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Source theory of molecular interactions

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The application of source theory to elementary collision processes is investigated and assessed. On the basis of causality and space–time uniformity it is shown how to arrive at explicit expressions for the T-matrix elements of a scattering process, and examples based on electron–hydrogen atom scattering processes are presented.

1. INTRODUCTION

Contemporary theories of molecular collision processes depend heavily on the S-matrix formalism, and the development of alternative schemes might seem likely to be unprofitable. In a series of papers and books Schwinger [1–6] has ignored this consideration and has presented a formal alternative, source theory, which is based on the postulates of causality and space–time uniformity. Source theory has been examined in relation to the electromagnetic properties of molecules [7]; in this paper we turn to the consideration of rudimentary types of molecular collisions.

The central idea of source theory is that collision processes may be described in terms of certain functions which have the property of being able to describe the injection of the initial components of a scattering process into a reaction zone or interaction region. The functions are realizations of the *source* of the initial reactants. The products emerging from the collision zone are subsequently detected by a source that now operates as a *sink* for the components. The logical appeal of this formalism is that any species may be considered as being determined by the sum of the collision processes that produce it. The role of the source is described by Schwinger as follows [4, p. 37]: " . . . if a particle is defined by the collisions that create it, the details of a specific reaction are not relevant and one can idealize the role of the other particles in the collision, recognizing that their function is solely to supply the needed balance of properties —they constitute the source for the particle of interest."

In this paper we examine the application of source-theoretical ideas to an 'elementary' problem, the collision between electrons and atomic hydrogen. The e–H system is the simplest three-particle problem in molecular collision theory, yet it contains all the essential ingredients to illustrate the application of the source-theoretical formalism. The major distinction between this treatment of the e–H scattering problem and the quite meagre applications of source theory so far is that we are interested in the non-relativistic domain. Covariant procedures are more elegant, but we are more concerned with chemical applications. Our chief purpose is to illustrate the ideas of source theory, and to arrive

at an assessment of its utility in treating problems of interest in chemical and molecular physics.

2. Essentials of source theory

The source function in coordinate space $S(\mathbf{r}, t)$ is related to the source function in momentum space $S(\mathbf{p}, \omega)$ by Fourier transformation. The source function is proportional to the amplitude $\langle \ldots (S) \ldots \rangle$ of a realizable process through the relations

$$\langle 1\phi_{\mathbf{P}}(S)0_- \rangle = iS(\mathbf{p}, \omega)\sqrt{(d\omega_{\mathbf{P}})}, \tag{2.1}$$

$$\langle 0_+(S)1\phi_{\mathbf{P}} \rangle = iS(-\mathbf{p}, \omega)\sqrt{(d\omega_{\mathbf{P}})}. \tag{2.2}$$

We use $\mathbf{P}$ to denote the four-vector $\{\mathbf{p}, \omega\}$. The subscripts $\pm$ specify the time-ordering of the system's evolution : $|0_-\rangle$ is the vacuum prior to the operation of the source, and $|0_+\rangle$ the vacuum state after its operation. The state $|1\phi_{\mathbf{P}}\rangle$ corresponds to a single particle in some state $\phi_{\mathbf{P}}$ of definite momentum energy, and so $\langle 1\phi_{\mathbf{P}}(S)0_- \rangle$ corresponds to its formation and $\langle 0_+(S)1\phi_{\mathbf{P}} \rangle$ to its annihilation. The square roots on the range $d\omega_{\mathbf{P}}$ ensure that the probability with which the source acts is proportional to $d\omega_{\mathbf{P}}$. The *total source* for the system has the decomposition $S = \sum_{\alpha} (S_\alpha^{(+)} + S_\alpha^{(-)})$, the superposition of all mechanisms (possibly infinite in number) by which the reactants are injected into the collision zone and the outgoing particles detected. We denote S by $\bullet$, the union of all sources $\circ$.

The fundamental quantity of interest is the *vacuum persistence amplitude* (V.P.A.), $\langle 0_+(S)0_- \rangle$. This is related to the action W through

$$\langle 0_+(S)0_- \rangle = \exp\,[iW(S)/\hbar] \tag{2.3}$$

as may be seen from the following.

The matrix element $\langle 0_-|1\phi_{\mathbf{P}} \rangle$ vanishes by orthogonality, but it may also be expressed in terms of source amplitudes as

$$\langle 0_-|1\phi_{\mathbf{P}} \rangle = \langle 0_-(S)0_+ \rangle \langle 0_+(S)1\phi_{\mathbf{P}} \rangle + \sum_{\mathbf{P}'} \langle 0_-(S)1\phi_{\mathbf{P}'} \rangle \langle 1\phi_{\mathbf{P}'}(S)1\phi_{\mathbf{P}} \rangle + \ldots \tag{2.4}$$

with higher terms negligible (weak source restriction). Now regard S as being composed both of $S^{(-)}$ and $S^{(+)}$, the former operating first and behaving as a source, and the latter operating second and as a sink, then the V.P.A. for the composite event is

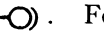
$$\langle 0_+(S^{(-)} + S^{(+)})0_- \rangle = \langle 0_+(S^{(+)})0_- \rangle \langle 0_+(S^{(-)})0_- \rangle + \sum_{\mathbf{P}} \langle 0_+(S^{(+)})1\phi_{\mathbf{P}} \rangle \langle 1\phi_{\mathbf{P}}(S^{(-)})0_- \rangle + \ldots . \tag{2.5}$$

Using the expressions for the single-particle amplitudes, restricting the V.P.A. to weak sources, and imposing the condition that there should be nothing but location in space–time to distinguish various components of a composite source (the principle of space–time uniformity), leads to

$$\langle 0_+(S)0_- \rangle = 1 + \tfrac{1}{2}i \int d\mathbf{R}\, d\mathbf{R}'\, S(\mathbf{R})\Delta(\mathbf{R} - \mathbf{R}')S(\mathbf{R}') \tag{2.6}$$

($\mathbf{R}$ is the four-vector $\{\mathbf{r}, t\}$), with

$$\Delta(\mathbf{R} - \mathbf{R}') = i \int d\omega_{\mathbf{P}} \exp i\mathbf{P} \,.\, (\mathbf{R} - \mathbf{R}'). \tag{2.7}$$

We shall denote Δ by $-\!\!\leftarrow\!\!-$, so that the diagrammatic form of equation (2.6) is $\langle 0_+(S)0_-\rangle = 1 + \frac{1}{2}i$  . For a collection of weak sources the generalization of equation (2.6) is simply the product of individual terms, and if the absence of coupling between sources in different space–time regions is incorporated through

$$\int d\mathbf{R}\, d\mathbf{R}'\, S_\alpha(\mathbf{R})\Delta(\mathbf{R}-\mathbf{R}')S_\beta(\mathbf{R}') = 0 \quad \text{if} \quad \alpha \neq \beta \tag{2.8}$$

we arrive at

$$\langle 0_+(S)0_-\rangle = \exp\left(\tfrac{1}{2}i\right.$$  $$\left.\right) \tag{2.9}$$

where

 $= \int d\mathbf{R}\, d\mathbf{R}'\, S(\mathbf{R})\Delta(\mathbf{R}-\mathbf{R}')S(\mathbf{R}'), \quad S(\mathbf{R}) = \sum_\alpha S_\alpha(\mathbf{R}).$ (2.10)

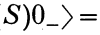
This is of the form that enables $2W/\hbar$ in equation (2.3) to be identified with . Furthermore, the vacuum persistence probability is

$$|\langle 0_+(S)0_-\rangle|^2 = \exp\{-\sum_{\mathbf{p}} |S_{\mathbf{p}}|^2\} \tag{2.11}$$

where $S_{\mathbf{p}} = S(\mathbf{P})\sqrt{(d\omega_{\mathbf{p}})}$. For multi-particle exchange the V.P.A. has the decomposition

$$\langle 0_+(S)0_-\rangle = \sum_n \langle 0_+(S^{(+)})n\rangle \langle n(S^{(-)})0_-\rangle, \tag{2.12}$$

with $S^{(-)}$ preceding $S^{(+)}$, and the connection with single-particle amplitudes is provided by

$$\langle 0_+(S)0_-\rangle = \langle 0_+(S^{(+)})0_-\rangle \exp\left(i\right.$$  $$\left.\right)\langle 0_+(S^{(-)})0_-\rangle, \tag{2.13}$$

where

 $= \int d\mathbf{R}\, d\mathbf{R}'\, S^{(+)}(\mathbf{R})\Delta(\mathbf{R}-\mathbf{R}')S^{(-)}(\mathbf{R}').$ (2.14)

The multi-particle amplitudes may be obtained by direct comparison of equations (2.12) and (2.13).

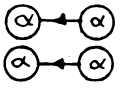
The detailed changes to this general scheme that occur when it is specialized to photon sources is the identification of S with a vector source $\mathbf{J}$. The ramifications were explored in an earlier paper [7]. In the case of electrons, S is identified with the source η, and Δ with the free-electron propagator $G(\mathbf{R}, \mathbf{R}')$ which satisfies

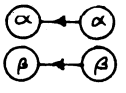
$$(ih\partial_t - p^2/2m)G(\mathbf{r}, t\,;\ \mathbf{r}', t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t'). \tag{2.15}$$

We note that the structure of the theory for electrons dictates that their sources should obey some exterior algebra [4].

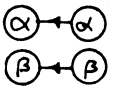
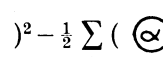
The first step in the calculation of collision cross sections is the reduction of the V.P.A. $\langle 0_+(S)0_-\rangle$ to a suitable form. The expansion of equation (2.3) into $1 + iW(\mathrm{S})/\hbar + (i^2/2!\hbar^2)W(S)^2 + \ldots$ leads to the identification of the following terms :

one-particle terms :  $= \int d\mathbf{R}_1\, d\mathbf{R}_2\, S_\alpha(\mathbf{R}_1)\Delta(\mathbf{R}_1-\mathbf{R}_2)S_\alpha(\mathbf{R}_2)$;

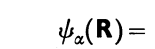
repeated one-particle terms :  ;

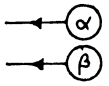
two-particle terms :  ;

and so on. The two-particle terms will be the terms of interest. The relevant part of the expansion of exp $(iW/\hbar)$ will be denoted $W^{(2)}$ and so, in the absence of interactions,

$(2/\hbar^2)W_0^{(2)} =$  $= \frac{1}{2}($  $)^2 - \frac{1}{2}\sum_\alpha ($  $)^2$. (2.16)

Connection with physical results is most easily made in terms of the *field* generated by the source :

$\psi_\alpha(\mathbf{R}) =$  $= \int d\mathbf{R}'\ \Delta(\mathbf{R}-\mathbf{R}')S_\alpha(\mathbf{R}')$. (2.17)

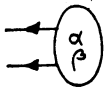
These fields play a fundamental role in subsequent developments. They lead, for example, to a stationarity condition that justifies the name of ' action ' for the quantity W. Non-interacting fields generated by the sources α and β are denoted $\psi_{\alpha\beta,0}$ and depicted  . The individual fields satisfy

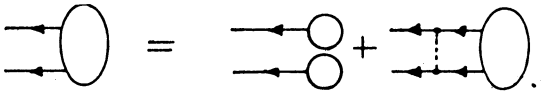
$$(i\hbar\partial_t - p^2/2m)\psi_\alpha(\mathbf{R}) = S_\alpha(\mathbf{R}) \tag{2.18}$$

and their product satisfies

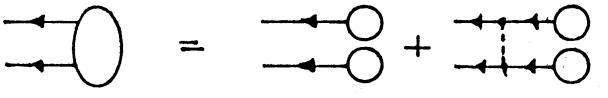
$$(i\hbar\partial_{t'} - p'^2/2m')(i\hbar\partial_t - p^2/2m)\psi_\alpha(\mathbf{R})\psi_\beta(\mathbf{R}') = S_\alpha(\mathbf{R})S_\beta(\mathbf{R}'). \tag{2.19}$$

3. Particle interactions

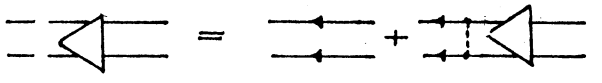
We have found it helpful to introduce and use the following diagrammatic analysis. The primitive two-particle interaction field $\psi_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2)$ is denoted  and is related to the free fields and the interaction potential $V_{\alpha\beta}(\mathbf{R}, \mathbf{R}') = V_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\delta(t-t')$ by the integral equation

 (3.1)

This expression may be dealt with by normal expansion techniques. In particular, the first-order term is given by the algebraic equation

 (3.2)

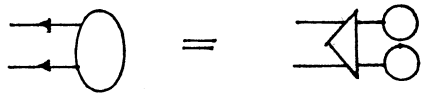
The interaction may be embedded in a modified propagator by introducing the integral equation

 (3.3)

The analytical interpretation of this expression is

$$\Delta(\mathbf{R}_1, \mathbf{R}_2\,;\ \mathbf{R}_1', \mathbf{R}_2') = \Delta_0(\mathbf{R}_1, \mathbf{R}_2\,;\ \mathbf{R}_1', \mathbf{R}_2')$$
$$+ i\hbar \int d\mathbf{R}_1''\, d\mathbf{R}_2''\ \Delta_0(\mathbf{R}_1, \mathbf{R}_2\,;\ \mathbf{R}_1'', \mathbf{R}_2'')V_{\alpha\beta}(\mathbf{R}_1'', \mathbf{R}_2'')\Delta(\mathbf{R}_1'', \mathbf{R}_2''\,;\ \mathbf{R}_1', \mathbf{R}_2') \tag{3.4}$$

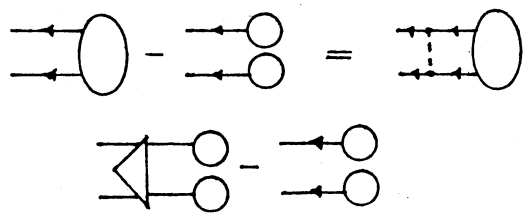
with $\Delta_0(\mathbf{R}_1, \mathbf{R}_2; \mathbf{R}_1', \mathbf{R}_2') = \Delta_0(\mathbf{R}_1, \mathbf{R}_1')\Delta_0(\mathbf{R}_2, \mathbf{R}_2')$. With this propagator we have



(3.5)

The second two-particle field introduced by Schwinger to complete the description of two-particle interactions is the *difference field* :

$\Phi_{\alpha\beta}(\mathbf{R}_1, \mathbf{R}_2) =$



(3.6)

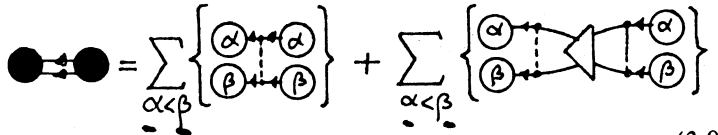
This field vanishes with V. The fields for interacting particles obey

$$\{(i\hbar\partial_{t'} - p'^2/2m')(i\hbar\partial_t - p^2/2m) - i\hbar V_{\alpha\beta}(\mathbf{R}, \mathbf{R}')\}\psi_{\alpha\beta}(\mathbf{R}, \mathbf{R}') = S_\alpha(\mathbf{R})S_\beta(\mathbf{R}'), \quad (3.7)$$

$$\{(i\hbar\partial_{t'} - p'^2/2m')(i\hbar\partial_t - p^2/2m) - i\hbar V_{\alpha\beta}(\mathbf{R}, \mathbf{R}')\}\Phi_{\alpha\beta}(\mathbf{R}, \mathbf{R}') = i\hbar V_{\alpha\beta}(\mathbf{R}, \mathbf{R}')\psi_\alpha(\mathbf{R})\psi_\beta(\mathbf{R}'). \quad (3.8)$$

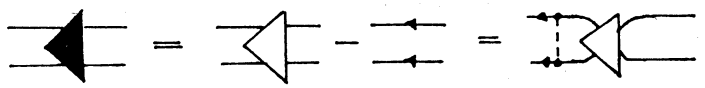
The form of the action composed of two-particle terms is $W_0^{(2)} + W_I^{(2)}$, where the non-interaction contribution is given by equation (2.16) and the interaction term is

$(2i/\hbar^2)W_I^{(2)} \equiv$



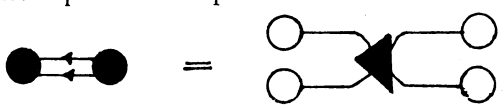
(3.9)

The first term represents the primitive interaction, and the second term the ' extended ' interaction. If the *difference propagator* (which vanishes with V)



(3.10)

is introduced, the last expression simplifies to



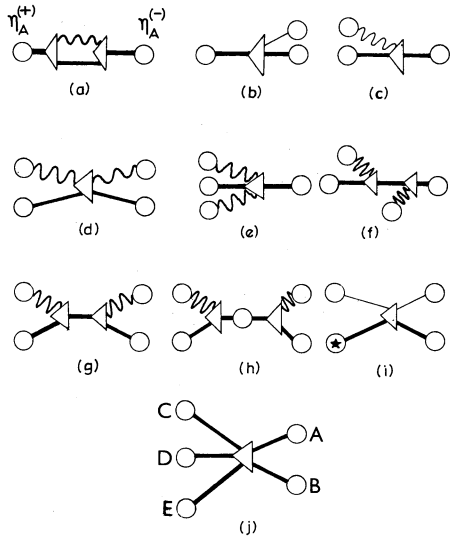
(3.11)

with summation over $\alpha < \beta$ understood.

For a more complicated system it is more convenient to think of all the appropriate terms depending on the interaction potentials as collected together into a single, composite interaction action, W_I. This leads to the simplifying feature that the expansion of the V.P.A. is $1 + (i/\hbar)W_I$ and higher-order terms of W_I are simply repetitions of the collision mechanism in different space–time regions.

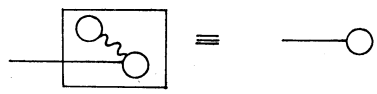
A collection of composite diagrams, with brief interpretations is shown in the figure. We also include diagrams relating to photon scattering. In the

diagrams —— denotes a non-composite particle, ~~~ a photon, and —— a bound particle (termed by Schwinger an H-particle, reflecting the fact that the hydrogen atom is the simplest example).



Types of source structure. (*a*) Self-energy, (*b*) $A^- \leftarrow A + e^-$, (*c*) $A + h\nu \leftarrow A^*$, (*d*) $A^* + h\nu' \leftarrow A + h\nu$, (*e*) $A + h\nu + h\nu' \leftarrow A^*$, (*f*) $A'' + h\nu'' \leftarrow A'$, $A' + h\nu' \leftarrow A$, (*g*) $A + h\nu' \leftarrow A^*$, $A^* \leftarrow A + h\nu$, (*h*) probe source, (*i*) $A^* + e^- \leftarrow A + e^-$, (*j*) $C + D + E \leftarrow A + B$.

Diagram (*a*) corresponds to a self-interaction or a vacuum polarization. Diagrams (*d*) and (*g*) illustrate the difference between direct scattering (*d*) and ' hot luminescence ' (*g*) [8]. Diagram (*h*) illustrates the method of examining intermediates with a *probe source*. In an actual act of creation a source will not in general liberate a unique particle type ; then the *extended source* should be regarded as a composition of the elementary sources. For example,



is a representation of an electron source : the initial source ejects a photon and an electron ; the experimental arrangement acts to eliminate the photon (a photon sink), and so the effective source is that shown on the right of the diagram. The sources in the figure are all of this simple, effective variety.

Sources restricted to single emission or absorption acts are termed *weak*.

4. Identical particles

The fundamental equation accounting for two-particle interactions is equation (3.9). We now turn to the consideration of interacting identical particles, and confine attention to fermions.

Consider a contribution to $W_0^{(2)}$ of the form

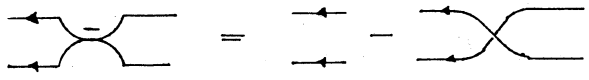
$$W_{\alpha\beta,0}^{(2)}=\hbar^2\int d\mathbf{R}_1\, d\mathbf{R}_2\, d\mathbf{R}_3\, d\mathbf{R}_4\, \eta_\alpha(\mathbf{R}_3)\eta_\beta(\mathbf{R}_1)G(\mathbf{R}_1,\mathbf{R}_2) \times G(\mathbf{R}_3,\mathbf{R}_4)\eta_\beta(\mathbf{R}_2)\eta_\alpha(\mathbf{R}_4). \quad (4.1)$$

The η notation for sources implies a limitation to electrons. This also implies the necessity of imposing an exterior, or anti-commutator algebra on the sources : $[\eta_\alpha(\mathbf{R}), \eta_\beta(\mathbf{R}')]_+=0$. In the case of identical particles, it may appear that the source label $(_\alpha, _\beta)$ is redundant. In the context of source theory, however, the function of the source is to inject into the collision zone and to detect the outcome of the collision process, particles characterized by the appropriate fundamental properties of charge, mass, spin, etc. The sources do not carry explicit reference to the subsequent (or previous) interactions that the particles they produce (or detect) experience. This information is conveyed by the field, and the explicit dependence on the interaction potential being contained in the propagators. It is necessary to distinguish the type of field which is to be identified with a particle generated by a specified source, since we have to allow for the possibility that different fundamental particle sources can yield identical particles characterized by entirely different fields. As an example, in electron–electron scattering, one electron is described by a free-electron field, while the other is described by a bound-state field.

From equation (4.1) the two-particle action of non-interacting fermions can be expressed in terms of the anti-symmetrized propagator :

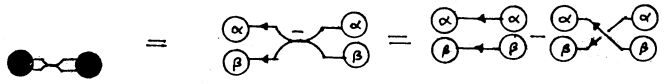
$$G_0(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4)=G(\mathbf{R}_1,\mathbf{R}_2)G(\mathbf{R}_3,\mathbf{R}_4)-G(\mathbf{R}_1,\mathbf{R}_4)G(\mathbf{R}_3,\mathbf{R}_2) \quad (4.2)$$

or



(4.3)

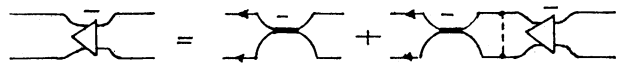
Then

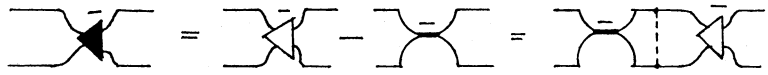


(4.4)

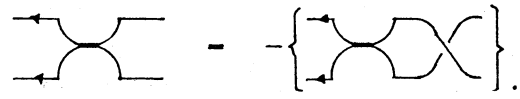
In the space–time region of the source components $\eta^{(-)}(\mathbf{R})$, $\eta^{(-)}(\mathbf{R}')$ or the components $\eta^{(+)}(\mathbf{R})$, $\eta^{(+)}(\mathbf{R}')$, which are disjoint, the identical particles are not influenced by each other and the form of the action is conveniently chosen to be that in equation (4.1). Schwinger, however, has shown how Fermi–Dirac statistics emerge in a direct manner in the formal structure of the theory. Nevertheless, there are reasons to be dissatisfied with the argument because the question of particle statistics for two electrons in different space–time regions is without meaning, and so the notion of Fermi–Dirac statistics as being intrinsic to the source rather than the field is unsatisfactory. Of course, it is argued that the statistics are a direct consequence of the algebraic properties of the source functions. An alternative scheme is to postulate the anti-symmetry of the propagator and to proceed from that to the algebraic structure of the sources, bearing in mind the necessity of maintaining positive vacuum persistence probabilities.

In the region of particle interactions the corresponding forms of the true and difference fermion propagators are solutions of

$\underline{G}$:  (4.5)

$\underline{G}_D$:  (4.6)

Note that the antisymmetry of G_0 is conveyed by the relation

 (4.7)

5. Electron–atom scattering

We concentrate on illustrating the scheme outlined above by treating the simplest of molecular collisions, electron-hydrogen atom scattering. The literature on this primitive problem is voluminous, but most of it can be traced through the review by Burke and Smith [9] and the books by Mott and Massey [10] and Bransden [11].

The experimental quantities of interest are the various cross-sections, and the theoretical route to them is through the transition matrix elements. The latter can be obtained from the V.P.A., and so that is the connection between sources, action, and measurement.

The V.P.A. can be decomposed as follows :

$$\langle 0_+(SS'S''\ldots)0_-\rangle = \sum_{\{n\}}\sum_{\{n'\}} \langle 0_+(S^{(+)}S'^{(+)}\ldots)\{n\}\rangle \langle\{n\}|\ |\{n'\}\rangle \times \langle\{n'\}(S^{(-)}S'^{(-)}\ldots)0_-\rangle \quad (5.1)$$

which represents a formal generalization of the expression in equation (2.5). The summations in this equation extend over all realizable mechanisms, and the primes denote sources with different characteristics. The V.P.A. on the left can be expanded in a number of ways ; for electrons, with sources obeying an anti-commutator algebra, we adopt the convention of retaining the same order of source functions on both sides of the equality. (Alternative conventions would correspond to a change of phase, which is of no relevance in cross-section calculations.) The transition matrix elements $\langle\{n\}|\ |\{n'\}\rangle$ connect particles, designated collectively by $\{n'\}$, entering the collision zone. Employment of the basic relations in equations (2.1) and (2.2) simplifies equation (5.1) to

$$\langle 0_+(SS'\ldots)0_-\rangle = \sum_{\{n\}}\sum_{\{n'\}} iS_{\{n\}}{}^{(+)}\, iS_{\{n\}}{}^{(+)'}\ldots\langle\{n\}|\ |\{n'\}\rangle iS_{\{n'\}}{}^{(-)} \times iS_{\{n'\}}{}^{(-)'}\ldots, \quad (5.2)$$

where $\{n\}$, $\{n'\}$ signify the nature of the source required to obtain the appropriate particles with the stipulated momentum-energy specifications. On considering the collision of two particles and their scattering the appropriate term in the expansion of exp $(iW/\hbar)$, that involving $W_I{}^{(2)}$, gives the transition matrix element for the process by comparison of the two expansions for $\langle 0_+(SS')0_-\rangle$.

For electron–hydrogen scattering, the direct mechanism is the most important contribution in the high-energy domain where the first Born approximation is

applicable. Then equation (5.2) reduces to

$$\langle 0_+(\eta\eta_{\mathrm{H}})0_-\rangle = \sum_{\{n\}}\sum_{\{n'\}} \langle 0_+(\eta^{(+)}\eta_{\mathrm{H}}{}^{(+)})\{n\}\rangle \langle\{n\}|\ |\{n'\}\rangle \times \langle\{n'\}(\eta^{(-)}\eta_{\mathrm{H}}{}^{(-)})0_-\rangle, \quad (5.3)$$

where the hydrogen atom source is denoted η_{H} and the free-electron source is η. The summation covers elastic and inelastic direct scattering, exchange scattering, and ionization. The right-hand side expands into

$$\{\langle 0_+(\eta^{(+)}\eta_{\mathrm{H}}{}^{(+)})1\phi_{\mathbf{pf}}\chi_{\mathrm{f}}\rangle \langle\chi_{\mathrm{f}}1\phi_{\mathbf{pf}}|\ |1\phi_{\mathbf{pi}}\chi_{\mathrm{i}}\rangle + \langle 0_+(\eta^{(+)}\eta_{\mathrm{H}}{}^{(+)})1\phi_{\mathbf{pf}}\Phi\rangle \langle\Phi 1\phi_{\mathbf{pf}}|\ |1\phi_{\mathbf{pi}}\chi_{\mathrm{i}}\rangle + \langle 0_+(\eta_{\mathrm{H}-}{}^{(+)})\Psi\rangle \langle\Psi|\ |1\phi_{\mathbf{pi}}\chi_{\mathrm{i}}\rangle + \ldots\}\langle\chi_{\mathrm{i}}1\phi_{\mathbf{pi}}(\eta^{(-)}\eta_{\mathrm{H}}{}^{(-)})0_-\rangle \quad (5.4)$$

where χ_{i} is the initial (ground) bound state of the atom, χ_{f} is the final state, and $1\phi_{\mathbf{p}}$ the corresponding states of the free electron. Φ is a continuum state of the atom (so that the second term corresponds to ionization) and Ψ is the H^- bound state (so that the third term corresponds to capture or absorption). This expression turns into

$$\langle 0_+(\eta\eta_{\mathrm{H}})0_-\rangle = i^4\,\eta_{\mathrm{f}}{}^{(+)}\,\eta_{\mathrm{Hf}}{}^{(+)}\langle\chi_{\mathrm{f}}1\phi_{\mathbf{pf}}|\ |1\phi_{\mathbf{pi}}\chi_{\mathrm{i}}\rangle\eta_{\mathrm{i}}{}^{(-)}\,\eta_{\mathrm{Hi}}{}^{(-)} + i^4\,\eta_{\mathrm{f}}{}^{(+)}\,\eta_{\Phi}{}^{(+)}\langle\Phi 1\phi_{\mathbf{pf}}|\ |1\phi_{\mathbf{pi}}\chi_{\mathrm{i}}\rangle\eta_{\mathrm{i}}{}^{(-)}\,\eta_{\mathrm{Hi}}{}^{(-)} + i^3\,\eta_{\Psi}{}^{(+)}\langle\Psi|\ |1\phi_{\mathbf{pi}}\chi_{\mathrm{i}}\rangle\eta_{\mathrm{i}}{}^{(-)}\,\eta_{\mathrm{Hi}}{}^{(-)} + \ldots . \quad (5.5)$$

Note that the momentum-energy source functions appear in this expression. For direct scattering, the appropriate term in the alternative expansion of $\langle 0_+(\eta\eta_{\mathrm{H}})0_-\rangle$ is obtained from the form of equation (3.9) appropriate to electrons :

$$W_{\mathrm{I}}{}^{(2)} = -\tfrac{1}{2}i\hbar^2 \int d\mathbf{R}_1\, d\mathbf{R}_2\, d\mathbf{R}_3\, d\mathbf{R}_4\, \eta_{\mathrm{H}}(\mathbf{R}_3)\eta(\mathbf{R}_1)G_{\mathrm{D}}(\mathbf{R}_1, \mathbf{R}_2\,;\ \mathbf{R}_3, \mathbf{R}_4) \times \eta(\mathbf{R}_2)\eta_{\mathrm{H}}(\mathbf{R}_4). \quad (5.6)$$

So far the source functions have been taken as real. We now extend this viewpoint and allow both sources and fields to be complex (the reasons for this will be amplified below). The complex field is simply

$$\psi_\alpha{}^*(\mathbf{R}) = \int d\mathbf{R}'\ \eta_\alpha{}^*(\mathbf{R}')G(\mathbf{R}', \mathbf{R}). \quad (5.7)$$

The modification of the action expression is then

$$W_{\mathrm{I}}{}^{(2)} = 2i\hbar^2 \int d\mathbf{R}_1\, d\mathbf{R}_2\, d\mathbf{R}_3\, d\mathbf{R}_4\, \eta_{\mathrm{H}}{}^*(\mathbf{R}_3)\eta^*(\mathbf{R}_1)G_{\mathrm{D}}(\mathbf{R}_1, \mathbf{R}_2\,;\ \mathbf{R}_3, \mathbf{R}_4) \times \eta(\mathbf{R}_2)\eta_{\mathrm{H}}(\mathbf{R}_4) \quad (5.8)$$

and equations (5.1) to (5.5) can be generalized to complex notation in an obvious way.

The first Born approximation to direct scattering is the following simplified form of equation (4.6) :

$$G_{\mathrm{D}}(\mathbf{R}_1, \mathbf{R}_2\,;\ \mathbf{R}_3, \mathbf{R}_4) = i\hbar \int d\mathbf{R}_1'\, d\mathbf{R}_3'\, G_0(\mathbf{R}_1, \mathbf{R}_1'\,;\ \mathbf{R}_3, \mathbf{R}_3') \times V(\mathbf{R}_1', \mathbf{R}_3')G(\mathbf{R}_1', \mathbf{R}_2\,;\ \mathbf{R}_3', \mathbf{R}_4) \sim i\hbar \int d\mathbf{R}_1'\, d\mathbf{R}_3'\, G(\mathbf{R}_1, \mathbf{R}_1')G(\mathbf{R}_3, \mathbf{R}_3') \times V(\mathbf{R}_1', \mathbf{R}_3')G(\mathbf{R}_1', \mathbf{R}_2)G(\mathbf{R}_3', \mathbf{R}_4). \quad (5.9)$$

When this is inserted into the expression for W_I we find

$$W_I^{(2)} \sim 2\hbar^3 \int d\mathbf{R}\, d\mathbf{R}'\, \psi_H^*(\mathbf{R})\psi^*(\mathbf{R}')V(\mathbf{R}, \mathbf{R}')\psi(\mathbf{R}')\psi_H(\mathbf{R}). \tag{5.10}$$

The fields are related to the sources and sinks by

$$\psi^*(\mathbf{R}) \equiv \psi^{(+)}(\mathbf{R}) = (i/\hbar^{1/2}) \sum_n \eta_n^{(+)*}\, \phi_{pn}^*(\mathbf{R}), \tag{5.11}$$

$$\psi(\mathbf{R}) \equiv \psi^{(-)}(\mathbf{R}) = (i/\hbar^{1/2}) \sum_n \eta_n^{(-)}\, \phi_{pn}(\mathbf{R}), \tag{5.12}$$

$$\psi_H^*(\mathbf{R}) \equiv \psi_H^{(+)}(\mathbf{R}) = (i/\hbar^{1/2}) \sum_n \eta_{Hn}^{(+)*}\, \chi_n^*(\mathbf{R}), \tag{5.13}$$

$$\psi_H(\mathbf{R}) \equiv \psi_H^{(-)}(\mathbf{R}) = (i/\hbar^{1/2}) \sum_n \eta_{Hn}^{(-)}\, \chi_n(\mathbf{R}). \tag{5.14}$$

Then, on restricting the discussion to the case when the hydrogen atom is initially described by the eigenfunction $\chi_i(\mathbf{R})$ and finally, after the scattering event, by $\chi_f(\mathbf{R})$, and where the incoming and outgoing electrons are described by $\phi_{pi}(\mathbf{R})$ and $\phi_{pf}(\mathbf{R})$, the action simplifies to

$$W_I^{(2)} = 2\hbar\{i^4\, \eta_{Hf}^{(+)*}\, \eta_f^{(+)*}\, \eta_i^{(-)}\, \eta_{Hi}^{(-)}\} \int d\mathbf{R}\, d\mathbf{R}'\, \chi_f^*(\mathbf{R})\phi_{pf}^*(\mathbf{R}') \times V(\mathbf{R}, \mathbf{R}')\phi_{pi}(\mathbf{R}')\chi_i(\mathbf{R}). \tag{5.15}$$

The transition matrix element for direct scattering is embodied by the first term of equation (5.5); and so, comparing the terms

$$\langle 0_+(\eta\eta_H)0_-\rangle \sim \eta_f^{(+)*}\, \eta_{Hf}^{(+)*}\, \eta_i^{(-)}\, \eta_{Hi}^{(-)} \langle \chi_f 1\phi_{pf}|\ |1\phi_{pi}\chi_i\rangle \tag{5.16}$$

and

$$\langle 0_+(\eta\eta_H)0_-\rangle \sim \tfrac{1}{2}(i/\hbar)^2\, W_I^{(2)}(\eta, \eta_H), \tag{5.17}$$

the latter coming from the expansion of equation (2.3), leads to

$$\langle \chi_f 1\phi_{pf}|\ |1\phi_{pi}\chi_i\rangle = (1/\hbar) \int d\mathbf{R}\, d\mathbf{R}'\, \chi_f^*(\mathbf{R})\phi_{pf}^*(\mathbf{R}') \times V(\mathbf{R}, \mathbf{R}')\phi_{pi}(\mathbf{R}')\chi_i(\mathbf{R}). \tag{5.18}$$

(The sign change comes about from the reordering of the sources for the comparison.)

When the scattering is an instantaneous event, the time component of $V(\mathbf{R}, \mathbf{R}')$ is the delta function $\delta(t-t')$. The time integration in the last expression is then trivial, with the result

$$\langle \chi_f 1\phi_{pf}|\ |1\phi_{pi}\chi_i\rangle = [\gamma(T)/\hbar] \int d\mathbf{r}\, d\mathbf{r}'\, \chi_f^*(\mathbf{r})\chi_i(\mathbf{r}')\phi_{pf}^*(\mathbf{r}')\phi_{pi}(r)V(\mathbf{r}, \mathbf{r}') \tag{5.19}$$

with

$$\gamma(T) = \int_{-T/2}^{T/2} dt\, \exp\{(it/\hbar)(E_i + E_{pi} - E_f - E_{pf})\}. \tag{5.20}$$

It follows that the transition rate is the conventional expression

$$\begin{aligned} dP/dt &= \lim_{T\to\infty} (1/T)|\langle \chi_f 1\phi_{pf}|\ |1\phi_{pi}\chi_i\rangle|^2 \\ &= (2\pi/\hbar)\delta(E_i + E_{pi} - E_f - E_{pf})|T_{i\to f}|^2 \end{aligned} \tag{5.21}$$

with $T_{i\to f}$, the conventional transition matrix element of $V(\mathbf{r}, \mathbf{r}')$ taken between the composite initial and final eigenstates of the system. If $V(\mathbf{r}, \mathbf{r}')$ is taken as the coulombic interaction energy of the two electrons and the single nucleus, the conventional expression for the differential cross section is obtained : this is the starting-point of existing theories.

In order to incorporate exchange into the scattering process the action has to be augmented by the term

$$W_I^{(2)} = -i\hbar^2 \int d\mathbf{R}_1\, d\mathbf{R}_2\, d\mathbf{R}_3\, d\mathbf{R}_4\, \eta_H^*(\mathbf{R}_3)\eta^*(\mathbf{R}_1)G_D(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \mathbf{R}_4) \times \eta(\mathbf{R}_2)\eta_H(\mathbf{R}_4), \quad (5.22)$$

where G_D is given by equation (4.6). This expression is developed by introducing the first-order approximation to G_D, equation (5.9), and the explicit functional forms for the fields (as for the direct term) and their expansions over eigenstates. This generates

$$W_I^{(2)} = \hbar^3 \int d\mathbf{R}\, d\mathbf{R}' \{\psi_H^*(\mathbf{R})\psi^*(\mathbf{R}') - \psi_H^*(\mathbf{R}')\psi^*(\mathbf{R})\}V(\mathbf{R}, \mathbf{R}') \times \{\psi(\mathbf{R}')\psi_H(\mathbf{R}) - \psi(\mathbf{R})\psi_H(\mathbf{R}')\}, \quad (5.23)$$

which simplifies to

$$W_I^{(2)} = 2\hbar^3 \int d\mathbf{R}\, d\mathbf{R}' \{\psi_H^{(+)}(\mathbf{R})\psi^{(+)}(\mathbf{R}')\psi^{(-)}(\mathbf{R}')\psi_H^{(-)}(\mathbf{R}) - \psi_H^{(+)}(\mathbf{R})\psi^{(+)}(\mathbf{R}')\psi^{(-)}(\mathbf{R})\psi_H^{(-)}(\mathbf{R}')\}V(\mathbf{R}, \mathbf{R}'). \quad (5.24)$$

Comparison of the two alternative expressions for the vacuum persistence amplitude then leads to

$$\langle \chi_f 1\phi_{pf} |\, | 1\phi_{pi}\chi_i\rangle = (1/\hbar) \int d\mathbf{R}\, d\mathbf{R}' \{\chi_f^*(\mathbf{R})\chi_i(\mathbf{R})\phi_{pf}^*(\mathbf{R}')\phi_{pi}(\mathbf{R}') - \chi_f^*(\mathbf{R})\chi_i(\mathbf{R}')\phi_{pf}^*(\mathbf{R}')\phi_{pi}(\mathbf{R})\}V(\mathbf{R}, \mathbf{R}') \quad (5.25)$$

when attention is confined to single initial and final states for both free and bound electrons. The same development as before leads at once to the identification of the transition matrix element as

$$T_{i\to f} = [\gamma(T)/\hbar] \int d\mathbf{r}\, d\mathbf{r}' \{\chi_f^*(\mathbf{r})\chi_i(\mathbf{r})\phi_{pf}^*(\mathbf{r}')\phi_{pi}(\mathbf{r}') - \chi_f^*(\mathbf{r})\phi_{pi}(\mathbf{r})\phi_{pf}^*(\mathbf{r}')\chi_i(\mathbf{r}')\}V(\mathbf{r}, \mathbf{r}') \quad (5.26)$$

in accord with conventional treatments. The development of this expression can be pursued by referring, for example, to the work of Bell and Moisewitsch [12].

The reason for employing the complex representation of sources can now be explained. First, consider the alternative, which is to employ the causally labelled fields $\psi = \psi^{(+)} + \psi^{(-)}$ and $\psi_H = \psi_H^{(+)} + \psi_H^{(-)}$. In this case the appropriate terms to select for the action underlying direct scattering, are those containing the source combination $\eta_H^{(+)}\eta_H^{(-)}\eta^{(+)}\eta^{(-)}$ (in some order). This choice is required because the composite particle and the free particle each needs to be generated and then detected. The introduction of these field decompositions into equation (5.10) leads to two distinct contributions, each one representing a direct scattering process, but with different arrangements of the non-commuting source factors. This minor but irksome difficulty can be overcome by the imposition of extra rules for comparing the V.P.A. expansions. The exchange contribution, however, settles the matter convincingly in favour of the complex

source formalism. In this case, substitution of the causal decomposition of ψ and ψ_H into the equivalent of equation (5.23) for real fields, leads to a term $\psi_H^{(+)}(\mathbf{R})\psi^{(+)}(\mathbf{R})\psi^{(-)}(\mathbf{R})\psi_H^{(-)}(\mathbf{R}')$ which is devoid of physical significance. Since source theory is built on the requirement that the expansion of exp $(iW/\hbar)$ have only physical terms or their repetition, it is clear that the complex source formalism conforms naturally and avoids the proliferation of rules of interpretation.

On turning to ionization, the simplest description is achieved by ignoring interferences between scattered and ejected electrons, and regarding the electrons as distinguishable. This corresponds to identifying the high velocity electrons with the fast incident electrons (and the low velocity electrons with the initially bound electrons).

Ionization is described by the second term of equation (5.4). The transition matrix element is obtained in the same manner as indicated by equations (5.10)–(5.20), with the following modifications. In equation (5.13) $\psi_H^{(+)}$ now designates the composite particle's electron excited into the continuum, in which case the appropriate expansion over eigenfunctions is

$$\psi_H^{(+)}(\mathbf{R}) = \sum_n i\eta_{Hn}^{(+)*}\,\Phi_n(\mathbf{R}). \tag{5.27}$$

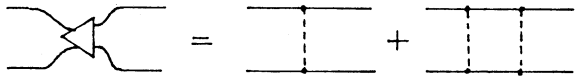
The T-matrix element is then

$$T_{i\to f} \sim \int d\mathbf{r}\, d\mathbf{r}'\; \Phi_f^*(\mathbf{r})\chi_i(\mathbf{r})\phi_{pf}^*(\mathbf{r}')\phi_{pi}(\mathbf{r}')V(\mathbf{r},\mathbf{r}'). \tag{5.28}$$

This may be employed in the calculation of the cross section in the normal way.

Absorption can also be treated within the framework of source theory, but there is a complication in the treatment of the electron–hydrogen system. The significant term in the expansion of the action now depends on the source factors $\eta_H^{(-)}\eta^{(-)}$, which eject the atom and the free electron from the collision zone, and on the detection source $\eta_H^{(+)}$ for the combined composite particle, the product of the event. The complication here is that absorption is possible only at very low incident electron energies. This prevents a simple truncation of the perturbation expansion of G_D.

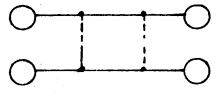
The *second Born approximation* can be obtained by extending the approximation for G_D to terms quadratic in the interaction potential. Equation (4.5) for direct scattering becomes



(5.29)

and after a little simplification, the corresponding form of the action is

$$(i/2\hbar^2)W^{(2)}_{(\text{2nd Born})} =$$



$$= \eta_{Hf}^{(+)*}\,\eta_{pf}^{(+)*}\,\eta_{pi}^{(-)}\,\eta_{Hi}^{(-)}\,\gamma(T)$$
$$\times \int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4\; \chi_f^*(\mathbf{r}_3)\phi_{pf}^*(\mathbf{r}_1)$$
$$\times V(\mathbf{r}_1,\mathbf{r}_3)G_E(\mathbf{r}_1,\mathbf{r}_2)G_E(\mathbf{r}_3,\mathbf{r}_4)V(\mathbf{r}_2,\mathbf{r}_4)$$
$$\times \phi_{pi}(\mathbf{r}_2)\chi_i(\mathbf{r}_4) \tag{5.30}$$

with G_E the energy transform of $G(t)$. On inserting the expansion

$$G_E(\mathbf{r}_1, \mathbf{r}_2)G_E(\mathbf{r}_3, \mathbf{r}_4) = -\left(\frac{m}{2\pi\hbar^3}\right)\sum_n \chi_n(\mathbf{r}_3)\left\{\frac{\exp(ik_n|\mathbf{r}_1-\mathbf{r}_2|)}{|\mathbf{r}_1-\mathbf{r}_2|}\right\}\chi_n^*(\mathbf{r}_4), \quad (5.31)$$

with the simplification

$$V_{fn}(\mathbf{r}) = \int \chi_f^*(\mathbf{r}')V(\mathbf{r}, \mathbf{r}')\chi_n(\mathbf{r}')\, d\mathbf{r}' \quad (5.32)$$

and comparing the action with equation (5.16), we arrive at

$$T_{i\to f}^{(2)} = \left(\frac{m}{2\pi\hbar^2 L^3}\right)\sum_n \int d\mathbf{r}_1\, d\mathbf{r}_2 \exp(-i\mathbf{k}_f \cdot \mathbf{r}_1)\, V_{fn}(\mathbf{r}_1) \times \left\{\frac{\exp(i\mathbf{k}_n|\mathbf{r}_1-\mathbf{r}_2|)}{|\mathbf{r}_1-\mathbf{r}_2|}\right\} V_{ni}(\mathbf{r}_2)\exp(i\mathbf{k}_i \cdot \mathbf{r}_2) \quad (5.33)$$

in accord with conventional treatments.

7. Conclusion

Source theory is a formalism for arriving at expressions which in a conventional calculation would be regarded as the starting-point. For those whose interest lies in the actual calculation of cross section for events, the formalism is superfluous because S-matrix techniques are much simpler and apparently adequate. The power of source theory is its ability to generate expressions for cross sections on the basis of two simple constructional principles, those of causality and space–time uniformity. Its disadvantage is that, since it is so heavily grounded in elementary particle physics, its application to processes of chemical interest is cumbersome, and they are too remote from the fundamental processes for which source theory was devised. As we found in a similar investigation of electromagnetic interactions, these principles can be elaborated to the point where they are seen to be the underlying features of traditional theories.

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