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APPROXIMATIONS IN THE THEORY OF REARRANGEMENT COLLISIONS AND APPLICATIONS TO A TRACTABLE MODEL OF CHARGE EXCHANGE SCATTERING

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Special Thesis

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James Quong
(Ph. D. Thesis)

August 19, 1966

Contents

Abstract. 1

I. Introduction. 3

II. A Soluble Model of Charge Exchange. 7

The Impact Parameter Method. 7

Three Body Systems. 8

Time Dependent Theory of Scattering. 10

The Numerical Solution To a Model of Ion Atom Scattering. 15

III. Approximate Scattering Theories. 23

A. Preliminary Remarks. 23

B. Ideas and Methods of Approximation Schemes. 25

C. Applications of Approximation Schemes Applied to the Tractable Model. 42

IV. Results and Discussion 56

Conclusions. 69

Acknowledgments. 72

Appendix A: The Variational Method For Time Dependent Theory. . 73

Appendix B: The Two Potential Formalism. 76

Appendix C: Mathematical Relationships Between Approximation Schemes. 80

References and Footnotes 83

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ABSTRACT

The approximation ideas and methods and the historic difficulties involved with the calculation of ion atom rearrangement scattering are examined and redeveloped. Five approximation schemes are selected to be tested. The transition probability for symmetric resonant charge exchange is calculated by these methods for a model one-dimensional scattering system whose exact solution, serving as the basis for comparison, is also attainable by numerical techniques. The impact parameter ideas concerning the uncoupling of the internal and external dynamics are built into the model.

None of the high energy theories are found to be adequate beyond the upper intermediate range; this suggests at least that the convergence of perturbation expansions is slow. The two improved first order schemes, for which the effects of nonorthogonality have been eliminated, are adequate only at upper intermediate energies.

The Born approximation always gives results too high.

An exchange mechanism is found to be operative for all energies up through the intermediate range. The two two-component coupled channel schemes, one employing atomic form factors, the other molecular form factors, together covers accurately this span of the spectrum.

Asymmetric resonant and nonresonant exchange are examined briefly at low and intermediate energies, to confirm predictions drawn from the previous work. The new results are that asymmetric resonant systems are qualitatively indistinguishable from symmetric resonant systems, and that the exchange mechanism is present also for nonresonant systems and may even be the controlling mechanism over the upper portion of the range of energy mentioned. At decreasing energies, however, the mechanism of the adiabatic approximation, tending to suppress exchange in nonresonant systems, becomes progressively more important and eventually becomes decisive. The formal statement, embodying the contents of the last two paragraphs, is that the coupled channel schemes provide an adequate theory for calculating the exchange probability, within the limitation imposed by off-manifold processes, over the low and intermediate ranges of energy for all three types of scattering systems.

I. INTRODUCTION

The term rearrangement scattering has generally been used to denote the type of scattering in which the particles comprising the scattering system in the final state are different from those comprising the initial state. The initial and final states are said to be states of different channels[1] and the process mentioned above a multichannel collision. The question may arise whether one is dealing with two different channels or two different states of the same channel. By our definition of channel, this question becomes a matter of defining formally different particles as distinct from states of the same particle. It will be convenient for us to use the convention where, for example, an inelastic subchannel is not considered a new channel. It is perhaps more common to regard a rearrangement process to be an exchange of one or more component-particles between the two particle systems colliding. There is no loss of generality in the latter definition as it is possible and even fashionable to treat most particles as composites. However, this latter definition is especially appropriate in atomic rearrangement scattering in that the structure of an atomic particle is well understood in terms of electrons and nuclei. Here the multichannel process is charge exchange, more precisely electron transfer, and therefore involves at least three particles. No confusion should arise from the use of the term particle at the two levels of description.

Charge exchange scattering between ion and atom, like all of nonrelativistic atomic scattering, is in principle a solved problem in that the fundamental two-body interaction, the Coulomb interaction,

is known. However, the exact solution for even the simplest systems involving composite particles is too complicated to compute, and recourse must be made to approximation schemes to obtain numerical results. Two considerations, which may not always be distinguishable, enter in the construction of approximation schemes for a particular class of problems. The first of these is involved in the selection of the physical features, believed to be most relevant, with which to define a physical model; the second consideration is that of mathematical convenience. An actual approximation scheme then often is the outcome of a compromise and is specifically tailored for the problem being investigated. We often find, inconveniently, the same mathematical approximation under different names in different situations and the same name shared by apparently different approximation. Much more important than an imprecision in nomenclature is that practically no approximation model is sufficiently reliable, theoretically, to serve as a standard for other calculations.

Ion atom rearrangement scattering, of which the proton-hydrogen charge exchange process is the simplest example, is typical in that of the many approximations used, only the adiabatic approximation is theoretically justified, and that only rigorously at zero kinetic energy. There are then no reliable calculations, and experimental verification of the ideas used is necessary. However, the amount of relevant experimental data is not extensive in that individual processes are difficult to isolate. In the absence of means to evaluate the various calculational methods, we have invented a nonreal, yet not entirely unphysical, model that we can treat not

only by the various approximation schemes, but also--to the extent of computer accuracy--exactly.

This mathematically tractable model is a nucleus and an atom, with one electron, colliding in a one dimensional world. The masses of the nuclei are assumed infinitely heavy, and consequently the ideas of the impact parameter method apply. In accordance the interaction between nuclei can play no physical role and is disregarded altogether. The problem then may be simply described as two potential wells of which one holds initially a bound electron in the ground state, moving past each other.

In Section II we shall describe the physical situation of the prototype scattering problem that our model attempts to simulate. The ideas, assumptions, and methods prevailing already in the prototype will be briefly mentioned. Then also in this section we shall present, rather abstractly, the method of numerical solution employed on our model problem to obtain the results that serve as experimental data to test some of the known approximation schemes.

In Section III, theoretical ideas and methods of approximation schemes will be explored and related in an attempt to bring out and clarify the useful concepts. This is important particularly because, for actual physical systems, only approximation calculations by numerous means and methods have been carried out. In part C of this section, five selected approximation schemes, believed to be pivotal for the understanding of charge exchange calculation schemes, are applied to model systems of ion atom scattering possessing symmetric degeneracy.

In Section IV, an appropriate example of our model system is briefly described. The "data" obtained on it and the results from the applied approximations schemes are presented, compared, and interpreted. The merits and applicability of the viewpoints and methods introduced earlier are discussed in the concluding paragraphs together with other final remarks.

II. A SOLUBLE MODEL OF CHARGE EXCHANGE

The Impact Parameter Method

In atomic scattering an alternative formalism, the impact parameter method,[2] may be employed to great advantage in theoretical treatments. This method is based on the fact that the high ratio of nuclear mass to electron mass permits the heavy particles to be well localized relative to atomic dimensions over most of the energy and angular range of interest. For example the relative motion of the nuclei in ion atom scattering may be described classically which for proton hydrogen scattering holds, depending on angle, down to a few electron-volts of kinetic energy. Usually the further assumption is made for computational convenience that the classical trajectory is undeviated and unaccelerated. This assumption holds for kinetic energies above about 1 keV for proton hydrogen; however the error made in the total charge exchange cross section in using the straight line trajectory is negligible down to a few hundred eV.[3] The theoretical description in the impact parameter method then reduces to a time dependent quantum mechanical treatment for the electrons, with the nuclei treated as moving centers of force acting only on the electrons, in place of the more general time independent wave treatment for all the particles. In this model, charge exchange scattering is always distinguishable from direct scattering even if the stripped and stripping particles are of the same species, for then in an experiment to detect that specie of core, exchange will correspond to backward scattering and direct will correspond to forward scattering of the incident particle. To the extent that actual large angle scattering

is known to be unimportant, this idea is valid.[4]

Three Body Systems

Let us consider only the scattering of a charged atom by a neutral atom. Among the many processes that can occur are elastic (coherent) scattering, single excitation of the neutral atom, single ionization of the neutral atom, single electron transfer from the neutral to the charged atom in the ground state, and single electron transfer from the neutral to the charged atom in an excited state. These five processes mentioned are the only ones that can occur in all the cases where there are actually or effectively only three bodies in the scattering system. The best known example of the former is the proton hydrogen system. An effective three body system would be one in which all the other electrons, presumably in closed shells, are largely inert. The Pauli exclusion principle can then be neglected. Although neither of the two colliding atomic particles is required to be neutral, we shall in this paper focus our attention for convenience only on ion atom scattering systems that on the "microscopic" level consists of an electron and two ions, each singly charged and effectively without internal structure. Typical examples of the five processes for proton hydrogen are the following:

Coherent scattering, $H^+ + H(1s) \rightarrow H^+ + H(1s)$. (1)

Excitation, $H^+ + H(1s) \rightarrow H^+ + H(nl)$. (2)

Ionization, $H^+ + H(1s) \rightarrow H^+ + H^+ + e^-$. (3)

Excited rearrangement, $H^+ + H(1s) \rightarrow H(nl) + H^+$. (4)

Rearrangement, $H^+ + H(1s) \rightarrow H(1s) + H^+$. (5)

Nomenclature. The nomenclature that we shall use is consistent with the IPM idea that the incident and target particles remain always distinguishable. Initially these particles are known species of ion and atom particles respectively and this combination will be defined as channel "i", the initial channel. The direct processes of (1) and (2) are single channel processes. As the process of predominate interest in this study is charge exchange, we shall name the channel, defined by the projectile being the uncharged atom and the target being the ion, the final channel or channel "f". Reactions (4) and (5) are rearrangement or multichannel processes. The remaining reaction (3), ionization, leaves the system in a third channel, the all free channel, about which little will be said.

Charge Exchange. A more general case of ion atom charge exchange is

$$H^{+} + He(1s^{2}) \rightarrow H(1s) + He^{+}(1s). \qquad (6)$$

The classic case of symmetric resonance is that given in reaction (5). Asymmetric resonance or accidental degeneracy occurs in reaction (7).

$$He^{++} + H(1s) \rightarrow He^{+}(2s) + H^{+}. \qquad (7)$$

We may note the fact that (7) is a case of excited rearrangement and that neither particle is neutral in the final channel. These distinctions are of no significance here.

Time Dependent Theory of Scattering

Without much loss in generality we shall express the impact parameter theory for a three body system possessing symmetric resonance. The two structureless nuclei are of the same species and in addition do not mutually interact. The wave function of the electron satisfy the time dependent Schrodinger equation that in units of $\hbar = 2m = a = 1$, is

$$\left[i \frac{\partial}{\partial t} - H(t) \right] \Psi(t) = 0 , \tag{8}$$

and the boundary condition

$$\Psi(t) \sim \psi_i(t) \quad \text{as} \quad t \to -\infty , \tag{9}$$

where the initial state $\psi_i(t)$, is a solution to

$$\left[i \frac{\partial}{\partial t} - H^i(t) \right] \psi_i(t) = 0 . \tag{10}$$

The Hamiltonian may be formally expressed as

$$H = K + V^f + V^i , \tag{11}$$

and formally separated in either prior or post forms

$$H = H^i + V^i = H^f + V^f . \tag{12}$$

More explicitly

$$H(t) = -\nabla^2 + V(\underline{x} - \underline{z}) + V(\underline{x} + \underline{z}) \tag{13}$$

where the internuclear coordinate $2\underline{z} = \underline{b} + \underline{v}_{lab} \cdot t$, and $\underline{b}$ is the impact parameter, and $\underline{v}_{lab}$ is the incident particle velocity in the laboratory coordinate system, which may be taken to be always in the direction $\hat{k}$. Clearly

$$H^i(t) = -\nabla^2 + V(\underline{x} + \underline{z}) \tag{15}$$

and

$$H^f(t) = -\nabla^2 + V(\underline{x} - \underline{z}) \ . \tag{16}$$

The mass of the electron is m, and a is some characteristic length of atomic dimensions. K is the usual kinetic energy operator, and the V's are the two body, local, electron-nucleus potentials; H^i and V^i are respectively the noninteraction and interaction Hamiltonians in the initial channel and H^f and V^f are the corresponding quantities in the final channel. The terms "prior" and "post" are used to imply "initial" and "final" respectively, e.g., the prior interaction V^i, the post interaction V^f. To avoid a cluttered notation, we are using the letters i and f to denote both channels and states. The precise meaning generally should be clear from the context as much of the ambiguity is removed when the process is known to be rearrangement for which the final state implies

also the final channel. The superscript when used is a channel label.

Let $\Psi(t)$ be the solution to the initial value problem defined by (8) and (9) for a set of values of $\underline{b}$ and $\underline{v}_{lab}$. The amplitude for rearrangement to the final state ψ_f is

$$T_{fi} = A_f(\infty) = \lim_{t \to \infty} \left[\psi_f(t), \Psi(t)\right] \tag{17}$$

where

$$\left[i \frac{\partial}{\partial t} - H^f(t)\right] \psi_f(t) = 0 \ . \tag{18}$$

The wave functions of the initial and final states are moving atomic orbitals translating respectively with the target and incident nuclei. When we make the reasonable approximation that the ratio of nuclear mass to electron mass is very large, $M/m \gg 1$, the velocity of the ion in the center of mass coordinate system is $\underline{v} = \underline{v}_{lab}/2$. Defining $\underline{k} = mv = \frac{1}{2}v$, we can express these wave functions as

$$\psi_i\ (\underline{x},t) = \varphi\ (\underline{x} + \underline{z})\ e^{-i\underline{k}\cdot\underline{x}\ -i\epsilon t\ -\ ik^2 t} \tag{19}$$

$$\psi_f\ (\underline{x},t) = \varphi\ (\underline{x} - \underline{z})\ e^{+i\underline{k}\cdot\underline{x}\ -\ i\epsilon t\ -\ ik^2 t}\ , \tag{20}$$

with the atomic orbital eigenfunctions and eigenvalues satisfying

$$\left[H^i - \epsilon\right] \varphi\ (\underline{x} + \underline{z}) = \left[H^f - \epsilon\right] \varphi\ (\underline{x} - \underline{z}) = 0\ . \tag{21}$$

The charge exchange transition probability is given by

$$P_{fi}(b,v) = |A_f(\infty)|^2 \tag{22}$$

which varies with the magnitudes of both the impact parameter and the velocity. The total cross section is then given by

$$\sigma_{fi}(v) = 2\pi \int_0^\infty db\ b\ P_{fi}(b,v) \quad . \tag{23}$$

The transition probability $P_{fi}(b,v)$ is by definition equal to $\sigma_{fi}(\theta,v)/\sigma(\theta,v)$ where σ_{fi} is the differential cross section for that particular final state and $\sigma(\theta,v)$ is simply the classical differential cross section at angle θ given by the impact parameter method for a particular potential. The IPM assumption that the trajectory is uncorrelated[5] to the internal transitions means $\sigma(\theta,v) = \sum_f \sigma_{fi}(\theta,v)$. It is then easy to show that the total cross section has the standard form,[6]

$$\sigma_{fi}(v) = \int_0^\pi d\theta \sin\theta\ \sigma_{fi}(\theta,v). \tag{24}$$

Another expression for the transition or T-matrix, T_{fi}, is obtained through the integral form of the Schrodinger equation (8) with boundary condition (9),[7]

$$\Psi(t) = \psi_i(t) + \int_{-\infty}^{t} G_0(t,t')\, V^i(t')\, \Psi(t')\, dt' \quad . \tag{25}$$

Using the post representation in which essentially the basic vectors are chosen to be the eigenstates of the post Hamiltonian, H^f, we get the expression

$$T_{fi} = \int_{-\infty}^{\infty} dt' \quad \langle f | V^f | \Psi \rangle \quad . \tag{26}$$

Expression (26) is the IMP analogue to the T-matrix expression derived from the Lippman Schwinger formalism. As noted previously, in the wave method all three particles are treated quantum mechanically using time independent theory. The three particle wave function Ψ, satisfies $(E - H)\Psi = 0$ with appropriate scattering boundary conditions. Converting the differential equation and boundary conditions into an integral equation we get the Lippmann Schwinger equation[8]

$$\Psi_i^{(\pm)} = \phi_i + \frac{1}{E \pm i\eta - H^i} \quad V^i \, \Psi_i^{(\pm)} \tag{27}$$

where the $(\pm)$ refers to the two asymptotic boundary conditions of outgoing and incoming spherical waves respectively. The representation convenient for rearrangement is[9]

$$\Psi_i^{(+)} = \frac{i\eta}{E + i\eta - H^f} \Phi_i + \frac{1}{E + i\eta - H^f} V^f \Psi_i^{(+)} , \tag{28}$$

and since the first term contains no outgoing waves in the final state[8,10] the transition matrix arises from the second term.

$$T_{fi} = \langle \Phi_f | V^f \Psi_i^{(+)} \rangle . \tag{29}$$

This is the post form of the T-matrix; the prior form corresponding to (29) is

$$T_{fi} = \langle \Psi_f^{(-)} | V^i \Phi_i \rangle \tag{30}$$

where

$$\Psi_f^{(-)} = \Phi_f + \frac{1}{E - i\eta - H^f} V^f \Psi_f^{(-)} . \tag{31}$$

<u>The Numerical Solution to An Impact Parameter Model of Ion Atom Scattering</u>

To this date, no real physical system--not even the proton hydrogen system--has been solved exactly in either the IPM or the time independent method. It is observed in the IPM that the heavy particle dynamics is essentially one dimensional in that the impact parameter, <u>b</u>, enters only parametrically in the theory. One expects then that many effects may validly be investigated in a purely one

dimensional problem in which the electronic wave function also is one dimensional. The case is especially good for rearrangement processes because, as we shall discuss in detail, almost all of the mathematical problems there arise from the multichannel feature and only incidentally from details of distribution in three space. There are three dimensional features that we cannot investigate with a one dimensional model. The first is the centrifugal barrier for orbital angular momentum numbers greater than zero. The second is the coupling between degenerate states differing in angular momentum. The third, which is related to the second, is the question regarding the appropriateness of using, as often done in approximation schemes, a rotating axis of quantization.

Because we shall employ nonanalytic potential functions, there will be unrealistic effects; these occur at energies, however, outside the range that we can meaningfully treat. Beyond the upper end there are large variations of the amplitudes with momentum transfer; and also the threshold dependence of the exchange cross section with v^{-1}, which decreases exponentially for analytic potentials, decreases only to some power determined by the order of the discontinuity in the nonanalytic potential function.

The initial value problem here, (8a) and (9a), is almost that of (8) and (9).

$$i \frac{\partial \Psi(t)}{\partial t} = H(t)\, \Psi(t) \tag{8a}$$

$$\Psi(t_0) = \psi_i(t_0) \ . \tag{9a}$$

The exact solution to (8a) and (9a) is formally

$$\Psi(t) = U(t,t_0)\ \psi_i(t_0) = \tau \exp\left[-i\int_{t_0}^{t} H(t')\ dt'\right]\ \Psi(t_0) \tag{32}$$

where τ is the time ordering operator.

The numerical method chosen to solve the above initial value problem involves an iterative procedure that at each step requires the solution to an equation analogous to (32), but for small time intervals. Thus

$$\Psi(t^{n+1}) = \tau \exp\left[-i\int_{t^n}^{t^{n+1}} H(t')\ dt'\right]\Psi(t^n) \tag{32a}$$

where $\Delta t = t^{n+1} - t^n$, and $n\Delta t = t - t_0$. (33)

For small Δt we may treat $H(t')$ in the integrand to be a constant, H^n, and eliminate the need for the time ordering operator. In obvious notation (32a) becomes

$$\Psi^{n+1} = e^{-i\ H^n\ \Delta t}\ \Psi^n \ . \tag{32b}$$

The finite difference analogue, mentioned earlier, is obtained by truncating (32b) to terms linear in Δt. However, the obvious and

straight forward course leads to

$$\Psi^{n+1} = [1 - i\, H^n\, \Delta t]\, \Psi^n \,, \tag{34}$$

an explicit finite difference scheme that unfortunately is unstable. Expressing (32b) as

$$e^{+i\, H^n\, \Delta t}\, \Psi^{n+1} = \Psi^n \tag{32c}$$

and truncating as before, we get the implicit scheme

$$\Psi^{n+1} = \frac{1}{1 + i\, H^n\, \Delta t}\, \Psi^n \,. \tag{35}$$

The operator $1/(1 + iH^n\, \Delta t)$, the formal inverse to $(1 + iH^n\, \Delta t)$, in practice implies a matrix inversion. Full implicit schemes like (35) are stable, and in most other physics problems this would be sufficient. The probabilistic interpretation of the quantum mechanical wave function, however, demands that the solution operator, operating on Ψ^n, in addition must be unitary. Writing (32b) formally as

$$\Psi^{n+1} = \frac{e^{-i\, H^n\, \Delta t/2}}{e^{+i\, H^n\, \Delta t/2}}\, \Psi^n \tag{32d}$$

we can readily derive

$$\Psi^{n+1} = \frac{1}{1 + i\, H^n\, \Delta t/2} \; \frac{1 - i\, H^n\, \Delta t/2}{1} \; \Psi^n \tag{36}$$

The scheme suitable for iteration, formally represented by Eq. (36), is stable and is furthermore unitary because H^n, the Hamiltonian, is Hermitian.

The finite difference schemes described formally by (34), (35), and (36) are also known respectively as forward, backward, and centered time difference schemes.

The Hamiltonian, H^n, is well chosen to be $H(t^{n+\frac{1}{2}})$. The two-dimensional finite difference equation implied by Eq. (36) is realized by quantizing the spatial coordinate and using for H^n the finite difference operator analogue--obtained straightforwardly from the linear differential operator.

For explicitness we shall henceforth write $H^{n+\frac{1}{2}}$, instead of H^n, for $H(t^{n+\frac{1}{2}})$.

$$H^{n+\frac{1}{2}} = -\frac{\delta^2}{(\Delta x)^2} + V_f^{\,n+\frac{1}{2}} + V_i^{\,n+\frac{1}{2}} . \tag{37}$$

Or more explicitly

$$H_j^{\,n+\frac{1}{2}} = -\frac{1}{(\Delta x)^2}\,(D_{j+1} - 2 + D_{j-1}) + V(x_j - z^{n+\frac{1}{2}}) + V(x_j + z^{n+\frac{1}{2}}) \tag{38}$$

where $z^{n+\frac{1}{2}} = v\, t^{n+\frac{1}{2}}$, Δx is the quantization interval, and $D_{j\pm 1}$ are displacement operators. The displacement operators are diagonal in momentum space, $D_{j\pm 1} = \exp(\mp i\, \Delta x\, p)$; the potentials however are not. Writing $H_j^{n+\frac{1}{2}}$ in a mixed representation, and letting $V \equiv V_i + V_f$,

$$H_j^{n+\frac{1}{2}} = \frac{2}{(\Delta x)^2}\,[1 - \cos(\Delta x\, p)] + V_j^{n+\frac{1}{2}} \tag{39}$$

$$= p^2 + V_j^{n+\frac{1}{2}} - p^4(\Delta x)^2/12 + - + \ldots\ldots , \tag{40}$$

we see that the leading term of the truncation error in the analogue Hamiltonian is quadratic in (Δx). By formally expanding the denominator of (36) it is easily shown that the truncation error there, as conventionally defined, is quadratic also in Δt. The leading terms of the total truncation error in our numerical solution of the Schrodinger equation is $\mathcal{O}[(\Delta t)^2] + \mathcal{O}[(\Delta x)^2]$.[11,12] The range of incident energies (or velocities), with which our numerical program can calculate meaningfully, is limited at both upper and lower ends by the truncation errors through the necessity of attaining believable accuracy without increasing significantly the computer time. These limitations become apparent when we realize that high velocities implies the presence of significant high momentum components that require a small spatial quantization interval, and also that low velocities means a long collision time and hence a large time

interval. It is not clear how to determine quantitatively the net effect of the truncation errors. Conservation of probability, which should be exact according to (36) and (39), is violated at most by a couple tenth of one percent owing to errors of round off. Round off may justifiably be ignored. The truncation error falsifies the distribution of the state function via (39) or (40) and also again by affecting differentially the component phases. An estimate of the accuracy based on experience and on heuristic checks of the calculation, among which varying Δt and Δx is one, is that the errors in the amplitudes typically range from less than one percent to several percent. More pertinent perhaps is the fact that partly because the error is systematic the precise uncertainty in the value need not, nor is it allowed to be, a significant factor in the interpretation.

The potentials in the model may at this point be chosen almost arbitrarily in that only numerical work is involved. However, it is desirable to have analytically, atomic and quasimolecular eigenfunctions, to use in the approximation models, which will be discussed in the next section. Consequently the potentials were chosen to be square wells of unit half width.

$$V(y) = - \lambda^2 u(y) \tag{41}$$

where

$$u(y) = 1 \quad \text{if} \quad |y| < 1 , \tag{42a}$$

$$u(y) = 0 \quad \text{if} \quad |y| > 1 , \tag{42b}$$

and for accuracy in the numerical calculation (36), define also

$$u(y) = \tfrac{1}{2} \quad \text{for} \quad |y| = 1 . \tag{42c}$$

The solution to (8a) and (9a) by the numerical method (36) yields at some appropriate time - t^n - after the scattering the state vector $\underline{\Psi}(t^n)$. Various scattering amplitudes may then be gotten by projection onto the appropriate channel states that are effectively orthogonal as far as our numerical work is concern. For instance the rearrangement amplitude is

$$T_{fi} = (\psi_f{}^n, \underline{\Psi}^n) = \langle f^n | \underline{\Psi}^n \rangle . \tag{17a}$$

At velocities too high for (17a) to be accurate, the rearrangement amplitude often may still be extracted by using the finite difference analogue of (26)

$$T_{fi} = \sum_{n=0}^{n=N} \Delta t \ \langle f^n | V_f{}^n \ \underline{\Psi}^n \rangle , \tag{26a}$$

which requires accuracy in the wave function only in the near zone of scattering.

III. APPROXIMATE SCATTERING THEORIES

A. Preliminary Remarks

The approximations that we will investigate on our model of ion atom charge exchange are here designated as follows:

(a) The Born

(b) The Modified Born - I

(c) The Modified Born - II

(d) The Coupled States Atomic

(e) The Coupled States Molecular

These and other approximation schemes are found in the literature under a variety of names and formulations. Since the mathematical statement of these approximations may not be very familiar and since the names chosen may be misleading, some preparatory remarks on these and other schemes will be helpful in understanding the position they occupy in the later discussion.

The approximation schemes used in rearrangement are usually more esoteric if not more profound than those used in single channel processes. The latter can be derived or traced rather directly from basic and simple theoretical notions such as those that lead to the use of perturbation theory for high energy scattering and to the use of eigenfunction expansions for low energy. For rearrangement these considerations are still applicable but more qualitatively. Schemes directly formulated from such general ideas are immediately plagued with difficulties associated with the presence of more than one channel. The two most important difficulties were the nonorthogonality

between the initial and final states and the difference between the initial and final channel boundary conditions. These have long been recognized and may from our present vantage be regarded as kinematic complications. The schemes modified to remove these defects are, however, much more complicated and do not possess the simple properties and conceptual clarity of the inadequate schemes. Their connection with the earlier work even appears remote from certain viewpoints. Indeed, it may be more logical and instructive to present the selected approximations afresh from a modern approach, but it is also desirable to relate to the older versions as they are the one encountered in other areas of scattering theory.

There are probably as many ways to classify approximation schemes as there are viewpoints to explore them. For convenience of presentation we shall group all approximation schemes under two types distinguished by the means in which mathematical simplification is achieved. No implication is made that the ideas of the schemes also fall into two groups or that all schemes can neatly be so classified. The first of the two types, which we shall call T-matrix approximations, involves the perturbation idea. Mathematically, an integral equation is reduced to an integral by the substitution in the T-matrix of an approximate state wave function for the exact state function. The second type includes those schemes where the integral equation is made tractable by restricting the range and domain of the Green's function to a subspace of the original Hilbert space. We shall use the term--Green's function approximation--for the latter type. T-matrix approximations includes the Born approximations, the Impulse

approximation, and among others the various two potential schemes. The Green's function approximation type includes the eigenfunction expansion method, and the perturbed stationary state method as some of the more familiar examples. An approximation scheme may involve both types of assumptions at different stages of the calculation. Also a Green's function approximation may be reduced to a T-matrix approximation by a justifiable further approximation; the two versions then are substantially the same although categorically different, which illustrates again that it can be misleading to take the classification too literally.

B. Ideas of Approximation Schemes

T-matrix Approximations

(a) Born Approximation

The simplest and best known of the T-matrix approximations is the Born Approximation. In the Lippmann Schwinger form this may be regarded as an approximation on $\underline{\Psi}_i^{(+)}$ by $\underline{\Phi}_i$ on the r.h.s. of (II-27) or equivalently as an approximation to T^f by V^f.

$$T^f = V^f \Omega_i^{(+)} \cong V^f \left(1 + \frac{1}{E + i\eta - H} V^i\right) \tag{1}$$

$$T_{fi}^{\text{Born}} = (\underline{\Phi}_f, V^f \underline{\Phi}_i) \tag{2}$$

The corresponding approximation in the prior form obtain from $\Psi_f^{(-)} \to \underline{\Phi}_f$, or $\Omega_f^{(-)} \to 1$ is

$$T_{fi}^{\text{Born}} = (\bar{\phi}_f, V^i \bar{\phi}_i) \ . \tag{3}$$

The analogous first order "Born" approximation in the impact parameter theory, which is the version of Brinkman Kramers,[13] from expression (II-26) is

$$T_{fi}^{BK} = -i \int dt' \ (\psi_f, V^f \ \psi_i) \tag{4}$$

It can be shown that the post (2) and prior (3) forms of the Born are equivalent by using the Hermiticity property of the total Hamiltonian. Likewise in the IPM, expression (4) is equivalent to

$$T_{fi}^{BK} = -i \int dt' \ (\psi_f, V^i \ \psi_i) \tag{5}$$

from the additional fact that the states of two channels are orthogonal asymptotically. There is then no post-prior discrepancy in the exact T-matrix nor in the Born approximation providing that exact wave functions are used.

The Born approximation historically has suffered from ambiguities in formulation not usually encountered in direct processes. These difficulties arise from the nonorthogonality of initial and final states, are now understood, and are eliminated in the refined Born treatments. There is a plurality of such schemes and we have the harder problem of deciding which modification is most correct. A

more serious difficulty is the indication that the Born series for rearrangement collisions does not converge.[14] The first Born, which is based on the reasonable idea of treating the prior interaction as a perturbation, may still be useful for energies not extremely high and may be part of another series that does converge.[3,15]

(b) Refined treatments

For energies toward the intermediate point where the relative velocity of the nuclei is near the orbital velocity of the electron, which in reference to the proton hydrogen system is about 25 keV, the Born approximation is expected to be inadequate. One could consider multiple scattering models such as for example the second Born or the Impulse approximations. However, a more precise formulation of the first order ideas may be sufficient to extend our ability to calculate into the intermediate region of energy. Historically, much of the motivation for this work was to remove the unsatisfactory feature of the Born where--due to the nonorthogonality mentioned before--a superfluous term in the potential may contribute to the Born transition probability. This should be of no surprise mathematically for this effect occurs also in coherent scattering. Here--within the context of the IPM--the exact contribution to the coherent amplitude introduced by such a term is a phase factor of modulus unity that the Born approximates by its first two terms. Hence depending on the argument of the phase factor, unitarity may be arbitrarily exceeded. The sensible prescription then is to drop such terms. For example the internuclear potential, contained formally in (2) and (3), cannot be included with theoretical consistency in the IPM forms (4), (5).[2] However, it is not always

apparent how to split the Hamiltonian or to know which terms to disregard.[16] We even suspect that the interaction in the Born formulations (2)-(5) corrected may contain already too much. Indeed, the internuclear potential has been reintroduced in later work[17] phenomenologically to cancel these additional effects in the Born. It is necessary then to clarify our concepts and employ more sophisticated models to derive more consistent first order schemes.

(1) Modified Born I.[2,9,18,19]

The important idea here is to single out the effective interaction believed to be responsible for the rearrangement process. For this usually the two potential idea is formally employed. Even when an interaction does not admit of a natural separation we may formally regard a part of it to be the principle interaction and the remainder the secondary interaction. Interpreting the equations literally, see Appendix A, the principle interaction is seen to be superimposed on the secondary interaction that acts as the background process. The reaction of interest, rearrangement, is attributed solely to the formal principle potential while the direct channel processes are included in the secondary potential.[18] The T-matrix is then, in the post description,

$$T_{fi} = (X_f^{(-)}, (V^f - U^f)\, \Psi_i^{(+)}) \quad . \tag{6}$$

The distorted wave approximation to (6) is

$$T_{fi}^{DW} = (X_f^{(-)}, (V^f - U^f)\, X_i^{(+)}) \; . \tag{7}$$

It is illustrative to note that the smallness of $(V^f - U^f)$ per se does not justify the above T-matrix approximation, which is based instead on $(V^i - U^i)$ being small. The potential treated as a perturbation is often not the one occurring in the T-matrix formula for rearrangement. Then the feedback consistency of single channel approximation recipes do not exist.

The actual choice of U^f is related directly to the ideas of the approximation scheme employed. In Mittleman,[18,20] U^f is generalized to be the optical potential responsible for all of the single channel final-state interactions. Then (6) may be recasted as

$$T_{fi} = (\underline{\Psi}_f^{(-)} | [\pi^f, V^f] \underline{\Psi}_i^{(+)}) \tag{8}$$

where $\pi^f = \sum_f |f\rangle\langle f|$.

And now approximating both incoming and outgoing waves by plane waves he obtains the following result.

$$T_{fi}^{MBI} = (\underline{\phi}_f | [\pi^f, V^f] \underline{\phi}_i) \ . \tag{9}$$

The IPM form of this is

$$T_{fi}^{MBI} = -i \int dt \, (\psi_f, (V^f - V^f |\psi_f\rangle\langle\psi_f|) \, \psi_i) \tag{9a}$$

$$= -i \int dt \, (V_{fi}^{\ f} - S_{fi} V_{ff}^{\ f}) \tag{9b}$$

where $(\psi_f, \psi_i) = S_{fi}$. (10)

A c-number potential, at most time dependent, would contribute equally to both terms in (9b) and hence have no net effect. The somewhat misleading term "effective orthogonality" is sometimes used to describe schemes like (8), (9), and (9b).

(2) Modified Born II.

The position taken here is that an inconsistency is kinematics has been made in the first Born of Eq. (5). It was recognized that the initial and final states are orthogonal asymptotically but not orthogonal at finite times. However, the channel states, strictly, are not physically defined at finite times. We may choose the definition formally to be

$$\psi'_{i,f}(t) = \frac{(1-s)^{\frac{1}{2}} + (1+s)^{\frac{1}{2}}}{2(1-s^2)^{\frac{1}{2}}} \psi_{i,f}(t) + \frac{(1-s)^{\frac{1}{2}} - (1+s)^{\frac{1}{2}}}{2(1-s^2)^{\frac{1}{2}}} \psi_{f,i}(t) \quad (11a,b)$$

where $s = S_{fi} = S_{if}$ (10a)

and the $\psi_{i,f}(t)$ are the wave functions given before (II-10, II-18).

As $t \to \infty$, $\psi'_{i,f}(t) \sim \psi_{i,f}(t)$, (12)

but the set (11a,b) is orthornormal at all times.

$$(\psi'_{i,f}, \psi'_{i,f}) = 1 \text{ ; and } (\psi'_{i,f}, \psi'_{f,i}) = 0 . \quad (13)$$

As we shall see there is little to be gained by using the orthonormal wave functions. Furthermore, if we imagine the perturbation V^i and V^f to be very weak then it is quite reasonable to make the normal definition of channel states used in the Born. Then, however, it is inconsistent to define the physical occupation of the state ψ_f by $(\psi_f(t), \Psi(t))$. The conception that the channels are somehow distinct at finite times leads to the sensible superposition

$$\Phi = \alpha\psi_i + \beta\psi_f \,. \tag{14}$$

Conversely, if a vector Φ lies in the Hilbert subspace spanned by ψ_i and ψ_f, the appropriate occupation numbers are α and β respectively. They are given by

$$\alpha = \frac{(\psi_i,\Phi) - S_{if}(\psi_f,\Phi)}{1 - S_{fi}^{\;2}} \tag{15a}$$

$$\beta = \frac{(\psi_f,\Phi) - S_{fi}(\psi_i,\Phi)}{1 - S_{fi}^{\;2}} \,. \tag{15b}$$

In (15a) and (15b) we may consider Φ to be the projection of an Φ', on to the subspace mentioned. $\Phi \equiv \pi\Phi'$, where

$$\pi = \frac{|f\rangle\langle f| + |i\rangle\langle i| - |f\rangle S_{fi}\langle i| - |i\rangle S_{if}\langle f|}{1 - S_{fi}^{\;2}} \,. \tag{16}$$

Returning to perturbation theory we have $\bar{\Psi}(t) \to \psi_i(t)$ and V^i is the perturbation. The incremental first order part of the wave function as obtained from the Schrodinger equation is $V^i\psi_i\,\delta t$. Neglecting other states we consider only[21]

$$\pi\, V^i\psi_i\,\delta t \equiv \dot{\alpha}\delta t\psi_i + \dot{\beta}\delta t\psi_f \quad . \tag{17}$$

From (15b), and (16) and noting that $\langle i,f|\pi = \langle i,f|$, we obtain an expression for $\dot{\beta}\delta t$ which we integrate to get the net transition amplitude to the final state.

$$\beta = T_{fi}^{\text{MB II}} = -i \int dt \; \frac{(\psi_f, V^i\,\psi_i) - S_{fi}\,(\psi_i, V^i\psi_i)}{1 - S_{fi}^{\;2}} \quad . \tag{18}$$

The version of (18) then correctly takes into account the distinction between the rearrangement and the coherent amplitude that we had formally assumed to exist. When $1 \gg S_{fi}$, such as at high velocities, we may neglect the denominator of (18). Then we have

$$T_{fi}^{\text{MB II}} = -i \int dt\, (V_{fi}^{\;i} - S_{fi}V_{ii}^{\;i}) \;, \tag{18a}$$

which is the prior version of (9b). With care then nonorthogonality is not a problem.

Green's Function Approximations

Two of the familiar examples of this class of approximation schemes are the eigenfunction expansion and the adiabatic approximation. In the eigenfunction expansion, as used in direct processes, there is an attempt to describe the system by only a few low lying eigenstates. Then the integral equation reduces to a matrix equation of a small number of dimensions. The convergence of this method is probably slow as continuum distortion is almost always an important effect. One may restore some of the missing second order effects through an optical potential formalism[18,22] or through employment of not the unperturbed stationary states but the perturbed stationary states. Clearly the inclusion into the representation of effects of the interaction Hamiltonian may range from the use of first order perturbed atomic orbitals to the use of quasimolecular orbitals. The term PSS is usually reserved for the latter, and in the time dependent context--the IPM--the PSS is equivalent to the adiabatic approximation. A useful statement of the theoretical idea justifying the AA is that--in the Heisenberg representation, the state vector in the discrete part of the spectrum remains a constant in the limit of infinitely slow rate of change of the Hamiltonian. The assumption that the conclusion is true even for finite rates of change of the Hamiltonian is known as the zeroth order adiabatic approximation, AA. In the AA then, the representation is chosen with respect to the set of eigenfunctions of the quasimolecule in the Heisenberg picture; the formal interaction Hamiltonian--in the time dependent Schrodinger

equation--that couples one state to another is proportional to the time rate of change of the total Hamiltonian. The atomic orbitals, which are discrete eigenstates of the prior or post unperturbed Hamiltonians (II-15,16), are also the asymptotic limits (infinite internuclear separation) of the quasimolecular eigenstates. It follows then that there is no rearrangement generally in the zeroth adiabatic approximation since by definition there are no transitions. Only in the case of symmetric resonance can rearrangement occur for now the two atomic orbitals of interest correspond to the asymptotic limit of different superpositions of two quasimolecular eigenstates, which are degenerate only at the asymptotic limit. This charge exchange phenomenon, well known as an instance of quantum mechanical resonance, reflects the fact that in the Schrodinger picture the state vector is not constant, the phase relationship of the two relevant amplitudes is time dependent through the splitting of the eigenenergies at finite internuclear separations, and that consequently the final and initial mixtures of the two states can correspond to the two different physical situations.

Unfortunately the adiabatic approximation is almost always inapplicable, and the ideas stemming from it would be rather misleading for understanding the actual rearrangement calculation correctly formulated. The initial and final states (II-19,20) are channel states possessing different boundary conditions; they are never eigenfunctions of Hamiltonians within the same Galilean coordinate system, much less eigenfunctions of the same Hamiltonian.

There is then no unique extension of the idea of initial and final channel states into the near zone of scattering. Hence no distinction can be made with precision between charge transfer by transition and charge exchange by quantum mechanical resonance. We shall show that we can recast our approximation schemes to display more prominently one effect or the other.

The Coupled Channel States

We have established that in rearrangement there is no natural and convenient Hamiltonian with which to define a representation, no unique interaction operator, and not one but two boundary conditions to consider. In principle nothing substantial has been lost. Formally only the use of conceptually clear and simple orthonormal expansions is precluded.

The physical picture of the scattering process that we will attempt to describe formally is the following. The state function, initially a translating atomic orbital is distorted by the passing ion. We have already described the possible asymptotic results. In the near zone we expect correlation effects to be most important especially at or below intermediate energies when the ion velocity is comparable to electron orbital velocity. We can thus neglect ionization per se and consider the state function to be a sum of two amplitudes, centered around each of the two moving nuclei in both position and momentum space. The state vector is then

$$\underline{\Psi}(t) = A_i(t)\,\psi_i(t) + A_f(t)\,\psi_f(t)\ . \tag{19}$$

The basic vectors $\psi_i(t)$, $\psi_f(t)$, spanning the Hilbert subspace to which $\underline{\Psi}(t)$ is confined, are required only to be well centered as mentioned and are otherwise arbitrary. They could contain the asymptotic boundary conditions as explicit momentum factors in accordance with the IPM idea that the nuclei are unaccelerated.

$$\psi_i(t) = \underline{\Phi}_i(t)\, e^{-i\,\underline{k}\cdot\underline{x}} \tag{20a}$$

$$\psi_f(t) = \underline{\Phi}_f(t)\, e^{+i\,\underline{k}\cdot\underline{x}}\ . \tag{20b}$$

Obviously, if $\underline{\Phi}_i$, $\underline{\Phi}_f$ contained sufficiently many terms the momentum factors could be omitted. However, these factors must be included in order to describe accurately the above model by only a few terms; perhaps a total of two terms in (19) may then be sufficient.

Expression (19) may be taken as an ansatz for the wave function with the A's determined from the variational expression (21)

$$\delta \int \underline{\Psi}^*(t)\,[i\,\frac{\partial}{\partial t} - H(t)]\ \underline{\Psi}(t)\,dt = 0\ . \tag{21}$$

We get ultimately, see Appendix B,

$$S\dot{A} = i\,T\,A\ , \tag{22}$$

and the unitarity condition $|\Psi(t)|^2 = 1$. (23)

S and T are 2 by 2 matrices: e.g.,

$$S_{if} = (\psi_i, \psi_f) \tag{10}$$

$$T_{if} = (\psi_i, (i \frac{\partial}{\partial t} - H) \psi_f) . \tag{24}$$

The matrix Eq. (22), which the Euler Lagrange equations reduce to, is precisely the set of coupled ordinary differential equations that the Schrodinger equation (II-8) assumes when expressed in the representation defined by having ψ_i, and ψ_f as the set of basic vectors. In other words, the two coupled equations may be written more familiarly as

$$(\psi_i, (i \frac{\partial}{\partial t} - H) \Psi) = 0 \tag{22a}$$

$$(\psi_f, (i \frac{\partial}{\partial t} - H) \Psi) = 0. \tag{22b}$$

(1) Coupled States - Atomic.

At high energies the atomic orbitals φ_i and φ_f, are expected to be good choices for $\phi_{i,f}$ in (20). In other words the asymptotic forms of the initial and final states are chosen to be the two basic states in (19).

$$\psi_i(t) = \varphi_i(\underline{x} + \underline{v}t) \exp[-i \underline{k}\cdot\underline{x} - ik^2t - i\epsilon_i t] \tag{25}$$

$$\psi_f(t) = \varphi_f(\underline{x} - \underline{v}t) \exp[+i \underline{k}\cdot\underline{x} - ik^2t - i\epsilon_f t] \tag{26}$$

where

$$(\epsilon_i - H^i(\underline{x}))\,\varphi_i(\underline{x}) = (\epsilon_f - H^f(\underline{x}))\,\varphi_f(\underline{x}) = 0 . \qquad (27)$$

For symmetric resonance the orbital labels may be dropped. Eqs. (25)-(27) are then those of (II-19) through (II-21). We repeat from Section II that

$$(i\frac{\partial}{\partial t} - H^{i,f})\,\psi_{i,f} = 0 . \qquad (28)$$

The CSA set of equations (22) with (28) may be reduced to our second version of the modified Borns by further making a first order approximation that uncouples the set. Clearly, the CSA is at least an improvement over the various Born schemes in that the "back coupling" matrix element is here taken into account (restoring unitarity), and consequently should describe some of the important multiple order effects.

There is no fundamental need to use exact atomic wave functions, although it is very convenient when they are available, as long as the coupled equations (22) are derived from (21) consistently using the actual basic functions. To formulate a two state scheme that is unambiguous in interpretation without further approximation, the minimal boundary conditions on $\Phi_{i,f}$ are

$$\bar{\phi}_i(t) \xrightarrow[\lim t \to -\infty]{} \varphi_i(t)$$

$$\bar{\phi}_f(t) \xrightarrow[\lim t \to +\infty]{} \varphi_f(t)$$

We shall impose the usual stronger condition,

$$\bar{\phi}_{i,f}(t) \xrightarrow[\lim t \to \pm\infty]{} \varphi_{i,f}(t)$$

In brief we will entertain as "correct" only one asymptotic form, that of the CSA. The type of distortion that the CSA allows in the wave function is characterized as pure correlation only, in that besides the unperturbed form, $A_i\psi_i$, there is an additional distribution corresponding to an unperturbed bound state with the incident particle. We should be able to improve our results at low energies by allowing for additional wave function distortion as an initial-state-interaction and a final-state-interaction in the spirit of two potential theory. In our methods here we don't actually choose explicitly the secondary interactions from which the distorted waves and principle interactions are obtained but rather we choose the distorted waves, $\psi_{i,f}$, with the principle interaction obtained in the process of derivation from (21) or (22). This is equivalent theoretically to specifying the diagonal form of the Green's function or specifying the propagators in the scattering process. The employment of a Green's function, anticipated to be more complete, should improve the convergence of the associated two state expansion.

(2) Coupled States - Molecular.

The propagators of this particular model are as usual specified formally by $\psi_{i,f}(t)$. For symmetric resonance, the appropriate forms of $\psi_{i,f}(t)$ are

$$\psi_i(t) = 2^{-\frac{1}{2}} [U^+(t) + U^-(t)] e^{-i\,\underline{k}\cdot\underline{x}} , \tag{29a}$$

$$\psi_f(t) = 2^{-\frac{1}{2}} [U^+(t) - U^-(t)] e^{+i\,\underline{k}\cdot\underline{x}} . \tag{29b}$$

Equations (29) are Eqs. (20) with $\bar{\phi}_{i,f}$ taken to be linear combinations of eigenfunctions of the quasimolecular ion. These molecular functions

$$[E^{\pm}(t) - H(t)]\ U^{\pm}(t) = 0 \tag{30}$$

are also eigenfunctions of parity, and have the correct asymptotic conditions. As $t \to \pm\infty$,

$$U^{\pm} \sim (\varphi_i \pm \varphi_f)/2^{\frac{1}{2}} \tag{31}$$

or

$$\varphi_{i,f} \sim (U^+ \pm U^-)/2^{\frac{1}{2}} \tag{31a}$$

For nonresonance, $U_{i,f} \sim \varphi_{i,f}$ as $t \to \pm\infty$,

where

$$(E_{i,f}(t) - H(t)) \, U_{i,f}(t) = 0 \; ; \tag{32}$$

and $\phi_{i,f}$ accordingly is taken to be $U_{i,f}$.

In the coupled channel schemes the basic functions $\psi_{i,f}$ are generally normalized but not orthogonal. An orthonormal set having the correct boundary conditions can be constructed from each set of $\psi_{i,f}$. See (11a,b). These functions do not simply translate with the nuclei in the near zone as depicted earlier; they are mixtures of two translating packets. Both sets however are formally equivalent; the exact solutions of the two corresponding sets of coupled equations are identical, but the respective "Born" approximations of the coupled states schemes are formally different.

The coupled channel states schemes are well suited to describe rearrangement through a very restricted type of multiple scattering. Furthermore, in the limited context of only two states we may display more apparently the effect of a generalized quantum mechanical resonance, by using the basic functions $\psi^{\pm}$, which are the sum and difference of $\psi_{i,f}$. In this representation the Schrodinger equations for the $A^{\pm}$, the wave function, are coupled, weakly coupled, and uncoupled for the cases respectively of nonresonant, asymmetric resonant, and symmetric resonant charge exchange. It follows from this, and unitarity, and the initial condition,

$$A^{+}(-\infty) = A^{-}(-\infty) \; , \tag{33}$$

that the rearrangement amplitude depends directly upon, and may be largely controlled by, the phase relation between the $A^{\pm}$ after the scattering. In the lower intermediate energy range the charged particle may be transferred to and from the ion several times during the collision. Resonant and nonresonant exchange may then be a difference in degree and not a difference in mechanism.

Support for the last statement is found, interestingly, when one investigates the case of accidental degeneracy. There it is easy to show that at large internuclear separation the molecular orbitals, obtained from degenerate perturbation theory, are the linear combinations $\varphi_i \pm \varphi_f$ and not φ_i and φ_f as traditionally believed. The immediate implication is that accidental degeneracy should resemble symmetric degeneracy more significantly than was formerly believed.[23,24] We exclude here the possibility where the energy curves of the actual molecular orbitals of interest, at finite internuclear separations, again approach each other closely.

C. Selected Approximation Schemes Applied to the Tractable Model

The Born Approximation

Another derivation of the Born amplitude is given as follows. Write the Schrodinger equation,

$$i \frac{\partial}{\partial t} \underline{\Psi}(t) = H(t) \underline{\Psi}(t) , \qquad \text{(II-8)}$$

in the post interaction picture and in the post Hamiltonian representation. This is equivalent to the variation of constants method. We then get

$$i\,\dot{A}_n(t) = \sum_m V_{nm}{}^f(t)\,A_m(t) \tag{34}$$

from $\Psi(t) = \sum_m A_m(t)\,\psi_m{}^f(t)$, (35)

$$[i\frac{\partial}{\partial t} - H^f(t)]\,\psi_m{}^f(t) = 0\,, \tag{36}$$

and $V_{nm}{}^f(t) = (\psi_n{}^f(t),\, V^f(t)\,\psi_m{}^f(t)\,)$. (37)

The final state amplitude is then given by

$$\begin{aligned} A_f(\infty) &= -i\sum_m \int_{-\infty}^{\infty} dt\, V_{fm}{}^f(t)\,A_m(t) \\ &= -i\int_{-\infty}^{\infty} dt \sum_m (\psi_f{}^f,\, V^f\,\psi_m{}^f)\,A_m \\ &= -i\int_{-\infty}^{\infty} dt\,(\psi_f(t),\, V^f(t)\,\Psi(t)\,) \end{aligned} \tag{38}$$

where the superscript has been omitted. The $A_f{}^{Born}(\infty) = T_{fi}{}^{Born}$ is gotten by using the zeroth order term of $\Psi(t)$ on the right hand side of (38).

$$T_{fi}{}^{Born} = -i\int_{-\infty}^{\infty} dt\,(\psi_f,\, V^f\,\psi_i) \tag{4}$$

$$V^f(x,t) = -\lambda^2\,u(x+vt), \quad \text{see (II-42)} \tag{39}$$

$$\psi_{i,f}(x,t) = \varphi(x \pm vt)\, e^{\mp i\frac{1}{2}vx - i\frac{1}{4}v^2 t - i\epsilon t} \tag{40}$$

$$\epsilon\varphi(x) = H^0(x)\,\varphi(x) = \left[-\frac{\partial^2}{\partial x^2} - \lambda^2 u(x) \right]\varphi(x) \tag{41}$$

The eigenvalue ϵ is given by $\arctan(\beta/\xi) = \xi$ (42)

where

$$\beta = (-\epsilon)^{\frac{1}{2}}, \quad \xi = (\lambda^2 - \beta^2)^{\frac{1}{2}} = (\lambda^2 + \epsilon)^{\frac{1}{2}} \tag{43a,b}$$

And the normalized ground state eigenfunction is

$$\begin{aligned} \varphi(x) &= (\beta/\beta+1)^{\frac{1}{2}} \cos \xi x \quad \text{for} \quad |x| \leq 1, \\ &= (\beta/\beta+1)^{\frac{1}{2}} \cos \xi\, e^{-\beta(|x| - 1)} \quad \text{for} \quad |x| > 1. \end{aligned} \tag{44}$$

Then

$$T_{fi}^{\text{Born}} = i\frac{\lambda^2}{v}\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dx\; \varphi(x-z)\, u(x+z)\, \varphi(x+z)\, e^{-ivx} \tag{45}$$

$$= i\frac{\lambda^2}{v}\int_{-\infty}^{\infty} d\sigma\, \varphi(\sigma)\, e^{-i\frac{1}{2}v\sigma} \int_{-1}^{+1} dy\, \varphi(y)\, e^{-i\frac{1}{2}vy} \tag{45a}$$

where in (45a) a change of variables, $\sigma = x-z$, $y = x+z$, $z = vt$, has been made and the relationship, $u(x) = \theta(1 - |x|)$, used. (46) $\theta(x)$ is the unit step function with the jump at $x = 0$.

Inserting (44) in (45a), and evaluating the integrals we get

$$T_{fi}^{\text{Born}} = i\,(\beta/\beta+1)\;\lambda^4\,\frac{(k\sin k\cos\xi - \xi\sin\xi\cos k)^2}{k^7\,(1-\xi^2/k^2)^2\,(1+\beta^2/k^2)} \tag{47}$$

where $k = \frac{1}{2}v$.

The high energy asymptotic limit of (47) is

$$T_{fi}^{\text{Born}} \xrightarrow[k\to\infty]{} i\,(\beta/\beta+1)\;\lambda^4\,\frac{\sin k\cos\xi}{k^5}\;; \tag{48}$$

the Born exchange probability asymptotically is inversely proportional to the fifth power of the kinetic energy or the tenth power of the velocity.

<u>The Modified Born I</u>

We may derive (9a,b) rapidly as follows. Expand the state function by

$$\Psi(t) = \sum_n A_n(t)\,\psi_n(t)\;, \tag{35}$$

where now

$$(i\,\frac{\partial}{\partial t} - H^f(t) - U^f(t)\,)\,\psi_n(t) = 0 \tag{49}$$

with U^f considered a final state interaction. The Schrodinger equation becomes

$$i\,\dot{A}_n(t) = \sum_m [V^f(t) - U^f(t)\,]_{nm}\,A_m(t)\,. \tag{50}$$

Choose $$U^f = \sum_{m,n}{}' \; |m;f\rangle \; V_{mn}{}^f \; \langle n;f| \tag{51}$$

to be the interaction responsible for all single channel processes within the final channel. The sum extends only over states of the final channel. Equation (50) is now

$$i\,\dot{A}_f(t) = (\psi_f(t),\ (V^f - \sum_m{}' \; V^f\,|\psi_m\rangle\langle\psi_m|)\,\Psi(t)\ ) \tag{52}$$

Now restrict U^f in (51) and the analogous initial state interaction to include only diagonal elements. The "distorted" Born approximation then to (52) is

$$i\,\dot{A}_f = (\psi_f,\ (V^f - V^f\,|\psi_f\rangle\langle\psi_f|)\ \psi_i) \tag{53}$$

where the $\psi_{f,i}$ differs from the zeroth order form used in the Born only in the phase factor involving the energies, which are now perturbed and time dependent. These phase factors are

$$\exp\ [-i\int_{-\infty}^{t} V_{ff}{}^f(t')\,dt'] \quad \text{for} \quad \psi_f \quad \text{and} \quad \exp\ [-i\int_{-\infty}^{t} V_{ii}{}^i(t')\,dt']$$

for ψ_i. When symmetric resonance exists these energy terms cancel in (53). The amplitude (9) follows immediately upon integrating (53). For nonresonance the distortion of the energies may be neglected as a further approximation justified at high energies.

$$i\,\dot{A}_f^{\,MBI} = V_{fi}{}^f - S_{fi}V_{ff}{}^f\ . \tag{53a}$$

The Modified Born II

Expand the wave function with respect to a nonorthogonal basic set as follows:

$$\Psi(t) = \sum_n{}' A_n{}^i(t)\, \psi_n{}^i(t) + \sum_m{}' A_m{}^f(t)\, \psi_m{}^f(t) + \gamma(t) \ . \quad (54)$$

The sums include only channel states; the third term γ, which completes the expansion, is orthogonal to both sets of channel states. Completeness of the sets $\psi^{i,f}$ however is actually not necessary in this derivation.

The Schrodinger equation is now the set of differential equations that in matrix form (using all $\psi_n{}^{i,f}$ as basic functions) is

$$i\, S\, \dot{A} = V\, A + (\text{term arising from } \gamma) \quad (55)$$

or $$i\, \dot{A} = S^{-1}\, V\, A + (\text{term arising from } \gamma) \ . \quad (55a)$$

V is appropriately V^i or V^f, and S is the matrix whose elements are the scalar products of the set of channel basic vectors.

Making a "Born" approximation

$$A_m{}^f(t) = 0 \ ; \quad A_n{}^i(t) = \delta_{ni} \ , \quad (56)$$

(55a) becomes

$$i\, \dot{A}_f{}^f = \sum_m (S^{-1})_{fm}\, V_{mi}{}^i \ . \quad (57)$$

Expressing $(S^{-1})_{fm}$ in terms of S_{ij}, we can write (57) as

$$i\,\dot{A}_f^{\,f} = \frac{1}{\mathrm{Det}\,(S_{fm})} \sum_m \frac{\partial\,\mathrm{Det}(S_{fm})}{\partial\,S_{mf}}\,V_{mi}^{\;i}\,. \tag{57a}$$

The MBII approximation is obtained by neglecting all intermediate indices other than those for the initial and final states.

$$i\,\dot{A}_f^{\,f} = (1 - S_{fi}^{\;2})^{-1}\,(V_{fi}^{\;i} - S_{fi}^{*}\,V_{ii}^{\;i}) \tag{58}$$

The S_{fi} may be chosen to be real; then $S_{fi} = S_{if} \equiv S_{fi}^{*}$

<u>The Coupled Two States</u>

The Schrodinger Equation for the coupled channel states given in (22) was

$$S\,\dot{A} = i\,T\,A\,. \tag{22}$$

And the two basic states implicit in (22) are those of (20a,b). It is useful, especially in our problem, to change the representation by the following simple unitary transformation operator

$$U = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\,. \tag{59}$$

Note that $U = U^{\dagger} = U^{-1} = \tilde{U} = U^{*}$ (60)

The transformed set of basic states are

$$\psi^{\pm} = 2^{-\frac{1}{2}} (\psi_i \pm \psi_f) , \tag{61}$$

that in the case of symmetric resonance are eigenstates of parity, $\mathcal{P}$, because then $\mathcal{P}\psi_{i,f} = \psi_{f,i}$. (62)

As both S and T are diagonal in the parity subspace the components in (22) are uncoupled in the symmetric resonance problem. The two independent equations are now written as

$$S^{\pm} \dot{A}^{\pm} = i\, T^{\pm} A^{\pm} , \tag{63}$$

whose solutions may immediately be written down as

$$A^{\pm}(\infty) = A^{\pm}(-\infty) \exp[i\delta^{\pm}(\infty)] \tag{64}$$

where

$$\delta^{\pm}(t) = \int_{-\infty}^{t} dt \; \frac{T^{\pm}(t)}{S^{\pm}(t)} \tag{65}$$

The initial conditions, using (59), are

$$\begin{aligned} A^{\pm}(-\infty) &= 2^{-\frac{1}{2}} [A_i(-\infty) \pm A_f(-\infty)] \\ &= 2^{-\frac{1}{2}} (1 \pm 0) = 2^{-\frac{1}{2}} . \end{aligned} \tag{66}$$

The rearrangement amplitude by (60), (64), and (66) is

$$T_{fi}^{CS} = A_f(\infty) = 2^{-\frac{1}{2}} (A^+(\infty) - A^-(\infty))$$

$$= \tfrac{1}{2} \left\{ \exp[i\delta^+(\infty)] - \exp[i\delta^-(\infty)] \right\} \tag{67}$$

$$= \exp[i(\delta^+ + \delta^-)/2]\, i \sin\tfrac{1}{2}(\delta^+ - \delta^-) \tag{67}$$

Since $\delta^{\pm}(t)$ is real, the rearrangement probability is

$$P_{fi} = |T_{fi}|^2 = \sin^2 \int_{-\infty}^{\infty} dt\, \tfrac{1}{2}\left(\frac{T^+}{S^+} - \frac{T^-}{S^-} \right) \tag{68a}$$

By (59) and (60),

$$T^{\pm} = \tfrac{1}{2}(T_{ii} + T_{fi}) \pm \tfrac{1}{2}(T_{if} + T_{fi}) \quad , \quad \text{and}$$

$$S^{\pm} = 1 \pm \tfrac{1}{2}(S_{if} + S_{fi}) \tag{69a}$$

By using (62) however, it is easy to show that

$$T_{ii} = T_{ff},\ T_{if} = T_{fi},\ S_{if} = S_{fi} \ ; \tag{62a}$$

and consequently

$$T^{\pm} = T_{ii} \pm T_{fi}$$

$$S^{\pm} = 1 \pm S_{fi} \ . \tag{69}$$

Finally (68a) may be written as

$$P_{fi} = \sin^2 \int_{-\infty}^{\infty} \frac{T_{fi} - S_{fi}T_{ii}}{1 - S_{fi}^{\ 2}} \, dt \, . \tag{68}$$

The CSA scheme uses the asymptotic forms (40) as the basic functions, $\psi_{i,f}(x,z,t)$. The internuclear coordinate, z, is just vt in our problem.

Then [25,26] $$P_{fi}^{\ CSA} = \sin^2 \int_{-\infty}^{\infty} \frac{V_{fi} - S_{fi}V_{ii}}{1 - S_{fi}^{\ 2}} \, dt \, , \tag{70}$$

where $$V_{ii} = V_{ii}^{\ i} = V_{ff}^{\ f}; \quad V_{fi} = V_{fi}^{\ i} = V_{fi}^{\ f} \, . \tag{71}$$

The last equality in (71) follows easily from the relation $\psi_i(x, -z, -t) = \psi_f^*(x,z,t)$.

Although the Born amplitude (38) can be evaluated analytically in (45) and (47), the time integration of the more complicated expressions (53), (58), and (70) can be carried out only numerically.

For the CSM scheme the basic functions are given essentially by (29).[27] Since a unitary phase factor, at most time dependent, common to both functions has no physical or theoretical significance, we shall for convenience actually employ

$$\psi_{i,f}(x, t) = 2^{-\frac{1}{2}}(U^+(x, z) \pm U^-(x, z))e^{\mp ikx - i\bar{E}(z) - ik^2t} \, , \tag{72}$$

with

$$\bar{E}(z) = \tfrac{1}{2}(E^{+}(z) + E^{-}(z)) \; . \tag{73}$$

$$z = vt$$

The eigenfunctions and eigenvalues of the quasimolecular ion are defined in equations (30), (31). Specifically for our problem

$$[H(x, z) - E^{\pm}(z)] \; U^{\pm}(x, z) = 0 \; , \tag{74}$$

$$U^{\pm}(x, z \to \pm \infty) = 2^{-\frac{1}{2}} \left(\varphi(x+z) \pm \varphi(x - z)\right) \; , \tag{75}$$

$$E^{+}(z \to \pm \infty) = E^{-}(z \to \pm \infty) = \epsilon \; . \tag{76}$$

The asymptotic quantities are of course just those used in the CSA throughout and are defined in (42) and (44). The Hamiltonian is

$$H(x, z) = -\frac{\partial^2}{\partial x^2} - \lambda^2 u(x + z) - \lambda^2 u(x - z) \; . \tag{77}$$

The matrix elements in the expression for the rearrangement probability (68) for this scheme and for our model system become, remembering that $z = vt$, $k = \frac{1}{2}v$, are

$$S_{fi}(t) = \tfrac{1}{2} \int_{-\infty}^{\infty} dx \; (U_{+}^{2}(t) - U_{-}^{2}(t)) \cos vx \; , \tag{78}$$

$$T_{ii}(t) = 0 \tag{79}$$

$$T_{fi}(t) = -\tfrac{1}{4}\,[E^{+}(t) - E^{-}(t)] \int_{-\infty}^{\infty} dx\, [U_{+}^{2}(t) + U_{-}^{2}(t)] \cos vx$$

$$- \tfrac{1}{2} \int_{-\infty}^{\infty} dx \sin vx\, (U_{+} - U_{-}) \left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial x}\right) (U_{+} + U_{-}) \,. \tag{80}$$

For the sake of compactness, not all the arguments have been written in and also the parity labels have been lowered to subscripts. The expressions for T_{ii} and T_{fi} do depend on the irrevelant phase factor that appears in (72); however, the combination $T_{fi} - S_{fi}T_{ii}$ appearing in the numerator of (68) is indeed an invariant expression with respect to overall time dependent phase transformations. The CSM transition probability (68), together with the relations (78)-(80), now takes the final form,

$$P_{fi}^{CSM} = \sin^2 \int_0^{\infty} dz\, \frac{\frac{E^{+}(z) - E^{-}(z)}{2v}(I_1 + I_2) + I_3 - I_4 + I_5 - I_6}{1 - \frac{1}{4}(I_1 - I_2)^2} \tag{81}$$

where

$$I_1(z) = \langle + | \cos vx | + \rangle \,, \tag{82a}$$

$$I_2(z) = \langle - | \cos vx | - \rangle \,, \tag{82b}$$

$$I_3(z) = \langle + | \sin vx \frac{\partial}{\partial z} | - \rangle \quad , \tag{82c}$$

$$I_4(z) = \langle - | \sin vx \frac{\partial}{\partial z} | + \rangle \quad , \tag{82d}$$

$$I_5(z) = \langle + | \sin vx \frac{\partial}{\partial x} | + \rangle \quad , \tag{82e}$$

$$I_6(z) = \langle - | \sin vx \frac{\partial}{\partial x} | - \rangle \quad , \tag{82f}$$

with $|\pm\rangle = |U^{\pm}(x, z)\rangle$. (83)

The quasimolecular eigenvalues $E^{\pm}(z)$ are implicit functions of z, whose analytic forms in addition change at $z = 1$. The eigenfunctions satisfy

$$U^{\pm}(x, z) = \pm U^{\pm}(-x, z) = \pm U^{\pm}(x, -z) \ . \tag{84}$$

Therefore only positive values of x and z need be considered. The implicit dependence of the functions $U^{\pm}$ on z actually enters through the eigenvalues $E^{\pm}$; i.e., $U^{\pm}(x; z) = U^{\pm}(x, E^{\pm}(z))$. The latter is an explicit function of x and a rather involved but explicit function also of E. The relatively simple spatial dependence of $U^{\pm}$ is given below.

$$U^{\pm}(x; z) = C^{\pm} \exp[-\beta^{\pm} x] \qquad \text{for } 1 + z < x \ ; \tag{85a}$$

$$= B^{\pm} \begin{matrix}\cos\\ \sin\end{matrix} (\xi^{\pm} x + \delta^{\pm}) \qquad \text{for} \quad |1-z| \leqslant x \leqslant 1 + z \; ; \tag{85b}$$

$$= \begin{cases} A^{\pm} \begin{matrix}\cosh\\ \sinh\end{matrix} (\beta^{\pm} x) \; , & (\text{if} \quad z \geqslant 1) \\ & \text{for} \quad |1-z| \geqslant x \; ; \\ A^{\pm} \begin{matrix}\cos\\ \sin\end{matrix} (\mu^{\pm} x), & (\text{if} \quad z \leqslant 1) \end{cases} \tag{85c,d}$$

with

$$\beta = E^{\frac{1}{2}}(z); \quad \xi = (\lambda^2 - \beta^2)^{\frac{1}{2}} \; ; \quad \mu = (2\lambda^2 - \beta^2)^{\frac{1}{2}} \; ; \tag{86}$$

and with

$$A^{\pm} = A^{\pm}(\beta^{\pm}) \; ; \; B^{\pm} = B^{\pm}(\beta^{\pm}) \; ; \; C^{\pm} = C^{\pm}(\beta^{\pm}); \quad \delta^{\pm} = \delta^{\pm}(\beta^{\pm}) \; . \tag{87}$$

The functions are continuous but not analytic throughout the range of either of the two arguments. Consequently, although the six integrals (82a-f) can be evaluated in closed form, it is impractical to do so owing to the large amount of work involved. The time integration in any event must be done numerically.

IV. RESULTS AND DISCUSSION

In an actual ion atom scattering problem the two independent variables are usually chosen to be the impact parameter and the energy (or velocity), and the dependent variable is the transition probability (or cross section). Our problem simulates a fixed impact parameter situation. And in the case of symmetric resonance our model contains formally only one free parameter, the coupling constant or equivalently the depth of the potentials. Units where $\hbar = 2m = a = 1$ are used throughout. For accidental degeneracy we have a second parameter, which is either the depth or the width of the second potential. For the general case of non degeneracy there are obviously three parameters. The number of bound states of an atom increases with the coupling constant. It is found from the solutions of the implicit eigenvalue equations that the number of excited atomic states is equal to the whole number of $\pi/2$ in λ, the square root of the coupling constant. The atomic orbitals are eigenstates of parity, alternatively even and odd, with the ground state always of even parity.

A scattering system is defined by each set of parameter values. An interesting system on which the results obtained are clean and relatively easy to interpret is the symmetric resonant case where λ^2, the coupling constant, is equal to $\pi^2/8$. The one and only bound state in this specie of atom has a binding energy, β^2, equal to the kinetic energy, ξ^2, inside the potential well. Here the decision on what to consider as the intermediate energy (or velocity) is

relatively unambiguous. We may note again for reference that for the proton hydrogen system this intermediate velocity corresponds to a laboratory kinetic energy of 25 keV. Numerical results were reliably obtained on this model system ranging over a factor of one thousand in energy. This covers what may conveniently be designated as the lower intermediate, the upper intermediate, and the (moderately) high energy regions that on the proton hydrogen system would be between $1\frac{1}{2}$ keV to $1\frac{1}{2}$ MeV in the laboratory system.

Figure 1 shows the rearrangement probabilities vs energy in the upper intermediate and high regimes. The intermediate point is 1.62 on the energy scale chosen. The solid line is the exact result and the various broken lines are results predicted by four of the approximation schemes. Three of these, the two modified Borns and the CSA, converge and are indistinguishable at high energies. They are definite improvements over the Born--more accurately the Brinkman Kramers--for energies not too high. At lower energies the two state representation is still very good but the higher order effects such as the depletion of the initial state through the back coupling term, must be included to prevent exaggeration of the transition amplitude as evidenced by the CSA curve. At high energy all four approximation schemes, which become in effect first order schemes, are inadequate. The belief is that transitions outside this manifold are important. The first order rearrangement amplitude varies asymptotically as v^{-5}. A first order direct amplitude would vary only as v^{-1}. It is clear then that in this three channel

problem (including ionization) that there is no unique perturbation expansion parameter and hence no unique power of the velocity to characterize an amplitude of a given order. Thus at high energies the second order effect may be comparable to the first order one. In other words, the continuum distortion, which is small to be sure at high energies, containing high momentum components may contribute via second order an effect comparable to the first order because the latter is falling off so rapidly with increasing momentum transfer. This is the case for proton hydrogen scattering.

Figure 2 displays results on the same system for both lower and upper intermediate energies. Here the rearrangement probability vs energy is presented for the exact problem and for the two coupled two states models, the CSA and the CSM. The dominant characteristics of the exact results, the oscillations, are described surprisingly well by the approximation schemes. As we have mentioned before the coupled two channel schemes contain formally the mechanism to predict these oscillations. It is not altogether clear how to distinguish a mechanism from its effects in a purely quantum mechanical context. We may simply refer instead to the notions of the qualitative structure of the mathematical formalism and its actual quantitative results. Anyhow, the predicted extrema of these oscillations, for symmetric resonance, saturates unitarity; there is no reasonable mechanism for nonsaturation in the two schemes. The test then is whether the positions of the actual maxima and minima are predicted by the approximations. The agreement is very good. As listed in Table 1.

Table 1. The location of the symmetric-resonant charge-exchange probability turning points in the spectrum as predicted by the CSA and CSM, and as given by the exact results. The intermediate energy value in these units is 1.62.

	1st. Max.	1st. Min.	2nd. Max.	2nd. Min.
CSA	1.06	0.430	0.236	0.150
CSM	1.13	0.382	0.203	0.127
EXACT	1.04	0.405	0.213	0.132

Below the half-intermediate value of 0.81, the CSM is more accurate; the CSA and the CSM results sandwich the exact result. At around 0.81, the CSA begins to converge toward the exact solution while the CSM begins to diverge from them both.

the trend of the data is in accordance with theoretical expectations; of the two, the CSA is relatively better at the higher energies while the CSM is relatively better at lower energies.

At first glance the failure of the exact rearrangement amplitude to reach the maximum and minimum of one and zero respectively suggests a serious inadequacy in the two states description. However, the oscillation minima are almost zero. Furthermore, the coherent amplitude, which is not shown, has similar oscillations that--in perfect agreement with the two states theory--are 90° out of phase with those of the rearrangement amplitude. This coincidence of the coherent maxima and minima with respectively the charge exchange minima and maxima substantiates the conclusion that the difference between the theoretical and actual maxima is due entirely to ionization, which for reasons not fully understood is slowly increasing with decreasing energy. The main point then is that the relative distribution of the state vector within the linear manifold spanned by the two bounded channels is well described by the coupled channel formulation.

We may now imagine the charge exchange process to proceed as follows in the lower intermediate energy regime. The electronic wave packet initially translates uniformly with the potential well of the target nuclei to which it is bound. Upon the approach of the beam nuclei the wave packet--no longer a steady state in the laboratory system--begins "tunneling" in both position and momentum space over to the other potential well. During the main collision period the

electron wave packet may thus, depending on the relative internuclear velocity, shift its location and momentum several times under the influence of the combined potentials. The collision phenomenon breaks off when the internuclear separation is large enough to inhibit further tunneling. The wave packet is then distributed largely around the values characterizing the two force centers in both position and momentum space. During the following relaxation period, most of the amplitude settles into the channel states although a small component (under 10 per cent) goes into ionization. In this picture the memory of which nucleus the electron was initially attached to should not be too significant. And for appropriate values of the velocity parameter the packet may end up completely on just one of the two potential wells; this corresponds to the extrema--either zero or maxima--charge exchange probability. Owing to the symmetries in the system, the amount of ionization should be independent of the type of extrema; and indeed the ionization, as found in the exact results, varies smoothly with energy.

A more crucial test is derived from the fact that on the basis of the foregoing physical picture resonance peaks should be found in the exchange amplitude also for asymmetric resonance and nonresonance systems. The data for these two cases are shown in Fig. 3. These nonsymmetric scattering systems differ primarily from the symmetric system only in that one of the nuclear potentials, chosen to be that of the incident particle V^i, is broader by a factor of 1.60. The

results in Fig. 3 show that the asymmetric resonant system behaves much like the symmetric resonant system. The curve for the non-resonant system does have similar structure but the peaks do not attain the maximum values.

We may summarize the intermediate energy data and their interpretation as follows:

(a) The two states coupled channel models are not completely adequate because the off-manifold processes--ionization in our examples--are in fact not negligible.

(b) The distribution of the on-manifold amplitude, however, is well described by two states models.

(c) The collision process may be pictured qualitatively as repeated exchange of the electron between the two ions. This description of the effect of the accumulated multiple order interactions is decidely less appropriate for the nonresonant situation.

In view of these remarks it is of advantage to use the quantity Δ, rather than the transition probability, to display our results.

$$\Delta = \sin^{-1} (P_f/[P_f + P_i])^{\frac{1}{2}} \tag{1}$$

where

$$P_{i,f} = |A_{i,f}|^2 . \tag{2}$$

This phenomenological parameter may be justified by the model implied by the statements (a) - (c). Consider the states $\psi_{\pm}(t)$, that satisfy

only the asymptotic conditions,

$$\psi_{\pm}(\pm\infty) = \psi_i(\pm\infty) \pm \psi_f(\pm\infty) \quad , \tag{3}$$

where $\psi_{i,f}(t)$ are the initial and final states. As the precise form otherwise of $\psi_{\pm}$ is not going to be relevant, we shall simply define

$$\psi_{\pm} = \psi_i \pm \psi_f \; . \tag{4}$$

After the scattering, we may express the transition probability by

$$P_f = |A_f|^2 = \tfrac{1}{4}\,|A_+ - A_-|^2 \tag{5}$$

where $A_f = \langle f|\underline{\Psi}\rangle$; $A_{\pm} = \langle \pm|\underline{\Psi}\rangle = A_i \pm A_f$ (6)

$$P_f = \tfrac{1}{4}(|A_+| - |A_-|)^2 + |A_+||A_-| \sin^2 \tfrac{1}{2}(\delta^+ - \delta^-) \tag{7}$$

where $A_{\pm} = |A_{\pm}|e^{i\delta\pm}$. (8)

Now

$$|A_+||A_-| = -\tfrac{1}{2}(|A_+| - |A_-|)^2 + \tfrac{1}{2}(|A_+|^2 + |A_-|^2) \tag{9}$$

$$= |A_i|^2 + |A_f|^2 - \tfrac{1}{2}(|A_+| - |A_-|)^2 \; . \tag{10}$$

Therefore

$$P_f = (P_i + P_f)\sin^2 \tfrac{1}{2}(\delta^+ - \delta^-) + \tfrac{1}{4}(|A_+| - |A_-|)^2 (1 - 2\sin^2 \tfrac{1}{2}(\delta^+ - \delta^-)) . \tag{11}$$

It is easy to establish that the second term on the r.h.s. of Eq. (11) is almost always negligible if the two states-- $\psi_\pm$ --do not couple strongly. For resonant systems this coupling is indeed either zero or weak. Furthermore, if ionization is negligible then $|A_+| \simeq |A_-| \simeq 1$, and the second term vanishes. In fact, however, ionization is not negligible. Let us take the pessimistic assumption that the ionization probability P_c arises from the strong coupling to the continuum of only one of the two states $\psi_\pm$ and estimate the magnitude of the second term in (11).

$$\tfrac{1}{4}(|A| - |A|)^2 = \tfrac{1}{4}(1 - (1 - 2P_c)^{\frac{1}{2}})^2 = \tfrac{1}{2}(1 - P_c - (1 - 2P_c)^{\frac{1}{2}}) = \tfrac{1}{4}P_c^{\,2} \tag{12}$$

Thus even for 25% ionization, the second term contributes only or less than .02 to P_f. In practice the second term $\leqslant$ .01; therefore

$$P_f \cong (P_i + P_f)\sin^2 \tfrac{1}{2}(\delta^+ - \delta^-) \; . \; . \; . \tag{13}$$

and the quantity Δ is to be identified with $\tfrac{1}{2}(\delta^+ - \delta^-)$. (14)

In Fig. 4 we have plotted the spectrum of Δ^{exact}, Δ^{CSM}, Δ^{CSA} Δ^{AA}, and Δ^{exact} (asymmetric), where for the exact results (1) has

been employed and for the models we have employed (14) & (III-65). The AA results were obtained as a special case of the CSM when instead of using $I_m(z; v)$ of (III-82) we used merely $I_m(z; 0)$. Note in Fig. 4 we have extended our range by another factor of ten in inverse energy.

Expression (1) determines Δ only to modulo π. To determine Δ absolutely we use the fact that, in accordance with the physical picture described in statement (c), the time development of $|A_f(t; E)|^2$ for a particular scattering at energy E should recapitulate the spectral distribution of the transition probability - $|A_f(\infty; E)|^2$ - between the energy values of ∞ and E. It is sufficient then to count the number of times $|A_f(t; E)|^2$ oscillates over the history of the scattering to determine the correct branch of Δ.

It is now apparent that the relevancy of the phenomenological parameter is model dependent. For this reason it is not useful to include the nonresonant case. On the other hand, for resonant systems, the conclusions about the mechanism that is operative at intermediate energies may be extrapolated to even lower energies, where direct comparisons of amplitudes is not feasible through the use of this "phase shift", Δ. In Fig. 4 the adiabatic approximation is too high throughout the entire range. For still lower energies the application of the impact parameter method itself is challengeable. We may conclude that over the range of energies that we can study meaningfully, the AA is wrong quantitatively for symmetric resonance and for accidental

degeneracy the commonly believed low energy behavior is wrong even qualitatively.

For the nonresonant case the coupled channel mechanism producing the pronounced structure in the rearrangement spectrum is masked rapidly with decreasing collision energy by a damping effect that qualitatively is in agreement with adiabatic theory.

We may now summarize all of our ideas usefully by conjuring up this qualitative description of charge exchange for all energies below the intermediate point. Let us form for convenient discussion three energy regimes within which the distinguishing features of the charge exchange spectrum are: in the highest -- III -- the oscillations reach the unitarity limit (the sum of the coherent and exchange probabilities) imposed by off manifold processes; in the middle -- II -- the above oscillations plus the damping of the peaks; in the lowest -- I -- the rapid decrease to zero of the envelope of the peaks near threshold. For exact resonance systems there is only regime III, the lower two being squeezed out so to speak. For nonresonance, with appreciable energy difference, the highest regime may not exist or may not be noticeable if displaced partly into the higher intermediate region. With small energy differences, i.e., near resonance, the two lower regimes are displaced down toward energies sufficiently low for the translational factors in the CSM matrix elements to be justifiably replaced by unity. With this approximation and one more--the use of LCAO molecular orbitals--we can locate in the mathematical

structure of the CSM equations the theoretical grounds for the features of the regimes. The CSM scheme, which contains accurately all of the above physics, also needs only to be examined at the lowest energies as there is little in dispute elsewhere. It is unnecessary to actually write down the CSM equations. We shall merely use our knowledge of the adiabatic theorem, which is that if the internuclear velocity is sufficiently slow for the change in the Hamiltonian during a Bohr transition period to be small compared to the energy difference of the transition then the transition between the two states of the Hamiltonian is unlikely. Charge exchange can then only occur through quantum mechanical resonance. To test this possibility, we find the two LCAO-MO by perturbation theory. Because the matrix elements fall off exponentially with increasing internuclear separation, with the diagonal exponent about twice that of the off diagonal term, the asymptotic forms of LCAO-MO, which are now exact, are always $\varphi_{\pm} \cong \varphi_i \pm \varphi_f$ for exact degeneracy and always $\varphi_{i,f}$ for nondegeneracy. Therefore, in the adiabatic region the resonance systems always proceed by quantum mechanical resonance and the nonresonance systems are always inert providing the energy curves never cross. This then is the basis for regime III at threshold for resonant systems and for the existence of regime I in nonresonant systems. At finite separations the LCAO-MO for nonresonance may approximately be any of the forms, $\varphi_{i,f}$; $\varphi_{\pm}$, or the general $p\varphi_i + q\varphi_f$, depending on the magnitude of the energy difference, $\epsilon_i - \epsilon_f$, relative to the off diagonal perturbation element, V_{if}. If the $\varphi_{\pm}$ forms do exist in the near

zone then regime III commences at velocities fast enough to be "sudden" in the far zone, where the unperturbed energies are small, but slow enough to be considered adiabatic in the near zone where the energy split is wide. Regime II appears at velocities satisfying either partially or in part the conditions for III. If the form $\varphi_{\pm}$ does not exist then there are only the two regimes I and II. At higher velocities where translational terms must be kept the description must be generalized to include the coupling effects existing even between appropriately chosen molecular orbitals.

The experimental evidence for asymmetric resonance agrees not with our resonant theory but rather with our near resonant theory. This is probably because exact asymmetric resonance in the actual world is rarely encountered. And what is measured is near resonant scattering. More serious perhaps is the fact that previous work has shown that asymmetric resonant exchange vanishes at threshold.[23,24] In these derivations an assumption is made that a "distorted Born" approximation, $A_i = 1$, on the coupled equations can validly be made when the off diagonal terms are small. They then get consistently $A_f = 0$, as $v \to 0$. Such approximation however beg the question. One could, in effect treat the off diagonal terms first, by using the distorted $(\pm)$ basis rather than the (i,f) basis and then treat the remaining terms as a perturbation. The result would then predict no perturbative effect as $v \to 0$, and therefore $A_{\pm} = \text{const.}$, which is the condition for quantum mechanical resonance. The correct conclusion about

charge exchange by this method of applying perturbation theory in two steps depends upon which quantities--the diagonal or the off diagonal terms--are in fact relatively small if either, or more pertinently upon which superposition type the asymptotic LCAO-MOs assume. This, we have already discussed.

Conclusion

The coupled channel schemes are decidely appropriate for the calculation of charge exchange within the low and intermediate energy range. For resonant systems--both symmetric and asymmetric--, one particular exchange mechanism is operative, while for nonresonant systems, adiabatic ideas are also in effect and are even dominant at low energies. All of this would be encompassed in the results of coupled two states schemes, had we had them for all three cases. These schemes are formulated to include explicitly the asymptotic boundary conditions; this theoretically amounts to just centering the nuclei in momentum space in consistency with that implied by the usual IPM. Although the translational terms are essential, the choice of the "form" factors is itself important for locating precisely the turning points in the spectrum. Atomic form factors are accurate at upper intermediate energies and molecular form factors are good over a surprisingly large range of energies. The coverage provided by the two forms is continuous with good overlap. Because the relevant coupled equations may also be derived variationally, approximate trial form factors should be also reasonably accurate.

Transitions to states off the linear manifold, beyond the scope of our type of two states schemes, shows up as a reduction in the rearrangement peaks from unity. Since ionization is involved, it is unlikely that this effect can be accurately reproduced by increasing the number of states coupled.

The near coincidence of the "phase shift" data for the two different resonant systems below the intermediate energy suggests the significance of the role played by the binding energy, which for the two cases was equal.

For energies above the upper intermediate we have no satisfactory theory. All of the attempts to calculate the charge exchange probability gave values too high.

It is perhaps appropriate here to dispel suggestions that certain values of the momentum transfer may be extraordinary and therefore responsible for resonant structure. No evidence for this was found. Nothing distinct happens at the intermediate point; and the singularity appearing in the analytic expression for the Born amplitude (II-47) is in fact removable. The zeros in the asymptotic form of the same expression are due to the sharp edges of the square wells employed and are above the range of energies treated here.

Finally, we note that the intermediate energy region, for which the lack of a theory motivated considerably this investigation, appears now to be better understood than the high and very low energy

regimes, which in view of the inadequacy of the earlier ideas can bear further study.

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Appendix A: THE VARIATIONAL METHOD FOR TIME DEPENDENT THEORY

The solution to the time dependent Schrodinger equation satisfies the stationary principle $\delta I = 0$, where

$$I = \int_{-\infty}^{\infty} dt \, (\underline{\Psi}(t), (i \frac{\partial}{\partial t} - H(t)) \, \underline{\Psi}(t)) \, . \tag{1}$$

The trial form of the wave function, as in the coupled channel schemes, is

$$\underline{\Psi}(t) = \sum_{n}^{N} A_n(t) \, \psi_n(t) \, , \tag{2}$$

where N is a finite integer. Substituting (2) into (1) we get, using the Einstein summing convention,

$$I = \int_{-\infty}^{\infty} dt \, (i \, A_m^* \, S_{mn} \, \dot{A}_n + A_m^* \, T_{mn} \, A_n) \, , \tag{3}$$

where $S_{mn} = (\psi_m, \psi_n)$, and (4)

$$T_{mn} = (\psi_m, (i \frac{\partial}{\partial t} - H) \, \psi_n) \, . \tag{5}$$

The stationary variation of I with respect to A_m^* , $\delta I = 0$, yields the Euler Lagrange equations,

$$\frac{\partial L}{\partial A_m^*} - \frac{d}{dt} \frac{\partial L}{\partial \dot{A}_m^*} = 0 \, , \tag{6}$$

with $$L \equiv (i\, A_m^* S_{mn} \dot{A}_n + A_m^* T_{mn} A_n) \,. \tag{7}$$

$$\frac{\partial L}{\partial A_m^*} = i\, S_{mn} \dot{A}_n + T_{mn} A_n \tag{8}$$

$$-\frac{d}{dt} \frac{\partial L}{\partial \dot{A}_m^*} = 0 \,. \tag{9}$$

From (6), (7), and (8) we get the desired result

$$S \dot{A} = i\, T A \quad , \text{q.e.d.} \tag{10}$$

We may verify directly that

$$T^\dagger = T - i \dot{S} \,. \tag{11}$$

$$T_{mn} = \langle m | i \frac{\partial}{\partial t} | n \rangle - \langle m | H | n \rangle \,. \tag{12}$$

$$i \dot{S}_{mn} = \langle m | i \dot{n} \rangle + \langle -i \dot{m} | n \rangle$$

$$= \langle m | i \frac{\partial}{\partial t} | n \rangle + \langle n^* | i \frac{\partial}{\partial t} | m^* \rangle \,. \tag{13}$$

$$(T^\dagger)_{mn} = T_{nm}^* = \langle n^* | -i \frac{\partial}{\partial t} | m^* \rangle - \langle m | H | n \rangle \tag{14}$$

where we have used the Hermitian property of H, $H_{nm}^* = H_{mn}$. From (12), (13), and (14) it is obvious that $T - T^\dagger = i \dot{S}$, from which (11) follows trivially.

The Schrodinger equation (10), and Eq. (11) imply conservation of probability. Left multiplying Eq. (10) by $A^{\dagger}$,

$$A^{\dagger} S \dot{A} = i A^{\dagger} T A \quad . \tag{15}$$

The corresponding adjoint equation is

$$\dot{A}^{\dagger} S A = -i A^{\dagger} T^{\dagger} A \text{ , using the obvious fact ,}$$

$$S_{mn} = S^{*}_{nm} \tag{16}$$

Adding (15) and (16) and eliminating $T^{\dagger}$ by (11), we obtain

$$0 = \dot{A}^{\dagger} S A + A^{\dagger} \dot{S} A + A^{\dagger} S \dot{A} = \frac{d}{dt} (A^{\dagger} S A) = \frac{d}{dt} (A^{*}_{m} S_{mn} A_{n}) =$$

$$\frac{d}{dt} (\Psi, \Psi) = 0, \text{ q.e.d.} \tag{17}$$

APPENDIX B: THE TWO POTENTIAL FORMALISM

There are many physical situations where the interaction Hamiltonian, V, is actually the sum of two potentials,

$$V = V_p + V_s \quad . \tag{1}$$

An example is proton nucleus scattering where the interaction is the sum of the nuclear and the coulomb potentials. The T-matrix is then

$$T_{fi} = (\Phi_f, (V_p + V_s)\, \Psi_i^{(+)}), \quad \text{with} \tag{2}$$

$$\Psi_i^{(+)} = \Phi_i + \frac{1}{E + i\eta - H_0} (V_p + V_s)\ \Psi_i^{(+)} \quad . \tag{3}$$

The noninteraction and the total Hamiltonians, H_0 and H respectively, are related as usual by $H = H_0 + V$. (4)

Sometimes it may be appropriate to treat the two potentials unsymmetrically in approximation work. One of these potentials, the "principle", is perhaps the interaction primarily responsible for the process of interest and may be treated validly by first order perturbation theory. The other, the "secondary" potential, may be too large to be ignored and also large enough to affect adversely the first order result. It is then handled as a background interaction, as both an initial-state-interaction and a final-state-interaction. The Lippmann-Schwinger equations for just this interaction are

$$\chi_{i,f}^{(\pm)} = \Phi_{i,f} + \frac{1}{E \pm i\eta - H_0} V_s \chi_{i,f}^{(\pm)}. \tag{5}$$

The principle interaction is now superimposed on the secondary interaction;

$$\Psi_i^{(+)} = \chi_i^{(+)} + \frac{1}{E + i\eta - H_0 - V_s} V_p \Psi_i^{(+)} . \tag{6}$$

Even without a natural separation, the interaction V may always be decomposed formally; $V = (V - U) + U$; the formal secondary interaction is U. The T-matrix may be shown to be, using (5) and the fact that all Hamiltonians are Hermitian,

$$T_{fi} = (\chi_f^{(-)}, (V - U) \Psi_i^{(+)}) + (\Phi_f, U \chi_i^{(+)}) . \tag{7}$$

The interaction U usually is so chosen that the second term may be dropped. Then the final form of the T-matrix is

$$T_{fi} = (\chi_f^{(-)}, (V - U) \Psi_i^{(+)}) . \tag{8}$$

The two potential formalism thus provides a structure for a more desirable split of the Hamiltonian, with the secondary interaction absorbed into the representation and the principle interaction expressed in a form suitable for perturbation expansions.

In rearrangement scattering, a two channel process, almost all of the above formalism carries through with due regard for the two

different representations present. The T-matrix in the post form is

$$T_{fi} = (\Phi_f, V^f \Psi_i^{(+)}) \quad . \tag{9}$$

$$\Psi_i^{(+)} = \Phi_i + \frac{1}{E + i\eta - H^i} V^i \Psi_i^{(+)} \quad , \tag{10}$$

where $H = H^i + V^i = H^f + V^f$. (11)

We now formally split off from V^i and V^f respectively an initial-state-interaction, U^i, and a final-state-interaction, U^f. The solutions to these are

$$\chi_{i,f}^{(\pm)} = \Phi_{i,f} + \frac{1}{E \pm i\eta - H^{i,f}} U^{i,f} \chi_{i,f}^{(\pm)} \tag{12}$$

The state vector in this "distorted" prior representation is

$$\Psi_i^{(+)} = \chi_i^{(+)} + \frac{1}{E + i\eta - H^i - U^i} (V^i - U^i) \Psi_i^{(+)} \quad . \tag{13}$$

The T-matrix may again be expressed as two terms:

$$T_{fi} = (\chi_f^{(-)}, (V^f - U^f) \Psi_i^{(+)}) + (\Phi_f, (U^f \frac{1}{d_f^+} d_i^+) \chi_i^{(+)}) \, , \tag{14}$$

with $$d_{i,f}^{\pm} = \frac{1}{E \pm i\eta - H^{i,f} - U^{i,f}} .$$

When the secondary interactions $U^{i,f}$ are chosen to contribute only to direct processes in respectively the initial and final channels, the second term in (14) vanishes.[28,29] The T-matrix is just the first term of (14); this, the post interaction form, is

$$T_{fi} = (\chi_f^{(-)}, (V^f - U^f)\, \Psi_i^{(+)}) . \tag{15}$$

The analogous expression in the prior interaction form is

$$T_{fi} = (\Psi_f^{(-)}, (V^i - U^i)\, \chi_i^{(+)}) , \tag{16}$$

where $\Psi_f^{(-)}$ satisfies an equation analogous to (10) or (13) but with the "incoming" scattered wave boundary condition.

Appendix C: MATHEMATICAL RELATIONSHIPS BETWEEN APPROXIMATION SCHEMES

C.1 At high velocities the following approximations may be made successively on the CSA result for charge exchange.

$$P_{fi}^{CSA} = \sin^2 \int_{-\infty}^{\infty} dt \; \frac{V_{fi} - S_{fi} V_{ii}^{i}}{1 - S_{fi}^{2}} \quad . \tag{1}$$

(i) Approximating the sine by its argument we get the Mod. Born II result,

$$P_{fi}^{CSA}(i) = P_{fi}^{MBII} = \left[\int_{-\infty}^{\infty} dt \; \frac{V_{fi} - S_{fi} V_{ii}^{i}}{1 - S_{fi}^{2}} \right]^2 \quad . \tag{2}$$

(ii) Neglecting the quadratic term, S_{fi}^{2}, in the denominator we get

$$P_{fi}^{CSA}(ii) = P_{fi}^{MBI} = \left[\int_{-\infty}^{\infty} dt \; (V_{fi} - S_{fi} - V_{ii}^{i}) \right]^2 \quad . \tag{3}$$

(iii) Dropping now the term proportional to S_{fi}, which may not be justified in all cases, we get the Born result,

$$P_{fi}^{CSA}(iii) = P_{fi}^{BK} = \left[\int_{-\infty}^{\infty} dt \; V_{fi} \right]^2 \quad . \tag{4}$$

C.2 At low velocities we may replace the translation factors by unity in the various coupled channel equations as an approximation that generally becomes exact at zero velocity (threshold). The adiabatic approximation scheme is so obtained from the CSM scheme. Conventionally

the AA scheme is obtained directly from an expansion of the state wave function about the two molecular orbitals that are relevant to the two atomic orbitals of interest. Rigorous derivation of the two component Schrodinger equation from such a starting point leads to ambiguous results that depend on the choice of coordinate system, except when $v = 0$. This is because the expansion is not properly posed for the two-channel problem in that the boundary conditions for the initial and final states are no longer included. The correct AA scheme, however, may be heuristically formulated with the exercise of great care, especially when approximate molecular functions are employed, in identifying and eliminating the spurious interaction terms that arise. The AA should be meaningful at low energies. It's asymptotic prediction, as $1/v \to \infty$, must agree qualitatively with the result known directly from our statement of the adiabatic theorem. This agreement must exist, even when "spurious" interaction terms are present (they vanish first as $v \to 0$), providing the analysis of the threshold behavior of the equations is correct.

The AA scheme, when LCAO molecular orbitals are used, is mathematically equivalent to the low energy approximation of the CSA. For symmetric resonance, the transition probability for this CSA* scheme is

$$P_{fi}^{CSA^*} = \sin^2 \int_{-\infty}^{\infty} dt \, \frac{V_{fi} - S_{fi} V_{ii}^{i}}{1 - S_{fi}^{2}} \tag{5}$$

where the translational factors have been omitted in the matrix elements in Eq. (5). This is identical to the LCAO-MO version of the P_{fi}^{AA} expression.

$$P_{fi}^{AA} = \sin^2 \int_{-\infty}^{\infty} dt \, \tfrac{1}{2}(E^{+}(z) - E^{-}(z)) \tag{6}$$

$$\tfrac{1}{2}(E^{+} - E^{-})_{LCAO} = \tfrac{1}{2}\langle + | H | + \rangle - \tfrac{1}{2}\langle - | H | - \rangle$$

$$= \tfrac{1}{2}\left\langle \frac{\varphi_i + \varphi_f}{[2(1+S)]^{\frac{1}{2}}} \middle| H \middle| \frac{\varphi_i + \varphi_f}{[2(1+S)]^{\frac{1}{2}}} \right\rangle - \tfrac{1}{2}\left\langle \frac{\varphi_i - \varphi_f}{[2(1+S)]^{\frac{1}{2}}} \middle| H \middle| \frac{\varphi_i - \varphi_f}{[2(1+S)]^{\frac{1}{2}}} \right\rangle$$

$$= \frac{V_{fi}^{i} - S V_{ii}^{i}}{1 - S^2}, \quad \text{because}$$

$(1 \pm S)^{-\frac{1}{2}}$ are "c" numbers, $H_{ii} = H_{ff} = V_{ii}^{i}$, and $H_{if} = H_{fi} = V_{fi}$. $S = S_{fi} = S_{if}$

Therefore the exact CSA scheme and the exact LCAO form of the CSM scheme converges at low energies. This then is a rough measure of the accuracy of the CSA at low energies or of the inaccuracy of the LCAO energies.

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$$\sigma(\theta;v) = -\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\tfrac{1}{2}b^2\right) = -\frac{b}{\sin\theta}\frac{db}{d\theta} .$$

The total cross section for a particular transition is by (II-23)

$$\sigma_{fi}(V) = 2\pi \int_0^\infty db\, b\, P_{fi}(b;v) = 2\pi \int_0^\infty db\, b\, \frac{\sigma_{fi}(\theta;v)}{\sigma(\theta;v)}$$

$$= 2\pi \int_0^\pi d\theta \sin\theta\, \sigma_{fi}(\theta;v) \quad , \text{ which is (II-24).}$$

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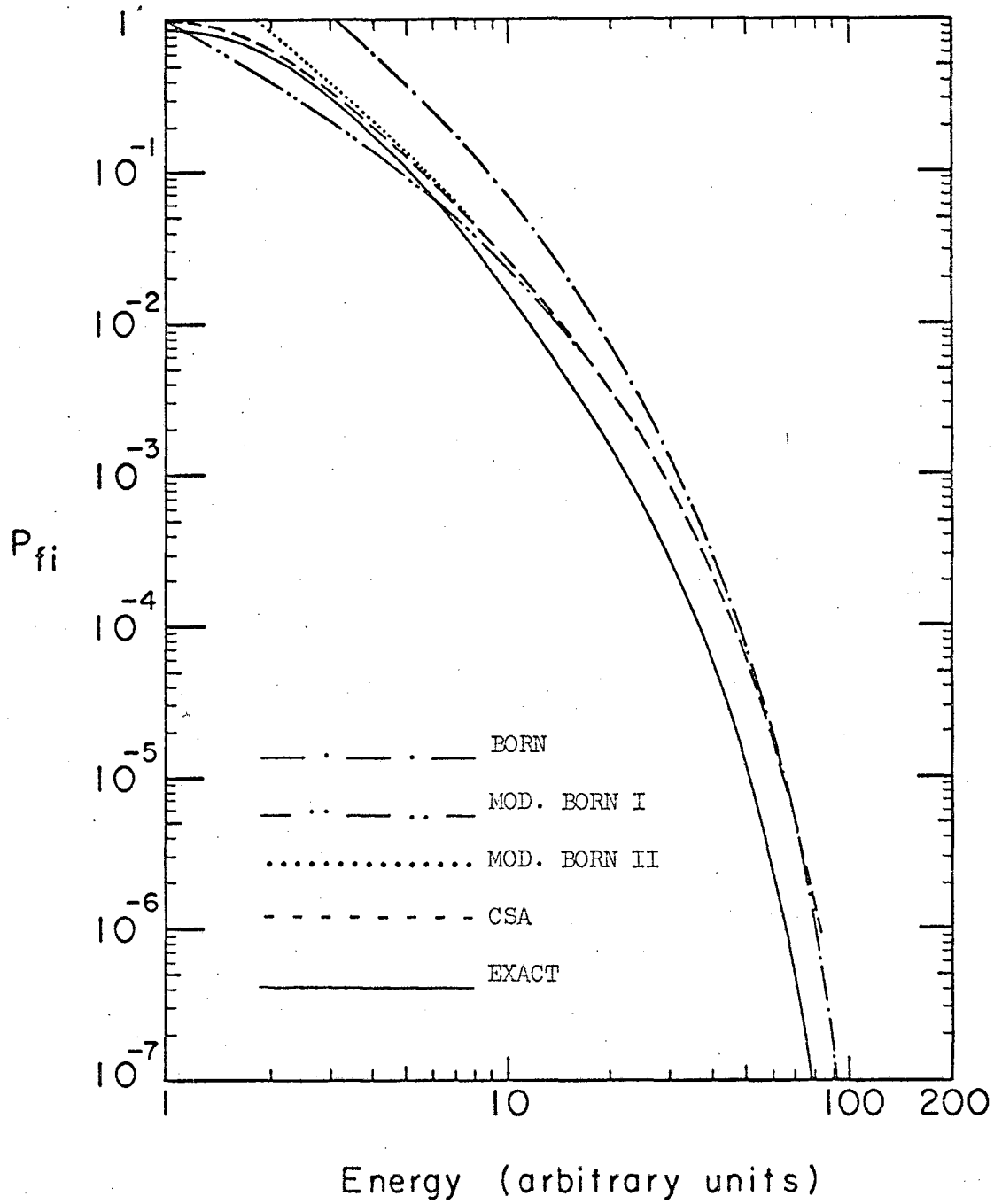

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Fig. 1. The charge exchange probability vs energy in the upper intermediate and high energy regions.

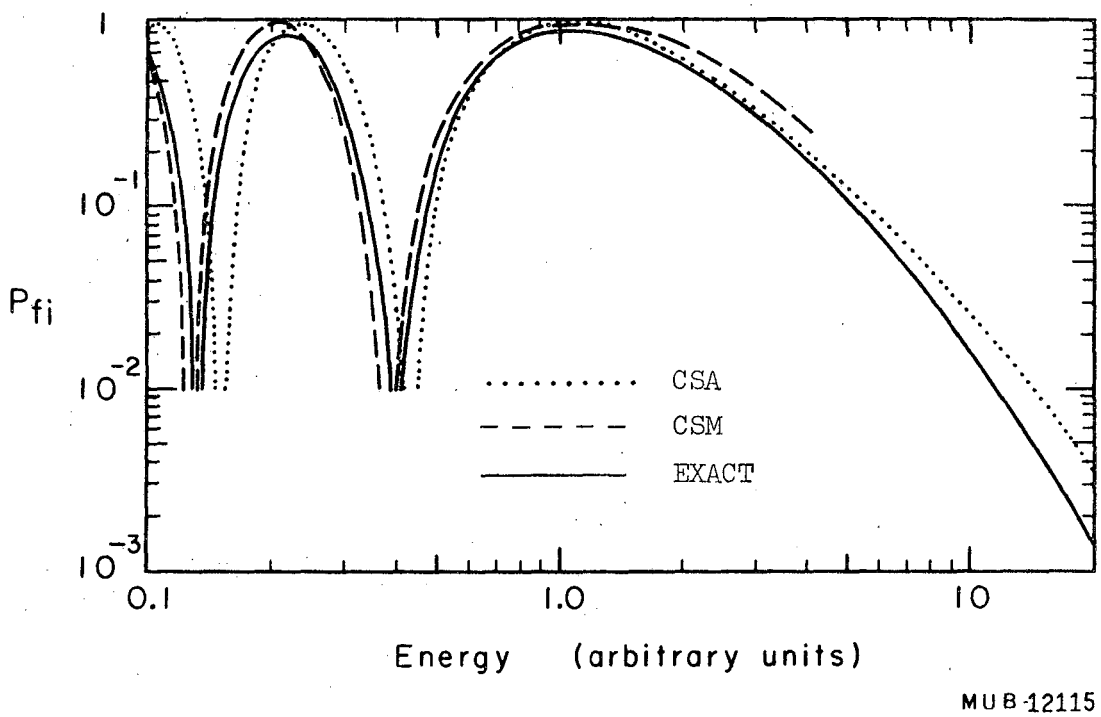

Fig. 2. The charge exchange probability vs energy in the lower and upper intermediate energy regions.

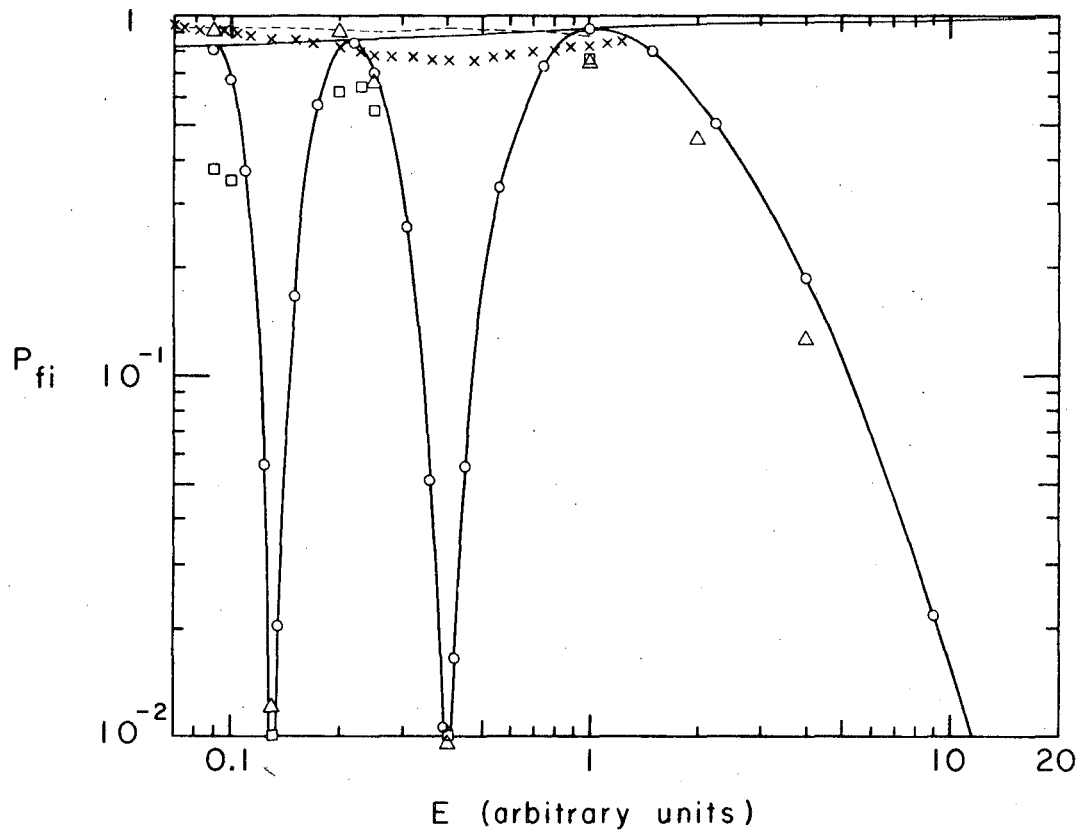

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Fig. 3. The exact rearrangement probability and the on-manifold unitarity limit vs energy.

Rearrangement	Unitarity	System
○——○——○	————	symmetric resonance
△ △ △	- - - - -	asymmetric resonance
□ □ □	x x x x x	nonresonance

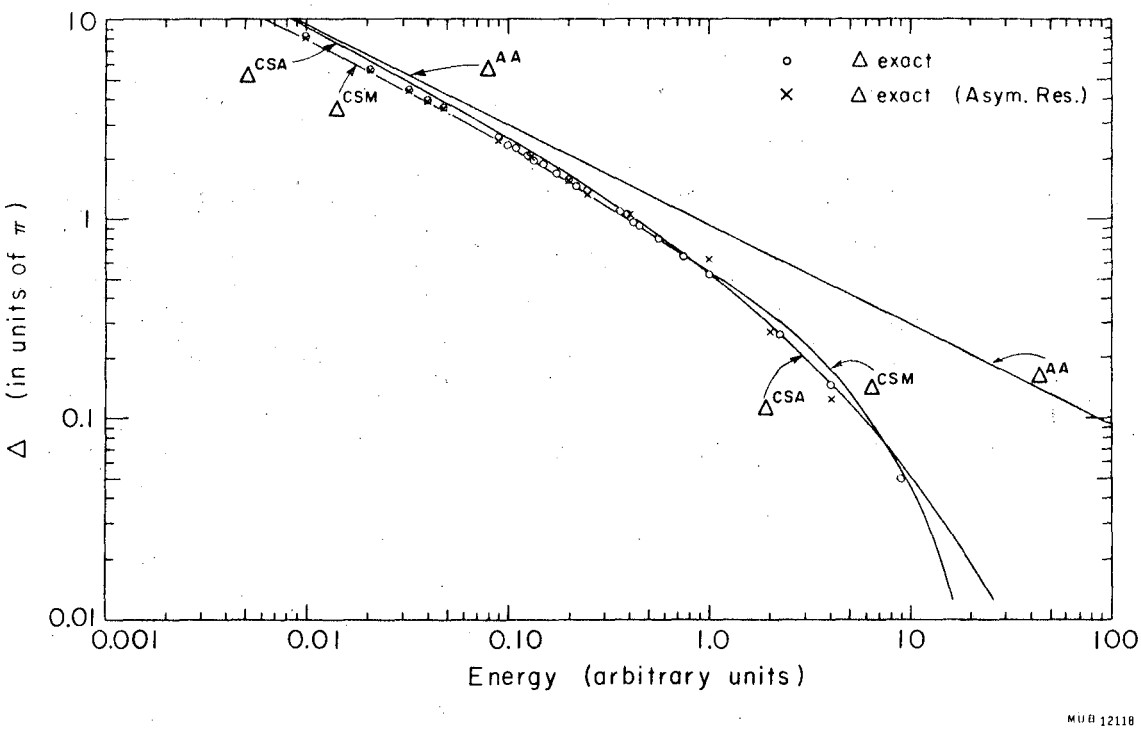

Fig. 4. The Δ vs energy for the low and intermediate regions.