Impact-Parameter Method for Proton–Hydrogen-Atom Collisions. I. The Time-Dependent Impact-Parameter Model*

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The impact-parameter method used to calculate cross sections in high-energy proton–hydrogen-atom collisions is considered. By making use of the observation that the scattering is almost completely in the forward direction, a complete time-dependent impact-parameter model is obtained from the Lippmann-Schwinger equation. As a direct consequence of the proper treatment of the continuum, two equivalent Schrödinger time representations are found in which to describe the model system of a point charge moving along a specified trajectory, and thereby perturbing a hydrogen atom. The unambiguous identification of the dynamical states of this model system, and the unambiguous definition of transition probabilities are obtained. The specification of the dynamical states of the time-dependent model system can be conveniently incorporated into the customary impact-parameter method by associating an additional boundary condition with the usual time-dependent Schrödinger equation. The familiar traveling atomic orbitals are not dynamical states of the system, but the discrete dynamical states approach the traveling orbitals as $|t| \to \infty$; and hence, the set of traveling atomic orbitals provides a description of the system which becomes correct asymptotically. One Schrödinger representation is the natural representation in which to obtain the amplitudes for electronic excitation. The other representation is the natural representation in which to obtain the amplitudes for charge exchange. A noniterative technique is used to solve the integral equations which describe the evolution of the state vector in the two time representations, and expressions are derived for the amplitudes for excitation and charge exchange. The amplitudes for excitation can be expressed in terms of the usual Coulomb integrals, and the amplitudes for charge exchange can be expressed in terms of usual exchange integrals.

I. INTRODUCTION

A. Perspective

The impact-parameter method, especially as formulated by Bates and McCarroll[1] and Bates,[2] has been a most fruitful approach for the study of inelastic and rearrangement scattering in high-energy proton–hydrogen-atom collisions (the keV energy range). Approximate cross sections for electronic excitation and charge exchange determined in extensive calculations have been reported recently.[3-7] This approach has crystallized into a definite model, which has been introduced by a series of postulates.[8,9] Some implications of recent work,[3,5-7] however, stimulated us to examine the fundamental basis of this model and the calculational procedure used to determine the approximate cross sections. This paper is the first in a series in which we hope to establish from first principles the time-dependent impact-parameter model, and to elucidate certain aspects of the calculational procedure. The model and its evolution has been clearly described by McDowell and Coleman.[8] However, to establish a perspective for this work, we shall briefly summarize some of the important elements of their review, and illustrate what appears to us to be fundamental inconsistencies raised by recent work.[3,5-7]

In the impact-parameter model, one assumes that the nuclear motion can be considered separately from the electronic motion; usually the Born-Oppenheimer separation is given as the justification for this assumption.[8] The protons are assumed to be distinguishable and to move along rectilinear trajectories separated by the impact parameter.[10] More precisely, let the vector $\vec{R}$ denote the position of proton 2 with respect to proton 1, and let the vectors $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}$, respectively, denote the positions of the electron with respect to proton 1, proton 2, and the midpoint of $\vec{R}$. The origin of a stationary coordinate system is chosen at the midpoint of $\vec{R}$ with axes aligned so that the relative motion takes place in the Y-Z plane; then the protons move according to

$$\vec{R}(t) = \vec{b} + vt\hat{Z}, \tag{1}$$

where $\vec{b}$ is the impact-parameter vector in the Y-Z plane, and v is the velocity of the incident proton. It is assumed that the electronic motion is governed by the Schrödinger equation

$$i\hbar\left(\frac{\partial}{\partial t}\right)_{\vec{r}}\psi(\vec{r},t)=H(\vec{r},t)\psi(\vec{r},t), \tag{2}$$

with the initial condition

$$\lim_{t\to-\infty}\psi=\psi_0 \tag{2a}$$

and with the model Hamiltonian

$$H=-\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2-\frac{e^2}{|\vec{r}-\frac{1}{2}\vec{R}(t)|}-\frac{e^2}{|\vec{r}+\frac{1}{2}\vec{R}(t)|}+\frac{e^2}{R(t)}, \tag{2b}$$

where m is the electronic mass, and e the electronic charge. Transition probabilities are to be determined from Eq. (2) for constant values of the impact parameter and velocity, and cross sections are determined by integrating the transition probabilities over all values of $\vec{b}$.

There have been attempts to justify this model *a posteriori*[8]: one attempts to show that certain quantities, such as transition probabilities or cross sections, obtained in this model correspond to the same quantities obtained from the complete quantum-mechanical treatment. In the limit of high energy, the equivalence of the approximate cross sections for excitation given by arbitrary orders of the Born approximation in the two treatments has been established.[11-14] McCarroll and Salin[15] have generalized the justification by allowing for the possibility of rearrangement; and have shown that in the limit of infinite nuclear mass the transition amplitudes obtained in the two treatments also correspond (apart from a phase factor), if one accepts the assumption of the uniform convergence of the expansion coefficients of one formal expansion to the expansion coefficients of another formal expansion. Although this assumption seems impossible to justify,[8] especially for rearrangement scattering, the work of McCarroll and Salin[15] does indicate that it is formally possible to define an equivalent impact-parameter model.[8]

It has not been possible to obtain an exact solution to Eq. (2); instead, approximate solutions are generated by expressing a wave function as a two-centered linear combination of a finite number of traveling hydrogenic orbitals[2,8]:

$$\psi_N=\sum_{n=1}^{N}[b_{n1}(t)\Phi_{n1}+b_{n2}(t)\Phi_{n2}], \tag{3}$$

where Φ_{nk} is a traveling hydrogenic orbital centered on proton k:

$$\Phi_{nk}=\phi_n(\vec{r}_k)\exp[\mp(i/\hbar)p_0z]\times\exp[-(i/\hbar)(\epsilon_n+\tfrac{1}{8}mv^2)t], \tag{4}$$

where $p_0=\frac{1}{2}mv$, and where ϕ_n and ϵ_n are, respectively, discrete hydrogenic eigenfunctions and eigenvalues. The upper sign applies if $k=1$ while the lower sign applies if $k=2$. The set of unknown functions $\{b_{nk}(t)\}$ are determined from the system of equation

$$\left\langle\Phi_{nk}\left|H-i\hbar\left(\frac{\partial}{\partial t}\right)_{\vec{r}}\right|\psi_N\right\rangle=0,$$

$$n=1,\ldots N,\quad k=1,2 \tag{5a}$$

with the initial condition

$$b_{nk}(-\infty)=\delta_{ni}\,\delta_{k1}, \tag{5b}$$

where it has been assumed that the traveling orbital Φ_{i1} describes the initial state of the system. The quantity

$$|b_{nk}(\infty)|^2$$

is interpreted as the probability of the transition from state Φ_{i1} to state Φ_{nk}.

Equation (3) is commonly referred to as an expansion, the set $\{\Phi_{nk}\}$ as a basis set, and the functions $\{b_{nk}(t)\}$ as expansion coefficients. In recent years much research has been directed towards determining the rate of convergence of Eq. (3) as the basis set is enlarged,[3,4,7,16-18] and searching for new basis sets (nonhydrogenic traveling orbitals) with improved convergence characteristics.[5,6] Wilets and Gallaher[7] used an eight-state basis set in their calculation, and for a few energies repeated their calculations using a 14-state basis. From their results and other arguments, Wilets and Gallaher[7] concluded that the hydrogenic expansion was converging slowly. However, numerical problems caused some of Wilets and Gallaher's[7] results to be inaccurate, and Rapp and Dinwiddie[3] repeated these calculations, and concluded that the expansion, at least as far as the cross sections for 1s exchange and the transitions to the 2s states are concerned, is converging fairly rapidly. In an attempt to use a basis set with improved convergence characteristics, Gallaher and Wilets[6] used a traveling Sturmian basis set. The Sturmian functions form a discrete complete set, and thus in principle one could account for the hydrogenic continuum. However, Gallaher and Wilets[6] demonstrated that the Sturmian basis has poor convergence properties. Part of the argument leading Wilets and Gallaher[7] to the conclusion that the hydrogenic expansion was slowly convergent was that the approximate wave function, Eq. (3), does not adequately represent the system in the middle of the collision. This observation led Cheshire, Gallaher, and Taylor[5] to use a pseudostate expansion. Certain members of the basis set were ar-

bitrary functions constructed to provide a large overlap with the lower bound state of He^+. No attempt has been made to determine the convergence of such an expansion.

The work of Gallaher and Wilets[6] with the Sturmian basis set, and that of Cheshire, Gallaher, and Taylor[5] with the pseudostate basis set, raises a fundamental question concerning the impact-parameter model, and the calculational procedure of Eq. (5). In these approaches it is possible to obtain transition probabilities which do not have limits as $t \to \infty$. For large t, the expression for a transition probability can be written as the sum of a constant term and a time-varying term. In the Sturmian calculation the time-varying term has been ignored.[6,19] Apparently there are also attempts being made to show that the time average of such a transition probability is a constant, and this average should be interpreted as a transition probability. Now the language of the impact-parameter model is that of time-dependent perturbation theory[20]: The eigenvectors of some unperturbed Hamiltonian form the basis of dynamical states available to the system. Initially ($t \to -\infty$) the system is described by one of these eigenvectors (α, for example). Subsequently, a time-dependent perturbation acts upon the system, and the state vector evolves according to the Schrödinger equation [or equivalently transforms under the unitary time-evolution operator $U(t, t' = -\infty)$]. The probability that the system has made a transition to another dynamical state (β, for example) is

$$P_{\beta\alpha} = |\langle \beta | U(t = \infty,\ t' = -\infty) | \alpha \rangle|^2 , \tag{6}$$

which is a *constant*. Part of the reason that one can obtain transition probabilities that do not have a limit as $t \to \infty$ is that the impact-parameter model as postulated is incomplete. One needs an unambiguous identification of the dynamical states available to the model system, and an unambiguous definition of a transition probability such as Eq. (6). Equivalently, as we will show, one needs to specify the boundary conditions associated with Eq. (2) in greater detail.[21]

Finally, the expansion shown in Eq. (3) is not an expansion in the normal sense, and one should not expect it to converge to the solution of Eq. (2). The reason for this is clear: Φ_{n1} and Φ_{n2} are members of two different complete sets, and as one proceeds to the limit, the basis set becomes linearly dependent. Of course, in principle, any finite set of these functions forms a linearly independent set; however, in practice, since only numbers of a finite length can be considered in most computations, the problem of redundancy might be encountered long before the limit is approached. Equation (5) would not be sufficient to determine the set of unknown expansion coefficients. One must therefore question the nature of the calculational procedure provided by the two-centered expansion, and the meaning of the numerical convergence, or lack of convergence, of the cross sections for the various processes.[3,7]

B. Objective

Starting with either time-dependent collision theory[22,23,24] or time-independent collision theory,[24-29] some aspects of the impact parameter model have been justified *a priori*. However, this work has not been in sufficient detail to provide a complete time-dependent impact-parameter model in which transition probabilities are unambiguously defined, or in sufficient depth to deal with the special problems introduced by the possibility of rearrangement. In this work, we start with time-independent scattering theory,[30] and by making use of the observation that the scattering is almost completely in the forward direction, obtain the impact-parameter model: i.e., obtain Eq. (2), the missing boundary condition, and, in general, the Schrödinger time representation (the identification of the dynamical states, the time evolution operator, and the definition of transition probabilities). A noniterative technique is used to formally solve the integral equations of evolution that are obtained, and expressions for "exact" transition amplitudes are derived. These expressions yield "exact" amplitudes in the sense that as standard numerical procedures are refined the calculated amplitudes approach the exact amplitudes.

In the second paper in this series, we consider the calculational procedure provided by the two-centered expansion. It has been attempted to justify the two-centered expansion and the Sturmian or pseudostate expansions as being possible trial functions in a variational calculation.[8,6,7] Equation (5) follows by requiring that a certain functional be stationary.[8,22,31,32] However, in the second paper of this series we show that this functional is not stationary about the exact wave function for the variations represented by these trial wave functions. The convergence of the two-centered traveling hydrogenic orbital expansion is also discussed. Variational methods based upon functionals which are stationary about the exact wave function for the types of variations represented by available trial wave functions are given in the second and fourth papers of this series. In the third paper, the use of nonhydrogenic expansion functions, such as pseudofunctions, is discussed.

Since we are interested in obtaining not only the impact-parameter equation, but also the definition of transition probabilities, which implies that the missing boundary condition associated with Eq. (2) must be found, we begin with the Lippmann-Schwinger equation written in a form to describe electronic excitation. We choose the relative linear momentum as one of the quantum numbers characterizing the abstract vector representing the three-particle system. Since the scattering is observed to be almost completely confined to the forward direction, we treat the relative linear momentum as an "almost good" quantum number, and thereby obtain, from the Lippmann-Schwinger equation, a reduced equation. The time-dependent theory is obtained by making the correspondence with time-dependent collision theory through the S matrix.[33,34] The reduced equation is by derivation the equation from which the amplitudes for electronic excitation are to be extracted. Transforming the Lippmann-Schwinger equation to a form which describes rearrangement scattering,[35] we obtain a second reduced equation. By derivation, this second equation is the equation from which the amplitudes for charge exchange are to be extracted, and the fact that there are two equations in this model is a direct consequence of the proper treatment of the continuum. We show that it is sufficient to solve either equation to obtain the amplitudes for excitation and charge exchange; however, in the solution it is necessary to account for the hydrogenic continuum. Finally, we transform the simplest reduced equation into the coordinate system in which Eq. (2) is written, and find that the set of traveling hydrogenic orbitals are not the basis of dynamical states of the unperturbed Hamiltonian. It is shown, however, that the discrete eigenvectors of the unperturbed Hamiltonian approach the traveling orbitals as $|t|\to\infty$; hence the traveling orbitals provide a description of the system which becomes asymptotically valid.

II. IMPACT-PARAMETER MODEL

The observation that the scattering is almost completely in the forward direction indicates that the incident proton travels in essentially a straight line, and so, to a good approximation, the protons can be assumed to be distinguishable. Thus we define the following arrangement channels to classify the possible modes of fragmentation of the three-particle collision:

arrangement channel 1: proton 2 is moving free with respect to hydrogen atom 1;

arrangement channel 2: proton 1 is moving free with respect to hydrogen atom 2;

arrangement channel 3: proton 2 is moving free with respect to the ionized hydrogen atom 1. Assuming that proton 2 is the incident proton, the states of arrangement channel 1 correspond to excitation of the hydrogen atom; those of arrangement channel 2 to charge exchange; and those of arrangement channel 3 to ionization. The following arrangement channel Hamiltonians are defined

$$H_1 = -\frac{\hbar^2}{2M_1}\nabla_{\vec{R}_1}^2 - \frac{\hbar^2}{2m_1}\nabla_{\vec{r}_1}^2 - \frac{e^2}{r_1}$$

$$= -\frac{\hbar^2}{2M_1}\nabla_{\vec{R}_1}^2 + h_1$$

and

$$H_2 = -\frac{\hbar^2}{2M_2}\nabla_{\vec{R}_2}^2 - \frac{\hbar^2}{2m_2}\nabla_{\vec{r}_2}^2 - \frac{e^2}{r_2}$$

$$= -\frac{\hbar^2}{2M_2}\nabla_{\vec{R}_2}^2 + h_2,$$

where for arrangement channel i, $\vec{R}_i$ is the relative coordinate vector, $\vec{r}_i$ is the internal coordinate vector for the hydrogen-atom Hamiltonian h_i, M_i is the relative mass, and m_i is the reduced mass. As is customary, we will assume that the electronic mass is negligible compared to the mass of the proton, and so the reduced mass becomes the electronic mass, and $\vec{R}_i$ becomes an interproton coordinate. The arrangement channel interactions are

$$V_1 = e^2/R_1 - e^2/|\vec{r}_1 - \vec{R}_1|,$$

$$V_2 = e^2/R_2 - e^2/|\vec{r}_2 - \vec{R}_2|.$$

Note that the arrangement-channel interactions vanish faster than $1/R_i$ as $R_i\to\infty$. The Hamiltonian for the complete system can be written as follows:

$$H = H_i + V_i.$$

The discrete eigenvectors of H_1 and H_2 form sets of vectors which respectively span the subspaces subtended by arrangement channels 1 and 2; these sets of vectors will be denoted as follows:

$$\{\Phi_\alpha(\vec{K}_{\alpha n}, n\alpha)\},$$

where α is an arrangement-channel index, $\hbar\vec{K}_{\alpha n}$ the relative linear momentum, and $n\alpha$ the set of quantum numbers needed to specify a bound state of the hydrogen atom in which proton α is the nucleus. These vectors are normalized as follows:

$$\langle\Phi_\alpha(\vec{K}'_{\alpha n'}, n'\alpha)|\Phi_\alpha(\vec{K}_{\alpha n}, n\alpha)\rangle = \delta(\vec{K}'_{\alpha n'} - \vec{K}_{\alpha n})\,\delta_{n'\alpha n\alpha},$$

and thus in the coordinate representation,

$$\Phi_\alpha = (1/2\pi)^{3/2} e^{i\vec{K}_{\alpha n}\cdot\vec{R}_\alpha}\phi_{n\alpha}(\vec{r}_\alpha),$$

where $\phi_{n\alpha}$ is a discrete eigenvector of the hydrogen atom Hamiltonian h_α. The magnitude of the linear momentum is, of course,

$$\hbar K_{\alpha n} = [(2M)(E-\epsilon_{n\alpha})]^{1/2},$$

where $\epsilon_{n\alpha}$ is the discrete eigenvalue of h_α corresponding to eigenvector $\phi_{n\alpha}$. The continuum eigenvectors of H_1 and H_2 belong to the space of arrangement channel 3, and they are written as follows:

$$\Phi_\alpha^+ = (1/2\pi)^{3/2} e^{i\vec{K}_\alpha\cdot\vec{R}_\alpha}\phi_\alpha^+(\vec{r}_\alpha;\vec{k}_\alpha),$$

where ϕ_α^+ is a continuum eigenvector of h_α which satisfies outgoing boundary conditions. These vectors are normalized as follows:

$$\langle \Phi_\alpha^+(\vec{K}'_\alpha,\vec{k}'_\alpha)|\,\Phi_\alpha^+(\vec{K}_\alpha,\vec{k}_\alpha)\rangle = \delta(\vec{K}'_\alpha-\vec{K}_\alpha)\delta(\vec{k}'_\alpha-\vec{k}_\alpha),$$

and a set of these vectors forms the orthogonal complement to the corresponding set of discrete eigenvectors spanning the space of arrangement channel 1 or 2. The total set is complete:

$$\sum_n \int d^3K_n\,\Phi_n\Phi_n^+ = 1, \tag{7}$$

where the arrangement-channel index has been suppressed, and the continuous indices for the eigenvectors of h are not distinguished from the discrete indices.

The complete state vector for the system is the solution to the Lippmann-Schwinger equation:

$$\Psi^+(\vec{K}_{1i},i1) = \Phi_1(\vec{K}_{1i},i1) + G_1^+(E)V_1\Psi^+(\vec{K}_{1i},i1), \tag{8}$$

where the Green's function is

$$G_1^+(E) = \lim_{\eta\to 0^+}\frac{1}{E-H_1+i\eta},$$

and it is understood that the limiting process is to be taken in a particular representation. In the coordinate representation,

$$G_1^+(\vec{R}_1,\vec{r}_1;\vec{R}'_1,\vec{r}'_1;E) = -\frac{M}{2\pi\hbar^2}\times\sum_{n1}\frac{e^{iK_{1n}|\vec{R}_1-\vec{R}'_1|}}{|\vec{R}_1-\vec{R}'_1|}\phi_{n1}(\vec{r}_1)\phi^*_{n1}(\vec{r}'_1)$$

and

$$\psi^+(\vec{R}_1,\vec{r}_1) = \Phi_1(\vec{R}_1,\vec{r}_1) + \int d^3R'_1\int d^3r'_1\,G_1^+(\vec{R}_1,\vec{r}_1;\vec{R}'_1,\vec{r}'_1)\times V_1(\vec{R}'_1,\vec{r}'_1)\Psi^+(\vec{R}'_1,\vec{r}'_1).$$

Consequently, as $R_1\to\infty$,

$$\Psi^+ \sim \Phi_1 + \sum_{n1}\left(-\frac{M}{2\pi\hbar^2}\int d^3R'_1\int d^3r'_1\,e^{-i\vec{K}_{1n}\cdot\vec{R}'_1}\phi^*_{n1}(\vec{r}'_1)V_1\Psi^+\right)\frac{e^{iK_{1n}R_1}}{R_1}\phi_n(\vec{r}_1) + (\text{other terms which decrease faster than } 1/R_1), \tag{9}$$

where the sum is only over the open-channel indices. The amplitude for the transition from the state Φ_1 to another state of arrangement channel 1 is from Eq. (9):

$$A_1(\vec{K}_{1n},nl;\vec{K}_{1i},i1) = -(M/2\pi\hbar^2)\int d^3R'_1\times\int d^3r'_1\,e^{-i\vec{K}_{1n}\cdot\vec{R}'_1}\phi^*_n(\vec{r}'_1)V_1\Psi^+.$$

The state vector also contains the information from which the amplitudes for charge exchange or ionization could be obtained. However, this information cannot be obtained from Eq. (8) because it is contained in those terms of Eq. (9) which are decreasing faster than $1/R_1$ (in particular those terms corresponding to ϕ_{n1} in the continuum).[35,36] To obtain this information, the Lippmann-Schwinger equation must be transformed into a more convenient form.[35] Consequently, each arrangement channel will be considered separately, and when the meaning is clear, the arrangement-channel index will be suppressed.

A. Arrangement Channel 1

From the observation that the scattering is almost completely in the forward direction, it is to be expected that the transition amplitude is a strongly peaked function of $\vec{K}_n$ about $\vec{K}_i$; i.e.,

$$A_1(\vec{K}_{1n},nl;\vec{K}_{1i},i1) \approx \delta(\vec{K}_{1n}-\vec{K}_{1i})A_1(n1,i1;\vec{K}_{1i}),$$

or in other words, $\vec{K}_{1i}$ is an "almost good" quantum number. Therefore we write[37]

$$\Psi^+(\vec{K}_{1i},i1) \approx |\vec{K}_{1i}\rangle\chi(i1;\vec{K}_{1i}),$$

and from the Lippman-Schwinger equation,

$$|\vec{K}_{i1}\rangle\chi \approx \Phi_1 + G_1^+(E)V_1|\vec{K}_{1i}\rangle\chi. \tag{10}$$

Inserting the complete set of states of H_1[Eq. (7)] and changing to a full equals to sign, Eq. (10) becomes (suppressing the arrangement-channel index)

$$|\vec{K}_i\rangle\chi = |\vec{K}_i\rangle\phi_i + \sum_n \int d^3K_n \times \frac{\phi_n|\vec{K}_n\rangle\langle\vec{K}_n|\phi_n^\dagger}{(\hbar^2/2M)(K_i'^2 - K_n^2) + i\eta} V_1|\vec{K}_i\rangle\chi\,, \qquad (11)$$

where

$$K_i'^2 = K_i^2 + (2M/\hbar^2)(\epsilon_i - \epsilon_n)\,.$$

In a partial coordinate representation, where[38]

$$\langle\vec{R}_1|(|\vec{K}_i\rangle\chi) \equiv (1/2\pi)^{3/2} \times e^{i\vec{K}_i\cdot\vec{R}_1}\chi(\vec{R}_1)$$

and

$$V_1(\vec{R}_1) \equiv \langle\vec{R}_1|V_1|\vec{R}_1\rangle\,.$$

Equation (11) becomes

$$\chi(\vec{R}_1) = \phi_i + \sum_n \phi_n \int d^3R_1' \left[\left(\frac{1}{2\pi}\right)^3 \int d^3K_n \frac{e^{i\vec{K}_n\cdot(\vec{R}_1 - \vec{R}_1')}}{(\hbar^2/2M)(K_i'^2 - K_n^2) + i\eta}\right] \phi_n^\dagger V_1(\vec{R}_1') e^{-i\vec{K}_i\cdot(\vec{R}_1 - \vec{R}_1')}\chi(\vec{R}_1')\,. \qquad (12)$$

Since

$$\left(\frac{1}{2\pi}\right)^3 \int d^3K_n \frac{e^{i\vec{K}_n\cdot(\vec{R}_1 - \vec{R}_1')}}{(\hbar^2/2M)(K_i'^2 - K_n^2) + i\eta} = -\frac{M}{2\pi\hbar^2}\frac{e^{iK_i'|\vec{R}_1 - \vec{R}_1'|}}{|\vec{R}_1 - \vec{R}_1'|}\,.$$

Equation (12) becomes

$$\chi(\vec{R}_1) = \phi_i + \sum_n \phi_n \left(-\frac{M}{2\pi\hbar^2}\int d^3R_1' \frac{e^{[iK_i'|\vec{R}_1 - \vec{R}_1'| - i\vec{K}_i\cdot(\vec{R}_1 - \vec{R}_1')]}}{|\vec{R}_1 - \vec{R}_1'|}\phi_n^\dagger V_1(\vec{R}_1')\chi(\vec{R}_1')\right), \qquad (13)$$

where

$$K_i' = K_i\left(1 + \frac{2M}{\hbar^2}\frac{(\epsilon_i - \epsilon_n)}{K_i^2}\right)^{1/2},$$

which since the incident kinetic energy is large, we approximate as

$$K_i' \approx K_i + (M/\hbar^2)[(\epsilon_i - \epsilon_n)/K_i]\,.$$

This is, of course, a good approximation for the bound-state contribution to the sum in Eq. (13), since

$$\epsilon_n \leq 13.6\ \text{eV}\,, \quad \hbar^2K_i^2/2M \geq 1\ \text{keV}\,.$$

The approximation begins to fail when the kinetic energy of the ejected electron approaches 1 keV. However, it is expected that these terms in the sum of Eq. (13) are negligibly small. Making this approximation, we obtain from Eq. (13)

$$\chi(\vec{R}_1) = \phi_i + \sum_n \phi_n\left[-\frac{M}{2\pi\hbar^2}\int d^3R_1' \frac{\exp[iK_i|\vec{R}_1 - \vec{R}_1'| - i\vec{K}_i\cdot(\vec{R}_1 - \vec{R}_1')]}{|\vec{R}_1 - \vec{R}_1'|}\exp\left(iM\frac{(\epsilon_i - \epsilon_n)|\vec{R}_1 - \vec{R}_1'|}{\hbar^2K_i}\right)\phi_n^\dagger V_1(\vec{R}_1')\chi(\vec{R}_1')\right],$$

or after removing the complete set of states of h_1

$$\chi(\vec{R}_1) = \phi_i - \frac{M}{2\pi\hbar^2}\int d^3R_1'\left(\frac{\exp[iK_i|\vec{R}_1 - \vec{R}_1'| - i\vec{K}_i\cdot(\vec{R}_1 - \vec{R}_1')]}{|\vec{R}_1 - \vec{R}_1'|}\right)\exp\frac{i}{\hbar}\left(\frac{(\epsilon_i - h_1)|\vec{R}_1 - \vec{R}_1'|}{v}\right), \qquad (14)$$

where the velocity is defined as $v = \hbar K_i/M$. We assume that the direction of $\vec{K}_i$ is $\hat{Z}$, and by following Glauber,[39] we obtain a high-energy approximation to the integral operator of Eq. (14) (See Appendix A for details)[40]; Eq. (14) then becomes

$$\chi(\vec{R}_1) = \phi_i - \frac{i}{\hbar v}\exp\left(\frac{i}{\hbar}(\epsilon_i - h_1)\frac{Z}{v}\right)\int_{-\infty}^{Z} dZ' \exp\left(\frac{-i}{\hbar}(\epsilon_i - h_1)\frac{Z'}{v}\right)V_1(X, Y, Z')\chi(X, Y, Z')\,. \qquad (15)$$

Note that the values of X and Y are constants of the motion. Reinserting the complete set of state of h_1, and letting Z become large, we obtain

$$\chi(\vec{R}_1) \sim \phi_i + \sum_n\left(\left\langle\phi_n\right| - \frac{i}{\hbar v}\int_{-\infty}^{\infty} dZ' \exp\left(\frac{-i}{\hbar}(\epsilon_i - h_1)\frac{Z'}{v}\right)V_1(Z')\chi(Z')\right\rangle\right)\phi_n \exp\left(\frac{i}{\hbar}(\epsilon_i - \epsilon_n)\frac{Z}{v}\right). \qquad (16)$$

Consequently, we see from Eq. (9) that the transition probability for electronic excitation is given in this approximation by

$$P_{ni}=\left|\left\langle \phi_n\right|-(i/\hbar v)\int_{-\infty}^{\infty}dZ'\exp[-(i/\hbar)(\epsilon_i-\epsilon_n)(Z'/v)]\,V_1(Z')\chi(Z')\right\rangle\Big|^2 . \tag{17}$$

In time-independent collision theory, the wave packet representing the incident particles is replaced by a plane wave for which a point of constant phase moves according to $Z=vt$. Therefore Eq. (17) can be written equally as well as

$$P_{ni}=\left|\left\langle \phi_n\right|-(i/\hbar)\int_{-\infty}^{\infty}dt\,e^{-(i/\hbar)(\epsilon_i-\epsilon_n)t}\,V_1(vt)\chi(vt)\right\rangle\Big|^2 . \tag{18}$$

Note that because of the established correspondence between time-independent collision theory and time-dependent collision theory,[33] the time t is "real time," and not just a convenient parameter.[26]

Equation (15) can be written as follows:

$$\chi(vt)=\phi_i-(i/\hbar)e^{(i/\hbar)(\epsilon_i-h_i)t}\int_{-\infty}^{vt}dt'\,e^{-(i/\hbar)(\epsilon_i-h_i)t'}\,V_1(vt')\chi(vt') . \tag{19}$$

Defining a new vector by the unitary transformation $\psi=e^{-(i/\hbar)\epsilon_i t}\chi$, Eq. 19 becomes

$$\psi(vt)=\phi_i e^{-(i/\hbar)\epsilon_i t}-\frac{i}{\hbar}e^{-(i/\hbar)h_1 t}\int_{-\infty}^{vt}dt'\,e^{(i/\hbar)h_1 t'}\,V_1(vt')\psi(vt') , \tag{20}$$

which by iteration can be written

$$\psi=\phi_i e^{-(i/\hbar)\epsilon_i t}-\frac{i}{\hbar}\int_{-\infty}^{vt}dt'\,e^{-(i/\hbar)h_1(t-t')}\,V_1(vt')e^{-(i/\hbar)h_1 t'}\,\phi_i$$
$$+\left(-\frac{i}{\hbar}\right)^2\int_{-\infty}^{vt}dt'\int_{-\infty}^{vt'}dt''\,e^{-(i/\hbar)h_1(t-t')}V_1(vt')e^{-(i/\hbar)(t'-t'')}\,V_1(vt'')e^{-(i/\hbar)h_1 t''}\,\phi_i+\cdots ,$$

or

$$\psi(vt)=U_1(t,t'=-\infty)\phi_i ,$$

where

$$U_1(t,t'=-\infty)=U_1^0(t,t'=-\infty)+\sum_n U_1^n(t,t'=-\infty) , \tag{21}$$

$$U_1^0(t,t'=-\infty)=e^{-(i/\hbar)h_1 t} , \tag{21a}$$

$$U_1^n(t,t'=-\infty)=\left(-\frac{i}{\hbar}\right)^n\int_{-\infty}^{vt}dt_1\int_{-\infty}^{vt_1}dt_2\cdots\int_{-\infty}^{vt_{n-1}}dt_n\,U_1^0(t,t_1)V_1(vt_1)U_1^0(t_1,t_2)$$
$$\times\cdots U_1^0(t_{n-1},t_n)V_1(vt_n)U_1^0(t_n,t'=-\infty) . \tag{21b}$$

It should be noted that the series defining U_1, Eqs. (21), is the usual expansion in powers of V_1 for the unitary time-evolution operator obtained in time-dependent perturbation theory.[20] Therefore we have obtained the Schrödinger time representation for the model system of a point charge moving along a prescribed path and perturbing a hydrogen atom. The eigenvectors of h_1 form the basis of dynamical states available to the model system. The system is initially described by a particular state ϕ_i. Subsequently, the perturbation of the moving point charge V_1 acts upon the system, and the state vector for the system ψ transforms under the unitary time-evolution operator U_1. The probability that the system has made a transition to the state ϕ_n is

$$P_{ni}=|\langle\phi_n|\,U_1(t=\infty,t'=-\infty)\,|\,\phi_i\rangle|^2$$
$$=\left|\left\langle\phi_n\right|-(i/\hbar)\int_{-\infty}^{\infty}dt\times e^{(i/\hbar)\epsilon_n t}\,V_1(vt)\psi(vt)\right\rangle\Big|^2 .$$

Equivalently, one can describe the evolution of the state vector according to a Schrödinger equation; taking the derivative of Eq. (20), one obtains

$$i\hbar\frac{\partial}{\partial t}\psi=[h_1+V_1(vt)]\psi , \tag{22}$$

with the boundary conditions[21]

$$\psi\sim\phi_{i1}e^{-(i/\hbar)\epsilon_{i1}t}\quad\text{as } t\to-\infty \tag{22a}$$

and

$$\psi \sim \sum_n (\delta_{n1i1} + A_{n1i1}) \times \phi_{n1} e^{-(i/\hbar)\epsilon_{n1}t} \quad \text{as } t \to \infty ,$$

where the arrangement-channel index has been explicitly indicated, and where the amplitude for the $i \to n$ transition is

$$A_{n1i1} = \left\langle \phi_{n1} \right| - (i/\hbar) \int_{-\infty}^{\infty} dt \times e^{(i/\hbar)\epsilon_{n1}t} V_1(vt)\psi(vt) \Big\rangle . \tag{22b}$$

Note that the boundary condition, or an equivalent restriction,[21] at $t \to \infty$ is not specified in the postulated impact-parameter model.

B. Arrangement Channel 2

As discussed, Eq. (8) is not in the form to extract the amplitudes for charge exchange, and as shown by Lippmann,[35] Eq. (8) must be transformed to a more suitable form. With a few algebraic manipulations, Eq. (8) can be written in the form convenient to describe rearrangement:

$$\Psi^+(\vec{K}_{1i}, i1) = \frac{i\eta}{E - H_2 + i\eta} \Phi_1(\vec{K}_{1i}, i1) + G_2^+(E) V_2 \Psi^+(\vec{K}_{1i}, i1), \tag{23}$$

where

$$G_2^+(E) = \lim_{\eta \to 0^+} \frac{1}{E - H_2 + i\eta}$$

and the limiting process ($\eta \to 0$) is to be taken in a particular representation. The first term of Eq. (24) is a source term; it is orthogonal to any state of arrangement channel 2 in the limit $R_2 \to \infty$.[34] Consequently, the amplitudes for transitions to the states of arrangement channel 2 are to be extracted from the second term of Eq. (23). Again it is assumed that $\vec{K}_{1i}$ is an "almost good" quantum number; therefore[37]

$$\Psi^+(\vec{K}_{1i}, i1) \approx |\vec{K}_{1i}\rangle \chi(i1; \vec{K}_{1i}),$$
$$|\vec{K}_{1i}\rangle \chi \approx \frac{i\eta}{E - H_2 + i\eta} \Phi_1 + G_2^+(E) V_2 |\vec{K}_{1i}\rangle \chi . \tag{24}$$

Following a procedure entirely analogous to that above, we reduce Eq. (24) and obtain

$$\psi(vt) = \sum_{n2} \phi_{n2} \langle \phi_{n2} | \phi_{i1} \rangle \times e^{-(i/\hbar)\epsilon_{n2}t} - \frac{i}{\hbar} e^{-(i/\hbar)h_2 t} \times \int_{-\infty}^{vt} dt' e^{(i/\hbar)h_2 t'} V_2(vt')\psi(vt') . \tag{25}$$

The first term in Eq. (25) follows from the source term in the Lippmann-Schwinger equation, and obviously corresponds to

$$e^{-(i/\hbar)h_2 t} \phi_{i1} = U_2^0(t, t' = -\infty)\phi_{i1} . \tag{26}$$

The transition probabilities are obtained from the second term of Eq. (25); hence by this approximation the probability for charge exchange is

$$P_{n2i1} = \left| \left\langle \phi_{n2} \right| - (i/\hbar) \int_{-\infty}^{\infty} dt' e^{(i/\hbar)\epsilon_{n2}t'} \times V_2(vt')\psi(vt') \right\rangle \Big|^2 , \tag{27}$$

which can be written as follows:

$$P_{n2i1} = |\langle \phi_{n2} | U_2(t = \infty, t' = -\infty) | \phi_{i1} \rangle|^2 ,$$

where the evolution operator is defined by the series

$$U_2(t, t' = -\infty) = U_2^0(t, t' = -\infty) + \sum_n U_2^n(t, t' = -\infty) , \tag{28}$$

$$U_2^n(t, t' = -\infty) = (-i/\hbar)^n \int_{-\infty}^{vt} dt_1 \cdots \int_{-\infty}^{vt_{n-1}} dt_n U_2^0(t, t_1) V_2(vt_1) U_2^0(t_1, t_2) \times \cdots U_2^0(t_{n-1}, t_n) V_2(vt_n) U_2^0(t_n, t' = -\infty) . \tag{28a}$$

The Schrödinger equation is easily obtained:

$$i\hbar \frac{\partial}{\partial t} \psi = [h_2 + V_2(vt)]\psi . \tag{29}$$

The boundary conditions are[21]

$$\psi(t) \sim \sum_{n2} \phi_{n2} \langle \phi_{n2} | \phi_{i1} \rangle \times e^{-(i/\hbar)\epsilon_{n2}t} \quad \text{as } t \to -\infty \tag{29a}$$

and

$$\psi(t) \sim \sum_{n2} \phi_{n2} \langle \phi_{n2} | \phi_{i1} \rangle \times e^{-(i/\hbar)\epsilon_{n2}t} + \sum_{n2} A_{n2i1} \times \phi_{n2} e^{-(i/\hbar)\epsilon_{n2}t} \quad \text{as } t \to \infty ,$$

where

$$A_{n2i1} = \left\langle \phi_{n2} \right| - (i/\hbar) \int_{-\infty}^{\infty} dt \times e^{(i/\hbar)\epsilon_{n2}t} V_2(vt)\psi(vt) \Big\rangle . \tag{29b}$$

Therefore, for the derived impact-parameter model there are two time-evolution operators, and hence two Schrödinger equations. The two Schrödinger equations differ in the identity of the protons and the boundary conditions that are to be applied to the solutions. The initial boundary condition associated with Eq. (22) is simple to apply; while the initial boundary condition associated with Eqs. (29) is in terms of the continuum eigenvectors of h_2, and hence difficult to apply. The fact that there are two time-evolution operators is a consequence of the fact that there are two S operators[34] $[U(t=\infty, t'=-\infty)]$ for the complete three-particle system.

By derivation, the amplitudes for excitation are to be obtained from the solution of Eq. (22), while the amplitudes for charge exchange are to be obtained from the solution of Eqs. (29). However, we note that in Eq. (22) or (29) there are the quantities $A_{n1,i1}$ or $A_{n2,i1}$ which correspond in a mathematical sense to transitions from ϕ_{i1} to the continuum states ϕ_{n1} or ϕ_{n2} of the operators h_1 or h_2. Further, we note that in the mathematical sense,

$$\psi(t) = U_1(t, t'=-\infty)\phi_{i1} = U_2(t, t'=-\infty)\phi_{i1},$$

hence

$$A_{n2,i1} + \langle \phi_{n2} | \phi_{i1} \rangle = \sum_{m1} \langle \phi_{n2} | \phi_{m1} \rangle \times (A_{m1,i1} + \delta_{m1 i1}) \times e^{i(\epsilon_{n2} - \epsilon_{m1})t} \tag{30}$$

or

$$A_{n1,i1} + \delta_{n1,i1} = \sum_{m2} \langle \phi_{n1} | \phi_{m2} \rangle \times (A_{m2,i1} + \langle \phi_{m2} | \phi_{i1} \rangle) \times e^{i(\epsilon_{n1} - \epsilon_{m2})t}, \tag{31}$$

and thus it is sufficient to solve either Eq. (22) or (29) to obtain both the amplitudes for excitation and charge exchange. However, since the only overlap elements in Eq. (30) or (31) that are not zero in the limit $t \to \infty$ are those with continuous indices, it is necessary to account for the hydrogenic continuum. Note that in addition to the perturbations V_1 or V_2 there must also be an infinitely large perturbation, since transitions to all states of h_1 or h_2 are possible. This of course follows from the assumption that the incident kinetic energy is very large [infinite in Eq. (14)]. Consequently, we can see no connection between the separation of nuclear and electronic motion that we have obtained and the Born-Oppenheimer separation,[8] since we have assumed that the kinetic-energy operator is an infinite perturbation rather than a small perturbation.

Finally it should be noted that Eq. (22), for instance, is written in a different set of coordinates than Eq. (2) of the impact-parameter model. Let $\mathcal{T}(t)$ be the transformation which at time t translates the origin of the electronic coordinate vector to the point $\frac{1}{2}\vec{R}_1(t)$. Associated with the transformation $\mathcal{T}$ is the unitary operator T[20]:

$$T(t) = e^{-(i/\hbar)\vec{p}\cdot\vec{R}_1(t)/2}, \tag{32}$$

where $\vec{p}$ is the electronic linear momentum operator. Applying the translation operator to Eq. (20) and with obvious manipulations, we obtain Eq. (2) with the boundary conditions:

$$\psi(\vec{r}, t) \sim \phi_i^T(\vec{r}) e^{-(i/\hbar)\epsilon_i t} \quad \text{as } t \to -\infty \cdot$$

and

$$\psi(\vec{r}, t) \sim \phi_i^T(\vec{r}) e^{-(i/\hbar)\epsilon_i t} + \sum_n A_{ni}\, \phi_n^T(\vec{r}) e^{-(i/\hbar)\epsilon_n t}$$

as $t \to \infty$. (32a)

The transformed basis vectors are related to the old basis vectors by

$$\phi_n^T = \sum_k T_{kn}\, \phi_k, \tag{33}$$

where

$$T_{kn} = \langle \phi_k | \exp[-(i/\hbar)\vec{p}\cdot\tfrac{1}{2}\vec{R}_1(t)] | \phi_n \rangle$$

are the elements of the translation matrix. One can demonstrate heuristically that as $|t| \to \infty$,

$$\phi_n^T \sim \phi_n(\vec{r}_1)\, e^{-(i/\hbar)p_0 z}, \tag{34}$$

which is the spatial part of the traveling orbitals [Eq. (4)]. One should note, however, that the set $\{\phi_n^T\}$ forms a basis of dynamical states in which the system is described for all times, while the traveling orbitals provide a description which is only asymptotically correct.

We will now consider other formal solutions to the integral equations of evolution which might be more useful for calculational purposes than Eqs. (21) and (28). In contrast to the iterative procedure used to derive Eq. (21) or (28), the procedure is noniterative, and is based upon replacing the integrals in Eqs. (20) and (25) by quadratures: Riemann sums in this case. A calculational procedure based upon this technique has been used to "solve" the Lippmann-Schwinger equation and thereby obtain "exact" scattering amplitudes for some time-independent-scattering problems.[41-43] The amplitudes are "exact" in the sense that as standard numerical procedures are refined the calculated amplitudes approach the

exact amplitudes. It is hoped that the formal expressions given below, or similar expressions obtained by replacing the integrals by other quadratures, will also be useful for obtaining accurate values for the excitation and charge exchange amplitudes.

Equations (20) and (25) can be conveniently written in atomic units as follows

$$\psi(\tau)=e^{-i\Gamma(\tau-\tau_0)}\phi_i-(i/v)e^{-i\Gamma(\tau-\tau_0)}\times\int_{\tau_0}^{\tau}d\tau'\,e^{i\Gamma(\tau'-\tau_0)}V(\tau')\psi(\tau'),\qquad(35)$$

where the index denoting the particular time representation has been suppressed, and we have defined

$$\Gamma=h/v,\quad \tau=vt.$$

The limiting process $\tau_0\to-\infty$ is understood; note that by definition

$$\lim_{\tau_0\to-\infty}e^{-i\Gamma_k\tau_0}\phi_{nk}=1,$$

where k denotes a particular time representation. In practice $|\tau_0|$ will be a large but finite number, and will be chosen by the requirement that the calculated transition probabilities be invariant to further increases in $|\tau_0|$. With the unitary transformation, defined as follows:

$$\Psi(\tau)=e^{-i\Gamma(\tau-\tau_0)}\psi(\tau),$$

Eq. (35) becomes

$$\Psi(\tau)=\phi_i-(i/v)\int_{\tau_0}^{\tau}d\tau'\,e^{i\Gamma(\tau'-\tau_0)}\times V(\tau')e^{-i\Gamma(\tau'-\tau_0)}\Psi(\tau'),\qquad(36)$$

and according to Eqs. (22b) and (29b), the transition amplitudes (apart from an unimportant phase factor) are given by

$$A_{fi}(t)=\langle\phi_f|\Psi(\tau)\rangle-\langle\phi_f|\phi_i\rangle.\qquad(37)$$

Equation (36) will be used to "step out" the solution Ψ from the initial state ϕ_i at τ_0 to the state at τ, and this result will be used in Eq. (37) to obtain an expression for the transition amplitudes. Consider a time $t_1=t_0+\Delta t$, where Δt is infinitesimal; from Eq. (36),

$$\begin{aligned}\Psi(\tau_1)&=\phi_i-(i/v)\int_{\tau_0}^{\tau_0+\Delta\tau}d\tau'\,e^{i\Gamma(\tau'-\tau_0)}\times V(\tau')e^{-i\Gamma(\tau'-\tau_0)}\Psi(\tau')\\&\approx\phi_i-i\Delta t\,V(\tau_0)\Psi(\tau_0)\\&=[1-i\Delta t\,V(\tau_0)]\,\phi_i,\end{aligned}$$

and from Eq. (37),

$$A_{fi}(t_1)\approx\langle\phi_f|-i\Delta t\,V(\tau_0)|\phi_i\rangle.$$

Obviously this process can be continued; at $t_2=t_1+\Delta t$,

$$\Psi(\tau_2)=\phi_i-(i/v)\int_{\tau_0}^{\tau_1}d\tau'\,e^{i\Gamma(\tau'-\tau_0)}V(\tau')e^{-i\Gamma(\tau'-\tau_0)}\Psi(\tau')-\frac{i}{v}\int_{\tau_1}^{\tau_2}d\tau'\,e^{i\Gamma(\tau'-\tau_0)}V(\tau')e^{-i\Gamma(\tau'-\tau_0)}\Psi(\tau')$$

$$\approx\{1-i\Delta t[V(\tau_0)+e^{i\Gamma(\Delta\tau)}V(\tau_1)e^{-i\Gamma(\Delta\tau)}]+(-i\Delta t)^2e^{i\Gamma(\Delta\tau)}V(\tau_1)e^{-i\Gamma(\Delta\tau)}V(\tau_0)\}\phi_i,$$

and so at time t_2,

$$A_{fi}(t_2)\approx\langle\phi_f|-i\Delta t[V(\tau_0)+e^{i\Gamma(\Delta\tau)}V(\tau_1)e^{-i\Gamma(\Delta\tau)}]|\phi_i\rangle+\langle\phi_f|(-i\Delta t)^2e^{i\Gamma(\Delta\tau)}V(\tau_1)e^{-i\Gamma(\Delta\tau)}V(\tau_0)|\phi_i\rangle.$$

In general at the nth step, we find

$$\begin{aligned}A_{fi}(t_n)\approx&\langle\phi_f|-i\Delta t[V(\tau_0)+\cdots e^{i\Gamma(n-1)\Delta\tau}V(\tau_{n-1})e^{-i\Gamma(n-1)\Delta\tau}]|\phi_i\rangle\\&+\langle\phi_f|(-i\Delta t)^2[e^{i\Gamma(\Delta\tau)}V(\tau_1)e^{-i\Gamma(\Delta\tau)}V(\tau_0)+\cdots e^{i\Gamma(n-1)\Delta\tau}V(\tau_{n-1})|e^{-\Gamma(n-1)\Delta\tau}V(\tau_0)\\&+\cdots e^{i\Gamma(n-1)\Delta\tau}V(\tau_{n-1})e^{-i\Gamma(\Delta\tau)}V(\tau_{n-2})e^{-i\Gamma(n-2)\Delta\tau}]|\phi_i\rangle\\&+\cdots\langle\phi_f|(-i\Delta t)^ne^{i\Gamma(n-1)\Delta\tau}V(\tau_{n-1})e^{-i\Gamma(\Delta\tau)}V(\tau_{n-2})\cdots e^{-i\Gamma(\Delta\tau)}V(\tau_0)|\phi_i\rangle=\sum_{N=1}^{n}A_{fi}^{(N)}(t_n),\end{aligned}\qquad(38)$$

where the Nth contribution to the transition amplitude is defined as follows:

$$A_{fi}^{(N)}(t_n)=\langle\phi_f|U_{Nn}|\phi_i\rangle,\qquad(39)$$

and where U_{Nn} is the Nth-type interaction at time t_n; for example,

$$U_{2n}=\sum_{j=0}^{n-2}\sum_{k\geq j+1}^{n-1}(i\Delta t)^2e^{i\Gamma(k\Delta\tau)}\times V(\tau_k)e^{-i\Gamma(k-j)\Delta\tau}V(\tau_j)e^{-i\Gamma(j\Delta\tau)}.$$

The various interactions appearing in Eq. (38) are shown in diagrammatic form in Fig. 1. At time

t_n, the number of interactions of type k is

$$n!/k!(n-k)!,$$

and the total number of interactions is 2^n. According to Eq. (38) the amplitude for the transition from ϕ_i to ϕ_f is the matrix element of the sum of diagrams shown in Fig. 1 between ϕ_i and ϕ_f. The diagrams are, of course, a direct result of the procedure used to approximate the integral operator in Eq. (36) and in general other sets of diagrams would be obtained by using other approximation methods. Finally, it should be noted that the integrals appearing in the interaction matrix elements can be performed analytically; for example,

$$\langle \phi_f | V(\tau_0) | \phi_i \rangle = \langle \phi_f | \phi_i \rangle / R(\tau_0) - Q_{fi}(\tau_0), \qquad (40)$$

where $Q_{fi}(\tau_0)$ is either a Coulomb or exchange integral depending upon whether time representation 1 or 2 is being used.

APPENDIX A

We consider the high-energy approximation to the integral operator in Eq. (14)[39]:

$$\int d^3R' \frac{\exp[iK|\vec{R}-\vec{R}'| - i\vec{K}\cdot(\vec{R}-\vec{R}')]}{|\vec{R}-\vec{R}'|} \times \exp\left(\frac{i}{\hbar}\frac{(\epsilon_i - h)}{v}|\vec{R}-\vec{R}'|\right) V(\vec{R}')\chi(\vec{R}'). \qquad (A1)$$

We let $\vec{\mathfrak{R}} = \vec{R} - \vec{R}'$, and so the integral becomes

$$\int d^3\mathfrak{R} \frac{e^{i(K\mathfrak{R} - \vec{K}\cdot\vec{\mathfrak{R}})}}{\mathfrak{R}} \times \exp\left(\frac{i}{\hbar}\frac{(\epsilon_i - h)\mathfrak{R}}{v}\right) V(\vec{R}-\vec{\mathfrak{R}})\chi(\vec{R}-\vec{\mathfrak{R}}). \qquad (A2)$$

Essentially we assume that since K is large, the product

$$\exp\left(\frac{i}{\hbar}\frac{(\epsilon_i - h)\mathfrak{R}}{v}\right) V(\vec{R}-\vec{\mathfrak{R}})\chi(\vec{R}-\vec{\mathfrak{R}})$$

varies slowly within an interval $1/K$ and so most of the contribution to the integral comes when the exponential

$$e^{i(K\mathfrak{R} - \vec{K}\cdot\vec{\mathfrak{R}})} \approx 1,$$

that is, for $\vec{\mathfrak{R}}$ parallel to $\vec{K}$.

Let the direction of $\hat{K}$ define the positive z axis; then in spherical polar coordinates the integral can be written

$$\int_0^\infty \mathfrak{R}\, d\mathfrak{R}\, e^{iK\mathfrak{R}} \exp\left(\frac{i}{\hbar}\frac{(\epsilon_i - h)}{v}\mathfrak{R}\right) \times \int_0^{2\pi} d\phi \int_{-1}^{1} d\xi\, F(\mathfrak{R}, \xi, \phi) e^{-iK\mathfrak{R}\xi}, \qquad (A3)$$

where $\xi = \cos\theta$ and $F(\mathfrak{R}, \xi, \phi) = V(\vec{R}-\vec{\mathfrak{R}})\chi(\vec{R}-\vec{\mathfrak{R}})$. We shall suppose that F is sufficiently smooth so that the ξ integral can be integrated by parts n times; the result is

$$\frac{i}{K\mathfrak{R}} F e^{-iK\mathfrak{R}\xi}\Big|_{-1}^{1} + \frac{i}{(K\mathfrak{R})^2} F' e^{-iK\mathfrak{R}\xi}\Big|_{-1}^{1} + \cdots.$$

Since K is large only the first term will be taken, and so

$$\int_{-1}^{1} d\xi F(\mathfrak{R}, \phi, \xi) e^{-iK\mathfrak{R}\xi} \approx \frac{i}{K\mathfrak{R}}[F(\xi=1)e^{-iK\mathfrak{R}} - F(\xi=-1)e^{+iK\mathfrak{R}}],$$

and thus Eq. (A3) becomes

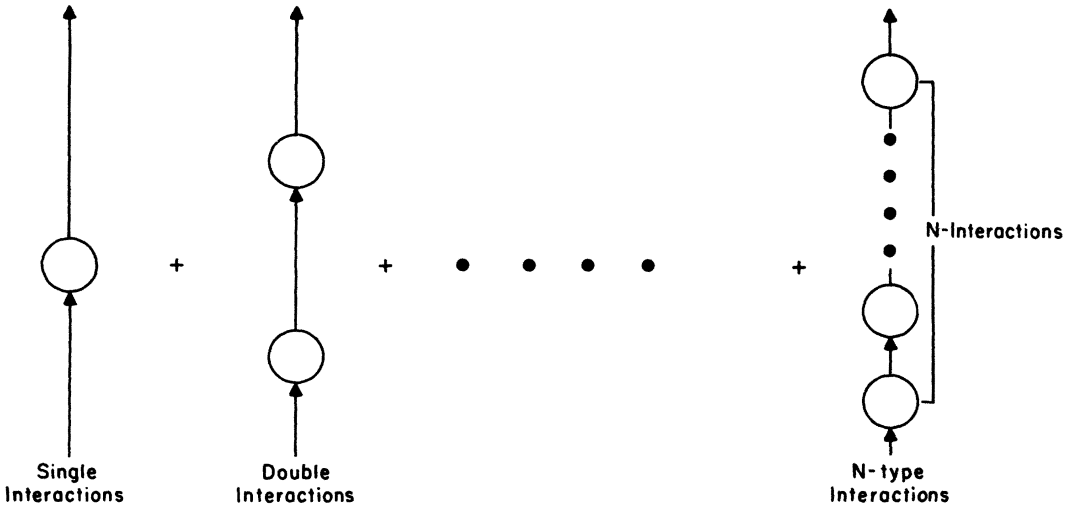

FIG. 1. Sum of the interactions appearing in Eq. (38) in diagrammatic form.

$$\frac{i}{K}\int_0^\infty d\mathfrak{R}\exp\left(\frac{i}{\hbar}\frac{(\epsilon_i-h)}{v}\mathfrak{R}\right)\int_0^{2\pi}d\phi\,[F(\xi=1)-F(\xi=-1)e^{2iK\mathfrak{R}}]. \tag{A4}$$

Since K is large, the second term is small compared to the first, and so Eq. (A4) becomes

$$\frac{2\pi i}{K}\int_0^\infty d\mathfrak{R}\left[\exp\left(\frac{i}{\hbar}\frac{(\epsilon_i-h)}{v}\mathfrak{R}\right)V(\vec{\mathbf{R}}-\vec{\mathfrak{R}})\chi(\vec{\mathbf{R}}-\vec{\mathfrak{R}})\right](\vec{\mathbf{R}}-\vec{\mathfrak{R}})\,||\,\hat{K}=\frac{2\pi i}{K}\int_0^\infty dz\exp\left(\frac{i}{\hbar}\frac{(\epsilon_i-h)}{v}z\right)V(Z-z)\chi(Z-z)$$

$$=\frac{2\pi i}{K}\exp\left(\frac{i}{\hbar}\frac{(\epsilon_i-h)}{v}Z\right)\int_{-\infty}^{Z}dZ'\exp\left(-\frac{i}{\hbar}\frac{(\epsilon_i-h)}{v}Z'\right)V(Z')\chi(Z'),$$

where in the last step we have used the fact that $Z'=Z-z$.

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[38]Note that in this partial coordinate representation $\chi(\vec{R}_1)$ is a vector and $V_1(\vec{R}_1)$ is an operator.
[39]R. J. Glauber, *Lectures in Theorectical Physics* (Interscience, New York, 1958), Vol. I., p. 315.
[40]The similarity between the impact-parameter approximation and the eikonal and Glauber approximations should be noted. The impact-parameter approximation differs from the Glauber approximation in that all momentum transfer to the incident particle is neglected.
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