sample despite the presence of 67 atomic percent of silicon, the ideal resistivity at the ice-point, about 13.9 micro-ohm cm , being comparable with that of pure metallic elements. The resistivity was constant between $4.2^{\circ}$ and $1.5^{\circ} \mathrm{K}$ at about 16 percent of the ice-point value, which in comparison with corresponding data on solid solution alloys suggests that the deviation from stoichiometric composition was probably less than 1 percent.

The enlarged portion of Fig. 4 indicates that in zero field quite a sharp superconducting transition was observed at $1.455^{\circ} \mathrm{K}$. The curves for restoration of resistance by a magnetic field at temperatures below the transition point were also studied and as shown in Fig. 5 were found to be of a rather gradual type. However, a plot of the field at which the first trace of resistance was restored against $T^{2}$ (cross points, Fig. 2) gave a straight line parallel to the critical field line obtained from induction measurements. Thus, allowing for the fact that the transition temperature of the electrical resistivity specimen $\left(1.455^{\circ}\right)$ is slightly higher than that of the magnetic specimen $\left(1.432^{\circ} \mathrm{K}\right)$, the
field at which resistance begins to be restored is probably quite close to the thermodynamic critical field in the present case.

## CONCLUSION

Cobalt disilicide crystallizes in the calcium fluoride structure, in which, to our knowledge, no other superconducting compound has previously been found. Although this structure is usually regarded as typical for ionic compounds, ${ }^{4}$ the present work indicates a clear exception in the case of $\mathrm{CoSi}_{2}$. It remains to be seen whether similar exceptions are provided by other isomorphous intermetallic compounds such as $\mathrm{NiSi}_{2}$ and $\mathrm{AuAl}_{2}$, but it may be remarked for the present that neither of these compounds showed magnetic evidence of superconductivity down to $1.1^{\circ} \mathrm{K}$.

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[^0]
# Variational Principles for Three-Body Scattering Problems* 

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Several stationary expressions for the direct and the exchange scattered amplitudes in three-body collisions are derived.

## I. INTRODUCTION

THREE-BODY scattering problems have been solved approximately either by a Born approximation ${ }^{1}$ or by variational methods involving a differential operator. ${ }^{2}$ We shall discuss here several generalizations for three-body problems of the variational principle proposed by Schwinger ${ }^{3}$ for two-body problems.

Important prototypes of three-body scattering problems are those involving the scattering of electrons by

[^1]hydrogen atoms and the scattering of neutrons by deuterons. In both these cases the indistinguishability of the scattered particle and one of the scatterers creates some special difficulties due to the symmetry conditions imposed on the solution by the Pauli principle. In this paper we shall assume that two of the particles are identical and that exchange effects are consequently important.
In Sec. II of this paper we formulate the problem and indicate how a knowledge of the direct and exchange scattered amplitude enables us to satisfy the Pauli principle without explicitly working with symmetrical or antisymmetrical wave functions. In Sec. III we derive a stationary expression for the direct scattered amplitude, and in Sec. IV we derive a stationary expression for the exchange scattered amplitude.

Finally, we derive in Sec. V still another stationary expression for the scattered amplitudes which is more likely to converge to the correct solution when the trial field is the iterated unperturbed field.

## II. GENERAL CONSIDERATIONS

In the problem which we treat, particle 1 is incident on a system consisting of particles 2 and 3 bound in their lowest state. The scattering cross section for this process can be found by considering the solution of the following Schrödinger equation with suitable boundary conditions:

$$
\begin{align*}
&\left\{\nabla_{1}^{2}+\nabla_{2}^{2}+2\left[E-v\left(r_{1}\right)\right.\right. \\
&\left.\left.-v\left(r_{2}\right)-V\left(r_{12}\right)\right]\right\} \Psi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=0 . \tag{1}
\end{align*}
$$

In setting down this equation we have chosen $m_{1}=m_{2}$ $=\hbar=1$ and $m_{3}=\infty . \mathbf{r}_{1}$ and $\mathbf{r}_{2}$ are the position vectors of particles 1 and 2 with respect to the origin of coordinates, which is the position of particle 3. $r_{12}$ is the distance between particles 1 and 2. $E$ is the total energy of the system and the $V$ 's are the potentials between the particles. The results in all but the last section of this paper can be generalized in a useful way to $m_{3}$ finite by introducing the following change of variables in the Schrödinger equation,

$$
\begin{align*}
\rho & =\mathbf{r}_{2}-\mathbf{r}_{3} \\
R & =\mathbf{r}_{1}-\left[\left(m_{2} \mathbf{r}_{2}+m_{3} \mathbf{r}_{3}\right) /\left(m_{2}+m_{3}\right)\right]  \tag{2}\\
P & =\left(m_{1} \mathbf{r}_{1}+m_{2} \mathbf{r}_{2}+m_{3} \mathbf{r}_{3}\right) /\left(m_{1}+m_{2}+m_{3}\right)
\end{align*}
$$

and eliminating the coordinates of the center of mass.
We can now best specify the appropriate boundary conditions for the solution $\Psi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$ by separating off the incident wave. If we let $\phi_{0}\left(\mathbf{r}_{2}\right)$ describe the bound state of particles 2 and 3 , then we may write

$$
\begin{equation*}
\Psi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\exp \left(i k_{0} \mathbf{n}_{0} \cdot \mathbf{r}_{1}\right) \phi_{0}\left(\mathbf{r}_{2}\right)+\psi\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) . \tag{3}
\end{equation*}
$$

Here $n_{0}$ is the direction and $k_{0}=\left(E-\epsilon_{0}\right)^{\frac{1}{2}}$ the wave number of the incident particle; $\epsilon_{0}$ is the binding energy of particles 2 and $3 . \psi\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$, the scattered part of the solution, should be regular everywhere, and should behave either like an outgoing wave or a decreasing exponential as $r_{1}$ (or $r_{2}$ ) goes to infinity. A simple means for choosing the correct function $\psi\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$ is to assume that the energy $E$ has a small imaginary part and then to require that $\psi\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$ vanish exponentially as either $r_{1}$ and/or $r_{2}$ goes to infinity.

The boundary conditions on $\Psi_{0}$ are, therefore, that

$$
\operatorname{Lim}_{r_{1} \rightarrow \infty} \Psi_{0}=\exp \left(i k_{0} \mathbf{n}_{0} \cdot \mathbf{r}_{1}\right) \phi_{0}\left(\mathbf{r}_{2}\right)
$$

$$
\begin{equation*}
+\left(\sum_{n}+\int\right) f_{n}(\theta, \phi) \frac{\exp \left(i k_{n} r_{1}\right)}{r_{1}} \boldsymbol{\phi}_{n}\left(\mathbf{r}_{2}\right) \tag{4a}
\end{equation*}
$$

$\operatorname{Lim}_{r_{2} \rightarrow \infty} \Psi_{0}=\left(\sum_{n}+\int\right) g_{n}(\theta, \phi) \frac{\exp \left(i k_{n} r_{2}\right)}{r_{2}} \phi_{n}\left(\mathbf{r}_{1}\right)$.
In Eq. (4) $\phi_{n}(\mathbf{r})$ are the eigenstates, with energy $\epsilon_{n}$, of the Hamiltonian

$$
\begin{equation*}
h=\nabla^{2}+2[\epsilon-v(r)] . \tag{5}
\end{equation*}
$$

$k_{n}{ }^{2}=E-\epsilon_{n}$, and the symbol $\left(\sum_{n}+\boldsymbol{J}\right)$ signifies a summation over discrete states and an integration over the
continuum states. By analogy with the three-dimensional wave equation, and from physical considerations, it is presumed but has never been proven that Eq. (1) with the boundary conditions (4) specifies a unique solution $\Psi_{0}$. The coefficients $f_{n}$ and $g_{n}$ for those terms in (4) for which $k_{n}$ is not imaginary, are called the scattered amplitudes for direct and exchange scattering.

A knowledge of $f_{n}$ and $g_{n}$ enables one to determine the effect of the Pauli principle on the cross section. ${ }^{4}$ A solution $\Psi_{0}{ }^{\prime}$ of (1) which satisfies this principle and the physical boundary conditions can be constructed from $\Psi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$ as follows:

$$
\begin{equation*}
\Psi_{0}{ }^{\prime}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\Psi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \pm \Psi_{0}\left(\mathbf{r}_{2}, \mathbf{r}_{1}\right) \tag{6}
\end{equation*}
$$

where the plus sign is taken for the antisymmetric spin state and the minus sign for the symmetric spin state. The scattering cross section for an unpolarized incident beam is given by

$$
\begin{equation*}
\sigma_{n}=\frac{k_{n}}{k_{0}}\left(w_{a}\left|f_{n}+g_{n}\right|^{2}+w_{s}\left|f_{n}-g_{n}\right|^{2}\right), \tag{7}
\end{equation*}
$$

where $w_{a}$ and $w_{s}$ are statistical weight factors for the antisymmetric and symmetric spin states, respectively.

## III. DIRECT SCATTERING

The first step in formulating a Schwinger variational principle is to replace Eq. (1) by an integral equation which includes the boundary conditions. For the case of direct scattering we consider

$$
\begin{equation*}
\zeta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=2\left[v\left(r_{1}\right)+V\left(r_{12}\right)\right] \tag{8}
\end{equation*}
$$

as a perturbation and introduce the Green's function for the operator

$$
\begin{equation*}
H_{0}=\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}+2\left[E-v\left(r_{2}\right)\right] ; \tag{9}
\end{equation*}
$$

this Green's function satisfies the equation

$$
\begin{equation*}
H_{0} G=-\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}{ }^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right) . \tag{10}
\end{equation*}
$$

A convenient representation of $G$ is

$$
\begin{align*}
& G\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
& \quad=\left(\sum_{n}+\int\right) \phi_{n}\left(\mathbf{r}_{2}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{2}{ }^{\prime}\right) \frac{\exp \left(i k_{n}\left|\mathbf{r}_{1}-\mathbf{r}_{1}{ }^{\prime}\right|\right)}{4 \pi\left|\mathbf{r}_{1}-\mathbf{r}_{1}{ }^{\prime}\right|} \tag{11}
\end{align*}
$$

In terms of $G$ the solution $\psi_{0}$ of Eq. (1) can be written as
$\Psi_{0}=\Phi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)-\int G\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)$
$\times \zeta\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \Psi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime}$.
In Eq. (12)

$$
\begin{equation*}
\Phi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\exp \left(i k_{0} \mathbf{n}_{0} \cdot \mathbf{r}_{1}\right) \phi_{0}\left(\mathbf{r}_{2}\right) \tag{12}
\end{equation*}
$$

The scattered amplitude $f_{n}$ can be found by taking the limit of the right-hand side of (12) as $r_{1} \rightarrow \infty$; this gives

[^2]the following result:
\[

$$
\begin{align*}
& f_{n}=-\frac{1}{4 \pi} \int \exp \left(-i k_{n} \mathbf{n} \cdot \mathbf{r}_{1}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{2}\right) \\
&  \tag{14}\\
& \times \zeta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \Psi_{0}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) d \mathbf{r}_{1} d \mathbf{r}_{2} .
\end{align*}
$$
\]

The Born approximation consists of replacing $\Psi_{0}$ in (14) by the unperturbed wave $\Phi_{0}$.

Starting with an integral equation it is a simple matter to write down a Schwinger variational principle. The usual algebraic complexities are simplified by first expressing this principle in operator form.

If $K$ is a self-adjoint operator and if in the domain of $K, x$ and $y$ are vectors which satisfy the equations

$$
\begin{align*}
& K x=a,  \tag{15a}\\
& K y=b, \tag{15b}
\end{align*}
$$

where $a$ and $b$ are vectors, then the expression

$$
\begin{equation*}
(y, K x) /(b, x)(y, a)=1 /(b, x) \tag{16}
\end{equation*}
$$

is stationary ${ }^{5}$ with respect to arbitrary variations of $x$ and $y$. The symbol ( $\alpha, \beta$ ) in Eq. (16) represents the inner products $\int \alpha^{*} \beta d \mathbf{r}$. The reciprocity condition is given by

$$
\begin{equation*}
(b, x)=(y, a) \tag{17}
\end{equation*}
$$

and is a consequece of the fact that $K$ is self-adjoint.
Our integral Eq. (12) corresponds to (15a), if we replace the abstract quantities in the latter according to the scheme

$$
\begin{align*}
& K \rightarrow \int d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}\left[\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right) \zeta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right)\right. \\
& \quad x \rightarrow \Psi_{0}\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right),  \tag{18}\\
& \left.a\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) G\left(\mathbf{r}_{1} \mathbf{r}_{2} ; \mathbf{r}_{1}^{\prime} \mathbf{r}_{2}^{\prime}\right) \zeta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right)\right] \\
&
\end{align*}
$$

For the equation corresponding to (15b) we choose
$\Psi_{n}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\Phi_{n}\left(\mathbf{r}_{1} \mathbf{r}_{2}\right)-\int G\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)$

$$
\begin{equation*}
\left.\times \zeta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) \Psi_{n}\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}\right) \tag{19}
\end{equation*}
$$

with

$$
\begin{equation*}
\Phi_{n}=\exp \left(i k_{n} \mathbf{n} \cdot \mathbf{r}_{1}\right) \phi_{n}\left(\mathbf{r}_{2}\right) \tag{20}
\end{equation*}
$$

Thus,

$$
\begin{align*}
& y \rightarrow \Psi_{n}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
& b \rightarrow \zeta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \Phi_{n}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \tag{21}
\end{align*}
$$

With the substitutions (18) and (21), Eq. (16) gives us a stationary expression for $-1 / 4 \pi f_{n}$.

## IV. EXCHANGE SCATTERING

In order to obtain the exchange scattered amplitude we consider

$$
\begin{equation*}
\eta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=2\left[v\left(r_{2}\right)+V\left(r_{12}\right)\right] \tag{22}
\end{equation*}
$$

[^3]as a perturbation and introduce the Green's function for the operator
\[

$$
\begin{equation*}
H_{0}^{\prime}=\nabla_{1}^{2}+\nabla_{2}^{2}+2\left[E-v\left(r_{1}\right)\right] ; \tag{23}
\end{equation*}
$$

\]

this Green's function satisfies the equation

$$
\begin{equation*}
H_{0}^{\prime} \mathcal{G}=-\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}^{\prime}\right) \tag{24}
\end{equation*}
$$

A convenient representation of $\mathcal{G}$ is

$$
\begin{align*}
& \mathcal{G}\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
& \quad=+\left(\sum_{n}+\int\right) \phi_{n}\left(\mathbf{r}_{1}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{1}{ }^{\prime}\right) \exp \frac{i k_{n}\left|\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right|}{4 \pi\left|\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right|} \tag{25}
\end{align*}
$$

The complication in this formulation is that the incident wave does not satisfy the equation

$$
\begin{equation*}
H_{0}{ }^{\prime} \Phi_{0}=0 . \tag{26}
\end{equation*}
$$

It is now most convenient to use the decomposition given by Eq. (3) to obtain the following integral equation for the scattered wave:

$$
\begin{align*}
& \psi\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \\
&=-\int \mathcal{G}\left(\mathbf{r}_{1} \mathbf{r}_{2} ; \mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \eta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \psi\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}^{\prime}  \tag{27}\\
&-\int \mathcal{G}\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \zeta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \Phi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime} .
\end{align*}
$$

The exchange scattered amplitude is found by taking the limit of the right-hand side of (27) as $r_{2} \rightarrow \infty$; this gives the following result:

$$
g_{n}=g_{n}{ }^{\prime}+b
$$

where

$$
\begin{aligned}
& g_{n}{ }^{\prime}=-\frac{1}{4 \pi} \int \exp \left(-i k_{n} \mathbf{n} \cdot \mathbf{r}_{2}{ }^{\prime}\right) \phi_{n}\left(\mathbf{r}_{1}{ }^{\prime}\right) \eta\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
& \times \psi\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime}=-\frac{1}{4 \pi} \int \Phi_{n}\left(\mathbf{r}_{2}{ }^{\prime}, \mathbf{r}_{1}{ }^{\prime}\right) \\
& \times \eta\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \psi\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime}, \\
& b=-\frac{1}{4 \pi} \int \exp \left(-i k_{n} \mathbf{n} \cdot \mathbf{r}_{2}{ }^{\prime}\right) \phi_{n}\left(\mathbf{r}_{1}{ }^{\prime}\right) \zeta\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
& \left.\times \exp \left(i k_{0} \mathbf{n}_{0} \cdot \mathbf{r}_{1}{ }^{\prime}\right) \phi_{0}\left(\mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime}\right)=-\frac{1}{4 \pi} \int \Phi_{n}\left(\mathbf{r}_{2}{ }^{\prime}, \mathbf{r}_{1}{ }^{\prime}\right) \\
& \\
& \\
& \times\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \Phi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime} .
\end{aligned}
$$

The Born approximation involves setting $\psi \equiv 0$ in (29) and thus gives $g_{n}=b$.

Our result for $g_{n}$ in the Born approximation does not agree with that given by Mott and Massey, ${ }^{6}$ namely,

$$
-\frac{1}{4 \pi} \int \Phi_{n}\left(\mathbf{r}_{2}^{\prime}, \mathbf{r}_{1}^{\prime}\right) \eta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) \Phi_{0}\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}
$$

[^4]The two results are equivalent ${ }^{7}$ when $\phi_{n}$ corresponds to a bound state, since their difference,

$$
\int \Phi_{n}^{*}\left(\mathbf{r}_{2}^{\prime}, \mathbf{r}_{1}^{\prime}\right)\left[v\left(r_{1}^{\prime}\right)-v\left(r_{2}^{\prime}\right)\right] \Phi_{0}\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}
$$

can be shown to be equal to zero as follows: Since $H_{0}{ }^{\prime} \Phi_{n}{ }^{*}\left(\mathbf{r}_{2}, \mathbf{r}_{1}\right)$ $=0$, replace $v\left(r_{1}{ }^{\prime}\right) \Phi_{n}{ }^{*}\left(\mathbf{r}_{2}{ }^{\prime}, \mathbf{r}_{1}{ }^{\prime}\right)$ by $\frac{1}{2}\left\{\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}+2 E\right\} \Phi_{n}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)$. Similarly replace $v\left(r_{2}{ }^{\prime}\right) \Phi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)$ by $\frac{1}{2}\left\{\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}+2 E\right\} \Phi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)$ Then integrate by parts.
However, when $\phi_{n}$ is in the continuum, the result of Mott and Massey in the Born approximation diverges, whereas Eq. (29) does not. The procedure that Mott and Massey use is open to question since they expand the entire solution including the incident wave in terms of the orthonormal set $\phi_{n}\left(\mathbf{r}_{1}\right)$. This procedure is not valid, as is shown in the Appendix.

We now proceed as in Sec. III to formulate a stationary expression for $g_{n}{ }^{\prime}$. Equation (27) corresponds to (15a) with

$$
\begin{align*}
& K \rightarrow \int d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}\left[\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right) \eta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)\right. \\
& \left.x \rightarrow \psi, \quad+\eta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \mathcal{S}\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) \eta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right)\right]  \tag{30}\\
& a \rightarrow-\eta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) \\
& \\
& \quad \times \int \mathcal{S}\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) \zeta\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) \Phi_{0}\left(\mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}^{\prime}\right) d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}
\end{align*}
$$

For the equation corresponding to (15b) we choose

$$
\begin{align*}
\chi_{n}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)=\Phi_{n}\left(\mathbf{r}_{2}, \mathbf{r}_{1}\right) & -\int \mathcal{S}\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
& \times \eta\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \chi_{n}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime} . \tag{31}
\end{align*}
$$

Thus

$$
\begin{align*}
& y \rightarrow \chi_{n}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)  \tag{32}\\
& b \rightarrow \Phi_{n}\left(\mathbf{r}_{2}, \mathbf{r}_{1}\right) \eta\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right) .
\end{align*}
$$

With the substitutions (30) and (32), Eq. (16) gives us a stationary expression for $-1 / 4 \pi g_{n}{ }^{\prime}$. A similar variational expression could be derived for $-1 / 4 \pi f_{n}$.

## V. OTHER FORMULATIONS

While the expressions corresponding to Eq. (16) with the replacements discussed in Secs. III and IV are stationary, their utility frequently depends to a large extent on whether or not one can use the unperturbed field as a trial function. There is some question as to whether the expressions derived in Secs. III and IV converge upon successive iterations of the unperturbed field. This applies especially to the case of exchange scattering. ${ }^{8}$ In order to avoid this difficulty it might be useful to formulate additional stationary expressions for the scattered amplitude such that the use of the unperturbed field in their evaluation would be the first step in a converging process.

To do this we consider $2 V\left(r_{12}\right)$ of Eq. (1) as a perturbation. This step restricts the usefulness of the pro-

[^5]cedure to the situation in which one of the particles of the system has an infinite mass. Otherwise the unperturbed problem would be a true three-body problem and the Green's function for the unperturbed operator would in general be unobtainable.

Following the procedure of Sec. IV we introduce the Green's function corresponding to the operator

$$
\begin{equation*}
H_{0}{ }^{\prime \prime}=\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}+2\left[E-v\left(r_{1}\right)-v\left(r_{2}\right)\right] ; \tag{33}
\end{equation*}
$$

this function is given by

$$
\begin{align*}
& \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) \\
&=\left(\sum_{n}+\int\right) \phi_{n}\left(\mathbf{r}_{1}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{1}{ }^{\prime}\right) \gamma_{n}\left(\mathbf{r}_{2}, \mathbf{r}_{2}{ }^{\prime}\right)  \tag{34a}\\
&=\left(\sum_{n}+\int\right) \phi_{n}\left(\mathbf{r}_{2}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{2}{ }^{\prime}\right) \gamma_{n}\left(\mathbf{r}_{1}, \mathbf{r}_{1}{ }^{\prime}\right) \tag{34b}
\end{align*}
$$

In Eqs. (34a) and (34b) $\gamma_{n}\left(r, r^{\prime}\right)$ is the Green's function for the operator

$$
\begin{equation*}
h_{n}=\nabla^{2}+2\left[E-\epsilon_{n}-v(r)\right] . \tag{35}
\end{equation*}
$$

We shall use Eq. (34a) to investigate the asymptotic behavior of the solution when $r_{2} \rightarrow \infty$ : when $r_{1} \rightarrow \infty$ we shall use (34b).
The solution of Eq. (1) satisfying the boundary conditions is

$$
\begin{align*}
& \Psi_{0}=\phi_{i}\left(\mathbf{r}_{1}\right) \phi_{0}\left(\mathbf{r}_{2}\right)-2 \int \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) V\left(r_{12}{ }^{\prime}\right) \\
& \times \Psi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime} . \tag{36}
\end{align*}
$$

In Eq. (36), $\phi_{i}\left(\mathbf{r}_{1}\right)$ is a solution of the equation $h_{0} \phi_{i}(\mathbf{r})=0$ which at infinity describes an incoming wave approaching the origin along the direction $\mathbf{n}_{0}$.

The scattered amplitudes can be found from the asymptotic forms of the Green's function ${ }^{9}$ :

$$
\begin{align*}
\operatorname{Lim}_{r_{2} \rightarrow \infty} \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)= & -\left(\sum_{n}+\int\right) \phi_{n}\left(\mathbf{r}_{1}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{1}{ }^{\prime}\right) \\
& \times \frac{\exp \left(i k_{n} r_{2}\right)}{4 \pi r_{2}} F_{n}\left(\mathbf{r}_{2}{ }^{\prime}, \pi-\Theta\right)  \tag{37a}\\
\operatorname{Lim}_{r_{1} \rightarrow \infty} \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right)= & -\left(\sum_{n}+\int\right) \phi_{n}\left(\mathbf{r}_{2}\right) \phi_{n}{ }^{*}\left(\mathbf{r}_{2}{ }^{\prime}\right) \\
& \times \frac{\exp \left(i k_{n} r_{1}\right)}{4 \pi r_{1}} F_{n}\left(\mathbf{r}_{1}{ }^{\prime}, \pi-\Phi\right) \tag{37b}
\end{align*}
$$

In Eqs. (37), $F_{n}$ is a solution of the equation

$$
\begin{equation*}
h_{n} F_{n}=0, \tag{38}
\end{equation*}
$$

[^6]which at infinity represents a wave approaching the origin at an angle of $\pi-\Theta$ (or $\pi-\Phi$ ) with the $z$ axis; $\Theta(\Phi)$ is the angle between $\mathbf{r}_{2}$ and $\mathbf{r}_{2}{ }^{\prime}\left(\mathbf{r}_{1}\right.$ and $\left.\mathbf{r}_{1}{ }^{\prime}\right)$.

From Eq. (37a) and (37b) one can immediately write down the amplitudes for direct and exchange scattering:
$\alpha_{n}=-\frac{1}{2 \pi} \int \phi_{n}{ }^{*}\left(\mathbf{r}_{2}{ }^{\prime}\right) F_{n}\left(\mathbf{r}_{1}{ }^{\prime} ; \pi-\Phi\right) V\left(r_{12}{ }^{\prime}\right)$ $\times \Phi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime}$,
and

$$
\begin{align*}
& \beta_{n}=-\frac{1}{2 \pi} \int \phi_{n}{ }^{*}\left(\mathbf{r}_{1}{ }^{\prime}\right) F_{n}\left(\mathbf{r}_{2}{ }^{\prime}, \pi-\Theta\right) V\left(r_{12}{ }^{\prime}\right)  \tag{39}\\
& \times \Phi_{0}\left(\mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime} . \tag{40}
\end{align*}
$$

Equations (39) and (40) give correctly the inelastically scattered amplitudes as well as the elastically scattered exchange amplitude. To determine the direct elastically scattered amplitude ${ }^{\prime} f_{0}$ it is necessary to add to $\alpha_{0}$ the coefficient of the outgoing spherical wave contained in $\phi_{i}(\mathbf{r})$ as $r \rightarrow \infty$.

In formulating the stationary expression we shall again require, as in Secs. III and IV a solution of Eq. (1) satisfying different boundary conditions. The solution whose inhomogeneous term is $F_{n}{ }^{*}\left(\mathbf{r}_{1}{ }^{\prime}, \pi-\Phi\right) \phi_{n}\left(r_{2}\right)$ will be designated by $\Psi_{n}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$, and the solution whose inhomogeneous term is $F_{n}{ }^{*}\left(\mathbf{r}_{2}, \pi-\Theta\right) \phi_{n}\left(r_{1}\right)$ will be designated by $\lambda_{n}\left(\mathbf{r}_{1}, \mathbf{r}_{2}\right)$.
A stationary expression for $-1 / 4 \pi \alpha_{n}$ can be found using Eq. (16) with the following replacements:

$$
\begin{gather*}
K \rightarrow \int d \mathbf{r}_{1}{ }^{\prime} d \mathbf{r}_{2}{ }^{\prime}\left[\delta\left(\mathbf{r}_{1}-\mathbf{r}_{1}{ }^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right) 2 V\left(r_{12}\right)\right. \\
\left.+4 V\left(r_{12}\right) \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}{ }^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) V\left(r_{12}{ }^{\prime}\right)\right] \\
x \rightarrow \Psi_{0}, \quad y \rightarrow \Psi_{n},  \tag{41}\\
a \rightarrow \phi_{i}\left(\mathbf{r}_{1}\right) \phi_{0}\left(\mathbf{r}_{2}\right), \quad b \rightarrow F_{n}{ }^{*}\left(\mathbf{r}_{1}, \pi-\Phi\right) \phi_{n}\left(\mathbf{r}_{2}\right)
\end{gather*}
$$

Similarly one can find the stationary expression for $-1 / 4 \pi \beta_{n}$ as follows:

$$
\begin{gathered}
K \rightarrow \int d \mathbf{r}_{1}^{\prime} d \mathbf{r}_{2}^{\prime}\left[\delta\left(\mathbf{r}_{1}-\mathbf{r}_{2}{ }^{\prime}\right) \delta\left(\mathbf{r}_{2}-\mathbf{r}_{2}{ }^{\prime}\right) 2 V\left(r_{12}\right)\right. \\
\left.+4 V\left(r_{12}\right) \Gamma\left(\mathbf{r}_{1}, \mathbf{r}_{2} ; \mathbf{r}_{1}^{\prime}, \mathbf{r}_{2}{ }^{\prime}\right) V\left(r_{12}{ }^{\prime}\right)\right] \\
x \rightarrow \Psi_{0}, \quad y \rightarrow \lambda_{n} \\
a \rightarrow \phi_{i}\left(\mathbf{r}_{1}\right) \phi_{0}\left(\mathbf{r}_{2}\right), \quad b \rightarrow F_{n}{ }^{*}\left(\mathbf{r}_{2}, \pi-\Phi\right) \phi_{n}\left(\mathbf{r}_{1}\right) \\
\text { APPENDIX }
\end{gathered}
$$

We shall show that when a plane wave $\exp \left(i k_{0} r \cos \theta\right)$ is expanded in terms of a complete set of eigenfunctions
of the Hamiltonian the expansion coefficients must contain singularities such as $\delta$ functions. If we assume that the Hamiltonian is spherically symmetric, it will be sufficient to consider the expansion of $\sin \left(k_{0} r\right)$ in terms of the eigenfunctions of the ordinary differential operator

$$
\begin{equation*}
-d^{2} / d r^{2}+V(r) \tag{A.1}
\end{equation*}
$$

Let $u_{n}(r)$ be the discrete eigenfunctions and $\phi(r, k)$ be the continuum eigenfunctions of (A.1); that is

$$
\left[d^{2} / d r^{2}+k^{2}-V(r)\right] \phi(r, k)=0
$$

We have the asymptotic formula $\phi(r, k) \sim \sin (k r+\eta)$, where $\eta$ is the phase shift. Put

$$
\phi(r, k)=\sin (k r+\eta)+w(r, k)
$$

Then $w(r, k)$ will approach zero as $r$ becomes infinite. From the well-known relation,

$$
\sum_{n} u_{n}(r) u_{n}\left(r^{\prime}\right)+\frac{2}{\pi} \int_{0}^{\infty} \phi(r, k) \phi\left(r^{\prime}, k\right) d k=\delta\left(r-r^{\prime}\right)
$$

we get the expansion

$$
\begin{aligned}
\sin k_{0} r=\sum_{n} u_{n}(r) \int_{0}^{\infty} & \sin k_{0} r^{\prime} u_{n}\left(r^{\prime}\right) d r^{\prime} \\
& +\frac{2}{\pi} \int_{0}^{\infty} \phi(r, k) d k \int_{0}^{\infty} \phi\left(r^{\prime}, k\right) \sin k_{0} r^{\prime} d r^{\prime}
\end{aligned}
$$

Now the expansion coefficient in the continuum spectrum is

$$
\begin{array}{r}
\frac{2}{\pi} \int_{0}^{\infty} \sin \left(k_{0} r^{\prime}\right) \phi\left(r^{\prime}, k\right) d r^{\prime}=\frac{2}{\pi} \int_{0}^{\infty} \sin \left(k_{0} r^{\prime}\right) \sin \left(k r^{\prime}+\eta\right) d r^{\prime} \\
+\frac{2}{\pi} \int_{0}^{\infty} \sin \left(k_{0} r^{\prime}\right) w\left(r^{\prime}, k\right) d r^{\prime}
\end{array}
$$

The second term is a well-behaved function of $k$, but for the first term we have

$$
\begin{align*}
& \frac{2}{\pi} \int_{0}^{\infty} \sin \left(k_{0} r^{\prime}\right) \sin \left(k r^{\prime}+\eta\right) d r^{\prime} \\
& =k \cos \eta \frac{\left[\delta\left(k-k_{0}\right)+\delta\left(k+k_{0}\right)\right]}{k}-\frac{2}{\pi} \sin \eta \frac{k}{k^{2}-k_{0}^{2}} \\
& =\cos \eta \delta\left(E-E_{0}\right)-\frac{1}{\pi} \frac{\sin \eta}{E-E_{0}}, \tag{A.2}
\end{align*}
$$

if we put $k^{2}=E, k_{0}{ }^{2}=E_{0}$. This coefficient is singular.


[^0]:    ${ }^{4}$ A. F. Wells, Structural Inorganic Chemistry (Clarendon Press, Oxford, 1945), p. 275.

[^1]:    * This work was performed at Washington Square College of Arts and Science, New York University, and was supported by contract with the U. S. Air Force through sponsorship of the Geophysics Research Division, Air Force Cambridge Research Center, Air Research and Development Command.
    ${ }^{1}$ For a resume of the literature see N. F. Mott and H. S. W. Massey, Theory of Atomic Collisions (Clarendon Press, Oxford, 1949), second edition.
    ${ }^{2}$ W. Kohn, Phys. Rev. 74, 1793 (1948) ; S. S. Huang, Phys. Rev. 76, 477 (1949) ; H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) A205, 483 (1951); M. Verde, Helv. Phys. Acta, 22, 339 (1949) ; A. Troesch and M. Verde, Helv. Phys. Acta 24, 39 (1951).
    ${ }^{3}$ J. Schwinger, hectographed notes on nuclear physics, Harvard University, unpublished.

[^2]:    ${ }^{4}$ Reference 1, Chap. VIII.

[^3]:    ${ }^{5}$ N. Marcuvitz-Sec. III D, Recent Developments in the Theory of Wave Propagation, New York University, Institute for Mathematics and Mechanics (1949).

[^4]:    ${ }^{6}$ Reference 1, Chap. VIII.

[^5]:    ${ }^{7}$ We are indebted to Major G. W. Griffing for this remark.
    ${ }^{8} \mathrm{~W}$. Kohn, private communication.

[^6]:    ${ }^{9}$ Reference 1, Chap. IV. It should be remarked that Eqs. (27), hold only for a $v(r)$ which goes to zero faster than $1 / r$. For the Coulomb field one obtains a logarithmic phase factor in the exponential in the usual way

