

Bounds on Scattering Phase Shifts for Compound Systems*

LEONARD ROSENBERG AND LARRY SPRUCH

*Physics Department, Washington Square College and Institute of Mathematical Sciences,
New York University, New York, New York*

(Received November 9, 1960)

An extension of recently developed methods determines a rigorous upper bound on $(-k \cot \eta)^{-1}$, where η is the phase shift, for the general one-channel scattering process. The method, unfortunately, requires truncation of the various potentials, but it should generally be possible, in practice, to so truncate the potentials that the difference between the phase shifts of the original problem and of the problem for which a bound is obtained is insignificant.

In the course of the development it is necessary to introduce, for compound system scattering, an absolute definition of the phase shift, not simply a definition modulo π . The definition chosen is to take the projection of the full scattering wave function on the ground-state wave function of the scattering system, and to treat the resultant one coordinate wave function as if it were the scattering wave function for a particle on a center of force. Though irrelevant with regard to the determination of a bound on $\cot \eta$, it is interesting that at least for some simple cases this definition automatically increases the phase shift by at least π whenever the Pauli principle introduces a spatial node into the scattering wave function. The triplet scattering of electrons by hydrogen atoms provides an example.

1. INTRODUCTION

IN a series of papers,¹⁻⁴ it has been shown that for the one-channel problem, to which the present paper is restricted, it is possible to replace certain variational principles for scattering theory by much more powerful minimum principles. More specifically, a rigorous upper bound on the scattering length, A , was first obtained for the relatively simple case of the (zero-energy) scattering of a particle by a static central potential which is not sufficiently attractive to bind the particle.¹ Using the Hylleraas-Undheim theorem,⁵ it proved to be possible³ to extend the method to the scattering of a particle by a static central potential (henceforth to be denoted simply as one-body scattering) when bound states do exist. (The interaction with the electromagnetic field is assumed to have been turned off, so that capture can not take place.) The generalization to the scattering of one compound system by another, for zero initial relative kinetic energy of the two scattering systems, was trivial.²

The method was then extended to treat positive energy scattering.⁴ The presentation was there restricted to the one-body problem, taking into account bound states when they exist. The quantity bounded from above in this case is $(-k \cot \eta)^{-1}$, where η is the phase shift; this, of course, reduces to A as k goes to zero. Unlike the situation at zero energy, it was, unfortunately, necessary to restrict the potentials to

those which vanish identically beyond some given point R . While the rigorous bounds obtained do not then generally apply directly to the real problem of interest (account must be taken of the truncated portion of the potential), it should be emphasized that the effects of the artificial restrictions on the potentials may be made to be quite small; indeed, in principle, we may come as close as desired to the true problem, by choosing the point R beyond which the potential must vanish to be further and further out. In practice the necessary labor increases as the point is moved out, but it increases sufficiently slowly so that it should ordinarily be possible to choose the point R far enough out so as not to have introduced any serious truncation error without having unduly increased the work required.

It is the purpose of the present paper to provide the further extension to the problem of the positive energy scattering of one compound system by another. (For the one-channel scattering with which we are presently concerned, this is the final possible extension.) As for positive energy one-body scattering, the various potentials must be truncated.

In the extension of the formalism for positive energy scattering from the one-body problem to the case of compound system scattering, certain new features arise which were not present in the zero-energy case and which require some study. The development of a bound in the method that we have used always effectively involves the expansion of the difference function, the difference between the trial function and the exact function, in terms of some complete set of functions. More precisely, the question is always whether or not the difference function satisfies the boundary conditions which are necessary if it is to be possible to use it as one of the trial functions in the application of the Hylleraas-Undheim theorem. For one-body scattering, it was shown⁴ that the complete set could be taken to

* The research reported in this article was sponsored by the Geophysics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command, the Office of Ordnance Research, and the Office of Naval Research.

¹ L. Spruch and L. Rosenberg, *Phys. Rev.* **116**, 1034 (1959); *J. Appl. Phys.* **31**, 2104 (1960), especially Appendix B.

² L. Spruch and L. Rosenberg, *Phys. Rev.* **117**, 1095 (1960).

³ L. Rosenberg, L. Spruch, and T. F. O'Malley, *Phys. Rev.* **118**, 184 (1960).

⁴ L. Rosenberg and L. Spruch, *Phys. Rev.* **120**, 474 (1960). In Eq. (5.4c) $-kR$ should be replaced by $\theta - (P+1)\pi$. In the last integral of (2.5), u_l and $\phi_{l\ell}$ should be interchanged.

⁵ E. A. Hylleraas and B. Undheim, *Z. Physik* **65**, 759 (1930).

be the eigenfunctions either of an associated potential strength eigenvalue problem or of an associated energy eigenvalue problem. The former was found to be preferable, but both gave rigorous bounds. It will be demonstrated in Sec. 4 that the potential strength eigenvalue approach admits of a straightforward generalization to include the case of compound system scattering. The energy eigenvalue approach, on the other hand, will not, in general, be applicable for compound system scattering. It is possible to make the energy eigenvalue approach applicable, but unfortunately only by introducing certain rather restrictive boundary conditions on the trial function (see Sec. 5). The origin of the necessity of these restrictive conditions, for many-body scattering, lies in the fact that for any given R , the wave functions of the virtually excited states, while decaying, have not vanished identically.

The technique for getting bounds on phase shifts using the associated potential strength eigenvalue problem⁶ was first given by Kato for the one-body problem and later extended to some restricted cases of scattering by compound systems⁷; in this latter work numerical calculations for e^+H scattering were included. We note that using the method of the present paper it would now be quite feasible to perform the e^+H calculation for higher values of the kinetic energy of the incident positron.

It might be noted that the same remarks are applicable for compound system scattering with regard to the error introduced by truncation as were applicable for one-body scattering. As examples, consider the scattering of electrons or positrons by hydrogen. An estimate based on the method of the present paper is that for R of the order of 15 Bohr radii, only about three or four eigenstates need be accounted for,⁸ right up to the threshold energies for inelastic scattering, i.e., 7 ev for e^+H and 10 ev for e^-H .

2. DEFINITION OF THE PHASE SHIFT

The formal development of a bound is based on a consideration of the associated potential strength eigenvalue problem noted above. One here encounters the necessity of having a definition of the phase shift which is unambiguous. This is in contrast with the normal requirements where one need only know some trigonometric function of η , that is, one need merely know η modulo π . Despite the fact that theorems have

been surmised which involve the value of η (not simply of η modulo π), and despite the fact that phase shift values are often discussed for scattering by compound systems, to our knowledge no definition of η has been given which is applicable to general compound system scattering. While the above theorems and values undoubtedly have some meaning,⁹ and certainly so within the context of some approximation, such as the static approximation, it is clear that an unambiguous definition of the phase shift is very much called for. One would, of course, like to choose a definition which is the most natural possible generalization of the definition for one-body scattering, but this general question doesn't arise in our present concern in obtaining a bound on $\cot\eta$.

We now propose a definition of the phase shift for the scattering of one compound systems by another. (As always in the present paper, we are concerned with systems and energies for which the open channels can be decomposed and analyzed in terms of uncoupled channels.) To avoid irrelevant kinematical complications, we give the definition for the particular case of the zero orbital angular momentum scattering of a neutron by a nucleus of angular momentum I . We further assume, purely for convenience, that the total angular momentum J , and its z projection, J_z , satisfy $J = J_z = I + \frac{1}{2}$. (In Sec. 4 the description of the method for obtaining a bound on $k \cot\eta$ will be given in terms of this system.) We define the function

$$g(q_i) = \int F_i \chi_{\frac{1}{2}}(i) \Psi d\tau_i, \quad (2.1)$$

where q_i is the distance between neutron i and the center of mass of the nucleus which consists of all the particles except neutron i . F_i is the ground-state wave function of this nucleus, Ψ is the full scattering wave function, and $\chi_{\frac{1}{2}}(i)$ is the spin function for neutron i . The integral is over all coordinates except q_i , and is understood to represent a summation over all spin indices as well. The phase shift is defined by treating $g(q_i)$ as a one-body wave function and applying one of the standard definitions of the phase shift for static potential scattering, namely

$$\eta = \lim_{m \rightarrow \infty} (m\pi - kq_i^{(m)}),$$

where $q_i^{(m)}$ is the m th zero in $g(q_i)$.

We note that from the relation

$$\Psi \rightarrow \text{const} \chi_{\frac{1}{2}}(i) F_i \sin(kq_i + \eta)/q_i,$$

it follows that $g(q_i) \rightarrow \text{const} \sin(kq_i + \eta)$ as $q_i \rightarrow \infty$ which guarantees that η modulo π as defined by Eq. (2.1) is correct.

⁹ It seems likely, for example, that when finally some definition will have been introduced of sufficient utility to be generally acceptable, the phase shifts that follow from this definition will generally be the same as those that have been quoted.

⁶ T. Kato, Progr. Theoret. Phys. (Kyoto) 6, 395 (1951). We might note that a somewhat similar eigenvalue problem has recently been studied by M. Rotenberg (to be published).

⁷ L. Spruch and L. Rosenberg, Phys. Rev. 117, 143 (1960).

⁸ This estimate was arrived at with the aid of a rather crude approximation, namely, by assuming that the incoming particle is unaffected by the hydrogen atom. It is nevertheless adequate for the purpose intended, i.e., to indicate that there exists a significant range of energies in which the calculation can be performed without an undue amount of labor. Of course the actual bound obtained will not depend on any such free wave approximation.

An Application: Triplet Electron Hydrogen Scattering

It has been stressed that for the purposes of obtaining a bound, the question of the justification of our definition of the phase shift does not arise. However, since the question of a useful definition of the phase shift for compound system scattering is a very interesting one in its own right, it may be worth noting that the definition given enables us to see, in a few simple cases at least, how contributions to the zero-energy phase shift arise by virtue of the Pauli principle. (Such contributions have been discussed previously¹⁰ on the basis of an approximate model, the so-called static, or no-polarization approximation.) As an example we consider the zero-energy scattering of electrons by atomic hydrogen in the triplet (spatially antisymmetric) case. We wish to show that the antisymmetry of the wave function implies that the phase shift is at least π . According to our definition, as applied to this problem, we need only show that the function,

$$g(q_1) = \int_0^\infty q_2^2 dq_2 \int_0^\pi \sin\theta_{12} d\theta_{12} F(q_2) \Psi(q_1, q_2, \theta_{12}), \quad (2.2)$$

has at least one node. Here q_1 and q_2 are the magnitudes of the electron position vectors, θ_{12} is the angle between those vectors, and $F(q_2)$ is the hydrogenic ground-state function. (The subscript on F is redundant in this particular discussion and will not be retained here.) The spins have been accounted for. We form the integral

$$\begin{aligned} \int_0^\infty F(q_1) g(q_1) q_1^2 dq_1 &= \int_0^\infty q_1^2 dq_1 \int_0^\infty q_2^2 dq_2 \\ &\times \int_0^\pi \sin\theta_{12} d\theta_{12} F(q_1) F(q_2) \Psi(q_1, q_2, \theta_{12}). \end{aligned}$$

This integral clearly vanishes since Ψ is antisymmetric in the electronic coordinates while $F(q_1)F(q_2)$ is symmetric. The fact that the ground-state function $F(q_1)$ is nodeless leads to the desired result, namely $\eta \geq \pi$.¹¹

After the present work was completed, we learned from Dr. A. Temkin that he has considered the identical definition of the phase shift for compound system scattering, and further that he has obtained the identical result for the zero-energy triplet e^-H phase shift.

An extension of the triplet e^-H phase-shift result to positive energy scattering is discussed in Sec. 4.B.

¹⁰ P. Swan, Proc. Roy. Soc. (London) **A228**, 10 (1955).

¹¹ The zero-energy triplet phase shift is generally taken to be π . We note that this has only been established within the context of the static approximation. Indeed, as observed above, no definition of the phase shift for the true problem has previously been advanced.

3. DEFINITION OF THE PROBLEM FOR WHICH THE BOUND IS TO BE OBTAINED

For purposes of clarity we begin with the case in which the mass of one of the scattering systems can be effectively taken to be infinite. A prototype problem would then be the scattering of an electron by a neutral atom of atomic number Z . To describe the assumed potentials, we first define three regions in configuration space. The first region contains that portion of configuration space for which all of the $Z+1$ electrons are within a sphere of radius R centered about the nucleus of the atom. Region (2) is further subdivided into $Z+1$ parts; region (2i) contains that portion of space for which all but the i th electron are within the sphere of radius R , while the i th electron is not, where i runs from 1 through $Z+1$. Region (3) consists of the rest of space, that is, the part for which two or more electrons are outside of the sphere.

In region (1), the potentials are the true (in this case, Coulomb) potentials. In region (2i), all but the i th electron interact as before, but the i th electron is assumed not to interact with the others. In region (3), the potentials are taken to be infinitely repulsive.

We return now to the particular problem discussed in Sec. 2, namely, the zero orbital angular momentum scattering of a neutron by a nucleus consisting of Z protons and N neutrons. We again divide space into 3 regions, but because the center of mass is not now fixed it is necessary to introduce the auxiliary parameters, S_i . These are defined, for any distribution of particles, as the radius of the smallest sphere whose center is at the center of mass of the $N+Z$ particles excluding neutron i and which contains all these $N+Z$ particles. (i , of course, now runs from $Z+1$ through $Z+N+1$.) The three regions are chosen to be

- (1) $q_i < R$,
 $S_i < [(N+Z-1)/(N+Z+1)]R$, for each neutron
- (2i) $q_i > R$,
 $S_i < [(N+Z-1)/(N+Z+1)]R$,
 $i = Z+1, Z+2, \dots$ or $Z+N+1$
- (3) the rest of configuration space.

The limit on S_i has been chosen such that the $N+1$ regions which make up region (2) are nonoverlapping.

The potentials are assumed to satisfy the following requirements. In region (1) the particles interact via two-body central potentials which allow for space and spin exchange. As discussed in reference 4 we exclude tensor forces since we are restricting ourselves to one-channel processes, and we are considering nonzero scattering energies. In region (2i) the potentials are of the same form as in (1) except that the interaction between neutron i and the rest of the system vanishes. The potentials are taken to be infinitely repulsive in region (3).

It will now be obvious how to define the problem for other systems, such as the scattering of one compound system by another,¹² where each nucleus may carry a net charge.⁴

As shown in reference 2, the generalization of the Kato identity for the problem under consideration takes the form

$$k \cot(\eta - \theta) = k \cot(\eta_i - \theta) + (2\mu/\hbar^2) \int \Psi_i^* (H - E) \Psi_i d\tau - (2\mu/\hbar^2) \int \Omega^* (H - E) \Omega d\tau, \quad (3.1)$$

where now the wave function Ψ , which is a solution of $(H - E)\Psi = 0$, satisfies the boundary conditions

$$\begin{aligned} \Psi = & (-1)^i (N+1)^{-1/2} \chi_{\frac{1}{2}}(i) \{ F_i \sin(kq_i + \eta) / [q_i \sin(\eta - \theta)] \\ & + \sum_{\alpha} a_{\alpha} F_i^{(\alpha)} f_i^{(\alpha)}(\mathbf{q}_i) \}, \\ & \text{in region (2i), } Z+1 \leq i \leq Z+N+1; \\ \Psi = & 0 \quad \text{in region (3).} \end{aligned}$$

Here θ satisfies $0 \leq \theta < \pi$ but is otherwise arbitrary. E is the total energy, the sum of the relative kinetic energy and of E_0 , where E_0 is the ground-state energy of the target nucleus. The incident relative wave number k therefore satisfies

$$\hbar^2 k^2 / 2\mu = E - E_0.$$

The $F_i^{(\alpha)}$ represent normalized excited state wave functions of the system which does not include the i th particle, while the $f_i^{(\alpha)}$ are free particle decaying functions. If, for example, α denotes a nuclear state with zero total angular momentum, then

$$f_i^{(\alpha)} = e^{-\kappa_{\alpha} q_i} / q_i,$$

where

$$-\kappa_{\alpha}^2 \hbar^2 / (2\mu) + E_{\alpha} = E,$$

with E_{α} representing the energy of the α th nuclear excited state. If α represents a nuclear state with angular momentum L , then $F_i^{(\alpha)} f_i^{(\alpha)}$ will involve a sum of products, each containing a pair of angular momentum eigenfunctions. Ψ_i satisfies similar boundary conditions with η and a_{α} replaced by η_i and $a_{\alpha i}$, respectively. It is our purpose to obtain a lower bound on the error integral, $\int \Omega^* (H - E) \Omega d\tau$, where $\Omega \equiv \Psi_i - \Psi$, thereby providing an upper bound on $k \cot(\eta - \theta)$.

4. BOUND ON $k \cot(\eta - \theta)$ AND ON η

a. Associated Potential Strength Eigenvalue Problem

We consider the equation

$$(H - E)\Phi = \mu \rho \Phi,$$

¹² In this case, incidentally, the definition of a one-body scattering function, in terms of which the phase shift is defined, will require that we multiply the true scattering function by the product of the ground-state wave functions of the isolated systems before performing an integration. Correspondingly, E_0 will be the sum of the ground-state energies.

where ρ is positive, but otherwise arbitrary, in region (1) and vanishes elsewhere. Φ satisfies the boundary conditions

$$\begin{aligned} \Phi = & (-1)^i (N+1)^{-1/2} \chi_{\frac{1}{2}}(i) \{ \text{const } F_i \sin[kq_i + \delta(\mu)] / q_i \\ & + \sum_{\alpha} b_{\alpha} F_i^{(\alpha)} f_i^{(\alpha)}(\mathbf{q}_i) \}, \\ & \text{in region (2i), } Z+1 \leq i \leq Z+N+1; \\ \Phi = & 0 \quad \text{in region (3).} \end{aligned} \quad (4.1)$$

The eigenfunctions Φ_n and their corresponding eigenvalues μ_n are defined by the condition¹³

$$\delta(\mu_n) = \theta + n\pi.$$

In the following, we make the reasonable assumption that for finite μ and for positive scattering energies $\delta(\mu)$ is a continuous function of μ ; this is, of course, known to be true in the one-body problem.

In order to apply the Hylleraas-Undheim theorem, which leads to the desired bound, it is necessary to establish the existence of a lowest eigenvalue. By virtue of the monotonicity of $\cot \delta(\mu)$ the continuity of $\delta(\mu)$ leads to the monotonicity of $\delta(\mu)$ itself with respect to μ . We therefore need only show that $\delta(-\infty)$ is finite. In fact, as in the one-body case, we have $\delta(-\infty) = -kR$. Thus, for $\mu = -\infty$ the corresponding wave function, $\Phi(-\infty)$, vanishes in region (1) and has the form given in Eqs. (4.1) in regions (2) and (3). According to our definition of the phase shift (see Sec. 2), $\delta(-\infty)$ is determined by examining the function

$$g(q_i, -\infty) = \int F_i \chi_{\frac{1}{2}}(i) \Phi(-\infty) d\tau_i.$$

We clearly have

$$\begin{aligned} g(q_i, -\infty) = & 0, & q_i < R \\ = & \text{const} \sin[kq_i + \delta(-\infty)] / q_i, & q_i \geq R \end{aligned}$$

from which the stated value of $\delta(-\infty)$ is immediately deduced.

The boundary conditions satisfied by the difference function Ω are given by

$$\begin{aligned} \Omega = & (-1)^i (N+1)^{-1/2} \chi_{\frac{1}{2}}(i) \{ \text{const } F_i \sin(kq_i + \theta) / q_i \\ & + \sum_{\alpha} c_{\alpha} F_i^{(\alpha)} f_i^{(\alpha)}(\mathbf{q}_i) \}, \\ & \text{in region (2i), } Z+1 \leq i \leq Z+N+1; \\ \Omega = & 0 \quad \text{in region (3),} \end{aligned}$$

which is of the form satisfied by the eigenfunctions Φ_n . Therefore, Ω is an allowable trial function in an application of the Hylleraas-Undheim theorem to the associated potential strength eigenvalue problem. The formal steps required to derive an upper bound on $k \cot(\eta - \theta)$ are then identical to those described in reference 4. The upper bound obtained, the basic

¹³ The fact that the Hamiltonian, H , is Hermitian under the assumed boundary conditions for the Φ_n is easily verified; the required calculation is quite similar to the one by which the Kato identity was established (see reference 2) and we omit the details.

result of the present paper, is

$$k \cot(\eta - \theta) \leq k \cot(\eta_i - \theta) + (2\mu/\hbar^2) \int \Psi_i^* (H - E) \Psi_i d\tau - (2\mu/\hbar^2) \sum_{n=-P}^{-P+T'-1} \frac{1}{\mu_{nt}} \left| \int \Phi_{nt}^* (H - E) \Psi_i d\tau \right|^2, \quad (4.2)$$

where the Φ_{nt} are trial functions which satisfy the boundary conditions

$$\Phi_{nt} = (-1)^i (N+1)^{-\frac{1}{2}} \chi_{\frac{1}{2}}(i) \{ \text{const } F_i \sin[kq_i + \theta]/q_i + \sum_{\alpha} b_{\alpha i} F_i^{(\alpha)} f_i^{(\alpha)}(\mathbf{q}_i) \}, \quad (4.3)$$

in region (2i), $Z+1 \leq i \leq Z+N+1$;

$$\Phi_{nt} = 0 \quad \text{in region (3);}$$

as well as the conditions

$$\int \Phi_{nt}^* \Phi_{mt} \rho d\tau = \delta_{nm}, \quad (4.4)$$

$$\int \Phi_{nt}^* (H - E) \Phi_{mt} d\tau = \mu_{nt} \delta_{nm}, \quad \mu_{nt} < 0.$$

We here have the condition that

$$\theta - (P+1)\pi \leq -kR < \theta - P\pi. \quad (4.5)$$

Note that the restrictions $\mu_{nt} < 0$ impose some minimum requirements of accuracy on the trial functions Φ_{nt} . The inequality of Eq. (4.2) is valid provided that the number of trial functions T' which have been found with the required properties is equal to the exact (in general, unknown) number T of eigenfunctions with negative eigenvalues. In almost every case, however, it should be possible on the basis of the numerical calculations involved in the determination of the negative trial eigenvalues μ_{nt} to be fairly certain that T' does in fact equal T .

b. Conditional Inequality

In the one-body case, it was shown⁴ that by the use of the conditional inequality¹⁴ one could obtain a rigorous bound on η even when one could not be sure that $T' = T$, that is, even when one did not have a rigorous bound on $k \cot(\eta - \theta)$. It was found that

$$\eta > \eta_L',$$

where η_L' is defined by the equations

$$k \cot(\eta_L' - \theta) = \text{right-hand side of the one-body equivalent of Eq. (4.2),}$$

$$T'\pi + \theta - (P+1)\pi < \eta_L' < (T'+1)\pi + \theta - (P+1)\pi. \quad (4.6)$$

This lower bound on η , while rigorous, will be too low by roughly $(T - T')\pi$ if T' is less than T . (T' can never be greater than T , for we can never find more

negative potential strength eigenvalues than actually exist.) The lower bound then obtained will then be useless with regard to a comparison with the experimental data, though it may still be useful as the starting point for further theoretical calculation.¹⁴

The above developments can be taken over directly, with complete rigor, for the many-body case. There is nevertheless one respect in which the use of the conditional inequality differs for the many-body problem when identical particles are present from its use for the one-body scattering problem. Thus, account must be taken of the additional nodes which arise from the symmetry requirements on the wave function, or the lower bound η_L' , while rigorous, may be too low by a multiple of π even when the number of eigenstates with negative eigenvalues μ_n has been correctly accounted for. The effect of the Pauli principle can perhaps be better understood through a comparison of one-body scattering and the triplet (spatially antisymmetric) scattering of electrons by hydrogen atoms. For both systems, we have that $\delta(-\infty) = -kR$. [For $\mu = -\infty$, the one-body scattering function vanishes for $0 \leq q \leq R$, as does the equivalent one-body scattering function, $g(q_i)$.] However, while $\delta(\mu)$ is a continuous function of μ in the neighborhood of $\mu = -\infty$ for one body scattering, it is *not* continuous for e^-H triplet scattering. It is to be recalled that the e^-H problem under consideration is the true problem modified by the introduction of a cutoff and a repulsive barrier. The proof given in Sec. 2 that $\eta \geq \pi$ at zero energy can then be immediately extended for $k \neq 0$ to show that $kR + \eta > \pi$. To see this, we note that in the definition of $g(q_1)$, Eq. (2.2), the range of integration, 0 to ∞ , can be replaced by 0 to R since $F(q_2)$ exists only in that range. It then follows, using the same symmetry argument as was used at zero energy, that the integral

$$\int_0^R F(q_1) g(q_1) q_1^2 dq_1 = \int_0^R q_1^2 dq_1 \int_0^R q_2^2 dq_2 \times \int_0^\pi \sin \theta_{12} d\theta_{12} F(q_1) F(q_2) \Psi(q_1, q_2, \theta_{12})$$

vanishes. It follows that $g(q_1)$ has a node for some $q_1 < R$, which in turn, as has been previously shown,⁷ implies the inequality $kR + \eta > \pi$. The argument is independent of the form of the potential so that we have, more generally, $kR + \delta(\mu) > \pi$ for all finite μ . Therefore, with the integer P defined as in Eq. (4.5) we would, in the application of the conditional inequality technique to this problem, replace Eq. (4.6) by the form

$$(T'+1)\pi + \theta - (P+1)\pi \leq \eta_L' \leq (T'+2)\pi + \theta - (P+1)\pi,$$

which gives rise to a more accurate lower bound on η .

5. USE OF ENERGY EIGENFUNCTIONS

It was shown in reference 4 that in the one-body case the introduction of an associated energy eigenvalue

¹⁴ L. Spruch, Phys. Rev. **109**, 2149 (1958).

problem will lead to similar though less general results than obtained using the associated potential strength eigenvalue problem. When the scatterer is a compound system, however, the energy eigenvalue approach is not valid, since by definition the energy eigenfunctions vanish at the box [i.e., at the boundary of region (1)], while the difference function Ω does not; Ω is therefore not an allowable trial function in the application of the Hylleraas-Undheim theorem. Here the distinction between an allowable trial function and a function which can be expressed in terms of a complete set of functions is essential. If we were merely interested in the latter case we would not have required that the function satisfy particular boundary conditions.

In the one body problem, the difference function, there denoted by w , *does* vanish at the box. There, the form of w is known to be

$$w(r) = \text{const} \sin(kr + \theta), \quad r \geq R,$$

so that by the appropriate choice of R , it is a trivial matter to arrange to have $w(R) = 0$. In compound system scattering, however, Ω contains, in addition to a term proportional to the above form, contributions from the virtually excited states, with unknown amplitudes. There is then no choice of R which will cause Ω to vanish, though clearly one can still arrange to have the nondecaying component of Ω vanish at the edge of region (1).

It is, of course, true that by choosing R large enough, it is possible to make the effect of the decaying states quite small. However, there is a reason for not making R too large; there are then too many energy eigenstates which must be accounted for in the determination of a bound. Furthermore, one does not really know how large R must be made before the effect of the decaying states is truly small. Not only does one then have an approximate if well-defined problem (the potentials having been truncated), but one has an "approximate bound" on that approximate problem.

Recently, Percival¹⁵ has attempted to extend a technique^{16,17} introduced for obtaining a bound on the phase shift for one-body scattering to the compound system scattering case. The approach was restricted to the very special case where no Pauli exchange can take place between particles in the scattered and scattering systems, but even for this extremely restrictive case, we can find no rigorous justification for this approach. This is not very surprising, since we have just seen that the straightforward energy eigenvalue approach does not lead to a rigorous bound, and, as indicated in reference 4, there is an intimate connection for the one-body case between the energy eigenvalue approach and that of Percival and of Risberg. It seems worthwhile nevertheless to give some details as to why the Percival approach is not rigorous for many-body scattering.

It will be recalled that in one-body scattering, there is a simple connection between the wave function for the eigenstate with energy E_j of a particle confined to the region R within which $V(r)$ exists and the scattering wave function at the energy E_j for the potential $V(r)$ truncated at R ; the scattering wave function is simply the extension of the eigenstate wave function, continuous in value and slope at R . There is no such simple connection in the case of compound system scattering. Once again, the origin of the difference is the existence of virtually excited states, for a wave function which vanishes at the edge of region (1) must contain terms of the form

$$F_i^{(\alpha)}(e^{-\kappa\alpha(q_i-R)} - e^{+\kappa\alpha(q_i-R)})/q_i,$$

where for simplicity we consider the case for which $F_i^{(\alpha)}$ represents a nuclear state of zero total angular momentum. Due to the presence of the exponentially increasing term, the smooth continuation of the eigenstate wave function into the rest of configuration space cannot represent a scattering wave function.

It is true that for R "large enough," the approach is not unreasonable, and that is really all that Percival claims, but one does not obtain a rigorous bound on any well-defined problem.

It may be of some interest that the results of the present paper can be used to show that there exists a modification of the Percival approach which can be justified. The modification is not a trivial one since it involves placing an additional restriction on the trial functions. This modified form, being a special case of our general development, has the interesting property that it *does* include the effects of the Pauli principle.

Thus, suppose we choose for ρ some constant value in region (1). (It must of course vanish elsewhere.) Furthermore, we choose the boundary conditions satisfied by the trial function Ψ_t to be of the form

$$\begin{aligned} \Psi_t &= (-1)^i (N+1)^{-1} \chi_{\frac{1}{2}}(i) \{ F_i \sin(kq_i + \eta_i) / \\ &\quad [q_i \sin(\eta_i - \theta)] \}, \\ &\quad \text{in region (2i), } Z+1 \leq i \leq Z+N+1; \\ \Psi_t &= 0 \quad \text{in region (3);} \end{aligned}$$

that is, no sum over excited states appears. Similarly, we choose the trial eigenfunctions Φ_{ni} such that the coefficients of the terms in the sum over excited states vanish. With the choice $kR + \theta = m\pi$, m an integer, the functions Φ_{ni} vanish at the boundary of region (1), i.e., they are allowable trial energy eigenfunctions in region (1). Indeed, with our choice of ρ the boundary conditions along with the conditions given by Eqs. (4.4) are just those placed on trial energy eigenfunctions in the application of the Hylleraas-Undheim theorem. The resultant inequality for $k \cot(\eta - \theta)$, along with an application of the conditional inequality, then leads to a modification of the Percival result which *is* rigorous and which *does* allow for identical particles. However,

¹⁵ I. C. Percival, Phys. Rev. **119**, 159 (1960).

¹⁶ I. C. Percival, Proc. Phys. Soc. (London) **70**, 494 (1957).

¹⁷ V. Risberg, Arch. Math. Naturvidenskab. **53**, 1 (1956).

since one here requires the use of trial functions whose flexibility is restricted by the physically unnatural conditions mentioned above (the exact function does *not* satisfy those conditions) there is a limitation on the accuracy of the bound that can be obtained. In fact, it may well not be possible to find the appropriate number of trial functions Φ_n of the prescribed restricted form (i.e., we might *necessarily* have $T' < T$) in which case the bound obtained on η will be too low by approximately $(T - T')\pi$.

It should be emphasized that while we obtain valid results using (restricted) trial energy eigenfunctions Ω is nevertheless not an allowable trial function in an energy eigenvalue problem. The difficulty has been bypassed by the use of the associated potential strength

eigenvalue problem as the starting point. The point is that in this latter approach one places conditions only upon the oscillatory term, through having specified the phase shift $\delta(\mu_n)$; no restrictions are placed on the amplitudes of the virtually excited decaying states.

The primary purpose of the present paper is the derivation of Eqs. (4.2), (4.3), and (4.4). The analysis of previous work presented in this section is simply a byproduct. We have presented the analysis for two reasons. Firstly, it sheds some light on the methods of the present paper as well as on previous work. Secondly, there will be occasions when for practical reasons one would use trial functions of the restricted form; that is what was done, for example, in the analysis of the scattering of positrons by hydrogen atoms.⁷

PHYSICAL REVIEW

VOLUME 121, NUMBER 6

MARCH 15, 1961

Isotope Shift in the Arc Spectrum of Nickel*†

DANIEL J. SCHROEDER AND J. E. MACK‡
University of Wisconsin, Madison, Wisconsin

(Received September 19, 1960)

The isotope shift in 31 spectral lines in the nickel arc spectrum has been determined by the use of a Fabry-Perot interferometer. The normal mass shifts were calculated ($\approx +0.025$ cm⁻¹ between Ni⁵⁸ and Ni⁶⁴) and subtracted from the observed isotope shifts. The differences were attributed to the specific mass and field effects. The relative shifts of levels of four configurations were deduced from the observed line shifts, these being the "complex" configurations $3d^8 4s^2$ and $3d^8 4s 4p$ and the two-electron configurations $3d^9 4s$ and $3d^9 4p$. It was shown that the shifts due to the specific mass effect are a significant part of the observed shifts. Perturbations due to interconfiguration interactions were postulated to explain some of the observed shifts. The isotope shift to be expected between Ni⁵⁸ and Ni⁶⁴ on the basis of field effect calculations is about -0.02 cm⁻¹ for a single $4s$ electron, while the

shifts observed are as large as $+0.190$ cm⁻¹. A large fraction of this shift must therefore be attributed to the specific mass effect. By noting the deviations of the relative shifts between adjacent pairs of even isotopes from those predicted by mass effect theory, it was possible to deduce the relative field effect. The relative level shift resulting from the field effect is nearly the same for the adjacent isotope pairs 60-62 and 62-64 while the relative level shift for the isotope pair 58-60 is approximately 0.004 cm⁻¹ larger than that for the other adjacent isotope pairs. The arrangement of neutrons in the outermost nuclear shells is believed to account for this difference. Within the experimental error the level shift of the Ni⁶⁴ relative to the neighboring even isotopes is such that there is no odd-even staggering of the levels.

INTRODUCTION

ISOTOPE shift of spectral lines can be divided into two classes, that caused by the mass effect and that resulting from the field effect. The mass effect consists of two parts, normal and specific, and results from the nucleus having a finite mass. The normal mass effect can be calculated exactly while the specific mass effect, present in spectra of atoms with more than one electron, is very difficult to calculate precisely. Both of these effects decrease with increasing Z . The field effect, which increases with increasing Z , arises because of the

deviation of the nuclear electric field from a Coulomb field and can be used to study details of nuclear structure. This is probably the most important consequence of isotope shift studies.

In the very light elements the mass effect dominates and can account qualitatively for the observed shifts. In the heaviest elements the mass effect is negligible and the field effect can roughly account for the observed shifts. In the elements of intermediate mass the two effects are comparable. As a result, the shifts observed are small because the mass and field effects within the levels are often in such a direction as to oppose one another. In order to use the field effect in the determination of nuclear properties, it is necessary that the contributions of the mass and field effects to the observed shifts be known. For elements of intermediate mass it is difficult to determine experimentally the relative contributions of these two effects.

* Supported by the Department of Army, Chicago Ordnance District, the National Science Foundation and, through the research committee of the University, the Wisconsin Alumni Research Foundation.

† This report is based on a thesis submitted to the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree.

‡ Currently on leave as Scientific Attaché, Stockholm, Sweden.