Static Green's Function for Elastic Electron-Hydrogen Scattering and Resonances*†

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One version of the variational bound formulation of scattering theory requires the evaluation of integrals involving the Green's function $G^P(E)$ for the static, or one-body, approximation in which there is a hydrogen atom in the ground state throughout the scattering process. We obtain explicit expressions for $G^P(E)$ for the problem of the elastic scattering of electrons by atomic hydrogen, for both singlet and triplet states and for arbitrary total orbital angular momentum, in terms of solutions of integrodifferential equations. The triplet $L=0$ case requires special treatment because the hydrogenic ground-state function is a solution of the homogeneous (static) equation; this makes the integrodifferential operator, as it stands, singular, and the operator must be modified. In all cases, the integrodifferential equations are transformed into integral equations which are solved numerically. The numerical evaluation of $G^P(E)$ also enables one to determine the resonance energies for scattering as the eigenvalues of a (nonlinear) operator. The method developed is applicable to a number of other problems.

I. INTRODUCTION

THE primary obstacle in the application of the variational bound formulation of scattering theory to the study of the parameters that characterize a scattering process is the determination of the static Green's function $G^P(E)$. This paper will be concerned with the determination of $G^P(E)$ for the scattering of electrons by hydrogen atoms for both the singlet and the triplet cases and for arbitrary orbital angular momentum L. We restrict ourselves to incident kinetic energies below 10.2 eV, the threshold for excitation. In a previous paper,[1] hereafter referred to as I, numerical variational bounds were obtained on the $L=0$ singlet and triplet phase shifts for two energies. The question of how to obtain $G^P(E)$ was reserved for the present paper, which uses the notation and definitions of I. In this paper we also stress the fact that a knowledge of $G^P(E)$ can be applied to the calculation of resonance energies.

$G^P = G^P(E)$ is uniquely defined by the integro-partial-differential equation

$$P(H-E)PG^P = -P, \qquad (1.1)$$

and by boundary conditions that follow from the equation

$$P\Psi - P\Psi^P = G^P PHQ\Psi \qquad (1.2)$$

and from the known form of the boundary conditions satisfied by $P\Psi - P\Psi^P$. Here P is the symmetrized

operator which projects out that component of the wave function in which one or the other electron (or possibly both in the singlet case) is in the hydrogenic ground state [see Eq. (I-2.9)], $Q = 1 - P$, H is the full Hamiltonian [see Eq. (I-2.1)], Ψ is the full wave function, and $P\Psi^P$ is the determinable scattering solution in the static approximation in which there is a hydrogen atom in its ground state throughout the scattering process; $P\Psi^P$ satisfies

$$P(H-E)P\Psi^P = 0. \qquad (1.3)$$

$P\Psi - P\Psi^P$ is regular when either electron is at the origin. Its asymptotic behavior follows from Eqs. (I-2.5) and (I-2.16a), and is given by, for r_1 or $r_2 \to \infty$,

$$P\Psi - P\Psi^P \to (1+\epsilon S_{12})R(r_1)\,\mathcal{Y}_{L0L}{}^M(\Omega_{12})[\cot(\eta-\theta)$$
$$-\cot(\eta^P-\theta)]\sin(kr_2-\tfrac{1}{2}L\pi+\theta)/(2^{1/2}r_2), \quad (1.4)$$

where

$$\mathcal{Y}_{L0L}{}^M(\Omega_{12}) = (4\pi)^{-1/2}Y_{LM}(\Omega_1),$$

and

$$R(r) = 2a_0^{-3/2}\exp(-r/a_0),$$

where a_0 is the Bohr radius. The exchange operator S_{12} interchanges $\mathbf{r}_1$ and $\mathbf{r}_2$, and θ is an arbitrary normalization constant. The η^P are the phase shifts in the static approximation. The η are the exact phase shifts and are the quantities ultimately to be determined, *after* G^P has been determined. η appears in (1.4) within the square bracket, and does not otherwise affect the asymptotic form of $P\Psi - P\Psi^P$.

In e^+H scattering, the determination of G^P can be readily reduced to the determination of the Green's function for a one-body Hamiltonian with a local interaction; this latter Green's function is easily constructed (numerically) from the regular and irregular solutions of the static equation. This method of construction is not applicable to e^-H scattering where the determination of G^P reduces to the determination of a one-body Green's function associated with a nonlocal interaction, a consequence of exchange.

[1] I. Aronson, Y. Hahn, P. M. Henry, C. J. Kleinman, and L. Spruch, Phys. Rev. **153**, 73 (1967).

II. THE STATIC GREEN'S FUNCTION

In the discussion that follows we often write r_i, r_i', r_i, and r_i' as simply $\mathbf{i}$, $\mathbf{i}'$, i, and i', respectively, for $i=1$ or 2. G^P is an integral operator, and the equation for its kernel $G^P(1,2;1',2')$ is obtained by applying (1.1) to $\delta(1-1')\delta(2-2')$; this results in

$$P(H-E)PG^P(1,2;1',2') = -P\delta(1-1')\delta(2-2').\quad (2.1)$$

To determine the form of G^P, we consider the symmetry conditions that G^P must satisfy. These are

$$G^P(1,2;1',2') = G^P(2,1;2',1')\quad (2.2)$$

and

$$G^P(1,2;1',2') = G^P(1',2';1,2).\quad (2.3)$$

The latter equation is just the expression of field-source symmetry. Equation (2.2), which represents symmetry under the interchange of the two identical particles, is a result of the requirement, which follows from (1.2) and the symmetry properties of $P\Psi - P\Psi^P$ and $Q\Psi$, that the operation of G^P on a wave function of a definite symmetry preserve the symmetry. To see that this leads to (2.2), let $f_\epsilon(1,2)$ be a function which has the property that

$$f_\epsilon(1,2) = \epsilon f_\epsilon(2,1),\quad (2.4)$$

where ϵ may be either $+1$ or -1. Here and in the following, ϵ, when used as a subscript, denotes the symmetry under the interchange of 1 and 2 indicated by (2.4). (We will not bother to use the ϵ index on wave functions.) Apart from the symmetry requirement, f_ϵ is arbitrary. More generally, the subscript ϵ will indicate that for otherwise arbitrary functions f and h

$$f_\epsilon(1',2') = \epsilon f_\epsilon(2',1')$$

and

$$h_\epsilon(1,2;1',2') = \epsilon h_\epsilon(2,1;1',2')$$
$$= \epsilon h_\epsilon(1,2;2',1')[=h_\epsilon(2,1;2',1')].$$

Let

$$F_\epsilon(1,2) \equiv \int G^P(1,2;1',2')f_\epsilon(1',2')d\mathbf{r_1}'d\mathbf{r_2}',\quad (2.5)$$

where our notation indicates that we are demanding that $F_\epsilon(2,1) = \epsilon F_\epsilon(1,2)$. Interchanging 1 with 2 and 1' with 2', and using (2.4) and the symmetry of F_ϵ, we find that

$$\epsilon F_\epsilon(1,2) = \epsilon \int G^P(2,1;2',1')f_\epsilon(1',2')d\mathbf{r_1}'d\mathbf{r_2}'.$$

Cancelling the ϵ and comparing with (2.5), it follows, since f_ϵ is arbitrary and can be of either symmetry, that (2.2) must be satisfied.

In addition to (2.2) and (2.3) we have

$$PG^P(1,2;1'2') = G^P(1,2;1',2'),\quad (2.6)$$

since, as seen from (1.1), only the projection of G^P onto P space is relevant. If we let S_{12}' be an operator which

interchanges the 1' and 2' coordinates, $\frac{1}{2}(1+\epsilon S_{12}')$ will be a symmetry projection operator. Introducing G_ϵ^P defined by

$$G_\epsilon^P(1,2;1',2') = \frac{1}{2}(1+\epsilon S_{12}')G^P(1,2;1',2'),\quad (2.7)$$

with the use of the ϵ notation to be justified below, it follows that

$$G^P(1,2;1',2') = \sum_{\epsilon=-1,+1} G_\epsilon^P(1,2;1',2'),\quad (2.8)$$

and that

$$G_\epsilon^P(1,2;1',2') = \epsilon G_\epsilon^P(1,2;2',1').\quad (2.9)$$

The G_ϵ^P clearly represent the components of G^P which are symmetric and antisymmetric under the interchange of the primed coordinates. It is readily shown that the G_ϵ^P satisfy the same three conditions, (2.2), (2.3), and (2.6), that G^P satisfies. In addition, it follows from (2.3) and (2.9) that

$$G_\epsilon^P(1,2;1',2') = G_\epsilon^P(1',2';1,2)$$
$$= \epsilon G_\epsilon^P(1',2';2,1) = \epsilon G_\epsilon^P(2,1;1',2'),\quad (2.10)$$

so that G_ϵ^P is also symmetric or antisymmetric under the interchange of the unprimed coordinates, thereby justifying the use of ϵ as a subscript. From (2.10) it is clear that only G_{+1}^P makes a contribution when G^P operates on a function with even symmetry, corresponding to the singlet case, and only G_{-1}^P in the case of a function with odd symmetry, the triplet case. In fact, we shall see that these two parts of the Green's function are independent of each other.

The most general form that G_ϵ^P can assume that is consistent with (2.2), (2.3), (2.6), and (2.9) is

$$G_\epsilon^P(1,2;1',2')$$
$$= 2\times\tfrac{1}{2}(1+\epsilon S_{12})\tfrac{1}{2}(1+\epsilon S_{12}')[v(1)\mathcal{Y}_{LOL}(\Omega_{12})v(1')$$
$$\times \mathcal{Y}_{LOL}*(\Omega_{12}')g(\epsilon;2,2')/(r_1 r_1' r_2 r_2')],\quad (2.11)$$

where

$$v(r) \equiv rR(r),$$

and where the $g(\epsilon;2,2')$ satisfy

$$g(\epsilon;2,2') = g(\epsilon;2',2).\quad (2.12)$$

Note that $g(\epsilon;2,2')$ is a symmetric function for both values of ϵ. (We are dealing here with the interchange of 2 and 2', not of the 1 and 2 or 1' and 2' that occurred in our previous symmetry consideration involving ϵ; we therefore do not write ϵ as a subscript.) To verify (2.11), one begins by writing G_ϵ^P as a sum of $2^4=16$ terms, where each term is a product of factors specifying, for each of the four coordinates 1, 2, 1', and 2', whether the function is a ground-state function or a function orthogonal to the ground state. [Some characteristic terms are $cv(r_1)v(r_1')v(r_2)v(r_2')/(r_1r_1'r_2r_2')$, $v(r_1)v(r_2) \times f_1(\mathbf{r_1}',\mathbf{r_2}')/(r_1r_1'r_2r_2')$, $v(r_1')f_2(\mathbf{r_1},\mathbf{r_2},r_2')/(r_1r_1'r_2r_2')$, where the functions f_1 and f_2 are orthogonal, in each of their coordinates, to $v(r)$, e.g., $\int f_1(\mathbf{r_1}',\mathbf{r_2}')v(r_1')d\mathbf{r_1}'=0$.]

By successively requiring this expression to satisfy (2.6), (2.2), (2.3), and (2.9), we arrive at (2.11).

The problem of obtaining $G_\epsilon{}^P$ thus reduces to that of finding the $g(\epsilon; r, r')$, which may be considered as one-particle Green's functions. We note for future reference that there exists some arbitrariness in $g(-1; r, r')$ for $L=0$, for if one adds to $g(-1; r, r')$ the function $v(r)w(r') + v(r')w(r)$, where $w(r)$ is arbitrary, the value of $G_{-1}{}^P(1,2; 1'2')$ is unchanged because of the presence of the symmetry projection operators in (2.11).

To obtain the equation satisfied by the $g(\epsilon; r, r')$, we operate on (2.1) with $\frac{1}{2}(1+\epsilon S_{12'})$, use the fact that the operator $P(H-E)P$ commutes with $\frac{1}{2}(1+\epsilon S_{12'})$, use (2.8), and find that

$$P(H-E)PG_\epsilon{}^P(1,2; 1',2')$$
$$= -\tfrac{1}{2}(1+\epsilon S_{12'})P\delta(1-1')\delta(2-2'). \quad (2.13)$$

Operating on this equation with P_1 and performing the detailed analysis we arrive at the equation

$$(1+\epsilon S_{12'})v(1')\mathcal{Y}_{L0L}{}^*(\Omega_{12'})U(\epsilon; 2,2')=0, \quad (2.14)$$

where

$$U(\epsilon; 2,2') \equiv D(2)g(\epsilon; 2,2')$$
$$+\epsilon \int W(2,1)g(\epsilon; 1,2')dr_1+\delta(2-2'). \quad (2.15)$$

All integrals, here and elsewhere, are from 0 to ∞. D and W are given by

$$D(r)=\frac{\hbar^2}{2m}\left[-\frac{d^2}{dr^2}+\frac{L(L+1)}{r^2}\right.$$
$$\left.-\frac{2}{a_0}\left(\frac{1}{a_0}+\frac{1}{r}\right)e^{-2r/a_0}-k^2\right], \quad (2.16)$$

and

$$W(r_1,r_2)=v(r_1)v(r_2)\left[-(E-2E_{T0})\delta_{L0}\right.$$
$$\left.+\frac{e^2}{2L+1}\frac{r_<{}^L}{r_>{}^{L+1}}\right], \quad (2.17)$$

where $r_<$ and $r_>$ are the smaller and larger, respectively, of r_1 and r_2. To obtain equations involving 2 and 2' only, we multiply (2.14) by $\mathcal{Y}_{L0L}(\Omega_{12'})$ and integrate over $\Omega_{12'}$, which gives

$$U(\epsilon; 2,2')=0, \quad L\neq 0 \quad (2.18)$$

and

$$U(\epsilon; 2,2')/v(2')=-\epsilon U(\epsilon; 2,1')/v(1'), \quad L=0. \quad (2.19)$$

Each side of (2.19) is clearly a function of 2 alone. We designate the function by $\phi(\epsilon; 2)$, so that

$$\phi(\epsilon; 2)\equiv U(\epsilon; 2,2')/v(2'), \quad (2.20)$$

and (2.19) becomes

$$\phi(\epsilon; 2)=-\epsilon\phi(\epsilon; 2), \quad L=0. \quad (2.21)$$

This is a trivial identity for $\epsilon=-1$, but letting $\epsilon=+1$, it follows that $\phi(+1; 2)$ must vanish, and (2.20) gives

$$U(+1; 2,2')=0, \quad L=0. \quad (2.22)$$

Combining (2.18), (2.20), and (2.21) we have

$$U(\epsilon; r, r')=\delta_{L0}\delta_{\epsilon,-1}\phi(-1; r)v(r'). \quad (2.23)$$

From (2.23) and (2.15) it follows that the integro-differential equation which must be satisfied by $g(\epsilon; r, r')$ is given by

$$D(r)g(\epsilon; r, r')+\epsilon\int ds\, W(r,s)g(\epsilon; s, r')$$

$$= -\delta(r-r')+\delta_{L0}\delta_{\epsilon,-1}\phi(-1; r)v(r'), \quad (2.24)$$

where $\phi(-1; r)$ is as yet undetermined. The presence of the additional term on the right-hand side of (2.24) in the special case of $L=0$ and $\epsilon=-1$ has its origin in the fact that only for $L=0$ and $\epsilon=-1$ does the corresponding homogeneous equation have a spurious solution which vanishes asymptotically and at the origin. This spurious solution, which exists for all k^2, is given by $v(r)$, i.e.,

$$D(r)v(r)-\int ds\, W(r,s)v(s)=0. \quad (2.25)$$

This equation is identical with the static equation obtained for $u^P(2)$ by substituting the form

$$P\Psi^P=(1+\epsilon S_{12})v(1)u^P(2)\mathcal{Y}_{L0L}(\Omega_{12})/(2^{1/2}r_1r_2)$$

into (1.3), and it is clear that $u^P(2)=v(2)$ represents the null solution for the particular case $L=0$ and $\epsilon=-1$. To determine the function $\phi(-1; r)$, we first note that the existence of the solution $v(r)$ of (2.25) imposes a restriction on the form of $\phi(-1; r)$. The necessary condition for the existence of a solution to (2.24) in the case $L=0$ and $\epsilon=-1$ is that the right-hand side of this equation be orthogonal to $v(r)$, which requires that

$$\int \phi(-1; r)v(r)dr=1.$$

Aside from this condition, $\phi(-1; r)$ is arbitrary. This lack of uniqueness is related to the lack of uniqueness of $g(-1; r, r')$ for $L=0$ pointed out earlier. For computational reasons it is desirable to eliminate terms in $g(-1; r, r')$ which, because of cancellation, make no contribution to $G_{-1}{}^P(1,2; 1',2')$. This is accomplished by demanding that

$$\int g(-1; r, r')v(r')dr'=0. \quad (2.26)$$

[Since $g(-1; r, r')$ is symmetric under the interchange of r and r', $g(-1; r, r')$ will thus also be orthogonal to $v(r)$.] The function $\phi(-1; r)$ must then be $v(r)$, which

follows by multiplying (2.24) by $v(r')$, integrating over r', and using (2.26).

Rewriting (2.24), with $\phi(-1;r)$ replaced by $v(r)$, we have

$$D(r)g(\epsilon;r,r')+\epsilon\int ds\, W(r,s)g(\epsilon;s,r')$$

$$=-\delta(r-r')+\delta_{L0}\delta_{\epsilon,-1}v(r)v(r').\quad (2.27)$$

The boundary conditions on $g(\epsilon;r,r')$ follow, through (2.11), from the boundary conditions on G^P, which in turn are determined from (1.2). $g(\epsilon;r,r')$ vanishes at the origin, and, using the asymptotic form for $P\Psi-P\Psi^P$ given by (1.4), one finds that $g(\epsilon;r,r')$ has an asymptotic dependence given by $\sin(kr-\frac{1}{2}L\pi+\theta)$ as $r\to\infty$.

To facilitate the solution of (2.27) we transform this equation into an integral equation. Introduce g_0, defined as that solution of

$$D(r)g_0(r,r')=-\delta(r-r')\quad (2.28)$$

which satisfies the same form of boundary conditions that g does. g_0 is readily constructed from the regular and irregular solutions of the homogeneous equation obtained from (2.28) by setting the right-hand side equal to zero. It then follows that

$$g(\epsilon;r,r')=g_0(r,r')+\epsilon\int dt\, g_0(r,t)\int ds\, W(t,s)g(\epsilon;s,r')$$

$$-\delta_{L0}\delta_{\epsilon,-1}\int dt\, g_0(r,t)v(t)v(r').\quad (2.29)$$

We note that in the case $L=0$ and $\epsilon=-1$ the solution of (2.29) is not unique. To see this, note that (2.25) leads to the relationship

$$v(r)=-\int dt\, g_0(r,t)\int ds\, W(t,s)v(s).\quad (2.30)$$

It is then clear that to any solution of (2.29) the quantity $cv(r)v(r')$ can be added, the resultant still satisfying (2.29) and the boundary conditions, and remaining symmetric. However, imposing the orthogonality condition (2.26) uniquely determines $g(-1;r,r')$.

III. METHOD OF SOLUTION

In order to determine the solution of (2.29), we write this equation in matrix form,

$$(I-\epsilon g_0W)g=g_0-\delta_{L0}\delta_{\epsilon,-1}g_0vv^T,\quad (3.1)$$

where g_0, W, and g are now matrices, I is the unit matrix, v is a column vector, and the superscript T denotes the transpose. If $I-\epsilon g_0W$ is a nonsingular operator, (3.1) can be solved directly for g by inversion. In all but the one case $L=0$ and $\epsilon=-1$ there is no reason to believe that $I-\epsilon g_0W$ has a zero eigenvalue,

and in fact numerical computations do not show any singularities. For these cases we have immediately that

$$g=(I-\epsilon g_0W)^{-1}g_0.\quad (3.2)$$

In the special case of $L=0$ and $\epsilon=-1$, the operator $A\equiv I+g_0W$ is singular, since it follows from (2.30) that

$$(I+g_0W)v=0.\quad (3.3)$$

There is nevertheless no difficulty in determining g from (3.1). Since $g(-1;r,r')$ has been chosen to be orthogonal to $v(r')$, it follows that in (3.1) the part of W proportional to v^T can be dropped, or, more generally, multiplied by an arbitrary constant. We can therefore replace (3.1) by

$$(I+g_0W_c)g=g_0-g_0vv^T,\quad (3.4)$$

where

$$W_c(r,r')\equiv cv(r)v(r')+e^2v(r)v(r')/r_>,\quad (3.5)$$

and where $c\neq-(E-2E_0)$ but is otherwise an arbitrary constant. We then have $W_c\neq W$, and there is no reason to suspect that A_c, defined by

$$A_c\equiv I+g_0W_c,$$

does not have an inverse,[2] except perhaps at isolated values of c.

Introducing B, defined by

$$B\equiv g_0-g_0vv^T,$$

(3.4) becomes

$$A_cg=B,$$

and we have

$$g=A_c^{-1}B.\quad (3.6)$$

We verify that g, as given by (3.6), is in fact a symmetric solution of (3.1). Using (3.3) and (3.5) we obtain the relationship

$$A_c^{-1}B=B^T(A_c^{-1})^T,\quad (3.7)$$

which proves the symmetry of g. Using (3.7) and the result that $v^TB^T=0$, it follows that

$$Ag=AA_c^{-1}B=A_cA_c^{-1}B-[c+(E-2E_0)]$$
$$\times g_0vv^TA_c^{-1}B=B,$$

which shows that the g obtained with the modified matrix A_c satisfies the original equation (3.1).

Equations (3.2) and (3.6) were solved numerically by introducing a finite mesh for r and r', converting these two equations into finite matrix form, and performing matrix inversions. We note that the accuracy of the calculation is improved by solving, not for g directly, but rather for g_1, defined by

$$g_1\equiv g-g_0,$$

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[2] In the results that follow, one needs to assume the existence of the right inverse only. However, since A_c can be symmetrized by operating on the left with W, it follows that the right inverse is also the left inverse.

which satisfies the equation for $L=0$ and $\epsilon=-1$,

$$(I+g_0W_c)g_1 = -(g_0W_cg_0+g_0vv^T), \qquad (3.8)$$

and for all other cases,

$$(I-\epsilon g_0W)g_1 = \epsilon g_0Wg_0. \qquad (3.9)$$

Here g_1 is the difference of two functions each of whose second derivatives has the same δ-function behavior, and thus discontinuities in the derivatives of g_1 occur first in third order. The integrations involving g_1 implied by the matrix multiplications in (3.8) and (3.9) are then more accurate than those involving g in (3.2) and (3.4).

IV. APPLICATION TO PHASE SHIFTS

The methods discussed above were used to calculate G^P numerically for $L=0$ singlet and triplet e^-H scattering at two energies below the excitation threshold. G^P was then used in the determination of variational lower bounds on the phase shifts in e^-H scattering; the results are given in I. The contribution of terms involving G^P to the phase shift was found to be very small, much smaller than in e^+H scattering,[3] but, since the size of the contribution was not known in advance, terms containing G^P had to be retained. (It would clearly be extremely useful to be able to know in advance, when true, that G^P had little effect; it would even be useful if one could determine in advance only that the inclusion of G^P increased the phase shift, since one could then obtain a bound without retaining G^P.)

It is not necessary to know G^P itself; one is ultimately interested in the evaluation of integrals involving G^P, and various methods have been devised which replace the need to evaluate G^P by the need to solve inhomogeneous differential equations. These approaches[4-8] represent variations of the original variational bound formulation.[9,10] The variations are relatively minor from a formal point of view, but may be of great practical importance; this remains to be seen. The explicit use of G^P has the advantage that terms involving G^P are evaluated once and for all, so that questions of convergence do not arise. Furthermore, once G^P has been obtained, it can be applied to trial functions with different sets of variational parameters without having

to solve any new equations. On the other hand, in addition to the initial effort of finding G^P, its use has the disadvantage that trial functions with many different parameters require the evaluation of many double integrals. To aid in judging the relative effectiveness of the original G^P approach, we note that using a mesh of 120 by 120 points, the computation of G^P for one energy takes about 2 min on the CDC 6600 and gives an accuracy of about one part per thousand. With G^P known, the calculation of a phase shift at one energy with a trial function that contains 25 linear variational parameters takes about 1 min; the time increases as the square of the number of parameters.

V. COMPOUND RESONANCE ENERGIES AS AN EIGENVALUE PROBLEM, AND THEIR ACCURATE NUMERICAL DETERMINATION

$G^P(E)$ can readily be calculated at any energy below 10.2 eV, the threshold for excitation, and, in particular, both at and near the narrow compound resonances in the scattering of electrons by atomic hydrogen. Though our numerical calculations have been restricted to lower energy values, where there are no resonances, the methods can readily be extended to the accurate evaluation of the positions of these resonances. All that is required is a trivial modification of the Feshbach projection-operator formalism of scattering by a compound system.[11]

If one is satisfied with only moderate accuracy and with a *post hoc* justification of the omission of certain terms, the positions of the resonance energies $\mathcal{E}_r^*$ can in some cases be relatively easy to obtain. In the case of the lowest resonance, $\mathcal{E}_1^*$, for e^-H scattering, even the initial determination,[12] based on a seemingly crude close-coupling approximation, was rather accurate. (As physical insight into the nature of the resonance developed, it became clear that the close-coupling approximation was not too crude for this problem since it included the dominant terms, the contributions associated with the hydrogenic $2s$ and $2p$ states.) $\mathcal{E}_1^*$ was determined by evaluating the phase shift η at a sequence of closely spaced energies.

Apart from the possibility of missing narrow resonances, a study of η as a function of the energy E is a very reasonable but somewhat unsatisfying approach. There are advantages associated with the specification of the $\mathcal{E}_r^*$ as the eigenvalues of some *known* operator. In nuclear physics one often obtains an estimate of the $\mathcal{E}_r^*$ by determining the eigenvalues of the "wrong" operator (e.g., QHQ, see below), and corrects by introducing an energy shift. It is well known that there is a "right" operator whose eigenvalues are the $\mathcal{E}_r^*$ themselves. In fact, there are a number of right opera-

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[12] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

tors, and we wish to stress that there is one form for the right operator, a form containing $G^P(E)$, which can be obtained numerically for some interesting if relatively simple problems involving light atoms, including the scattering of electrons by H atoms. Furthermore, once an $\mathcal{E}_r{}^*$ has been obtained, the partial cross section for all energies near $\mathcal{E}_r{}^*$ can be obtained by the evaluation of η (by a variational bound calculation, for example) at any *one* energy close to $\mathcal{E}_r{}^*$.

In Feshbach's approach, compound resonances are states in which the incident particle can form a bound state with an *excited* target state, the coupling to the target ground state having been artificially turned off. No particular stress was placed on forms in which the scattering parameters could be calculated numerically from first principles, the emphasis being on the determination of the *form* of $\sigma(E)$ and on the development of physical insights into the origin of resonances. Thus, complex wave functions were used, and a number of Green's functions were used. (In nuclear physics, *no* Green's function is calculable.) We will briefly rederive some of Feshbach's results in a partial-wave form, which is less general but more amenable to numerical calculation, and in a form in which only real functions appear and in which only the calculable Green's function, $G^P(E)$, appears.

It was transparent from the beginning that Feshbach's formulation could serve to determine the $\mathcal{E}_r{}^*$, but $G^P(E)$ had not been determined. For e^-H scattering, one knows immediately from the origin of compound resonances that a crude upper bound on $\mathcal{E}_1{}^*$ is provided by the energy of the $n=2$ state. The first application[13] of the Feshbach formulation provided a crude (and nonrigorous) *lower* bound on $\mathcal{E}_1{}^*$ by ignoring the $G^P(E)$ term in the "right" operator, $[Q\mathcal{K}(E)Q$, see below], thereby arriving at QHQ, and showing that the lowest eigenvalue of QHQ was greater than or equal to 8.6 eV. A number of subsequent calculations[14] have provided very accurate estimates of the lowest eigenvalues of QHQ, but these calculations provide no *a priori* justification for the neglect of the $G^P(E)$ term; the justification is normally based upon agreement with the experimental data. [It is not even clear, considering the number of significant figures that are often retained, that one is truly justified in neglecting the contribution from the $G^P(E)$ term.] This criticism cannot be leveled at some later work[6]—an adaptation of the variational bound formulation which incorporates the advantages of the close-coupling approximation without sacrificing accuracy—in which, however, η is again calculated at a series of energy values.

The $\mathcal{E}_r{}^*$ can be determined by an analysis of the equations[15]

$$\tan\eta(E) = \tan\eta^P(E) - (2m/k\hbar^2)$$
$$\times (P\Psi^P(E), PHQ\Psi(E)) \quad (5.1)$$

and

$$Q[\mathcal{K}(E) - E]Q\Psi(E) = -QHP\Psi^P(E), \quad (5.2)$$

where

$$Q\mathcal{K}(E)Q \equiv Q[H + HPG^P(E)PH]Q. \quad (5.3)$$

Introducing the Green's function $G^Q(E)$ defined by

$$Q[\mathcal{K}(E) - E]QG^Q(E) = -Q \quad (5.4)$$

and by the boundary condition that $G^Q(E)$ vanish as any of its radial arguments approaches ∞, we can rewrite (5.2) as

$$Q\Psi(E) = G^Q(E)QHP\Psi^P(E).$$

Equation (5.1) then becomes[16]

$$\tan\eta(E) = \tan\eta^P(E) - (2m/k\hbar^2)$$
$$\times (QHP\Psi^P(E), G^Q(E)QHP\Psi^P(E)). \quad (5.5)$$

[Feshbach's Eq. (4.23) in the second paper of Ref. 11 is the analog for the scattering amplitude, with a complex $G^Q(E)$, of Eq. (5.5).] Taking $\tan\eta = \infty$ to be the definition of a resonance, it follows that the $\mathcal{E}_r{}^*$ are the poles of $G^Q(E)$, that is, the discrete energy eigenvalues defined by

$$Q\mathcal{K}(E_r{}^*)Q\Phi_r{}^* = \mathcal{E}_r{}^*Q\Phi_r{}^*. \quad (5.6)$$

The $\mathcal{E}_r{}^*$ are thus defined by a nonlinear eigenvalue problem. This should normally cause no real difficulty, since $G^P(E)$ does not "know" of the existence of compound resonances and will therefore be smooth at energies near $\mathcal{E}_r{}^*$. The iteration process in which one starts by guessing at a value $\mathcal{E}_{r0}{}^*$ for $\mathcal{E}_r{}^*$, inserts $\mathcal{E}_{r0}{}^*$ into the left-hand side of Eq. (5.6) and determines the next estimate $\mathcal{E}_{r1}{}^*$, should converge very rapidly. (A possible but by no means necessary guess for $\mathcal{E}_{r0}{}^*$ could be the rth eigenvalue of QHQ.)

Note that resonances cannot be said to occur when η^P is an odd multiple of $\frac{1}{2}\pi$. Though $\tan\eta^P$ is then infinite, $(P\Psi^P, PHQ\Psi)$ may also be infinite due to the presence in the denominator of $P\Psi^P$ of the term $\sin(\eta^P - \frac{1}{2}\pi)$ [see Eq. (I-2.16)]. $\tan\eta$ need not therefore be infinite.

The above analysis corresponds to the particular choice $\theta = \frac{1}{2}\pi$ in the notation of Ref. 9. Choosing a slightly different normalization in the asymptotic form of Ψ, corresponding to $\theta = 0$, we find, with primes in-

[13] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

[14] See P. G. Burke, Advan. Phys. **14**, 521 (1965); K. Smith, Rept. Progr. Phys. **29**, 373 (1966), for comprehensive reviews. The most recent calculation of the eigenvalues of QHQ is that by A. K. Bhatia, A. Temkin, and J. F. Perkins, Phys. Rev. **153**, 177 (1967). This paper also contains references to the earlier work.

[15] See Ref. 5, Eqs. (2.12) and (2.7b). In (2.12) we set $\theta = \frac{1}{2}\pi$; the additional factor of 4π is the result of a slightly different normalization than used here.

[16] Equation (5.5) and its analog for multichannel scattering can also serve as very convenient starting points in the determination of an *upper* bound on $\tan\eta$ and on the elements of the inverse of the reactance matrix, respectively. See Ref. 8.

dicating a different normalization from that used above,

$$\cot\eta(E) = \cot\eta^P(E) + (2m/k\hbar^2)(P\Psi'^P(E), PHQ\Psi'(E))$$
$$= \cot\eta^P(E) + (2m/k\hbar^2)$$
$$\times (QHP\Psi'^P(E), \mathcal{G}'^Q(E)QHP\Psi'^P(E)). \quad (5.7)$$

The advantages of the choice $\theta = \frac{1}{2}\pi$ over the choice $\theta = 0$ are now clear. In the latter case, the determination of the $\mathcal{E}_r{}^*$, corresponding to $\cot\eta = 0$, requires a study of both terms on the right-hand side of (5.7) simultaneously.

To study the energy variation of the partial cross section, we introduce the eigenvalue problem, for *each* E,

$$Q\mathcal{K}(E)Q\Phi_n(E) = \mathcal{E}_n{}^Q(E)\Phi_n(E). \quad (5.8)$$

[Note that $\mathcal{E}_n{}^Q(\mathcal{E}_n{}^*) = \mathcal{E}_n{}^*$, and that $\Phi_n(\mathcal{E}_n{}^*) = \Phi_n{}^*$.] We can then write $\mathcal{G}^Q(E)$ in bilinear form,

$$\mathcal{G}^Q(E) = \sum_n \Phi_n{}^Q(E)\rangle \langle\Phi_n{}^Q(E)/[E - \mathcal{E}_n(E)],$$

where $\sum_n$ represents the sum over any discrete eigenvalues that may exist and an integral over the continuum. Introducing

$$\tfrac{1}{2}\Gamma_n(E) \equiv (2m/k\hbar^2)(P\Psi^P(E), PHQ\Phi_n{}^Q(E))^2 \quad (5.9)$$

for all n, including $n = r$, and introducing

$$b_r(E) \equiv \tan\eta^P(E) - \sum_n{}' \tfrac{1}{2}\Gamma_n(E)/[E - \mathcal{E}_n(E)], \quad (5.10)$$

where the prime indicates the exclusion of the $n = r$ term, (5.5) becomes

$$\tan\eta(E) = b_r(E) - \tfrac{1}{2}\Gamma_r(E)/[E - \mathcal{E}_r(E)]. \quad (5.11)$$

With the partial cross section given by $(4\pi/k^2)\sin^2\eta(E)$, the total cross section is given by

$$\sigma(E) = \frac{4\pi}{k^2}\frac{\tan^2\eta(E)}{1 + \tan^2\eta(E)} + \sigma'(E),$$

with $\tan\eta(E)$ given by (5.11), and with $\sigma'(E)$ representing the cross-section contributions from all partial waves other than the one for which the resonance under consideration occurs. This will normally be a useful form for E close to $\mathcal{E}_r{}^*$, perhaps in the energy domain $|E - \mathcal{E}_r{}^*| \ll |E - \mathcal{E}_{r\pm1}{}^*|$, for $E_r(E)$, $\Phi_r{}^Q(E)$, $\Gamma_r(E)$, $b_r(E)$, and $\sigma'(E)$ will be slowly varying functions of E which can be approximated by their values at $E = \mathcal{E}_r{}^*$, that is, by $\mathcal{E}_r{}^*$, $\Phi_r{}^*$, $\Gamma_r(\mathcal{E}_r{}^*)$, $b_r(\mathcal{E}_r{}^*)$, and $\sigma'(\mathcal{E}_r{}^*)$, respectively. Having made a reasonably accurate determination of $\mathcal{E}_r{}^*$, $\Phi_r{}^*$, $P\Psi^P(\mathcal{E}_r{}^*)$, and, from (5.9), $\Gamma_r(\mathcal{E}_r{}^*)$, a reasonably good estimate of $b_r(\mathcal{E}_r{}^*)$ can be obtained from a careful estimate, possibly a variational bound estimate, of $\tan\eta(E')$, where $E' \simeq \mathcal{E}_r{}^*$ but $E' \neq \mathcal{E}_r{}^*$, through the use of (5.10). With

$$d_r(E) \equiv b_r(\mathcal{E}_r{}^*) - [\tfrac{1}{2}\Gamma_r(\mathcal{E}_r{}^*)/(E - \mathcal{E}_r{}^*)],$$

we then have, for E close to $\mathcal{E}_r{}^*$,

$$\sigma(E) \approx \frac{4\pi}{k^2}\frac{d_r{}^2(E)}{1 + d_r{}^2(E)} + \sigma'(\mathcal{E}_r{}^*).$$

VI. CONCLUDING REMARKS

The G^P considered in the present paper is effectively a one-channel Green's function since we are here concerned with an energy for which elastic scattering is the only possible process. For an energy for which there are n open channels, the problem becomes that of determining the elements $G_{ij}{}^P$, where $1 \leq i \leq n$ and $1 \leq j \leq n$, of the "static" Green's function, or, more appropriately, the Green's function in P space. The extension to this latter case should present no difficulty. It might be very laborious to carry out the numerical calculations, though, even for n small. The method of determining G^P can be trivially extended to the elastic scattering of electrons from hydrogen-like atoms. To the extent that the ground-state wave function can be considered known, it should also be possible to extend the method to a number of heavier neutral atoms and to some positron pick-up processes.

Note added in proof. The numerical determination of g was tedious but not too time consuming. The *form* in which $g(\epsilon; r, r')$ was obtained, as a set of values over a two-dimensional space, is much more disturbing, for all integrals over g had to be done numerically over a two-dimensional mesh, and these integrations, which had to be repeated for each choice of a set of variational parameters, occupied a large fraction of the machine time used. It would be extremely useful to have a representation of g as a product of functions or as a sum of products. This would seem to be precluded by the nonlocal character of W as given by (2.17). However, Mittleman noted that W is of a very special character and that (2.27) can be rewritten as a set of two coupled equations. Thus, setting $V(r) = e^2(a_0/2)^{1/2}R(r)$ for later convenience, and introducing

$$g_2(r, r') \equiv (2m/\hbar^2e^2)[(E - 2E_{T0})rr'\delta_{L0} - (e^2/2L+1)(r_<{}^{L+1}/r_>{}^L)], \quad (6.1)$$

$W(r, s)$ can be rewritten as

$$W(r, s) = -V(r)g_2(r, s)V(s).$$

Setting $D_1(r) = D(r)$, Eq. (2.27) becomes

$$D_1(r)g(\epsilon; r, r') - \epsilon V(r)\int g_2(r, s)V(s)g(s, r')ds$$
$$= -\delta(r - r') + \delta_{L0}\delta_{\epsilon, -1}rV(r)r'V(r'). \quad (6.2)$$

The boundary conditions on g are given below (2.27). The essential point to note is that g_2 is itself a Green's function, satisfying

$$D_2(r)g_2(r, s) = -\delta(r - s),$$
$$D_2(r) \equiv (\hbar^2/2m)[-d^2/dr^2 + L(L+1)/r^2].$$

Following Mittleman, we define the function

$$z(\epsilon; r,r') = -\epsilon \int g_2(r,s) V(s) g(\epsilon; s,r') ds . \quad (6.3)$$

We immediately find

$$D_1 g + V z = -\delta(r-r') + \delta_{L0}\delta_{\epsilon,-1} r V(r) r' V(r') \quad (6.4)$$
$$-\epsilon D_2 z + V g = 0 .$$

It follows from (6.3) that z has the same boundary conditions as g_2. The coupled equations for g and z, plus the boundary conditions on g and z, can readily be shown to lead to (6.2).

We note that, apart from a constant factor and the factor $r_1 r_2$, the second part of g_2 is the radial factor of P_L in an expansion of $1/r_{12}$. Thus g_2 is a Green's function only because the Coulombic $1/r_{12}$ interaction is itself a Green's function. The decoupling technique would therefore also work for a Yukawa interaction, a Green's function too, but it would *not* work for almost any other potential.

The set (6.4) is identical in form to the coupled equations which arise in a two-state close-coupling approximation for the incident kinetic energy equal to the threshold energy for excitation. The physical analogy cannot be pushed too far, but as a mathematical problem the work of Newton and Jost [R. G. Newton, J. Math. Phys. **1**, 319 (1960)] can now be used, with the trivial but annoying modifications that include the use of standing wave rather than outgoing wave boundary conditions and a g_2 which is defined for the region $0 < r' < \infty$, as required by (6.2), rather than $r < r' < \infty$ or $0 \le r' < r$.

To simplify the discussion, we treat here all cases other than the case of $L=0$, $\epsilon=-1$, which requires slight modifications. In order to construct g and z, we consider the matrix equations

$$\mathbf{M}\mathbf{u}=0 , \quad \mathbf{M}\mathbf{w}=0 , \quad (6.5)$$

where $\mathbf{M} \equiv \mathbf{D} + \mathbf{V}$ and

$$\mathbf{D} \equiv \begin{pmatrix} D_1(r) & 0 \\ 0 & -\epsilon D_2(r) \end{pmatrix} , \quad \mathbf{V} \equiv \begin{pmatrix} 0 & V(r) \\ V(r) & 0 \end{pmatrix} ,$$

$$\mathbf{u} \equiv \begin{pmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{pmatrix} , \quad \mathbf{w} \equiv \begin{pmatrix} w_{11} & w_{12} \\ w_{21} & w_{22} \end{pmatrix} ,$$

with the four column vectors in $\mathbf{u}$ and $\mathbf{w}$ representing four independent vector solutions of $\mathbf{M}$. The two column vectors in $\mathbf{u}$ will be taken to be regular at the origin, while the two column vectors in $\mathbf{w}$ will be irregular. We have combined the vector solutions into two matrix solutions for convenience of notation, but no new content is introduced thereby. We define the matrices

$$\mathbf{g}^{(0)} \equiv \begin{pmatrix} g_1 & 0 \\ 0 & -\epsilon g_2 \end{pmatrix} , \quad \mathbf{u}^{(0)} \equiv \begin{pmatrix} u_{11}^{(0)} & 0 \\ 0 & u_{22}^{(0)} \end{pmatrix} ,$$

$$\mathbf{w}^{(0)} \equiv \begin{pmatrix} w_{11}^{(0)} & 0 \\ 0 & w_{22}^{(0)} \end{pmatrix} ,$$

where $\mathbf{D}\mathbf{u}^{(0)}=0$, $\mathbf{D}\mathbf{w}^{(0)}=0$, with

$$u_{22}^{(0)} = e^{-2} r^{L+1} , \quad w_{22}^{(0)} = e^2 (2L+1)^{-1} r^{-L} - (E - 2E_{T0}) r \delta_{L0} ,$$
$$u_{11}^{(0)}(0) = 0 , \text{ and, as } r \to \infty ,$$
$$u_{11}^{(0)}(r) \to \sin(kr - \tfrac{1}{2}L\pi + \eta^D) ,$$
$$w_{11}^{(0)}(r) \to \sin(kr - \tfrac{1}{2}L\pi + \theta)/[k \sin(\theta - \eta^D)] .$$

Then the Wronskians are given by

$$u_{11}^{(0)} w_{11}^{(0)\prime} - u_{11}^{(0)\prime} w_{11}^{(0)} = -1 ,$$
$$u_{22}^{(0)} w_{22}^{(0)\prime} - u_{22}^{(0)\prime} w_{22}^{(0)} = -1 .$$

The Green's functions g_1 and g_2 are given by

$$g_1(r,r') = -(2m/\hbar^2) u_{11}^{(0)}(r_<) w_{11}^{(0)}(r_>)$$
$$g_2(r,r') = -(2m/\hbar^2) u_{22}^{(0)}(r_<) w_{22}^{(0)}(r_>)$$

such that $D_1 g_1 = -\delta$, and g_2 agrees with (6.1). It is convenient to (uniquely) define $\mathbf{u}$ and $\mathbf{w}$ by

$$\mathbf{u} = \mathbf{u}^{(0)} + \mathbf{g}^{(0)} \mathbf{V} \mathbf{u} , \quad \mathbf{w} = \mathbf{w}^{(0)} + \mathbf{g}^{(0)} \mathbf{V} \mathbf{w} .$$

Since $\mathbf{M}$ is symmetric, the Wronskian

$$W[\alpha_1, \alpha_2] \equiv \alpha_1^T \alpha_2' - \alpha_1'^T \alpha_2$$

of any two matrix solutions α_1 and α_2 of $\mathbf{M}\alpha=0$ is a constant matrix. Due to the boundary conditions on $\mathbf{u}$ and $\mathbf{w}$ as specified in terms of $u_{11}^{(0)}$, $w_{11}^{(0)}$, $u_{22}^{(0)}$, and $w_{22}^{(0)}$, we have

$$W[\mathbf{u},\mathbf{u}]=0 , \quad W[\mathbf{w},\mathbf{w}]=0 . \quad (6.6)$$

The constant matrix $\mathbf{K}$ is defined by $W[\mathbf{u},\mathbf{w}] = -\mathbf{K}$. We define $\mathbf{v} = \mathbf{w}\mathbf{K}^{-1}$, so that $W[\mathbf{u},\mathbf{v}] = -\mathbf{1}$ and $\mathbf{M}\mathbf{v}=0$, where $\mathbf{K}^{-1}$ exists if the set $\mathbf{u}$ and $\mathbf{w}$ are linearly independent. $\mathbf{v}$ has the same boundary conditions as $\mathbf{w}$. The g and z are then given by

$$g = -(2m/\hbar^2)[u_{11}(r_<)v_{11}(r_>) + u_{12}(r_<)v_{12}(r_>)]$$
$$z = -(2m/\hbar^2) \begin{cases} u_{21}(r)v_{11}(r') + u_{22}(r)v_{12}(r') , & r < r' \\ v_{21}(r)u_{11}(r') + v_{22}(r)u_{12}(r') , & r > r' . \end{cases}$$

That g and z satisfy the coupled equations for $r<r'$ and $r>r'$ follows trivially from (6.5), and they have the proper boundary conditions by construction. We will now show that $(\hbar^2/2m)g$ has a unit discontinuity in its first derivative, and that z and z' are smooth at $r=r'$. [The conditions on z and z' follow from the second equation in (6.4).] Following Newton, we consider a solution λ of $\mathbf{M}\lambda=0$ with the 8 boundary conditions

$$\lambda(r=r_0)=0 , \quad \lambda'(r=r_0)=1 , \quad (6.7)$$

for an arbitrary r_0. Then λ can be written as $\lambda = \mathbf{u}\mathbf{a} + \mathbf{v}\mathbf{b}$, where $\mathbf{a}$ and $\mathbf{b}$ are constant matrices to be determined by the boundary conditions on λ. Evaluating the Wronskians at $r=r_0$, using (6.6) and (6.7), we find

$$W[\mathbf{u},\lambda] = -\mathbf{b} = \mathbf{u}^T(r_0) , \quad W[\mathbf{v},\lambda] = \mathbf{a} = \mathbf{v}^T(r_0) ,$$

so that

$$\lambda(r) = \mathbf{u}(r)\mathbf{v}^T(r_0) - \mathbf{v}(r)\mathbf{u}^T(r_0) .$$

Setting $r=r_0$, it follows from (6.7) that

$$\mathbf{u}\mathbf{v}^T - \mathbf{v}\mathbf{u}^T = 0 , \quad \mathbf{u}'\mathbf{v}^T - \mathbf{v}'\mathbf{u}^T = 1 , \quad (6.8)$$

since r_0 is arbitrary. Due to antisymmetry the first equation in (6.8) gives only one relation, which corresponds to the continuity of z at $r=r'$. The second equation gives 4 relations, of which only 3 are independent of the first equation, which include the smoothness of z' and the proper jump condition on g' at $r=r'$.

The noniterative determination of g for a potential containing two nonlocal components, one separable and the other a Green's function, can be considered an extension of the techniques used by Yamanouchi, Percival, and Marriot for the noniterative determination of a wave function for such nonlocal interactions. G^P could in fact have been obtained somewhat more directly by first rewriting (1.1) in the form of coupled

equations, analogous to (6.4), and then considering the regular and irregular wave function solutions of the coupled homogeneous equations.

For the case of $L=0$, $\epsilon=-1$, the second term in the right-hand side (rhs) of (6.2) can be shown to cancel the effect of the first term in the rhs of (6.1). Thus one obtains g by simply dropping the $(E-2E_{T0})rr'$ term in g_2 and the $(E-2E_{T0})r$ term in $w_{22}{}^{(0)}$, and also dropping the second term in the rhs of (6.2).

One of us (L.S.) would like to express his warm thanks to Dr. Mittleman for his original suggestion that the equation for g could be decoupled, so that it should be possible to write g as a sum of products, and for some helpful comments.

Collision Spectroscopy. I. Analysis of the Scattering of He⁺ by Ne and Ar†

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Experimental data on the differential scattering of He⁺ by Ne and Ar in the energy range from 10 eV to 100 keV are plotted in a reduced coordinate system suggested by a scaling law for the forward scattering. The resulting curves are used to determine the interaction potential. The repulsive interaction dominating at higher energies shows pronounced shell-structure effects, leading to the deduction of the screening constants for the L and M shells of Ar and for the K and L shells of Ne. At lower energies a polarization attraction appears, allowing deduction of the polarizabilities of Ne and Ar. A simple analytic potential is constructed, including a polarizability term appropriately damped inside the outer shell, which fits the data over the entire range. In addition to the pure elastic scattering, effects of inelastic interactions are diagnosed. A prominent curve crossing is located and the scattering pattern arising from it is interpreted by a semi-classical theory. In collisions with closer encounters, a different type of inelastic process appears which apparently involves a more intense coupling than the curve crossing and which appears to open up a number of competing inelastic channels.

I. INTRODUCTION

THE connection between the electronic states of a diatomic system and its collision properties is best studied in differential scattering where the large amount of available information provides a stringent test of our theoretical understanding. Such experiments are now producing a growing mass of data of spectroscopic quality which deserve detailed interpretation. These data can be used to test predictions derived from prior theoretical knowledge about the electronic states of the system, but it is also possible to deduce a great deal of information about these states empirically from an analysis of the scattering spectra. It is to such an analysis that this paper is devoted.

Symmetric systems provide the most information because of the structure in the interference patterns that arise in them. For example, in the system He⁺+He, oscillations appear in the elastic scattering pattern due both to electronic symmetry (g and u states) and nuclear symmetry.[1] These oscillations can be used to deduce detailed empirical information about potentials for the states involved. Similarly, in Ne⁺+Ne, Jones[2] has observed an additional symmetry effect due to participation of II as well as Σ states in the scattering. Most theoretical information on the potentials is available for symmetric systems with 4 or fewer elec-

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[2] P. R. Jones, T. L. Batra, and H. A. Ranga, Phys. Rev. Letters **17**, 281 (1966).