# Theoretical treatment of collisions of Rydberg atoms with neutral atoms and molecules. Semiquantal, impulse, and multistate-orbital theories

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The semiquantal treatment of ionization in $A$-$B(n)$ collisions, based on encounters between the Rydberg electron $e$ and incident atom or molecule $A$, is derived from the full quantal impulse approximation. The useful transformation between the dynamical variables natural to these treatments is provided. Various levels of approximation are then deduced and necessary criteria for validity of application of the basic impulse expression to various types of $A$-$B(n)$ processes—ionization, excitation, and quasielastic—in different energy regions are emphasized, including those associated with the additional assumption of "on-the-energy-shell" $(e$-$A)$ encounters. It is pointed out for cases involving quasielastic collisions at thermal energies that models based on $(e$-$A)$ encounters alone may not provide either a full or proper description of the underlying mechanism. A new treatment of (in) elastic transitions via $(A$-$B^+)$ encounters at thermal energies and beyond is introduced and formulated. Preliminary assessment indicates that the proposed new mechanism is significant and could well be dominant in quasielastic $A$-$B(n)$ processes.

## I. INTRODUCTION

In the semiquantal treatments previously proposed[1] for the collision process

$$A(i)+B(n)\rightarrow A(j)+B^{+}+e \qquad (1.1)$$

involving a target $B(n)$ in a highly excited Rydberg state with principal quantum number $n$, electron ejection from the target is assumed to proceed via a binary collision between the Rydberg electron $e$ and the projectile $A$ initially in internal state $i$. An $(e$-$A)$ inelastic collision includes the possibility of a simultaneous transition $(i\rightarrow j)$ within the atomic or molecular system $A$. This treatment is successful[2] for ionization of $B$ with or without simultaneous excitation/ionization of $A$ in fast neutral-neutral collisions, and it has been recently applied[3] to ionization in excited atom-excited atom collisions $(i<n)$. The treatment yields the correct high-energy limit when the speed $v_A$ of $AB$ relative motion is $\gg v_e$ the orbital speed of the Rydberg electron, is valuable for both $v_A\sim v_e$, and for much slower collisions with $v_A\ll v_e$. The treatment is valid *provided* the momentum and energy transferred to $e$ via the $e$-$A$ encounter are much greater than the momentum and energy imparted to $e$ by its parent core $B^+$ during the duration of the collision.

The basic treatment[1] yields the cross section for the process in which the internal energy of an (electron-ion) pair, or of any ion-pair system, is changed by an amount between $\epsilon$ and $\epsilon+d\epsilon$ via the binary $(e$-$A)$ collision, and as such is therefore more suited to target ionization than to discrete excitation of the target from level $n_i$ to $n_f$. Apart from inserting[1] $d\epsilon=n_f^{-3}$ within the formalism for very high $n_f$, the rigorous generalization of the semiquantal treatment to target excitation is not immediately obvious. Moreover, its relationship with the conceptually similar quantal impulse approximation is not transparent, although several authors[4-6] have discussed it from various standpoints, but not in terms of its true antecedent. Nakamura *et al.*,[7] in a recent series of papers show for the simple case when the scattering amplitude for $(e$-$A)$ collisions is a function only of momentum change $\vec{P}$ (as in Born's approximation) that the semiquantal treatment for this special case follows quite naturally from the impulse and Born expressions for ionization (1.1), as expected, since the quantal impulse (QIA), semiquantal (SQ), and Born expressions for ionization all coalesce in this (high-energy) limit. As previously shown,[1] at very high energies the SQ treatment yields the free collision approximation of Dmitriev and Nikolaev,[8] again as expected.

In this paper, we shall present the derivation of the general semiquantal treatment SQ (without any simplifying assumptions) from the full quantal impulse approximation (QIA), its proper antecedent, and expose any underlying assumptions with the eventual aim of constructing a hierarchy of schemes, capable of systematic improvement, for the valid description of $A$-$B(n)$ collisions. In so doing, the rigorous generalization of SQ to target excitation then becomes apparent.

Effort will also be made to establish and to clarify rigorous criteria for validity of the basic QIA and its derivatives, in contrast to intuitive conditions, normally acceptable but with origins difficult to trace within the various levels of approximation. This procedure entails some review of the impulse procedure (originally developed by Chew,[9] and extended by Chew and Wick,[9] and by Chew and Goldberger,[9] for high-energy neutron-deuteron scattering) and will reveal certain implications of critical importance to $A$-$B(n)$

 

collisions in general. Since most applications of the impulse approximation in atomic collision physics have been to high-energy $e$, $H^+$-H(1$s$) direct and charge-transfer collisions with ground-state hydrogen (for which it is not too successful, cf. Coleman[10]) this critical investigation is required for $A$-$B(n)$ collisions at all impact energies.

The present investigation will also show, for quasielastic $A$-$B(n)$ collisions, in particular, at thermal energy, that the quantal impulse expression (as commonly used) and its derivatives provide only a partial description of the basic mechanism by focusing attention only on the ability of ($e$-$A$) encounters to provide changes in energy and/or angular momentum. In angular momentum $l$-changing collisions[11] at thermal energies, for example, we show that a significant and sometimes dominant contribution to the required cross section arises from proper consideration of encounters between the slow incident atom $A$ and the core $B^+$ of the target, in direct contrast with that assumed, without examination, in other studies.[5,6,12] A new mechanism which produces electronic transitions in the target $B(n)$ via $A$-$B^+$ encounters will be discussed, and a new theoretical formulation of the cross section for the resulting process will be developed. The resulting theory will be important not only for $l$ changing and other quasielastic and elastic processes, but also will complement expressions for the shift and shape of spectral lines originating from highly excited levels which are collision broadened by neutral perturbers. This shift was predicted by Fermi[13] on the basis of $S$-wave scattering in slow $e$-$A$ collisions, and was generalized by Alekseev and Sobel'man[14] who assumed that $e$-$A$ collisions alone were responsible for elastic and inelastic transitions within the framework of the impulse approximation.

The layout of the paper is as follows. Section II describes the basic impulse approximation and its derivatives for most $A$-$B(n)$ collisions, and illustrates the various levels of approximation. In Sec. III, useful limiting cases and validity criteria are explored. The full and important derivation of the general semiquantal expression from the basic impulse approximation is then presented in Sec. IV. In Sec. V, a new theory of transitions occurring in $A$-$B(n)$ collisions via $A$-$B^+$ encounters is presented and formulated. Its implications are then discussed in Sec. VI. Finally, for completeness, reference, and in order to isolate an important expression which is actually more basic than the usual impulse expression, and which is valuable to interpretation of thermal energy collisions when various distortion ($A$-$B^+$) effects cannot be ignored, we have included in the Appendix a derivation of the full quantal impulse expression from the two-potential formula, which permits greater clarity of effects arising in $A$-$B(n)$ collisions.

## II. BASIC IMPULSE APPROXIMATION AND DERIVATIVES

Let the center of mass of the target system composed of the Rydberg electron labeled 1 and its core $C$ labeled 2 be at rest at the origin for spatial coordinates $\vec{r}_i$ of particle $i$ with relative momentum wave vector $\vec{k}_i$ and mass $M_i$. The impulse approximation to the full $T$-matrix element,

$$T_{fi}(\vec{k}_3,\vec{k}_3')=\langle\phi_f(\vec{r}_1)\times\exp(i\vec{k}_3'\cdot\vec{r}_3)\,|\,V(\vec{r}_1,\vec{r}_3)\,|\,\Psi_i^+(\vec{r}_1,\vec{r}_3;\vec{k}_3)\rangle\,, \tag{2.1}$$

for *inelastic* scattering of an incident projectile 3, from wave vector $\vec{k}_3$ initially to $\vec{k}_3'$ finally, by pair interactions

$$V(\vec{r}_1,\vec{r}_3)=V_{31}(\vec{r})+V_{3C}\left(\vec{r}_3+\frac{M_1}{M_1+M_2}\vec{r}_1\right),\quad \vec{r}=\vec{r}_1-\vec{r}_3 \tag{2.2}$$

with the (electron 1-core $C$) target atom with internal eigenfunctions $\phi_n(\vec{r}_1)$, is (cf. Appendix for rigorous derivation) obtained, in effect, by ignoring the projectile 3-core $C$ interaction $V_{3C}$ and by approximating the exact solution $\Psi_i^+$, with the appropriate outgoing boundary condition for scattering under Hamiltonian H, by the exact solution for (1-3) scattering in the laboratory frame under Hamiltonian $(\mathrm{H}-V_{3C}-V_{1C})$. The (1-3) scattering in isolation is described by

$$\Phi(\vec{r}_1,\vec{r}_3;\vec{k}_1,\vec{k}_3)=\exp(i\vec{K}\cdot\vec{R})\psi(\vec{k},\vec{r}),$$

$$\vec{K}=\vec{k}_1+\vec{k}_3,\quad \vec{k}=(M_3\vec{k}_1-M_1\vec{k}_3)/(M_1+M_3)\,. \tag{2.3}$$

The electron momentum $\vec{k}_1$ is, however, not constant but is smeared out with amplitude,

$$g_i(\vec{k}_1)=(2\pi)^{-3/2}\int\phi_i(\vec{r})\exp(-i\vec{k}_1\cdot\vec{r}_1)d\vec{r}_1\,, \tag{2.4}$$

determined fully by its interaction $V_{1C}(\vec{r}_1)$ with the core so that the impulse wave function for scattering in the complete system is

$$\Psi_i^+\approx\Psi_i^{\mathrm{imp}}=\frac{1}{(2\pi)^{-3/2}}\int g_i(\vec{k}_1)\Phi(\vec{k}_1,\vec{k}_3;\vec{r}_1,\vec{r}_3)d\vec{k}_1\,. \tag{2.5}$$

The weak binding of the Rydberg electron is therefore switched off during the assumed strong (1-3) interaction between the projectile and the Rydberg electron and, serves only to establish the correct initial and final atomic states $\phi_{i,f}$

of the target system. Solution (2.3) for the (1-3) mutual scattering in the *absence* of interaction with the core has been expressed as the product of a plane wave for the free motion with total momentum $\vec{K}$ of the (1,3) center of mass, and of the wave function $\psi(\vec{k},\vec{r})$ for the (1-3) relative motion at momentum $\vec{k}$ under potential $V_{31}(\vec{r})$ which, of course, need not be weak (as for Born's approximation). Thus, for $A$-$B(n)$ collisions (2.5) includes *undistorted* motion of the (Rydberg electron-$A$) center of mass (which is *not* a valid assumption at thermal energies) but effectively exact ($e$-$A$) relative motion.

Substitution of (2.2)–(2.5) yields the basic impulse $T$-matrix element,[10]

$$T_{fi}(\vec{k}_3,\vec{k}_3')=\int g_f^*(\vec{k}_1')g_i(\vec{k}_1)T_{13}(\vec{k},\vec{k}')\times d\vec{k}_1\{\delta[\vec{P}-(\vec{k}_1'-\vec{k}_1)]d\vec{k}_1'\}, \quad (2.6)$$

for this case when $V_{3C}$ is neglected, where

$$T_{13}(\vec{k},\vec{k}')=\langle\exp(i\vec{k}'\cdot\vec{r})\,|V_{13}(\vec{r})|\,\psi(\vec{k},\vec{r})\rangle \quad (2.7)$$

is the exact $T$ matrix for potential scattering by $V_{13}$. A consequence of the impulse approximation, implicit in the Dirac $\delta$ function in (2.6), is that linear momentum is conserved in the (1-3) collision, i.e.,

$$\vec{K}=\vec{k}_1+\vec{k}_3=\vec{k}_1'+\vec{k}_3', \quad (2.8)$$

such that the momentum of 1 after being scattered is

$$\vec{k}_1'=\vec{k}_1+(\vec{k}_3-\vec{k}_3')\equiv\vec{k}_1+\vec{P}, \quad (2.9)$$

in terms of the momentum change $\vec{P}$ in the collision. The final momentum of (1-3) relative motion is

$$\vec{k}'=\frac{M_3}{M}(\vec{k}_1+\vec{k}_3)-\vec{k}_3'\equiv\vec{k}+\vec{P}, \quad (2.10)$$

where $M$ is the sum $(M_1+M_3)$.

The conservation of momentum (2.8) is not a consequence of the assumed planar (1-3) center-of-mass motion but arises (cf. Appendix) irrespective of this assumption. As indicated by (2.10), off-the-energy-shell elements of the $T_{13}$ matrix for free-free (1-3) scattering are, in general, required in the impulse approximation (2.6), even for the case ($k_3=k_3'$) of elastic scattering of the projectile 3. This originates from the effect of switching off the core interactions $V_{31}+V_{3C}$ during the brief time $\tau_c$ of the impulsive (1-3) encounter, thereby implying that energy can only be controlled to within imprecision $\Delta E_I\sim\hbar/\tau_c$. This also implies that the energy dependence of the electron 1-projectile 3 collision cross section $\sigma_{13}$ must not exhibit too rapid a variation as would occur, for example, in the neighborhood of an electron-atom resonance with the formation of a temporary-bound negative ion, or in the vicinity of a Ramsauer minimum for $e$-Ar, Kr, and Xe scattering. When the speed $v_1$ of 1 is $\gg v_3$, the speed of 3, $\tau_c\sim A_1 n$(a.u.) where $A_1(a_0)$ is the ($e$-$A$) interaction distance, such that during $\tau_c$ the energy imprecision $\Delta E_I\sim(A_1 n)^{-1}$ a.u. is comparable with the small impact energy $\frac{1}{2}v_1^2$. For $v_3\gg v_1$, however, $\Delta E_I\sim v_3/A_1$ which is $\ll\frac{1}{2}v_3^2$ the relative energy over which $\sigma_{13}$ generally varies slowly.

The integral cross section for elastic and elastic scattering of 3 by the bound (1,2) system, in the center of mass of the 3-(1,2) system with reduced mass $M_{AB}$, is

$$\sigma_{if}(k_3)=\left(\frac{M_{AB}}{M_{13}}\right)^2\frac{k_3'}{k_3}\times\int|\langle g_f(\vec{k}_1+\vec{P})\,|\,f_{13}(\vec{k},\vec{k}')\,|\,g_i(\vec{k}_1)\rangle_{\vec{k}_1}|^2 d\hat{k}_3'. \quad (2.11)$$

in which

$$f_{13}(\vec{k},\vec{k}')=-\frac{1}{4\pi}\left(\frac{2M_{13}}{\hbar^2}\right)T_{13}(\vec{k},\vec{k}') \quad (2.12)$$

is the (on- and off-the-energy-shell) amplitude for ($\vec{k}\to\vec{k}'$) scattering in the center of mass of the (1-3) system with reduced mass $M_{13}$. The component of momentum (2.9) of the final state $f$ is selected in (2.11) in accord with the conservation of momentum (2.8). Interference terms are in general present between scattering and momentum amplitudes in (2.11). The $T$ matrix for elastic scattering in the forward direction is

$$T_{ii}(\vec{k}_3,\vec{k}_3)=\int g_f^*(\vec{k}_1)g_i(\vec{k}_1)T_{13}(\vec{k},\vec{k})d\vec{k}_1,$$

$$\vec{k}=\frac{m_3}{M}\vec{k}_1+\frac{m_1}{M}\vec{k}_3, \quad (2.13)$$

in which $T_{13}$ is evaluated on the energy shell.

The following interesting derivatives and simplifications to (2.11) arise upon use of (A) the optical theorem, (B) a plane-wave final state, (C) closure, (D) the peaking approximation, (E) $f_{13}(\vec{P})$ depending only on momentum change $\vec{P}$, and (F) constant $f_{13}$.

### A. Optical theorem

When distortion in the scattering of 3 by the core $C$ is neglected in the incident wave which is then taken as a plane wave, the imaginary component of the full $T$ matrix for (3-1) and (3-$C$) scattering arises only (cf. Appendix) from (3-1) scattering such that the total cross section for all elastic and inelastic events is, with the aid of the optical theorem, given by

$$\sigma_{tot}(k_3)=\left(\frac{1}{k_3}\right)\left(\frac{2M_{AB}}{\hbar^2}\right)T_{ii}(\vec{k}_3,\vec{k}_3)\,, \tag{2.14}$$

which, with (2.13), yields

$$\sigma_{tot}(k_3)=\left(\frac{1}{v_3}\right)\int |g_i(\vec{k}_1)|^2[v_{13}\sigma_{13}^T(v_{13})]d\vec{k}_1\,, \tag{2.15}$$

where $\sigma_{13}^T$ is the total cross section for 1-3 scattering at relative speed $v_{13}$, and $v_3$ is the speed of the incident atom 3. No interference terms are present in (2.15). This cross section is *an upper limit* to any collision process satisfying specific criteria for validity of the impulse approximation (see Appendix) and shows that the rate ($v_3\sigma_{tot}$) for all $A$-$B(n)$ elastic and inelastic processes is essentially limited by the total rate of free Rydberg electron-$A$ collisions, with free-momentum amplitude specified by the momentum wave function for the initial state of $B(n)$. While the validity criteria for application can in general be satisfied by most energy-changing processes in $A$-$B(n)$ collisions it is worth noting at this stage that the appropriate mechanism may be not fully described by a (1-3) impulsive encounter alone. For example, in angular momentum $l$ mixing within the same principal quantum number $n$, under conditions normally met in the experiments, any description based on the above impulse approximation (2.11), or its limit (2.15), or on further simplification to (2.11), appears[15] to be quite inadequate for correct interpretation of the current experiments on $l$-mixing collisions. These collisions in fact demand a mechanism quite different from that based on the Rydberg electron-projectile atom collision alone, which in fact may contribute only a small percentage (~10%) of the measured cross section.

### B. Plane-wave final state of particle initially bound

When the bound electron is ejected from the atom, and is described as a plane wave,

$$\phi_f(\vec{r}_1)=\frac{1}{(2\pi)^{-3/2}}\exp(i\vec{\kappa}_1'\cdot\vec{r}_1)\,, \tag{2.16}$$

then (2.4) yields

$$g_f(\vec{k}_1')=\delta(\vec{k}_1'-\vec{\kappa}_1')\,, \tag{2.17}$$

such that (2.6) reduces to

$$T_{fi}(\vec{k}_3,\vec{k}_3')=g_i(\vec{k}_1)T_{13}(\vec{k},\vec{k}'),\quad \vec{k}_1=\vec{\kappa}_1'-\vec{P}\,. \tag{2.18}$$

The differential cross section for scattering of the incident particle 3 into solid angle $d\hat{k}_3'$, and for ejection of the initially bound electron into the continuum with momentum in the interval $d\vec{k}_1'$ about $\vec{k}_1'$, is therefore

$$\left[\frac{d\sigma_{if}}{d\hat{k}_3'd\vec{k}_1'}\right]=\left(\frac{M_{AB}}{M_{13}}\right)^2\frac{k_3'}{k_3}|g_i(\vec{k}_1)|^2|f_{13}(\vec{k},\vec{k}')|^2\,. \tag{2.19}$$

This approximation, in addition to the "impulse" requirement, assumes that the effect of the core is acknowledged only in the preparation of the initial state $i$, and is "switched off" thereafter. It is this quantal result (2.19) that leads directly to the semiquantal theory previously proposed (see Sec. IV). Moreover, the total cross section $\sigma_{tot}$ for all elastic and inelastic events in $A$-$B(n)$ collisions as obtained from the "semiquantal" origin (2.18) yields a result identical with that (2.15) deduced from the full quantal impulse expression (2.6). If the incident projectile $A$ is an atom or molecule which undergoes a transition $\alpha\to\beta$ while interacting with the Rydberg electron, then the above relations (2.6), (2.11), and (2.19) hold, but with $T_{13}$ being the $T$ matrix for $e$-atom inelastic scattering such that $|f_{13}|^2$ is replaced by $|f_{13}^{\alpha\to\beta}|^2$.

### C. Closure

Since the momentum eigenfunctions $g_n(\vec{k}_1)$ form a complete set,

$$\underset{f}{S}g_f(\vec{k}_1')g_f(\vec{k}_1'')=\delta(\vec{k}_1'-\vec{k}_1'')\,, \tag{2.20}$$

with the result that the differential cross section for all elastic and inelastic transitions in $B$ from the initial state $i$, and for scattering to within unit $d\hat{k}_3'$ is, by closure on (2.11), given by

$$\left(\frac{d\sigma_i^T}{d\hat{k}_3'}\right)=\frac{\bar{k}_3'}{k_3}\left(\frac{M_{AB}}{M_{13}}\right)^2\left(\int |g_i(\vec{k}_1)|^2|f_{13}(\vec{k},\vec{k}')|^2d\vec{k}_1\right),$$

$$\vec{k}^{(\prime)}=\frac{M_3}{M}(\vec{k}_1+\vec{k}_3)-\vec{k}_3'\,, \tag{2.21}$$

*provided* (a) that the incident momentum $\vec{k}_3$ is sufficiently high to excite all the atomic states including the continuum and (b) that $k_3'$, which is $(k_3^2-2\epsilon_{fi}/M_{AB})^2$ for a given $i\to f$ transition of energy $\epsilon_{fi}$, can either be replaced by $k_3$ or by some average $\bar{k}_3'$. Realistic averages at high $k_3$ may be provided by choosing $\epsilon_{fi}$ to be either zero, or the logarithmic mean energy,

$$\ln\langle\epsilon_{fi}\rangle=\underset{j}{S}f_{ij}\ln\epsilon_{ij}/Sf_{ij}\,, \tag{2.22}$$

where $f_{ij}$ is the oscillator strength for $i\to j$ excitation in the target system. Note that interference terms present in (2.11) have disappeared in (2.21). This approximation is necessarily a high-energy approximation with projectile energy $E_3\gg\epsilon_{fi}$.

### D. Peaking approximation

When the (1-3) scattering amplitude $f_{13}$ in the basic impulse expression (2.6) varies slowly with

$\vec{k}$ relative to the product $g_f^* g_i$ of the momentum amplitudes, assumed to be peaked about $\vec{k}_1' \equiv \vec{k}_i + \vec{P} \approx 0$, then it may be taken outside the integral (2.6) to yield the peaking approximation,[10]

$$T_{fi}^P(\vec{k}_3, \vec{k}_3') = F_{fi}(\vec{P}) T_{13}(\vec{k}, \vec{k}') , \qquad (2.23)$$

where

$$F_{fi}(\vec{P}) = \int g_f^*(\vec{k}_1 + \vec{P}) g_i(\vec{k}_1) d\vec{k}_1$$
$$\equiv \langle \psi_f(\vec{r}) | \exp(i\vec{P}\cdot\vec{r}) | \psi_i(\vec{r}) \rangle \qquad (2.24)$$

is the inelastic form factor for $i \to f$ transitions in the target atom. The differential cross section for scattering of 3 accompanied by discrete transitions in the target is then

$$\left(\frac{d\sigma_{if}}{d\vec{k}_3'}\right) = \left(\frac{M_{AB}}{M_{13}}\right)^2 \frac{k_3'}{k_3} |F_{fi}(\vec{P})|^2 |f_{13}(\vec{k}, \vec{k}')|^2 . \qquad (2.25)$$

For target ionization, when the continuum electronic wave function is normalized to $\delta(\vec{k}_1' - \vec{\kappa}_1')$, as in (2.16), then (2.25) yields the required cross section per unit interval $d\vec{k}_1'$. Although the peaking approximation (2.23) has enjoyed much popularity in nuclear physics (via the neutron-deuteron problem) and although its success in $H^+$-H(1$s$) atomic collisions is somewhat limited (cf. Coleman[10]), it has not as yet been tested for $A$-$B(n)$ collisions involving highly excited Rydberg states.

### E. $T_{13} = T_{13}(\vec{P})$

When the $T$ matrix for (1-3) scattering is a function only of momentum change,

$$\vec{P} = \vec{k}' - \vec{k} = \vec{k}_1' - \vec{k}_1 = \vec{k}_3 - \vec{k}_3' , \qquad (2.26)$$

which normally holds only in the Born high-energy region, then it can be taken outside the integral in (2.6) to give

$$T_{fi}(\vec{k}_3, \vec{k}_3') = T_{13}(\vec{P}) F_{fi}(\vec{P}) . \qquad (2.27)$$

When $T_{13}$ is described by the Born approximation for $e$-$A$ scattering, then (2.27) becomes,

$$T_{fi}^B(\vec{P}) = T_{13}^B(\vec{P}) F_{fi}(\vec{P}) \qquad (2.28)$$

which is identical with the actual Born approximation to $A$-$B$ inelastic scattering. Because of this identity, a quick and simple (although less satisfactory) method of deriving the impulse approximation for $A$-$B$ scattering is simply to replace in the Born approximation for $A$-$B$ inelastic scattering the inherent Born $T$ matrix, $T_{13}^B$ for $e$-$A$ scattering, by the actual $T$ matrix $T_{13}$, a procedure which yields the peaking approximation (2.23). The basic impulse expression is, of course (2.6), rather than its simplified version (2.23) or (2.27). The version (2.27) for use in $A$-$B(n)$ collisions involving Rydberg atoms is, in addition to the impulse requirements, restricted to situations in which $e$-$A$ scattering is a function *only* of $\vec{P}$ and is that used extensively by Matsuzawa[16] some in situations where it may not describe the actual state of affairs, either in terms of validity[16] or in mechanism.[6]

In the former case,[16] the rapid energy variation of the cross section for resonant formation of $A^-$ negative ions at thermal incident speeds when $v_3 \ll v_1$ is alien to the spirit of the impulse mechanism which, because of its violation of total energy conservation due to neglect of $e$-core and $A$-core interaction energies during the collision demands that the energy variation in the ($e$-$A$) encounter be sufficiently slow throughout the appropriate range of free momentum of the Rydberg electron [see also (A16) of the Appendix]. The latter case[6] involves only an ($e$-$A$) encounter for quasielastic scattering at thermal energies when the ($B^+$-$A$) encounter also plays a significant role (see Sec. VI), and when the impulse procedure for $l$ changing may not even be valid [see Sec. IIIC (iv)].

The full impulse expression (2.11) and both the semiquantal derivatives (2.19) and (2.21) provide, via a general $f_{13}(\vec{k}, \vec{k}')$ a scattering description much more general than (2.27).

### F. Constant $T_{13}$

When the $e$-atom scattering amplitude $f_{13}$ is a constant scattering length $A$, then (2.11) yields the integral cross section

$$\sigma_{if}(k_3) = \frac{2\pi A^2}{k_3^2} \left(\frac{M_{AB}}{M_{13}}\right)^2 \int_{(k_3 - k_3')}^{(k_3 + k_3')} |F_{fi}(\vec{P})|^2 P\, dP , \qquad (2.29)$$

while, (2.15) for the total cross section gives

$$\sigma_{tot}(k_3) = \frac{4\pi A^2}{v_3} \int v_{13} |g_i(\vec{k}_1)|^2 d\vec{k}_1 , \qquad (2.30)$$

$$\sigma_{tot}(k_3) \to \begin{cases} 4\pi A^2, \quad v_3 \gg v_1 & (2.31) \\ \dfrac{\langle v_1 \rangle}{v_3} 4\pi A^2, \quad v_3 \ll v_1 & (2.32) \end{cases}$$

where $\langle v_1 \rangle$ is the mean speed of the Rydberg electron. However, at high impact speeds $v_3$, $T_{13}$ is never constant such that (2.31) is never attained in practice.

## III. LIMITING CASES AND VALIDITY CRITERIA

Some simplification to the basic expression (2.6) for the impulse $T$ matrix occurs in the following two limits of $v_3 \gg v_1$ and $v_3 \ll v_1$, respectively.

### A. $\nu_3 \gg \nu_1$

When the incident speed $v_3$ is much greater than the orbital speed $v_1$ then by inserting the momenta,

$$\vec{k} = \frac{M_1 M_3}{M}(\vec{v}_1 - \vec{v}_3) \approx -M_{13}\vec{v}_3 , \quad (3.1)$$

$$\vec{k}' \approx -M_{13}\vec{v}_3 + \vec{P} , \quad (3.2)$$

and

$$\vec{k}_1' = \vec{k}_1 + \vec{P} , \quad (3.3)$$

in the basic integral (2.6), the impulse $T$ matrix reduces to

$$T_{fi}(\vec{k}_3, \vec{k}_3') = T_{13}(-M_1\vec{v}_3, -M_1\vec{v}_3 + \vec{P})F_{fi}(\vec{P}) , \quad (3.4)$$

such that in the (1-3) electron-atom collision the electron can be considered as moving towards the stationary projectile with the same velocity as the incoming fast projectile. In the limit of fast incident speeds, $T_{13}$ can be described in terms of the Born (real) amplitude,

$$f_{13}^{\alpha\beta}(P) = -\frac{1}{4\pi}\frac{2M_{13}}{\hbar^2}[F_{\beta\alpha}^A(\vec{P}) - Z_A\delta_{\alpha\beta}]/P^3 , \quad (3.5)$$

where $F_{\beta\alpha}^A$ is the inelastic form factor for the transition $(\alpha \to \beta)$ in the projectile $A$ of nuclear charge $Z$. Also, in this limit, ejection of the Rydberg electron can be described by a plane wave, such that the bound-free form factor $F_{fi}$ for the target $B$ becomes

$$F_{\vec{k}_1', i}(\vec{P}) = g_i(\vec{k}_1' - \vec{P}) \equiv g_i(\vec{k}_1) , \quad (3.6)$$

the momentum amplitude of the initial Rydberg state. The cross section for scattering into $d\hat{k}_3'$, accompanied by electron ejection into all of the continuum, is

$$\frac{d\sigma_i^I}{d\hat{k}_3'} = \left(\frac{M_{AB}}{M_{13}}\right)^2 \frac{k_3'}{k_3} |f_{13}^{\alpha\beta}(P)|^2 \int |g_i(\vec{k}_1' - \vec{P})|^2 d\vec{k}_1' , \quad (3.7)$$

in which $d\vec{k}_1' = d\vec{k}_1$, for fixed $\vec{P}$, such that the integral in (3.7) is unity. Hence the integral cross section for electron loss in the target is

$$\sigma_i^I(v_3) = \frac{1}{v_3^2}\int_{(v_3 - v_3')}^{(v_3 + v_3')} |f_{13}^{\alpha\beta}(P)|^2 P\,dP , \quad (3.8)$$

the final speed $v_3'$ of the projectile being chosen consistent with ionization of the target and possible excitation of the projectile, and is thus identical, as expected, with the cross section for collisions between a stationary atom $A$ and an electron moving initially with speed $v_3$, in which sufficient momentum is transferred so that detachment of the electron from $B$ occurs, together with possible excitation of $A$. This is the basis of the free collision model introduced intuitively by Dmitriev and Nikolaev,[8] and used by Victor[17] in electron-loss calculations. Here we have shown that the model is a natural consequence of the quantal and semiquantal impulse approximations with the above appropriate simplifications (3.4)–(3.6).

Also, in this limit, $v_3 \gg v_1$, the total cross section for all elastic and inelastic events is, from (3.4), simply

$$\sigma_{\text{tot}}(v_3) = \sigma_{13}^T(v_3) , \quad (3.9)$$

the total cross section for $e$-projectile collisions. This is an upper limit to cross sections obtained from (3.4) for any process at high energies.

### B. $\nu_1 \gg \nu_3$

The mean relative speed of the $(A$-$B)$ system with reduced mass $M_{AB}$ in atomic mass units (amu),

$$v_3 = \frac{1.15\times 10^{-3}}{M_{AB}^{1/2}}\left(\frac{T}{300}\right)^{1/2} \text{a.u.} \quad (3.10)$$

at temperature $T$ (K), is much less than the orbital speed $v_1$ of the Rydberg electron for principal quantum numbers,

$$n \ll 870 M_{AB}^{1/2}\left(\frac{300}{T}\right)^{1/2} , \quad (3.11)$$

which is sufficiently large so as to be satisfied in most cases of interest for thermal atoms $A$. Hence,

$$\vec{k} = M_{13}(\vec{v}_1 - \vec{v}_3) \approx M_{13}\vec{v}_1 = \vec{k}_1 \quad (3.12)$$

and

$$\vec{k}' = \vec{k} + \vec{P} \approx \vec{k}_1 + \vec{P} , \quad (3.13)$$

so that (2.6) and (2.11) yield

$$T(\vec{k}_3, \vec{k}_3') = \int g_f^*(\vec{k}_1 + \vec{P}) g_i(\vec{k}_1) T_{13}(\vec{k}_1, \vec{k}_1 + \vec{P}) d\vec{k}_1 \quad (3.14)$$

and

$$\left(\frac{d\sigma_{if}}{d\hat{k}_3}\right) = \left(\frac{M_{AB}}{M_{13}}\right)^2 \frac{k_3'}{k_3} \times \left| \int g_f^*(\vec{k}_1 + \vec{P}) g_i(\vec{k}_1) f_{13}(\vec{k}_1, \vec{k}_1 + \vec{P}) d\vec{k}_1 \right|^2 , \quad (3.15)$$

with interference effects between the amplitudes included. Under quasielastic conditions when the momentum transfer $P$ is small in comparison with the orbital momentum, $f_{13}$ is evaluated on the energy shell. The scattering amplitude $f_{13}$ for $e$-$A$ collisions with low wave numbers $k \sim 1/n$ can then be written as the first few terms of the partial-wave expansion,

$$f_{13}(\vec{k},\vec{k}')=\frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\delta_l}\sin\delta_l P_l(\cos\theta),\quad k=k' \tag{3.16}$$

where the phase shifts $\delta_l(k)$ are in general tabulated functions of $l$ and $k$ as for the case of ground-state rare gases.[18] Alternatively, according to effective-range expansion theory at low energies,[19]

$$\frac{\tan\delta_0}{k}\approx\frac{\sin\delta_0}{k}=-A-\tfrac{1}{3}\pi\alpha k - \tfrac{4}{3}\alpha A k^2\ln k + O(k^2)\,, \tag{3.17}$$

where $A$ is the zero-energy scattering length, and where $\alpha$ is the polarizability of the atom. Also, for small phase shifts for $l>1$,[19]

$$\frac{\tan\delta_l}{k}\approx\frac{\sin\delta_l}{k}=\frac{(\pi\alpha k)}{[(2l-1)(2l+1)(2l+3)]} + O(k^2(l=1),k^3(l>1))\,, \tag{3.18}$$

with the result that the (1-3) scattering amplitude is

$$f_{13}(\theta)=-(A+\tfrac{1}{3}\pi\alpha k+\tfrac{4}{3}\alpha A k^2\ln k)(1-iAk) - \tfrac{1}{4}\pi\alpha P+\tfrac{1}{3}\pi k+O(k^2)\,, \tag{3.19}$$

where the momentum change $P$ in (3.19) originates from the use of the identity

$$\sum_{l=0}^{\infty}\frac{P_l(\cos\theta)}{(2l-1)(2l+3)}=-\tfrac{1}{2}\sin\tfrac{1}{2}\theta\,. \tag{3.20}$$

Although the imaginary component of $f_{13}$, which is included in (3.19) to $O(k)$ via $\delta_0$ alone, is small in comparison to the real component, it nevertheless ensures that the optical theorem is satisfied in the zero-energy limit. Either (3.16) or (3.19) can be substituted directly into (3.15) for determination of the appropriate cross section. Finally, the integral cross section for all elastic and inelastic events, for the case $v_1\gg v_3$ is

$$\sigma_{\rm tot}(v_3)=\frac{1}{v_3}\int|g_i(k_1)|^2 v_1\sigma_{13}^T(v_1)dv_1\equiv\frac{\langle v_1\sigma_{13}^T(v_1)\rangle}{v_3}\,, \tag{3.21}$$

the averaged rate for electron-atom collisions divided by the projectile speed $v_3$. Thus (3.21) is therefore an upper limit to cross sections for any process in this energy region ($v_1\gg v_3$). This expression can also be uncovered (via the optical theorem) from the analysis of Alekseev and Sobel'man[14] for the width and shift of lines originating from excited levels perturbed by neutral particles. The bound (3.21) is in direct contrast to (3.9), which is limited only by the cross section for electron-atom collisions in the energy region with $v_3\gg v_1$. Both results of course represent the limiting cases of (2.15), predicted both by (2.6) and (2.18) the full impulse and semiquantal expressions.

Although the expressions (3.4) for $v_3\gg v_1$ and (3.15) for $v_1\gg v_3$, together with their derivatives, can be applied to a wide selection of $A$-$B(n)$ energy-change processes, it is worth noting that the (1-3) binary encounter impulse mechanism may *not* furnish a full or even correct description of the process at a given impact energy, particularly in those cases when the measured (accurate) cross sections exceed the specified maxima (3.9) and (3.21) to the impulse cross sections (see Sec. VI).

### C. Validity criteria

The customary validity criteria for justification of the impulse approximation to 3-(1,2) collisions (where the core $C$ and 2 are synonomous) are as follows:

(i) The (1,2) separation $R_{12}\approx n^2a_0\gg A_{1,2}$, the scattering lengths, or amplitudes, for (1-3) and (2-3) collisions at relative speeds $v_{13}$ such that 3 never interacts simultaneously with 1 and 2, which therefore behave as separate scatterers.

(ii) The reduced wavelength $\lambda\sim k^{-1}$ for (1-3) relative motion $\ll R_{12}$, so that the amplitude $f_{13}$ for 1-3 scattering is not affected by the presence of 2, (and vice versa), i.e., the scatterers are independent, and interference effects from scattering by each center can be ignored.

(iii) Contribution from (2-3) collisions to inelastic scattering is neglected.

(iv) The momentum $P$ transferred (impulsively) to 1 during the collision time $\tau_c\sim(A/v_{13})$ must be $\gg$ the momentum imparted to 1 during the same time via the interaction $V_{12}$ with the core, i.e.,

$$P\gg|\langle\psi_{nl}|-\vec{\nabla}V_{12}|\psi_{nl}\rangle|\tau_c\approx\frac{\tau_c}{n^3(l+\frac{1}{2})}\,. \tag{3.22}$$

Since the orbital period $T_n$ of the Rydberg electron $\sim n^3$ a.u., then

$$\tau_c\ll T_n(l+\tfrac{1}{2})P\,. \tag{3.23}$$

If $V_{12}$ varies sufficiently slowly (but need not be necessarily small!) over the range $A_1$ of the collision interaction $V_{13}$, such that the force $\vec{F}(\equiv-\vec{\nabla}V_{12})$ due to the core is small in comparison with the impulsive force $(-\vec{\nabla}V_{13})$ due to the Rydberg electron-projectile interaction, then (3.22) is satisfied; in this sense $V_{12}$ can be regarded as "quasiclassical."

For ionizing collisions, $P\sim 1/n$, then $\tau_c\ll T_n$ for circular orbits ($l\sim n$), and $\tau_c\ll T_n/n$ for highly eccentric orbits ($l \sim 0$). Hence the requirement, $\tau_c \sim A_1/v_{13} \ll n^2$, covers electron ejection from all orbits. With aid of the factor $-\exp(i\epsilon t/\hbar)$ (appearing in time-dependent theory), this condition implies that the energy $\epsilon$ transferred during $\tau_c$ ($\sim h/\tau_c \gg |\epsilon_n| \sim n\hbar/T_n$) must be much greater than the energy $\epsilon_n$ imparted to 1 via $V_{12}$. This condition is obviously more restrictive than the condition $\tau_c \ll T_n$, which is commonly assumed, and which is only valid for $l \sim n$ and $P \sim 1/n$.

For nonionizing collisions, $P$ by (3.22) cannot become arbitrarily small, as could occur for quasielastic or $l$-changing collisions. At thermal energies, the electron speed $v_1 \sim 1/n$ a.u. is greater than the incident speed $v_3 \sim 10^{-4}$ a.u. of $A$ for most $n$ of interest, and the collision time $\tau_c \sim A_1 n$ for $e$-rare gas atom scattering [where $A_1 \sim (1\text{-}7)a_0$] such that (3.22) implies that $P \gg A_1/n^2(l+\frac{1}{2})$. The angular-momentum change (for fixed $n$) due to ($e$-$A$) impulsive encounters at $R_{12}$ from $B^+$ must satisfy,

$$\Delta L \sim P\langle R_{12}\rangle \sim \tfrac{1}{2}P[3n^2 - l(l+1)] \gg \tfrac{1}{2}A_1[3n^2 - l(l+1)]/n^2(l+\tfrac{1}{2}) \tag{3.24}$$

which is, in general, fulfilled only at the highest initial $l$ when the permitted $\Delta L \gg A_1/(l \sim n)$. Small initial $l$ require large changes $\Delta L \gg A_1$ for validity of the impulse model (since then the momentum imparted by the core on the highly elliptical orbits becomes considerably strengthened over that for circular orbits). The above considerations are absent in any previous $l$-changing study.[5,6,12]

Conditions (i) and (ii) combined imply separate independent scattering centers, such that $R_{12}^2 \gg \lambda A_1$, which in turn, implies negligible effect arising from multiple scattering, the amplitude of the scattered wave emanating from 1 being negligible compared with that of the incident wave when both reach the spectator particle 2, and vice versa.

Although the above conditions (i)–(iv), (deduced intuitively), are consistent with various assumptions in the derivation of the impulse approximation, their origin within the mathematical description requires further clarification (cf. Appendix). As shown in the Appendix, there are two distinct classes of interaction which satisfy the impulse approximation, i.e., those associated with the quasiclassical character of (slow-varying) $V_{12}$, [which is equivalent to condition (iv)] and those which satisfy the "weak-binding" condition $E_{13} \gg |\epsilon_n|$. The weak-binding condition is sometimes unnecessarily restrictive (cf. Appendix). The further neglect of core distortion on (1-3) scattering implies conditions (i) and (ii) while assumption of core inertiality implies condition (iii).

While the basic impulse approximation (2.6) and its derivatives (2.19), (2.21), (2.24), (3.4), and (3.15) do not insist on conservation of energy in the (1-3) binary collision, tacit assumption is nevertheless usually made, both for simplification, and for possible use of measured and calculated $e$-atom cross sections, which essentially provide only on-the-energy-shell contributions. This assumption entails considerations, in addition to these (i)–(iv) above.

### D. On and off the energy shell

The energy transferred to particle 1 in the (1,3) collision is

$$\epsilon = \frac{1}{2M_1}(k_1'^2 - k_1^2), \tag{3.25}$$

where

$$\vec{k}_1^{(\prime)} = \frac{M_1}{M}\vec{K} + \vec{k}^{(\prime)}, \tag{3.26}$$

in terms of the conserved momentum $\vec{K}$ of the (1,3) center of mass and of the momentum $\vec{k}^{(\prime)}$ associated with the relative motion before and after the collision. The energy departure from on the energy shell is

$$\Delta T_{\rm rel}(1,3) = \frac{1}{2M_{13}}(k'^2 - k^2) = \left(\frac{M_1}{M_{13}}\right)\left(\epsilon - \frac{1}{M}\vec{K}\cdot\vec{P}\right), \tag{3.27}$$

where $\vec{P}$ is the momentum change $(\vec{k}' - \vec{k})$. The magnitudes of

$$\vec{k} = M_{13}(\vec{v}_1 - \vec{v}_3) \equiv M_{13}\vec{g}, \tag{3.28}$$

and of

$$\vec{k}' = \vec{k} + \vec{P}, \tag{3.29}$$

are in general different, except when

$$P = 2M_{13}g_{13}\sin\tfrac{1}{2}\psi, \tag{3.30}$$

where $\psi$ is the angle of scattering in the (1,3) center-of-mass reference frame. Hence, evaluation of $T_{13}(\vec{k},\vec{k}')$ on the energy shell implies that the energy and momentum charges are related by

$$\epsilon = \vec{V}_{13}\cdot\vec{P}, \tag{3.31}$$

where $\vec{V}_{13}$ is the velocity of the (1,3) center of mass. Thus,

$$\epsilon \to \begin{cases} 2M_{13}v_3^2\sin\frac{1}{2}\psi, & v_3 \gg v_1 \\ 2M_{13}v_3(\sin\frac{1}{2}\psi)/n, & v_1 \gg v_3 \end{cases} \tag{3.32}$$

for the above cases of limiting speeds. For energy changes, $\epsilon \sim \delta/n^3$, where $\delta$ ranges from the quantum defect for $l$-changing transitions within a given principal quantum number $n$, to 1 for transitions between neighboring energy levels, and to $n$ for ionizing transitions, then the former case ($v_3 \gg v_1$) demands scattering mainly in the forward direction

$$\sin\tfrac{1}{2}\psi = \left(\frac{v_1}{v_3}\right)^2\left(\frac{\delta}{n}\right) \ll 1, \quad v_3 \gg v_1 \tag{3.33}$$

with momentum change $P \sim \epsilon/v_3$, a situation easily achieved for all of the above types of transitions induced by fast heavy projectiles of speed $v_3$ impinging on effectively stationary electrons. Although the latter case, $v_1 \gg v_3$, is satisfied for thermal incident particles for $n$ given by (3.11), the momentum $M_1 v_1$ is still $\ll M_3 v_3$, in general, such that the (1,3) center-of-mass speed is determined by $v_3$ in both cases. Thus evaluation of $T_{13}$ on the energy shell alone implies that, for the latter case,

$$\sin\tfrac{1}{2}\psi = \left(\frac{v_1}{2v_3}\right)\frac{\delta}{n} \gg \frac{\delta}{n}, \quad v_1 \gg v_3 \tag{3.34}$$

for energy-changes $\delta/n^3$. Thus ionization ($\delta = n$) will essentially be prohibited (as expected), and excitation here will arise only from those scattering angles with $\psi \gg \sin^{-1}(1/n)$, i.e., for collisions with momentum change $P \gg n^{-2}$. Quasielastic and elastic scattering (as for small $\delta$ in $l$-changing collisions) demands the full angular range, but the inherent small momentum changes $P$ may violate condition (3.22). Moreover, as mentioned previously, and discussed in Sec. VI, the substantial contribution to $l$-changing collision arises not from Rydberg electron-projectile $A$ impulsive encounters, but from quite a different mechanism (cf. Sec. V), such that the above case $v_1 \gg v_3$ of the impulse treatment is only of partial utility. Moreover, it is important to note that the assumed neglect of the distortion of the incident atom due to the core within the derivation of the impulse expression [see (A8)] is generally *not* valid for slow incident atoms with $v_3 \ll v_1$. This deficiency, implicit in recent theoretical accounts of $l$ mixing, can, however, be remedied by a proposed new scheme in Sec. V.

## IV. DERIVATION OF THE SEMIQUANTAL EXPRESSION FROM THE QUANTAL IMPULSE APPROXIMATION

For ionization, quantum mechanics naturally provides the cross section for scattering of the projectile $A$ into solid angle $d\hat{k}_3'$, accompanied by ejection of the target Rydberg electron into momentum interval $d\vec{k}_1'$ about $\vec{k}_1'$. Classical mechanics (as used in the semiquantal theory[1]) naturally specifies the cross section per unit energy-change interval $d\epsilon$ about

$$\epsilon = \frac{1}{2m_1}(k_1'^2 - k_1^2), \tag{4.1}$$

per unit momentum-change interval $dP$ about

$$\vec{P} = \vec{k}_3 - \vec{k}_3' = \vec{k}_1' - \vec{k}_1, \tag{4.2}$$

per unit initial momentum interval $d\vec{k}_1$ about momentum $\vec{k}_1$ of the bound Rydberg electron. Thus,

$$\left(\frac{d\sigma}{d\vec{k}_1' d\hat{k}_3'}\right) d\vec{k}_1' d\hat{k}_3' = \left(\frac{d\sigma}{d\epsilon\, dP\, d\vec{k}_1}\right) d\epsilon\, dP\, d\vec{k}_1, \tag{4.3}$$

and each partial cross section is related to the other by the $5\times 5$ Jacobian of the appropriate transformation. The momentum $\vec{k}_3$ of incident relative $A$-$B(n)$ motion is taken along the $Z$ axis of a space-fixed spherical polar coordinate system, with $\vec{k}_1(k_1, \theta_1, \phi_1)$, $\vec{k}_1'(k_1', \theta_1', \phi_1')$, $\vec{k}_3'(k_3', \theta_3', \phi_3')$. Thus,

$$\cos\theta_1 = \hat{k}_1 \cdot \hat{k}_3 = (\alpha^2 k_1^2 + \beta^2 k_3^2 - k^2)/(2\alpha\beta k_1 k_3),$$
$$\alpha = \left(\frac{M_3}{M}\right), \quad \beta = \left(\frac{M_1}{M}\right) \tag{4.4}$$

can be replaced as independent variable by $k$. Hence,

$$\left(\frac{d\sigma}{d\epsilon dP dk_1 dk d\phi_1}\right) = k_1^2 \left(\frac{d\sigma}{d(\cos\theta_3')d\phi_3' dk_1' d(\cos\theta_1')d\phi_1'}\right) \times \frac{\partial(\cos\theta_3', \phi_3', k_1', \cos\theta_1', \phi_1')}{\partial(P, \epsilon, k_1, k, \phi_1)}. \tag{4.5}$$

Substitute the full impulse expression with the plane-wave final state, i.e., (2.19) for infinite $M_2$, into the rhs of (4.5) with the result,

$$\left(\frac{d\sigma}{d\epsilon dP dk_1 dk d\phi_1}\right) = \frac{k_1'^2}{J_{55}}\left(\frac{k_3'}{k_3}\right)\left(\frac{M_3}{M_{13}}\right)^2 \times |g_i(\vec{k}_1)|^2 |f_{13}(\vec{k}, \vec{k}')|^2, \tag{4.6}$$

where $f_{13}$ is the scattering amplitude for elastic or inelastic collisions of the Rydberg electron by the projectile atom or molecule $A$. The Jacobian of the five-dimensional $(P, \epsilon, k_1, k, \phi_1 \to \hat{k}_3', \vec{k}_1')$ transformation is

$$J_{55} = \frac{\partial(P, \epsilon, k_1, k, \phi_1)}{\partial(\cos\theta_3', \phi_3', k_1', \cos\theta_1', \phi_1')}, \tag{4.7}$$

which is now determined by the following (a)–(d) series of steps.

(a) From (4.2),

$$P^2(\cos\theta_3') = k_3^2 + k_3'^2 - 2k_3 k_3' \cos\theta_3', \tag{4.8}$$

such that,

$$\frac{\partial P}{\partial(\cos\theta_3')} = -\frac{k_3 k_3'}{P} \equiv A \tag{4.9a}$$

and

$$\frac{\partial P}{\partial(i)}=0\,, \tag{4.9b}$$

where $i$ denotes the remaining $(\phi_3',k_1',\theta_1',\phi_1')$ variables.

(b) When $T_{13}$ is evaluated on the energy shell (cf. Sec. III D),

$$k^2=k'^2+2M_{13}\Delta_3\,, \tag{4.10}$$

where $\Delta_3$ is the energy absorbed or released by the internal state of the projectile $A$ via an $(e\text{-}A)$ elastic/inelastic collision. Since

$$\vec{k}'=\alpha\vec{k}_1'-\beta\vec{k}_3'\,,\qquad \alpha=\left(\frac{M_3}{M}\right),\quad \beta=\left(\frac{M_1}{M}\right),\quad M=M_1+M_3\,, \tag{4.11}$$

then,

$$k^2(k_1',\theta_1',\theta_1',\phi_3')=\alpha^2k_1'^2+\beta^2k_3'^2-2\alpha\beta k_1'k_3'\cos\alpha_{13}'+2M_{13}\Delta_3\,, \tag{4.12}$$

where $\alpha_{13}'$, the angle between $\hat{k}_1'$ and $\hat{k}_3'$, is given by

$$\cos\alpha_{13}'=\cos\theta_1'\cos\theta_3'+\sin\theta_1'\sin\theta_3'\cos(\phi_1'-\phi_3')\,. \tag{4.13}$$

Thus, $k$ is expressed as an explicit function $k(k_1',\theta_1',\phi_1',\theta_3',\phi_3')$ and,

$$B\equiv\frac{\partial k}{\partial\phi_1'}=-\alpha\beta\left(\frac{k_1'k_3'}{k}\right)\frac{\partial(\cos\alpha_{13}')}{\partial\phi_1'}=-\alpha\beta\left(\frac{k_1'k_3'}{k}\right)\sin\theta_1'\sin\theta_3'\sin(\phi_1'-\phi_3')\,, \tag{4.14a}$$

$$B\equiv-\frac{\partial k}{\partial\phi_3'}\,, \tag{4.14b}$$

$$C\equiv\frac{\partial k}{\partial(\cos\theta_1')}=-\alpha\beta\left(\frac{k_1'k_3'}{k}\right)\frac{\partial(\cos\alpha_{13}')}{\partial(\cos\theta_1')}\,, \tag{4.14c}$$

$$D\equiv\frac{\partial k}{\partial(\cos\theta_3')}=-\alpha\beta\left(\frac{k_1'k_3'}{k}\right)\frac{\partial(\cos\alpha_{13}')}{\partial(\cos\alpha_3')}\,, \tag{4.14d}$$

$$E\equiv\frac{\partial k}{\partial k_1'}=\alpha^2\left(\frac{k_1'}{k}\right)-\alpha\beta\left(\frac{k_3'}{k}\right)\cos\alpha_{13}'\,. \tag{4.14e}$$

Note, as $\phi_1'$ (or $\phi_3'$) spans its full $(0\to2\pi)$ range, that a given value of $\alpha_{13}'$ in (4.13), and hence $k$ in (4.12) is passed through twice, for fixed $k_1'$, $\theta_1'$, and $\theta_3'$. On integration over $k$ between its limits, (4.14a) and (4.14b) will therefore be multiplied by a factor of 2 to acknowledge this weighting.

(c) With the aid of momentum conservation,

$$\vec{k}_1=\vec{k}_1'-\vec{P}=\vec{k}_1'-(\vec{k}_3-\vec{k}_3')\,, \tag{4.15}$$

such that the initial momentum can be expressed as

$$k_1^2(P\,|\,k_1',\theta_1',\phi_1',\theta_3',\phi_3')=k_1'^2+P^2-2k_1'k_3\cos\theta_1'+2k_1'k_3'\cos\alpha_{13}' \tag{4.16}$$

where, in addition, implicit dependence on the independent variables (only $\theta_3'$) arises via $P$. Hence in terms of $B$, $C$, and $D$ above,

$$C^+\equiv\frac{\partial k_1}{\partial(\cos\theta_1')}=-\left(\frac{k_1'k_3}{k_1}\right)-\gamma C,\quad \gamma=\frac{k}{\alpha\beta k_1}\,, \tag{4.17a}$$

$$D^+\equiv\frac{\partial k_1}{\partial(\cos\theta_3')}=-\left(\frac{k_3'k_3}{k_1}\right)-\gamma D\,, \tag{4.17b}$$

$$-\gamma B\equiv\frac{\partial k_1}{\partial\phi_1'}=\left(\frac{k_1'k_3'}{k_1}\right)\frac{\partial(\cos\alpha_{13}')}{\partial\phi_1'}\,, \tag{4.17c}$$

$$\gamma B\equiv\frac{\partial k_1}{\partial\phi_3'}\,, \tag{4.17d}$$

$$F\equiv\frac{\partial k_1}{\partial k_1'}=\left(\frac{k_1'}{k_1}\right)-\left(\frac{k_3}{k_1}\right)\cos\theta_1'+\left(\frac{k_3'}{k_1}\right)\cos\alpha_{13}'\,. \tag{4.17e}$$

(d) On resolving the initial momentum $\vec{k}_1$ along the X and Y axes, $\phi_1$ can be expressed as a function $\phi_1(k_1',\theta_1',\phi_1',\theta_3',\phi_3')$ by

$$\tan\phi_1(k_1',\theta_1',\phi_1',\theta_3',\phi_3')=\frac{\lambda_1'\sin\phi_1'+\lambda_3'\sin\phi_3'}{\lambda_1'\cos\phi_1'+\lambda_3'\cos\phi_3'}\,, \tag{4.18}$$

in which

$$\lambda_i'(k_i',\theta_i')=k_i'\sin\theta_i'\quad(i=1,3)\,. \tag{4.19}$$

It can then be shown from (4.18) that

$$\frac{\partial\phi_1}{\partial\phi_1'}=G=1-\frac{\partial\phi_1}{\partial\phi_3'}\,. \tag{4.20}$$

Derivatives ($J$, $K$, $L$, for example) with respect to the remaining variables $(\theta_3',k_1',\theta_1')$ are not required because of the relationship existing between those already determined with each other and with these below.

(e) Finally, since $\epsilon$ is expressed in (4.1) as an explicit function of $k_1'$, and implicitly of all the variables via $k_1(k_1',\theta_1',\phi_1',\theta_3',\phi_3')$,

$$\frac{\partial\epsilon}{\partial k_1'}=v_1'-v_1F\,, \tag{4.21a}$$

$$\frac{\partial\epsilon}{\partial(\cos\theta_1')}=-v_1C^+\,, \tag{4.21b}$$

$$\frac{\partial\epsilon}{\partial\phi_1'}=v_1\gamma B\,, \tag{4.21c}$$

$$\frac{\partial\epsilon}{\partial(\cos\theta_3')}=-v_1D^+\,, \tag{4.21d}$$

$$\frac{\partial\epsilon}{\partial\phi_3'}=-v_1\gamma B\,. \tag{4.21e}$$

TABLE I. The 5×5 Jacobian for the $(\hat{k}_3', \vec{k}_1' \equiv P,\ \epsilon,\ k_1,\ k,\ \phi_1)$ transformation. It reduces to $ABv_1'(C^+ + \gamma C)$ which, from (4.17a), is $(-v_1'k_1'k_3AB/k_1)$.

| | $\theta_3'$ | $\phi_3'$ | $k_1'$ | $\theta_1'$ | $\phi_1'$ |
|---|---|---|---|---|---|
| $P$ | $A$ | 0 | 0 | 0 | 0 |
| $\epsilon$ | $(-v_1D^+)$ | $(-v_1\gamma B)$ | $(v_1'-v_1F)$ | $(-v_1C^+)$ | $(v_1\gamma B)$ |
| $k_1$ | $D^+$ | $\gamma B$ | $F$ | $C^+$ | $(-\gamma B)$ |
| $k$ | $D$ | $-B$ | $E$ | $C$ | $B$ |
| $\phi_1$ | $J$ | $(1-G)$ | $K$ | $L$ | $G$ |

Table I provides a schematic representation of the completed Jacobian $J_{55}$, which finally reduces to

$$J_{55}=ABv_1'[C^+ + \gamma C] = -v_1'\left(\frac{k_1'}{k_1}\right)k_3AB\,, \qquad (4.22)$$

i.e., with the aid of (4.9a), (4.14a), and (4.17a),

$$J_{55}=\alpha\beta v_1'\frac{(k_1'k_3k_3')^2}{k_1kP}\sin\theta_1'\sin\theta_3'\sin(\phi_1'-\phi_3')\,. \qquad (4.23)$$

This must now be expressed in terms of the variables $(P,\epsilon,k_1,k,\phi_1)$ if the quantal→semiquantal transformation is required (as is the present objective); or in terms of the variables $(\theta_3',\phi_3',k_1',\theta_1',\phi_1')$ if the inverse transformation is needed.

In terms of speeds $v_1^{(\prime)}$, $v_3^{(\prime)}$, and $g^{(\prime)}$ associated with the momenta $\vec{k}_1^{(\prime)}$, $\vec{k}_3^{(\prime)}$, and $\vec{k}^{(\prime)}$, respectively,

$$g'^2=v_1'^2+v_3'^2-2v_1'v_3'\cos\alpha_{13}'\,, \qquad (4.24)$$

from (4.12), such that, with the aid of (4.13), it can be shown that

$$\sin^2\theta_1'\sin^2\theta_3'\sin^2(\phi_1'-\phi_3') = (1-S)^2+2S\cos\theta_1'\cos\theta_3' - (\cos^2\theta_1'+\cos^2\theta_3')\,, \qquad (4.25)$$

where

$$S=(v_1'^2+v_3'^2-g'^2)/(2v_1'v_3')\,. \qquad (4.26)$$

In terms of the (constant) velocity $\vec{V}_{13}$ of the (1,3) center of mass,

$$\vec{v}_1^{(\prime)}=\vec{V}_{13}+(M_{13}/M_1)\vec{g}^{(\prime)} \qquad (4.27)$$

and

$$\vec{v}_3^{(\prime)}=\vec{V}_{13}-(M_{13}/M_3)\vec{g}^{(\prime)}\,, \qquad (4.28)$$

for the initial (unprimed) and final (primed) velocities of both particles 1 and 3, respectively. Since, in the impulse approximation, the electron (1)–core (2) potential energy is "switched-off" during the brief encounter, the change in the (1-2) internal energy from $\epsilon_i$ to $\epsilon_f$ is

$$\epsilon=(\epsilon_f-\epsilon_i)=\tfrac{1}{2}M_{12}[(\vec{v}_1'-\vec{v}_2)^2-(\vec{v}_1-\vec{v}_2)^2]\,, \qquad (4.29)$$

where $\vec{v}_2$ is the unaffected velocity of the "spectator" core 2 relative to the (1,2) center of mass, i.e.,

$$\vec{v}_2=-\frac{M_1}{M_2}\vec{v}_1\,. \qquad (4.30)$$

With the aid of (4.27), (4.30), and (4.10), the energy change (4.29) is

$$\epsilon=M_{13}\vec{V}_{13}\cdot(\vec{g}'-\vec{g})+\frac{M_{13}^2}{(M_1+M_2)}\vec{g}\cdot(\vec{g}'-\vec{g}) - \frac{M_2M_3}{(M_1+M_2)(M_1+M_3)}\Delta_3\,. \qquad (4.31)$$

While the present analysis holds for arbitrary masses $M_1$, $M_2$, and $M_3$ moving with arbitrary velocities, we confine our subsequent analysis, in order to preserve clarity, to the case of infinite $M_2$ (tacitly assumed in Sec. II), and of zero $\Delta_3$; the resulting formulas can be readily generalized to cover all $M_2$ and $\Delta_3$. Thus,

$$\epsilon=\vec{V}_{13}\cdot\vec{P}=(M_1\vec{v}_1+M_3\vec{v}_3)\cdot(M_1/M)(\vec{v}_1'-\vec{v}_1)\,, \qquad (4.32)$$

and since

$$P^2=M_1^2(v_1'^2+v_1^2-2\vec{v}_1\cdot\vec{v}_1') \qquad (4.33)$$

and

$$g^2=v_1^2+v_3^2-2\vec{v}_1\cdot\vec{v}_3\,, \qquad (4.34)$$

it follows that

$$\cos\theta_1'=[2\epsilon+P^2/M_3+M_1(v_1^2+v_3^2-g^2)]/(2M_1v_1'v_3)\,. \qquad (4.35)$$

From (4.8),

$$\cos\theta_3=(v_3^2+v_3'^2-P^2/M_3^2)/(2v_3'v_3)\,. \qquad (4.36)$$

With the use of (4.35) and (4.36) it can be shown, after much lengthy analysis, that (4.25) can be expressed (and generalized so as to cover arbitrary $M_2$ and $\Delta_3$) as

$$\sin^2\theta_1'\sin^2\theta_3'\sin^2(\phi_1'-\phi_3') = \frac{P^2}{4M_3^2v_1'^2v_3'^2v_3^2}[(g_+^2-g^2)(g^2-g_-^2)]\,, \qquad (4.37)$$

where the limits to the relative speed for given energy and momentum changes are

$$g_\pm^2=\tfrac{1}{2}B\pm[(B/2)^2-C]^{1/2}\,, \qquad (4.38)$$

in which

$$B(\epsilon,P,v_1;v_3)=\frac{a}{(1+a)^2}\frac{P^2}{M_{13}^2}+\left(v_1^2+v_1'^2+v_3^2+v_3'^2+\frac{2\Delta_3}{M_{13}}\right) - \frac{4\epsilon(\epsilon+\Delta_3)}{P^2} \qquad (4.39)$$

and

$$C(\epsilon,P,v_1;v_3)=\frac{(v_1^2+av_3^2)}{1+a}\frac{P^2}{M_{13}^2}+(v_1^2-v_3^2)(v_1'^2-v_3'^2)+\frac{2\Delta_3}{M_{13}}(v_1^2+v_3^2)+\frac{4\Delta_3}{P^2}[v_1^2(\epsilon+\Delta_3)-\epsilon_{1,2}v_3^2]. \quad (4.40)$$

The mass-ratio parameter is defined as

$$a=\frac{M_2M_3}{M_1(M_1+M_2+M_3)}\to\frac{M_3}{M_1},\ \text{as } M_2\to\infty \quad (4.41)$$

while the speeds of 1 and 3 after the collision are determined from,

$$v_1'^2=v_1^2+2\epsilon/\tilde{M}_1,\quad \tilde{M}_1=M_1(1+M_1/M_2)\to M_1, \quad (4.42)$$

and

$$v_3'^2=v_3^2-2(\epsilon+\Delta_3)/M_{AB}. \quad (4.43)$$

Hence from (4.23) and (4.37),

$$\frac{k_1'^2}{J_{55}}=\frac{2kk_1M_1}{M_{13}^2k_3k_3'}[(g_+^2-g^2)(g^2-g_-^2)]^{-1/2}, \quad (4.44)$$

such that (4.6) yields

$$d\sigma=\frac{d\epsilon dP}{M_{13}^2v_3^2}\left[\frac{|g_i(\vec{k}_1)|^2k_1^2dk_1d\phi_1}{v_1}\right]\times\frac{|f_{13}(\vec{k},\vec{k}')|^2dg^2}{[(g_+^2-g^2)(g^2-g_-^2)]^{1/2}}, \quad (4.45)$$

the differential cross section for ejection of a bound particle with initial momentum $k_1$ in the interval $dk_1d\phi_1$ about $(k_1,\phi_1)$, with initial speed $g$ relative to the projectile in the interval $dg$ about $g$, such that the energy $\epsilon$ and momentum $P$ gained as a result of the (1-3) collision are in an interval $d\epsilon$ and $dP$ about $\epsilon$ and $P$, respectively.

For a hydrogenic system in state $(nlm)$, the momentum wave function

$$g_i(\vec{k}_1)=g_{nl}(k_1)Y_{lm}(\theta_1,\phi_1) \quad (4.46)$$

such that the average over $m$ states yields,

$$\frac{1}{(2l+1)}\int\sum_{m=-l}^{l}|g_i(\vec{k}_1)|^2d\phi_1=\tfrac{1}{2}g_{nl}^2(k_1). \quad (4.47)$$

Introduction of the normalized speed distribution,

$$F_{nl}(v_1)dv_1=g_{nl}^2(k_1)k_1^2dk_1, \quad (4.48)$$

we therefore have, on averaging (4.45) over the initial $m$ states and on $\phi_1$ integration,

$$d\sigma=\frac{d\epsilon dP}{M_{13}^2v_3^2}\frac{F_{nl}(v_1)dv_1}{2v_1}\frac{|f_{13}(P,g)|^2dg^2}{[(g_+^2-g^2)(g^2-g_-^2)]^{1/2}}. \quad (4.49)$$

Thus, the integral cross section for energy change in the range $\epsilon_1\to\epsilon_2$ is

$$\sigma_{SQ}(v_3)=\frac{1}{M_{13}^2v_3^2}\int_{\epsilon_1}^{\epsilon_2}d\epsilon\int_{v_{10}}^{\infty}\frac{F_{nl}(v_1)dv_1}{v_1}\int_{P^-}^{P^+}dP\int_{g_-}^{g_+}\frac{|f_{13}(P,g)|^2dg^2}{[(g_+^2-g^2)(g^2-g_-^2)]^{1/2}} \quad (4.50)$$

where the $e$-$A$ scattering amplitude $f_{13}(\vec{k},\vec{k}')$ is general, being written in terms of $P$ and $g$, and where a multiplicative factor of two has been inserted to acknowledge the fact, as $\phi_1'$ (or $\phi_3'$) spans the full $(0\to 2\pi)$ range for fixed $k_1'$, $\theta_1'$, and $\theta_3'$, that $g$ passes through its full $(g_-\to g_+)$ range *twice*, as previously noted from (4.12) and (4.13). This final expression (4.50) is identical to that derived from a different approach defined as the semiquantal treatment.[1] The limits, $P^\pm$ and $v_0$, follow from the requirement that $g_\pm$ in (4.38) are real, and can be shown to be[1]

$$P^+(\epsilon,v_1;v_3)=\min[M(v_1'+v_1),M_{AB}(v_3'+v_3)], \quad (4.51)$$

$$P^-(\epsilon,v_1;v_3)=\max[M|v_1'-v_1|,M_{AB}|v_3'-v_3|], \quad (4.52)$$

with the provisor, $P^+>P^-$, and

$$v_{10}^2(\epsilon)=\max[0,(2\epsilon/M)],\quad \epsilon\gtrless 0. \quad (4.53)$$

In ionization, for example, $\epsilon_1$ is the binding energy $I_n$ of the Rydberg electron, and $\epsilon_2$ is the maximum amount $(\frac{1}{2}M_{AB}v_3^2-I_n)$ of kinetic energy of relative motion available for electron ejection.

In situations where it may prove more convenient to express the general (1-3) scattering amplitude $f_{13}(\vec{k},\vec{k}')$ as a function of relative speed $g$ and scattering angle $\psi$, rather than of $g$ and $P$ as in (4.50), then the above analysis can essentially be repeated, but with

$$P^2=k'^2+k^2-2kk'\cos\psi, \quad (4.54)$$

such that the Jacobian of the appropriate transformation is

$$J_{55}'\equiv\frac{\partial(\cos\psi,\epsilon,k_1,k,\phi_1)}{\partial(\cos\theta_3',\phi_3',k_1',\cos\theta_1',\phi_1')}=-\frac{P}{kk'}\frac{\partial(P,\epsilon,k_1,k,\phi_1)}{\partial(\cos\theta_3',\phi_3',k_1',\cos\theta_1',\phi_1')}. \quad (4.55)$$

We can then show, again after much analysis and reduction, that

$$\sin\theta_1'\sin\theta_3'\sin(\phi_1'-\phi_3')=\frac{kk'}{v_1'k_3k_3'}[(1+a)(v_1^2+av_3^2)-ag^2]^{1/2}[(\cos\psi^+-\cos\psi)(\cos\psi-\cos\psi^-)]^{1/2} \tag{4.56}$$

for use in (4.23). The angular limits $\psi^\pm$ can be shown to be

$$\cos\psi^\pm(\epsilon,v_1,g;v_3)=\omega^{-1}(\alpha^2+\beta^2)^{-1}\{\alpha(\alpha+\bar\epsilon)\pm\beta[\omega^2(\alpha^2+\beta^2)-(\alpha+\bar\epsilon)^2]^{1/2}\}, \tag{4.57}$$

where $\omega$ is $g'/g$ in terms of the final relative speed $g'$, and where

$$\alpha(v_1,g;v_3)=\tfrac{1}{2}M_{13}\left[v_1^2-v_3^2+\left(\frac{1-a}{1+a}\right)g^2\right], \tag{4.58}$$

and

$$\beta(v_1,g;v_3)=\tfrac{1}{2}M_{13}[(2v_1^2+2v_3^2-g^2)g^2-(v_1^2-v_3^2)^2]^{1/2} \tag{4.59}$$

are determined by parameters prior to the collision. The energy

$$\bar\epsilon=\epsilon+\frac{a}{(1+a)}\Delta_3 \tag{4.60}$$

assimilates both the energy change $\epsilon$ in (1-2) binding and the change $\Delta_3$ in the internal energy of the incident atom (or molecule). For small energy transfers $\bar\epsilon$,

$$\cos\psi^+\approx 1-\bar\epsilon^2/2\beta^2+O(\bar\epsilon^3), \tag{4.61}$$

and

$$\cos\psi^-\approx 1-2(\beta^2+\alpha\bar\epsilon)/(\alpha^2+\beta^2)+O(\bar\epsilon^2), \tag{4.62}$$

such that quasielastic ($\epsilon\to 0$, $\Delta_3=0$) or energy-resonant collisions ($\bar\epsilon=0$) imply $\psi^+\to 0$ and $\psi^-\to(\alpha^2-\beta^2)/(\alpha^2+\beta^2)$.

The Jacobian (4.55) can be written as

$$J_{55}'(\epsilon,v_1,g,\psi)=\frac{k_3k_3'k_1'^2}{M_1kk_1}S(v_1,g;v_3)[(\cos\psi^+-\cos\psi)(\cos\psi-\cos\psi^-)]^{1/2}, \tag{4.63}$$

in which the function

$$S(v_1,g;v_3)=\frac{M_{13}}{(1+a)}[(1+a)(v_1^2+av_3^2)-ag^2]^{1/2}=\frac{M_{13}}{(1+a)}[(1+a)(v_1'^2+av_3'^2)-ag'^2]^{1/2}\equiv(d^2+\beta^2)^{1/2}/g \tag{4.64}$$

is invariant to the transformations (4.42), (4.43), and (4.10) between the post and prior collision speeds. Hence (4.6) yields

$$\sigma_{SQ}(v_3)=\frac{1}{v_3^2}\int_{\epsilon_1}^{\epsilon_2}d\epsilon\int_{v_{10}}^{\infty}\frac{F_{nl}(v_1)dv_1}{v_1}\int_{g^-}^{g^+}\frac{g\,dg}{S(v_1,g;v_3)}\int_{\psi^-}^{\psi^+}\frac{|f_{13}(g,\psi)|^2d(\cos\psi)}{[(\cos\psi^+-\cos\psi)(\cos\psi-\cos\psi^-)]^{1/2}}, \tag{4.65}$$

which is the required semiquantal result,[1] when allowance is made for the fact, as $\phi_1'$ (or $\phi_3'$) ranges from $0\to 2\pi$, that $\psi$ passes through the $(\psi^- - \psi^+)$ range twice. Although the analysis for the Jacobian assumed infinite core mass $M_2$, for simplicity, i.e., $a=M_3/M_1$ in (4.41) the generalization for arbitrary $M_2$ can be readily made with the result that both (4.50) and (4.65) follow with the mass ratio a taken as in (4.41).

Many simplifications to (4.50) and (4.65) follow, as in cases when $f_{13}$ is simply a constant, or either independent of $\psi$ or $g$, when use can be made of the integral

$$2\int_{x^-}^{x^+}\frac{dx}{[(x_+-x)(x-x_-)]^{1/2}}=2\pi \tag{4.66}$$

for $x\equiv\cos\psi$ and $g^2$, respectively. For example, when the scattered amplitude $f_{13}$ depends only on the momentum change $P$ (as in Born's approximation) then (4.50) yields

$$\sigma_{SQ}(v_3)=\frac{\pi}{M_{13}^2v_3^2}\int_{\epsilon_1}^{\epsilon_2}d\epsilon\int_{v_{10}}^{\infty}\frac{F_{nl}(v_1)dv_1}{v_1}\int_{P^-}^{P^+}|f_{13}(P)|^2dP. \tag{4.67}$$

Although this simplified result could have been deduced more directly from the impulse expression (2.19) with the assumption $f_{13}(\vec k'-\vec k)$, the full analysis given here is essential to general scattering amplitudes $f_{13}(\vec k,\vec k')$, i.e., the transformation from (2.19) to either (4.50) or (4.65).

Although the complete expressions (2.19), (4.50), and (4.65) have been designed for $A$-$B(n)$ neutral-neutral collisions in mind, since the impulse criteria that ($A$-$e$) and ($A$-$B^+$) interactions be short range relative to the ($e$-$B^+$) interaction are well satisfied, it is worth pointing out for $A^+$-$B$ collisions when $|f_{13}|^2$ is $(4\hbar^4/P^4a_0^2)$, the differential cross section for on-the-energy-shell Coulomb scattering which depends only on momentum change $\vec{P}$, that (4.67) reduces[20] to the standard expressions of the binary encounter theory[21] for charged particle-atom collisions. For this special case of Coulombic scattering amplitude $f_{13}^C(\vec{P})$ associated with charged particle-atom collisions, Vriens[22] derived the binary encounter expression from the quantal impulse formula. Bates and McDonough[23] have derived the binary encounter result from Born's approximation with $\sigma_{13}(\vec{P})$, and from the classical Thomas differential cross section[23] [which essentially involves the initial element $\frac{1}{2}(g/v_3)\sigma_{13}(\vec{k},\vec{k}')\times d\hat{k}'d(\cos\theta_1)$] for scattering of two free particles with general differential cross section $\sigma_{13}(\vec{k},\vec{k}')$.

In summary therefore, the present analysis in this section has provided the valuable transformation from scattering variables $(\vec{k}_1', \hat{k}_3')$ for the ejected and scattered particles, 1 and 3, respectively, which naturally occur in detailed quantum-mechanical treatments to the set of dynamical variables $(\epsilon, P, k_1, k, \phi_1)$ or $(\epsilon, \psi, k_1, k, \phi_1)$ which represents the natural choice in semiquantal, binary-encounter, and classical treatments. Within the basic impulse approximation the essential assumptions underlying the semiquantal description are a plane-wave description for the ejected electron and evaluation of the general scattering amplitude $f_{13}(\vec{k},\vec{k}')$ only on the energy shell as in (4.10).

## V. THE ($A$-$B^+$) ENCOUNTER IN $A$-$B(n)$ COLLISIONAL TRANSITIONS

In the full $T_{fi}$-matrix element (A10) for 3-(1,2) collisions, the contribution from (3-2) encounters is nonvanishing only for elastic scattering ($k_3 = k_3'$, $i=f$) so that inelastic transitions originate solely from (1-3) encounters, the second term of (A10), in which the distortion effect of the core interaction $V_{32}$ on the incident wave $\chi^+$ is neglected. Inelastic transitions can, however, arise *indirectly* from (3-2) encounters in the basic impulse expression (A8) which properly includes this distortion but which is much more complex for computation, a nine-dimensional integral rather than a three-dimensional integral as in (A10). Inclusion of inelastic transitions arising from *direct* collisions with the core demands the reformulation of the impulse procedure so as to acknowledge noninertiality of the core, i.e., finite $M_2$ rather than infinite $M_2$ as assumed in Sec. II. The reformulation in essence spoils the basic attraction of the original method, and involves solution based on approximate (perturbation) procedures. Effective allowance for inelastic transitions from (2-3) collisions can, however, be obtained within the sudden approximation, and in a more elaborate new treatment proposed below.

### A. Sudden approximation

Let the (3-2) encounter be sufficiently fast so that the collision time $\tau_c \ll T_n$, the orbital period of the Rydberg electron. The wave function $\psi_i(\vec{r})$ in state $i$ relative to a *fixed* core is therefore unaffected. Require, in addition $\tau_c \ll n^2a_0/v_3$, such that, during the encounter, the nucleus remains essentially fixed within the dimensions of the Rydberg atom. The (3-2) encounter suddenly transfers momentum $\vec{P}$ to 2 which then moves with velocity $\vec{v} = \vec{P}/M_{23}$ after time $\tau_c$. The electronic state $\psi_i$ is relative initially to a fixed core, and finally to a core moving with speed $v$. The overlap between the fixed and traveling orbitals provides the desired probability of transition, and can be obtained either in the coordinate system in which the nucleus is initially at rest, or more conveniently, in the system in which the nucleus is moving. Here, the initial wave function (with core traveling backwards with velocity $\vec{v}$) is,

$$\psi_i'(\vec{r}) = \psi_i(\vec{r})\exp(-iM_1\vec{v}\cdot\vec{r}/\hbar) \equiv \sum_n a_n\psi_n(\vec{r}) , \quad (5.1)$$

such that its projection $a_f$ onto a final state $\psi_f$ for the electron relative to a fixed core gives the probability $|\langle\psi_f|\psi_i'\rangle|^2$ in the sudden approximation[24] which yields,

$$P_{if} = |a_f|^2 = |\langle\psi_f(\vec{r})|\exp(-iM_1\vec{v}\cdot\vec{r}/\hbar)|\psi_i(\vec{r})\rangle|^2 \equiv |F_{fi}(M_1\vec{P}/M_{23})|^2 , \quad (5.2)$$

for transition $i \to f$. This mechanism can alternatively be viewed as originating from an instantaneous change of the electronic Hamiltonian, from one without motion of the center of mass (c.m.) of the electron shell to one with both relative and c.m. motions described by (5.1). The required cross section for collisional transitions is therefore,

$$Q_{if}^{23} = \int \left|\left\langle\psi_f\left|\exp\left(i\frac{M_1}{M_{23}}\vec{P}\right)\right|\psi_i\right\rangle\right|^2\left(\frac{d\sigma_{23}^{el}}{d\Omega}\right)d\Omega \equiv 2\pi\int_0^{\rho_{max}}|F_{fi}(M_1\vec{P}/M_{23})|^2\rho\,d\rho , \quad (5.3)$$

where the maximum impact parameter $\rho_{max}$, determined by the effective range of $V_{32}$, must be well within $n^2a_0$, which is generally the case (cf. Table

II, Sec. VI), and where $(d\sigma_{23}^{\rm el}/d\Omega)$ is the differential cross section for (2-3) elastic scattering.

Although this paper essentially describes neutral $A$-neutral $B(n)$ collisions, because the (3-1) and (3-2) interactions are short range (~polarization attraction) in comparison to the (1-2) Coulombic binding interaction, it is interesting to note that the impact parameter $\rho$ is related to the angle $\psi$ for scattering (in the 2-3 center-of-mass system) under the Coulombic interaction $(\alpha/R_{23})$ at relative energy $E$ by

$$\rho=(\alpha/2E)\cot\tfrac{1}{2}\psi,\quad E=\tfrac{1}{2}M_{23}v_{23}^2\,, \qquad (5.4)$$

and that the momentum change is

$$\vec{P}=2M_{23}\vec{v}_{23}\sin\tfrac{1}{2}\psi\,, \qquad (5.5)$$

such that the integral cross section (5.3) is given in the sudden approximation by

$$Q_{if}^S=\frac{8\pi\alpha^2}{v_{23}^2}\left(\frac{M_1}{M_{23}}\right)^2\int_{\tilde{P}_{\min}}^{\tilde{P}_{\max}}|F_{fi}(\tilde{P})|^2\frac{d\tilde{P}}{\tilde{P}^3}\,, \qquad (5.6)$$

where the maximum value of $\vec{P}$, the momentum change $2M_1v_{23}\sin\frac{1}{2}\psi$ corresponding to an electron-ion collision at speed $v_{23}$, is $\tilde{P}_{\max}=2M_1v_{23}$, and the minimum $\tilde{P}_{\min}$ is ill determined by $\psi_{\min}$ corresponding to $\rho=\rho_{\max}$ in (5.4), or else is approximated by $M_1(v_{23}'-v_{23})$ where $v_{23}$ is the final speed determined by energy conservation of the complete scattering system. Although multiplied by $(M_1/M_{23})^2$, the form of (5.6) is identical with the usual inelastic Born cross section,

$$Q_{if}^B=\frac{8\pi\alpha^2}{v_{32}^2}\int_{P^-}^{P^+}|F_{fi}(P)|^2\frac{dP}{P^3}\,, \qquad (5.7)$$

$$P^{\pm}=M_{23}(v_{23}'\pm v_{23})\,,$$

which arises solely from the (1-3) interaction. However, (5.6) permits momentum changes $\tilde{P}$ which are a factor of $(M_1/M_{23})$ smaller than those allowed in (5.7), i.e., $\tilde{P}_{\min}=(M_1/M_{23})(\epsilon_f-\epsilon_i)/v_{23}$ at high energy, thereby causing a non-negligible contribution to the overall inelastic cross section. This treatment (5.3) can be generalized to intermediate and thermal energies as follows.

### B. General treatment of inelastic transition via (2-3) collision

In the absence of the interaction $V_{13}$ between the incoming projectile 3 and the Rydberg electron 1, the Hamiltonian for the complete $A$-$B(n)$ system is

$$\mathcal{H}\equiv-\frac{\hbar^2}{2M_{12}}\nabla_r^2-\frac{\hbar^2}{2M_{AB}}\nabla_R^2+V_{23}(\vec{R}')-\frac{e^2}{r}\,, \qquad (5.8)$$

where the vector $\vec{R}'$ of 3 relative to 2 is, in terms of its position $\vec{R}$ relative to the (1,2) center of mass, and $\vec{r}$ the (1-2) vector separation, given by

$$\vec{R}'=\vec{R}+(M_1/M)\vec{r},\quad M=M_1+M_2\,, \qquad (5.9)$$

such that the (2-3) interaction can be expanded as

$$V_{23}(\vec{R}')=V_{23}(\vec{R})+(M_1/M)\vec{r}\cdot\vec{\nabla}V_{23}(\vec{R})+\cdots\,. \qquad (5.10)$$

The full scattering solution for $\mathcal{H}$ can be expanded in terms of the target basis $\{\phi_n(\vec{r})\}$, as

$$\Psi(\vec{r},\vec{R})=\sum_n F_n(\vec{R})\phi_n(\vec{r})\,, \qquad (5.11)$$

where the unknown $F_n$ for the (2-3) relative motion can be shown to satisfy the standard set of coupled, three-dimensional differential equations,

$$[\nabla_R^2+\kappa_f^2(\vec{R})]F_f(\vec{R})=(2M_{AB}/\hbar^2)\sum_{n\neq f}V_{fn}(\vec{R})F_n(\vec{R})\,, \qquad (5.12)$$

where

$$\kappa_f(\vec{R})=\left(k_{3f}^2-\frac{2M_{AB}}{\hbar^2}V_{ff}(\vec{R})\right)^{1/2}\,, \qquad (5.13)$$

are the local wave numbers for relative motion under the static interactions $V_{ff}(\vec{R})$, the diagonal element of the matrix,

$$V_{ji}(\vec{R})=V_{23}(\vec{R})\delta_{ji}+\left(\frac{M_1}{M}\right)\langle\phi_j(\vec{r})|\vec{r}|\phi_i(\vec{r})\rangle\cdot\vec{\nabla}V_{23}(\vec{R})+\cdots\,. \qquad (5.14)$$

A hierarchy of approximations readily follow from solution of (5.12) to various orders of sophistication. In particular, the multichannel eikonal treatment designed by Flannery and McCann[25] (for $e$-atom collisions) and the multistate orbital treatment of McCann and Flannery[26] (for heavy particles at thermal and higher energies, as here) represent efficient semiclassical methods of solution. As shown by McCann and Flannery,[26] the multistate-orbital treatment within a common trajectory for all static interactions $V_{ff}(\vec{R})$ yields

$$f_{ni}(\theta)=B_n(\rho,t\to\infty)\exp\left(-\frac{i}{\hbar}\int_{t_0}^t[V_{ff}\{\vec{R}(t)\}+\vec{R}\cdot\vec{P}(t)]dt\right)\left(\frac{d\sigma_{23}}{d\Omega}\right)^{1/2}\,, \qquad (5.15)$$

where $(d\sigma_{23}/d\Omega)$ is the classical differential cross section per steradian for scattering by the optical potential,

$$\mathcal{V}_{\rm opt}\{\vec{R}(t)\}=\sum_n\left(|B_n(t)|^2\epsilon_n+\sum_f B_f^*(t)B_n(t)V_{fn}\{\vec{R}(t)\}\exp(i\epsilon_{fn}t/\hbar)\right), \qquad (5.16)$$

which effectively couples the response in (5.11) of the Rydberg atom to the interaction $V_{23}(\vec{R}(t))$ in (5.10) back to the relative motion, and vice versa. This response is measured in terms of the transition amplitudes $B_f(t)$ which are solutions of[26]

$$i\hbar\frac{\partial B_f}{\partial t}(\rho,t)=\sum_f B_n(\rho,t)V_{fn}\{\vec{R}(t)\}\exp\left(\frac{i}{\hbar}\epsilon_{fn}t\right), \qquad (5.17)$$

where the time $t$, introduced in the stationary state description, is merely a dummy variable invoked only to represent variation along the trajectory specified by $\vec{R}(t)$. This trajectory common to all excitation channels is determined by the solution of Hamilton's equations,[27]

$$\frac{\partial Q_j}{\partial t}=\frac{\partial\overline{H}}{\partial P_j}\equiv\frac{1}{M_{AB}}P_j(t), \qquad (5.18)$$

and

$$\frac{\partial P_j}{\partial t}=-\frac{\partial\overline{H}}{\partial Q_j}=-\frac{\partial\mathcal{V}_{\rm opt}}{\partial Q_j}=-\sum_n\sum_f B_f^*(t)B_n(t)\frac{\partial V_{fn}(Q_j)}{\partial Q_j}\exp\left(\frac{i}{\hbar}\epsilon_{fn}t\right), \qquad (5.19)$$

for variation with time $t$ of the generalized coordinates $Q_j\equiv(X,\ Y,\ Z)$ of $\vec{R}(t)$ and of the associated conjugate momenta $P_j$ for motion of a particle of reduced mass $M_{AB}$ with Hamiltonian,

$$\overline{H}=\sum_{j=1}\frac{1}{2M_{AB}}P_j^2(\vec{R})+\mathcal{V}_{\rm opt}(\vec{R}). \qquad (5.20)$$

The solution for relative motion in (5.18) and (5.19) is coupled to the solution of (5.17) for the transition amplitudes $B_n$ via the optical potential (5.16). An essential feature of scattering by this effective potential $\mathcal{V}_{\rm opt}$ is that total energy of the system is conserved at all times throughout the collision, as is confirmed by showing with the aid of (5.16)–(5.20) that $d\overline{H}/dt=\partial\overline{H}/\partial t=0$.

When the trajectory is computed without the second term in (5.14), and when it is single valued, i.e., a specified scattering angle $\theta$ originates from one impact parameter $\rho$, then the required cross section is

$$\left(\frac{d\sigma_{fi}}{d\Omega}\right)=|B_f(\rho,t\to\infty)|^2\left(\frac{d\sigma_{23}}{d\Omega}\right), \qquad (5.21)$$

where the classical differential cross section is obtained from $V_{23}(\vec{R})$, and where $B_f$ is obtained by standard numerical procedures from (5.17), solved subject to $B_f(\rho,t=-\infty)\equiv\delta_{fi}$. The above equations represent the present treatment of inelastic transitions arising from 2-3 encounters.

That this treatment yields the correct high-energy limit (5.3) immediately follows by invoking the sudden approximation to the coupled set (5.17). This entails ignoring the exponential phase factors $(i\epsilon_{fn}t/\hbar)$ in (5.17), (since the collision time $t$ is assumed small in comparison with the time $\hbar/\epsilon_{fn}$ for transition between highly excited states $n$ and $f$). The resulting set of coupled equations can then be solved exactly[28] to yield

$$B_f(\rho,t\to\infty)=\left\langle\phi_f(\vec{r})\left|\exp\left[i\left(\frac{iM_1}{\hbar M}\right)\vec{r}\cdot\int_{-\infty}^{t\to\infty}\nabla V_{23}(\vec{R}(t))\cdot dt\right]\right|\phi_i(r)\right\rangle_{\vec{r}}, \qquad (5.22)$$

which can be verified by direct substitution in (5.17). Since $\vec{F}_{23}=-\nabla V_{23}$, such that the impulse

$$\int_{-\infty}^{\infty}\vec{F}_{23}dt=M_{23}(\vec{v}_{23}'-\vec{v}_{23})=M_2\vec{v} \qquad (5.23)$$

is the momentum $M_2\vec{v}$ transferred to the core 2, the probability of transition is therefore,

$$|B_f(\rho,t\to\infty)|^2=|\langle\phi_f(\vec{r})|\exp(iM_1\vec{v}\cdot\vec{r})|\phi_i(\vec{r})\rangle|^2, \qquad (5.24)$$

in accord with (5.2). This derivation is rather instructive in that it clearly identifies the role of the impulse within an elaborate quantum-mechanical description of the collision process. Since the right-hand side of (5.24) is the inelastic form factor squared which when summed over all final states $f$ yields

$$\sum_f|F_{fi}(\vec{P})|^2=1, \qquad (5.25)$$

unity for any momentum change $\vec{P}$, thereby implying probability conservation for $|B_f|^2$ in (5.24), such that the total cross section for *all elastic and inelastic events* is therefore,

$$\sigma_{if}^{\text{tot}} = \sigma_{23}\,. \tag{5.26}$$

Thus, the cross section $\sigma_{if}$ of any process based on the (2-3) collision mechanism is limited by the integral cross section $\sigma_{23}$ for (2-3) elastic scattering, which can be rather large. The detailed treatment is represented by the solutions of (5.17)–(5.19) with interaction matrix (5.14) in the expression (5.15) for the inelastic scattering amplitude $f_{fi}(\theta)$ in (5.15). When more than one impact parameter $\rho_i$ yields a specified classical scattering angle $\theta$, then interference effects occur between the phases associated with the various trajectories $\rho_i(\theta)$. Also, for scattering in the vicinity of the rainbow angle $\theta$, i.e., where $d\theta/d\rho \to 0$, an infinite number of trajectories $\rho_i$ form a caustic as $\theta \to \theta_r$, and special procedures involving Airy functions are required. To cover both of these possibilities, McCann and Flannery[26] have provided a three-dimensional uniform approximation, a direct generalization of the one-dimensional elastic scattering analysis of Berry[29] to inelastic events, which replaces (5.15) by a summation over all the contributing trajectories $\rho_i(\theta)$ with appropriate phase factors arising from the action (or eikonal) associated with each trajectory.

## VI. PARTICULAR APPLICATION: *l* MIXING IN RYDBERG-ATOM-RARE-GAS THERMAL COLLISIONS

The above quantal impulse, semiquantal, and multistate-orbital treatments for the cross section $\sigma_{if}$ of $A$-$B(n)$ collisional transitions based on both ($A$-$e$) and ($A$-$B^+$) encounters find extensive application, particularly to excitation and to ionization processes which involve momentum and energy changes in ($A$-$e$) encounters sufficiently large in comparison with the momentum and energy imparted by the Rydberg electron-core attraction during the ($A$-$e$) collision time. For many high-energy, weak-binding situations ($E_3 \gg |\epsilon_n|$), ($A$-$e$) encounters alone provide the dominant contribution to $\sigma_{if}$ and yield the correct high-energy Born limit for heavy-particle collisions when the Born cross section for ($e$-$A$) scattering is adopted.[1] Other cases such as quasielastic, $l$-changing collisions at thermal energy involve small momentum changes, and, because of the limitation (3.24), and of on-the-energy-shell considerations in III D, introduce severe tests of the hypothesis based on the sole ($A$-$e$) binary encounter. Important and sometimes major contributions then arise from the mechanism based on $A$-$B^+$ encounters, discussed in Sec. V, and limited by the ($A$-$B^+$) elastic scattering cross section $\sigma_{23}$ which can be rather large at thermal energies.

The full quantal and classical investigations of Flannery and Morrison[30] on $H^+$, $Na^+$, $K^+$-rare gas (He, Ne, Ar, Kr) elastic collisions show, as the momentum $k_3$ of (2-3) relative motion increases, that the elastic cross sections $\sigma_{23}$, are large (~$10^3$ Å$^2$) at thermal energies, and oscillate on a decreasing background. The amplitude of the quantum oscillations diminishes at energies $\gtrsim$ thermal where a very accurate representation of $\sigma_{23}$ is given by,

$$\sigma_{23}^{\text{el}}(k_3) \equiv \frac{4\pi}{k_3}\int_0^\infty 2l\sin^2\eta_l\,dl = 1.0688\times 10^3\left(\frac{\alpha M_{AB}}{k_3}\right)^{2/3} a_0^2\,, \tag{6.1}$$

where $\alpha\, a_0^3$ is the polarizability of the neutral, and $k_3$ (a.u.) is the momentum of relative motion of the ($A$-$B^+$) system with reduced mass $M_{AB}$ (amu). Expression (6.1) is obtained from the semiclassical phase shifts,[31]

$$\eta_l(k_3) = -\left(\frac{M_{AB}}{\hbar^2}\right)\int_{(l+1/2)/k_3}^\infty \frac{V_{23}(R)dR}{[k_3^2 - (l+\frac{1}{2})^2/R^2]^{1/2}}\,, \tag{6.2}$$

for the polarization attraction $V_{23} = -(\alpha e^2/2R^4)$. Cross sections calculated from (6.1) for $Na^+$-rare gas $Rg$ collisions at 430 K are presented in the fifth column of Table II.

In an effort to assess whether the binary ($A$-$e$) and ($A$-$B^+$) mechanisms discussed here offer realistic interpretation of the recent experiments[11] of $l$ mixing in Na($nl$)-$Rg$ collisions at thermal energies, i.e., when the orbital speed $v_1 \sim 1/n \gg v_3$, we note from (3.21) and (5.26) that the total cross section for all elastic and inelastic events at a given impact speed $v_3$ is

$$\sigma_{\text{tot}} = \sigma_{\text{tot}}^{(1\text{-}3)} + \sigma_{\text{tot}}^{(2\text{-}3)} = \langle v_1 \sigma_{13}^T(v_1)\rangle / v_3 + \sigma_{23}^{\text{el}}\,, \tag{6.3}$$

where $\sigma_{13}^T$ is the integral cross section for $e$-$A$ elastic and inelastic collisions consistent with the speed $v_1$, which is sufficiently small (~$1/n$) so as to allow ($e$-$A$) elastic scattering alone.

The minimum temperature $T$, corresponding to energy $\frac{3}{2}kT$ of relative motion, required to cause $n \to n+\Delta$ excitation and ionization of H($n$) are

$$T_E(\text{K}) = (10/n)^3\Delta(300) \tag{6.4}$$

and

$$T_I(\text{K}) = (23/n)^2\Delta(300)\,, \tag{6.5}$$

respectively. Since the quantum defects for $s$ and $p$ levels of Na are 1.35 and 0.855,[11,12] it is reason-

TABLE II. Maximum cross sections $\sigma_{tot}$ for Na(10 $l$)- rare gas $Rg$ collisions at 430 K, based on ($e$-$Rg$) elastic encounters with cross section $\sigma_{tot}^{13}$, and on ($Na^+$-$Rg$) elastic encounters with cross section $\sigma_{23}^{el}$. The relative speed, momentum, and polarizability of the incident $Rg$ atom 3 are $v_3$, $k_3$, and $\alpha$, respectively.

| $Rg$ | $v_3(10^{-4}$ a.u.) | $k_3$ (a.u.) | $\alpha$ ($a_0^3$) | $\sigma_{23}^{el}$ (Å$^2$) | $\sigma_{tot}^{13}$(Å$^2$) | $\sigma_{tot}$ (Å$^2$) | exp(Å$^2$) |
|---|---|---|---|---|---|---|---|
| He | 7.471 | 4.641 | 1.384 | $3.03\times10^2$ | $(6.67-7.64)\times10^2$ | $(0.97-1.1)\times10^3$ | $2.2\times10^3$ |
| Ne | 4.208 | 8.240 | 2.666 | $6.87\times10^2$ | $(0.75-2.33)\times10^2$ | $(7.6-9.2)\times10^2$ | $7.7\times10^2$ |
| Ar | 3.611 | 9.601 | 11.07 | $1.96\times10^3$ | $(2.20-0.43)\times10^3$ | $(4.2-2.4)\times10^3$ | $3.7\times10^3$ |
| Kr | 3.248 | 10.68 | 16.74 | $2.78\times10^3$ | $(1.91-0.39)\times10^4$ | $(2.2-0.7)\times10^3$ | |
| Xe | 3.119 | 11.11 | 27.26 | $3.95\times10^3$ | $(6.89-1.01)\times10^4$ | $(7.3-1.4)\times10^4$ | |

able to assume[11] that Na(10d)-$Rg$ collisions at 430 K will strongly couple only those angular momentum in $n=10$ with $l\geq 3$.

The electron rare-gas elastic cross sections $\sigma_{13}$ can be obtained from recent phase shifts calculated in the polarized-orbital, local-exchange approximation by Yau *et al.*[18] The cross sections were so normalized as to reproduce measurements (when available) of the scattering length $A$, since, for He, Ne, and Ar, the calculated scattering lengths were 13% lower, 11% lower, and 40% higher than the respective measurements.[32] The cross section $\sigma_{tot}^{(1-3)}$ arising from (1-3) collisions is presented in the sixth column of Table II. Here the first value in the range corresponds to $\sigma_{13}=4\pi A^2$ at zero electron-energy, while the second value is associated with $k=0.1$ a.u. This $k$ range corresponds to orbital electrons in levels $n\gtrsim 10$. Within this range, a rapid decrease[18] due to the Ramsauer-Townsend effect occurs in $\sigma_{13}$ for Ar, Kr, and Xe, a situation ill suited to the impulse treatment, as discussed above in Sec. II. The cross sections $\sigma_{tot}^{(1-3)}$ are lower than the measured $l$-mixing cross sections for He, Ne, and Ar in column 8 of Table II by factors of 3, (3-10), and (1.7-8), respectively. This inadequacy may be attributed to the neglect of distortion of the incident wave by the core interaction $V_{3C}$ (cf. Appendix), an effect not expected to be important during ($e$-$A$) interaction when $v_3 \ll v_1$, and to the incomplete description of the $l$-mixing mechanism. The latter omission, remedied as detailed in Sec. V, can be assessed by the maximum contribution $\sigma_{23}^{el}$ from (2-3) collisions. We note from Table II that $\sigma_{23}^{el}$ indeed contributes significantly particularly for the lighter systems, to the overall cross section $\sigma_{tot}$, which then becomes more consistent with the measured values.[11] Also the ($A$-$B^+$) collision tends to offset the dramatic effect exhibited for the Ar case by the Ramsauer-Townsend effect.

Although $\sigma_{23}^{el}$ is large, the effective scattering length for (2-3) elastic collisions alone (~5, 7, 13, 15, 18 Å for He–Xe, respectively) is still much less than the orbital radius (~88 Å) for the $n=10$ Rydberg electron, so that core distortion during ($e$-$A$) scattering can indeed be neglected. Limits to the cross section $\sigma_{tot}$ for higher $n$ can be obtained from Table II by scaling, by a factor $n^{-1}$ which arises via $v_1$ in (6.3).

Also, it is worth noting, since the cross section $\sigma_{tot}^{(1-3)}$ represents the upper limit to cross sections for *all* processes based on the impulse treatment (2.6) of ($e$-$A$) encounters in $A$-$B(n)$ collisions, that cross sections[6,12] based on any derivative of (2.6) which exceed $\sigma_{tot}^{(1-3)}$ have somewhat limited reliability.

A detailed theoretical account of $l$-mixing collisions, therefore, demands both (1-3) and (2-3) collision mechanisms. The former mechanism at low energy $v_3 \ll v_1$ could involve proper acknowledgment of the distortion of the incident wave by 2, within the appropriate impulse expression, i.e., the nine-dimensional integral (A8) rather than the three-dimensional integral (A10). The latter mechanism based on noninertiality of the core would demand the full treatment presented in Sec. V or appropriate reformulation of the impulse procedure. Such investigations are underway. It is interesting to note for the special case of Rydberg atom-*parent* atom collisions that Janev and Mikajlov[33] recently introduced a mechanism based on quasiresonant energy exchange within the quasimolecular ion lying within the orbit of the Rydberg electron. The mechanism proposed here is in a sense general to this in that the nuclei need not be identical.

## VII. SUMMARY AND CONCLUSIONS

In this paper we have derived the semiquantal treatment from the quantal impulse approximation (2.6) via appropriate transformation between the sets of dynamical variables naturally associated with each treatment. The actual transformation represents in itself, a very useful and valuable procedure. In so doing, the assumptions involved with the semiquantal description become apparent and are a plane-wave description for the ejected electron in the process,

$$A(i)+B(n)\rightarrow A(j)+B^{+}+e \qquad (7.1)$$

and evaluation of the general scattering amplitude for Rydberg electron-$A$ encounters only on the energy shell. The semiquantal method represents a very efficient procedure for calculation of integral or energy-differential cross sections for (7.1), rather than from the corresponding quantum expression (2.19) which is valuable for angular differential cross sections. The total cross section $\sigma_{\text{tot}}$ in the semiquantal treatment (2.18) for all elastic and inelastic events yields a result identical to that (2.15) obtained from the full quantal impulse expression (2.6).

The full impulse description (2.6) of $A$-$B(n)$ collisions is justified in two cases when (a) the interactions of $e$ and $A$ with the core $B^+$ are quasiclassical in that they exhibit a variation slow in comparison with that of the $(e$-$A)$ interaction within its range $f_{13}$ and when (b) a weak-binding situation exists, i.e., when the incident energy $E_3 \gg |\epsilon_n|(f_{13}/\lambda\!\!\!^{-})$, where $\lambda\!\!\!^{-}$ is the reduced wavelength of incident relative motion. The former case (a) necessarily implies that the force on $e$ due to the core $B^+$ is negligible in comparison with the impulsive force of the $(e$-$A)$ interaction, or that the momentum transferred to $e$ during the $(e$-$A)$ interaction time $\tau_c$ is much greater than the momentum imparted to $e$ via the core $B^+$ during the same time $\tau_c$. Case (b) reflects essentially a high-energy situation. Both cases are further restricted by the condition that distortion to the motion of $A$ by the core $B^+$ can be neglected. When this distortion is strong, as in thermal energy collisions with $v_1 \gg v_3$, then the more basic expression (A8) which is much more complex than the standard (and still fairly complicated) impulse expression (2.6) or (A10) must be used.

The above requirements are necessary for valid application of the impulse procedure (2.6) to $A$-$B(n)$ collisions. Those collisions involving small energy and momentum cases require particular scrutiny (as for $l$-changing collisions). The derivatives of (2.6) given in Secs. II and III involve additional considerations for validity of application, and the associated cross sections cannot exceed $\sigma_{\text{tot}}$ in (2.15). Evaluation of $f_{13}$ only on the energy shell requires the energy and momentum considerations of Sec. IIID.

More importantly, however, particularly for quasielastic transitions at thermal energies is the failure of the standard impulse result (2.6) to acknowledge the possibility of electronic transitions via direct $A$-$B^+$ encounters a new quantal description of the underlying mechanism has been formulated here. Preliminary assessment indicates that this additional mechanism yields important and perhaps dominant contributions to the overall cross section. This mechanism is in effect complementary to the impulsive $(e$-$A)$ mechanism in that it provides a description of the collision at lower impact energies in situations where the momentum and energy transferred is sufficiently small so as to violate the essential criteria for the impulse approximation.

In conclusion, the combination of the quantal impulse approximation Sec. II, or of its derivatives in Secs. II–IV when valid, and the new mechanism in Sec. V based on $A$-$B^+$ encounters provide interesting and complementary theoretical accounts of $A$-$B(n)$ collisions.

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## APPENDIX: IMPULSE EXPRESSION, QUASICLASSICAL, AND WEAK-BINDING VALIDITY CONDITIONS

*Basic Expression.* Although the quantal impulse approximation has been derived from many formal quantal directions[9,10,34-36] and from generalization of Born's approximation,[37] perhaps the method most natural and transparent for $A$-$B(n)$ collisions is based on the exact two potential expression[34] for the $T$-matrix element for scattering by interaction $(V_{13}+V_{3C})$ of the incident particle 3 (assumed without loss of generality to be structureless) with the Rydberg electron 1 and core C. In order to clarify several issues important to application for processes involving highly excited states, we will follow that direction. The two-potential formula[34] yields

$$T_{fi}=\langle \Phi_f | V_{3C}(\vec{r}_3)|\chi_i^+\rangle + \langle \chi_f^- | t_{13} | \chi_i^+\rangle , \qquad (A1)$$

where

$$\Phi_f(\vec{r}_1,\vec{r}_3)=\phi_f(\vec{r}_1)\exp(i\vec{k}_3\cdot\vec{r}_3), \qquad (A2)$$

$$\chi_i^{\pm}(\vec{r}_1,\vec{r}_3)=\phi_i(\vec{r}_1)\left[\chi^{\pm}(\vec{k}_{3i};\vec{r}_3)=\left(1+\frac{1}{E-(H_0+V_{3C})\pm i\epsilon}V_{3C}\right)\exp(i\vec{k}_{3i}\cdot\vec{r}_3)\right], \qquad (A3)$$

and the operator

$$t_{13}=V_{13}+V_{13}\frac{1}{E-(H_0+V_{3C})-V_{13}+i\epsilon}V_{13}\,, \qquad (A4)$$

is taken over distorted waves $\chi^{\pm}$, which are scattering solutions of $(H_0+V_{3C})$, with total energy $E$ for the $A$-$B(n)$ system and with appropriate ingoing and outgoing boundary conditions. The first term in (A1) is nonvanishing only for elastic scattering. The Hamiltonian for the isolated collision partners is

$$H_0=-\frac{\hbar^2}{2M_{1C}}\nabla_1^2-\frac{\hbar^2}{2M_{3C}}\nabla_3^2+V_{1C}(\vec{r}_1)\equiv\hat{\kappa}+V_{1C}\;; \qquad (A5)$$

where $\hat{\kappa}$ describes free motion of 1 and 3. The impulse approximation replaces $t_{13}$ by

$$t_{13}^{\rm imp}=V_{13}+V_{13}\frac{1}{E_\kappa-\hat{\kappa}-V_{13}+i\epsilon}V_{13}\,, \qquad (A6)$$

which is taken over intermediate eigenstates of $\hat{\kappa}$ with energy $E_\kappa$, i.e., over

$$\phi_\kappa^-(\vec{r}_1,\vec{r}_3)=\frac{1}{(2\pi)^3}\exp(i\vec{k}_1\cdot\vec{r}_1)\exp(i\vec{k}_3\cdot\vec{r}_3)$$

$$\equiv\frac{1}{(2\pi)^3}\exp(i\vec{K}\cdot\vec{R})\exp(i\vec{k}\cdot\vec{r})\,, \qquad (A7)$$

where $\vec{K}$ and $\vec{k}$ are the respective momenta of the (1,3) center of mass at $\vec{R}$ and of relative motion of 1 and 3 separated by $\vec{r}$. In (A6), interactions with the core are neglected and the free-particle energy is used instead of the total energy of the system. The second term of (A1) is then

$$\langle\chi_f^-|t_{13}|\chi_i^+\rangle=\int d\vec{\kappa}\,d\vec{\kappa}\,'\langle\chi_f^-|\phi_\kappa^-\rangle_{\vec{r}_1,\vec{r}_3}\times\langle\phi_{\kappa'}^-|t_{13}^{\rm imp}|\phi_\kappa^-\rangle_{\vec{r},\vec{R}}\langle\phi_\kappa^-|\chi_i^+\rangle_{\vec{r}_1,\vec{r}_3} \qquad (A8)$$

the $T$ matrix for free-particle scattering by $V_{13}$, weighted by the probability amplitudes that the actual initial and final states of the total scattering system have free total momentum components $\vec{\kappa}$ and $\vec{\kappa}\,'$, respectively. Because of the $\vec{R}$ integration in (A8), $t_{13}^{\rm imp}$ connects only those free-particle states $\phi_\kappa^-$ in (A7) which satisfy momentum conservation ($\vec{K}=\vec{K}'$) expressed by $\delta(\vec{K}-\vec{K}')$. The six-dimensional element $d\vec{\kappa}$ is either $d\vec{k}_1\,d\vec{k}_3$ or $d\vec{k}\,d\vec{K}$. The amplitude $\langle\phi_\kappa^-|\chi_i^\pm\rangle$ of the free-particle states is, from (A2) and (A7), simply the product of Fourier transforms of the atomic orbital $\phi_i(\vec{r}_1)$ and of the wave $\chi^\pm(\vec{k}_{3i},\vec{r}_3)$ distorted by $V_{3C}$. If this distortion is neglected, then the probability of amplitude of finding the initial state with free momentum $(\vec{k}_1+\vec{k}_{3i})$ is determined solely by $V_{1C}$, i.e., by

$$\langle\phi_\kappa^-|\chi_i^+\rangle=g_i(\vec{k}_1)\delta(\vec{k}_3-\vec{k}_{3i})\,, \qquad (A9)$$

where $g_i$ is the momentum eigenfunction (2.4) for the bound state.

Upon integration over $d\vec{k}_3\,d\vec{k}_3'$ in (A8) the full $T$ matrix (A1) is therefore,

$$T_{fi}(\vec{k}_3,\vec{k}_3')=[\langle\exp(i\vec{k}_3'\cdot\vec{r}_3)|V_{3C}|\chi^+(\vec{k}_3;\vec{r}_3)\rangle]\delta_{fi}+\int d\vec{k}_1 d\vec{k}_1' g_f^*(\vec{k}_1')g_i(\vec{k}_1)\langle\exp(i\vec{k}\,'\cdot\vec{r})|t_{13}|\exp(i\vec{k}\cdot\vec{r})\rangle\delta[\vec{P}-(\vec{k}_1'-\vec{k}_1)]\,, \qquad (A10)$$

in which $\vec{P}$ is the momentum transfer $(\vec{k}_3-\vec{k}_3')$ or $(\vec{k}\,'-\vec{k})$ such that the $\delta$ function expresses the momentum conservation which originated in (A8). When the distortion of $\chi^\pm$ is also neglected in the first term of (A1) or of (A10), then this first term simply reduces to the Born $T$ matrix—the Fourier transform of $V_{3C}$—for scattering of 3 by the core. Being real, it makes no contribution to the optical theorem,

$$\sigma_{\rm tot}(v_3)=\frac{1}{k_3}\left(\frac{2M_{AB}}{\hbar^2}\right)\mathrm{Im}\,T_{ii}(\vec{k}_3,\vec{k}_3)\,, \qquad (A11)$$

which therefore yields the total cross section for all elastic and inelastic events as

$$\sigma_{\rm tot}(v_3)=\frac{1}{v_3}\int|g_i(\vec{k}_1)|^2 v_{13}\sigma_{13}^T(v_{13})dk_1\,, \qquad (A12)$$

where $\sigma_{13}^T$ is the corresponding cross section for ($e$-$A$) collisions at relative speed $v_{13}$. Cross section (A12) is an upper limit for processes assumed to occur via the impulse mechanism, and is certainly valid for $v_3\gg v_1$. For incident speeds $v_3\ll v_1$, however, distortion of $\chi^+$ by $V_{3C}$ may not be ignored, such that the first term of (A10) will, in general, be complex and may therefore make a significant contribution to (A12).

*Basic Assumptions.* (a) The error introduced in the basic impulse approximation (A8) is assessed by the difference between $t_{13}$ of (A4) and $t_{13}^{\rm imp}$ of (A6). From the inverse-operator difference relation, $A^{-1}-B^{-1}\equiv A^{-1}(B-A)B^{-1}$, it follows that

$$t_{13}-t_{13}^{\rm imp}=V_{13}\frac{1}{E-(H_0+V_{3C})-V_{13}+i\epsilon}\times[E_\kappa+(V_{1C}+V_{3C})-E]\times\frac{1}{E_\kappa-\hat{\kappa}-V_{13}+i\epsilon}V_{13}\,, \qquad (A13)$$

which vanishes when the sum $V_C$ of the core interactions, $V_{1C}+V_{3C}$, is constant over the range $R_{13}$ of interaction of $V_{13}$. The basic impulse expression (A8) is, in general, therefore valid when $V_C$ varies only slowly (and need not be necessarily small) over $R_{13}$, i.e., the binding is quasiclassical and the force $\sim e^2/n^3(l+\frac{1}{2})$ due to the core is small, in comparison to the *impulsive* force, $-\vec{\nabla}V_{13}$, due to the Rydberg electron-projectile $A$ interaction. This assumption implies condition (iv) of Sec. III, and is important in regulating the permissible changes in energy and angular momentum. It also regulates the energy variation of the (1-3) collision cross section—too rapid a variation as in the vicinity of a Ramsauer minimum or a negative-ion resonance is alien to the neglect of the energy imparted to 1 by the core during the collision [cf. discussion following Eqs. (2.5) and (2.28)].

(b) Reduction of (A8) to the impulse expression (A10) normally adopted originates from the assumption that the distortion effect of $V_{3C}$ on the motion of 3 while interacting with 1 is negligible. This assumption implies that 1 and 2 behave in the two-potential formula (A1) as separate and independent scatterers [cf. conditions (i) and (ii) of Sec. III]. Although multiple scattering, which arises in $\langle\chi_f^-|t_{13}|\chi_i^+\rangle$ from $V_{3C}$ of (A3) with (A4), can now be neglected, the impulse approximate $\langle\Phi_f|t_{13}^{\rm imp}|\Phi_i\rangle$ can be used for $\langle\Phi_f|t_{13}|\Phi_i\rangle$ in multiple scattering sequences. If, in addition, (2-3) distortion is neglected in the first term of (A10), as is the custom, the contribution to (A10) from (3-$C$) collisions is real such that (A11) provides an *upper limit* to any collision process which satisfies specified criteria for validity of the impulse approximation.

(c) Inelastic transitions in $B$ are prohibited in *direct* encounters with the core (which is assumed to be inertial) whether or not core distortion is included. The formulation of the impulse model underlines (1-3) encounters as providing the basic mechanism and includes inelastic effects from (2-3) encounters only indirectly insofar as they affect (1-3) encounters, as in (A8). This provision may not furnish a full description particularly at thermal energies. The impulse treatment can, however, be generalized so as to cover arbitrary $M_2$ (rather than infinite $M_2$ as assumed in the present derivation) and hence include inelastic collisions via direct collision with the noninertial core. This involves replacing $V_{3C}(\vec{r}_3)$ in (A1)–(A4) by $V_{3C}(\vec{r}_3+(M_1/M)\vec{r}_1)$. The separation (A3) in $\vec{r}_1$ and $\vec{r}_3$ variables is, however, no longer possible, and approximate procedures must be used to obtain $\chi_i^{\pm}$. When distortion—the second term of (A3)—can be neglected, then, by expanding $V_{3C}$ as in (5.10) and by proceeding as before we obtain, in place of the first term of (A10),

$$T_{fi}^{2\text{-}3}(\vec{k}_3,\vec{k}_3')=\langle\phi_f(\vec{r}_1)\exp(i\vec{k}_3'\cdot\vec{r}_3)|V_{3C}(\vec{r}_3+(M_1/M)\vec{r}_1)|\phi_i(\vec{r}_1)\exp(i\vec{k}_i'\cdot\vec{r}_3)\rangle$$
$$=\langle\exp(i\vec{k}_3'\cdot\vec{r}_3)|V_{3C}(\vec{r}_3)|\exp(i\vec{k}_3\cdot\vec{r}_3)\rangle\delta_{fi}+(M_1/M)\langle\phi_f|\vec{r}|\phi_i\rangle\langle\exp(i\vec{k}_3'\cdot\vec{r}_3)|\vec{\nabla}V_{23}(\vec{r}_3)|\exp(i\vec{k}_3\cdot\vec{r}_3)\rangle \qquad (A14)$$

for the contribution of (2-3) collisions to inelastic transitions. The structure of (A14) bears a marked similarity to that obtained in Sec. V, particularly when the integral over the force $(-\vec{\nabla}V_{23})$ can be replaced by the momentum change $(M_2\vec{v})$ as in (5.23).

The above requirements (a)–(c) can be well satisfied for $A$-$B(n)$ collisions at sufficiently high $n$ and incident speeds $v_3\gg v_1$. However, for $v_1\gg v_3$, conditions associated with (a)–(c) may be seriously violated (cf. Sec III and VI).

There are two distinct classes of interactions which justify the replacement of $t_{13}$ by $t_{13}^{\rm imp}$. One class is associated with the "quasiclassical" condition (a) which is sufficient for validity of (A8). The other class satisfies the weak-binding condition[34] that the kinetic energy $E_3$ of relative motion,

$$E_3\gg(\Delta E_c)\sim\langle\psi_n(r)|V_{1C}(\vec{r})|\psi_n(\vec{r})\rangle,\ \langle\psi_n(\vec{r}_1)|-\frac{h^2}{2M_{12}}\nabla_1^2|\psi_n(\vec{r}_1)\rangle\approx|\epsilon_n| \qquad (A15)$$

is large relative to each of the averaged potential energy (or energy shift $\Delta E_c$ due to the core) and kinetic energy, taken, in general, of the order of the binding energy $|\epsilon_n|$. The impulse replacement may then still be valid in situations where the weak-binding condition (A15) is severely violated. According to Goldberger and Watson,[34] for example, the impulse replacement is satisfied for the case (A15) in which the contribution to (A8) arises mainly from on the energy shell, when the fractional error,

$$\frac{f_{13}}{\lambda\!\!\!^{-}}\,\frac{\Delta E_c}{\hbar}\left(\frac{\hbar}{E_3}+Q\right)\ll 1\,, \qquad (A16)$$

where $\lambda\!\!\!^{-}$ is the reduced wavelength $(\sim k_3^{-1})$ of the projectile particle 3 and where $f_{13}$ is the scattering amplitude for free Rydberg-electron 1-projectile 3 collisions, with time delay $Q$. In the absence of resonant scattering $(Q=0)$,

$$\frac{f_{13}}{\lambda\!\!\!^{-}}\,\frac{|\epsilon_n|}{E_3}\ll 1 \qquad (A17)$$

which is less stringent than the weak-binding requirement (A15) above, by allowing the possibility that $f_{13}$ can be greater than or less than $\lambda\!\!\!^{-}$.

In summary, therefore, the impulse replacement $t_{13}$ by $t_{13}^{imp}$ is valid for the two distinct situations of quasiclassical potentials $(V_{1C} + V_{3C})$ and of weak binding. While the case $v_1 \gg v_3$ may satisfy the quasiclassical condition, the neglect of distortion by the core in the incident wave as assumed in (A10) and the assumption of core inertiality may, however, be unrealistic. The more basic expression (A8) must then be used, and/or reformulation as in Sec. V or in (A14) must be performed.


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