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Improvement in the First Born Theory of Electron Scattering by Molecular Systems. I. Theory*

James M. Peek
Sandia Laboratories, Albuquerque, New Mexico 87115
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The asymptotic or Bethe expansion of the first Born cross section, for large magnitude of the initial collision velocity V, is considered for a particular electronic excitation of a molecular target. The sum of the Bethe cross section over the complete set of wave functions for nuclear motion in the final electronic state is shown to be asymptotic to the analogous sum of the Born cross section over states allowed by energy conservation. The closure relation is then used to simplify the matrix elements which define the Bethe cross section without further approximation. The advantages gained by this approach are demonstrated in the following paper by the treatment of a particular example.

I. INTRODUCTION

Accurate calculations in the first Born approximation for the scattering of fast electrons by various targets are becoming available in ever increasing numbers.[1] The reason for this belated activity with such a simple theory is primarily due to the paucity of accurate functions describing the target, especially excited state functions, and the nontrivial computational problems encountered once these functions are available. The treatment of molecular targets is further complicated by the decrease in symmetry, increase in the number of degrees of freedom, and increase in the number of individual excitation events that must be considered for the case of inelastic scattering. As a result, there are available very few calculations[2] that do not introduce approximations in addition to those occasioned by the first Born theory.

A summary of two popular approximations is given by Craggs and Massey.[3] After assuming the Born-Oppenheimer (BO) separation of electronic and nuclear variables for the target molecule, the additional assumption is made that the rotational and vibrational modes for the final state (i.e., the eigenstate of the target after scattering has taken place) are not coupled. The cross section is then summed over the final rotational modes. If the sum is extended to obtain a closure property for the rotational functions alone and if energy conservation requirements are ignored, one obtains some simplification in the first Born matrix element.[4] The extension of the sum over rotational functions to obtain closure is not, in general, compatible with the closure property possessed by the final rotation-vibration eigenstates. This will be called the C-M (Craggs and Massey) approximation and will be discussed in more detail in the following paper. Further simplification ensues by assuming the electronic Born matrix element, see Eq. (10), is a slowly varying function of the internuclear distance.[3] The total cross section now involves a Born matrix element for a given internuclear configuration, suitably averaged over spatial orientations, and modified by the well-known Franck-Condon factor.[3] This latter result has numerical difficulties only slightly more involved than the atomic target case and has been used for a number of studies.[5] Certain instances are known where the Franck-Condon approximation gives large errors[6,7] and recent work with optical phenomena questions this approach.[8] We are interested in approaches with fairly general validity so this approximation will not be given further attention.

Another simplification of the molecular scattering problem has been found useful for treating scattering events leading to electronic excitation. After assuming the Born-Oppenheimer separation of nuclear and electronic variables for the target, the cross section is summed over the complete set of final rotational-vibrational eigenfunctions of the target. The sum is performed by ignoring the dependence of the excitation energy ΔE on the final rotation-vibration state so the closure property of the final rotation-vibration functions can be used. In this way one obtains once again a computational problem only slightly more difficult than that found for the atomic target case. Typical examples of this approach can be found as shown.[6,9] In defense of this approach, one notes that the sum over final rotational-vibrational modes makes use of a rigorously correct closure relationship. This theory has also been tested by comparison with experiment for at least one system[7,10] and agreement typical of that found for other comparisons with first Born theory was obtained. This approach can be criticized because of the loss of energy conservation, usually maintained in the first Born approximation, and one only obtains data which depend on the initial electronic-rotational-vibrational states and final electronic state. Hence some of the rich structure expected, and found, from the resolution of rotational-vibrational modes in the final electronic state is lost.

In this paper we reconsider the approach described in the preceding paragraph which will be referred to as the "old closure approximation." The asymptotic expansion, for large magnitude of the collision velocity V, of the first Born total cross section is summed over the complete set of final rotational-vibrational eigenfunctions of the target. This sum over the asymptotic cross section is proven to be rigorously asymptotic to the sum of the Born cross section over final rotational-vibrational modes allowed by energy conservation. The closure property of the final rotational-vibrational functions is then used to simplify the asymptotic cross section without any further approximation. The major objection to the old closure theory, the loss of energy conservation, is thus removed. The development of this asymptotic closure cross section is presented in Sec. II. Only the first two terms of the asymptotic series are considered, analogous to the so-called Bethe cross section,[11] but extension to higher-order terms may be possible.

Detailed analysis of the asymptotic remainder term for the Bethe cross section is given in Sec. III. The asymptotic expansion of the sum of the Born cross section over discrete states of nuclear motion is shown to be the same sum over the Bethe cross section. The asymptotic expansion of the integration of the Born cross section over continuum modes of nuclear motion does not appear to be given by the same integration[12] over the Bethe cross section, if this integration is extended to obtain closure. Since the simplifications due to closure over various matrix elements usually are considerable, it is important to establish whether or not closure over the Born cross section has an asymptotic expansion. This problem is treated in Sec. IV. Conditions on the Born matrix element are found which are sufficient to prove that two terms in the asymptotic expansion of closure over the Born cross section are given by closure over the Bethe cross section.

Some concluding remarks are given in Sec. V.

Certain generalizations of the above conclusion seem possible. The proof probably holds for a molecular target with any number of nuclei, although only diatomic targets are discussed. The relationship between the closure argument given here and closure over electronic degrees of freedom will be made apparent by the discussion in Sec. II. Sections III and IV also comment on the changes necessary to treat the electronic case.

The ideas leading to the asymptotic closure theory are far from new, and the present work owes much to the paper by Inokuti, Kim, and Platzman[13] for inspiration. In addition, Bethe[11] has derived an asymptotic closure cross section for electron scattering by hydrogenic targets, and this particular problem has recently received further attention.[14] References 11 and 13, plus subsequent application,[15] deal with closure arguments for the electronic degrees of freedom while we are concerned with a given electronic transition with closure arguments applied to the rotation-vibration states. Also, with an exception to an appeal to the results available in closed form for hydrogenic targets,[11] the asymptotic nature of closure over the Bethe cross section has not been established.[16] Hence we believe the present application is new, the general error analysis is new, and that molecular scattering systems represent an area of very wide applicability for these ideas. The last point is due to the existence of a large body of experimental data that do not resolve the final rotational-vibrational structure. Also as interest develops in systems that have unusual initial rotational-vibrational populations, it is useful to have available a treatment that is both independent of simplifying assumptions about the structure of the target and that is reasonably easy to pursue.

II. CLOSURE AND THE BETHE CROSS SECTION

The first Born total cross section can be written

$$Q(N,N') = \mu^2 k_f (4\pi^2\hbar^4 k_i)^{-1} \int d\Omega(\hat{k}_f)\, |\langle \Psi(N') \exp(i\vec{k}_f \cdot \vec{r})|\, V_{\text{int}}\, |\Psi(N) \exp(i\vec{k}_i \cdot \vec{r})\rangle|^2 \tag{1}$$

for the scattering of a structureless charged particle by a target having eigenstates N and N' before and after collision. Obviously, we are ignoring the possibility of exchange between the incident and target particles. The following definitions should be noted: μ is the reduced mass for the electron plus target system and may be approximated by the electron mass for the case of electron scattering, k_i and k_f are the magnitudes of the momentum vectors of the incident particle before and after collision, $d\Omega(\hat{k}_f)$ is the element of solid angle for the scattered particle, the plane waves are the first Born functions describing the motion of the incident particle, and the interaction potential V_{int} between the target and incident particle, which is assumed to be an electron, is

$$V_{\text{int}} = -\sum_i e^2 Z_i / |\vec{r} - \vec{\rho}_i| + \sum_j e^2 / |\vec{r} - \vec{r}_j| . \tag{2}$$

Here e is the electron charge, Z_i is the charge number of the ith nucleus in the molecular system, the index i numbers the nuclei in the target, the index j numbers the target electrons, $\vec{\rho}_i$ is a vector, in a frame whose origin is at the center of mass of the nuclei, to the ith nucleus, $\vec{r}_j$ is a vector to the jth electron, and $\vec{r}$ is a vector to the incident particle. Atomic units will be used throughout the remainder of this paper. Following the usual development of the first Born total cross section by introducing the momentum transfer vector $\vec{K}=\vec{k}_i-\vec{k}_f$ and utilizing Bethe's integral[11]

$$\int d\vec{r}\exp(i\vec{K}\cdot\vec{r})/|\vec{r}-\vec{r}\,'|=4\pi K^{-2}\exp(i\vec{K}\cdot\vec{r}\,'),$$

Eq. (1) becomes

$$Q(N,N')=4V^{-2}\int d\Phi\int_{K_0}^{K_1}dK\,K^{-3}|E(N,N';\vec{K})|^2, \tag{3}$$

where V is the initial electron velocity, Φ is the azimuthal angle for $\vec{K}$, K_0 and K_1 are the minimum and maximum magnitudes of $\vec{K}$ allowed by energy conservation and

$$E(N,N';\vec{K})=\langle\Psi(N')|\sum_j\exp(i\vec{K}\cdot\vec{r}_j)-\sum_i Z_i\exp(i\vec{K}\cdot\vec{\rho}_i)|\Psi(N)\rangle. \tag{4}$$

Excluding the rather unique case of elastic scattering by a charged target, we proceed to develop the Bethe cross section by noting that the expansion

$$|E(N,N';\vec{K})|^2=\sum_{j=1}^{\infty}A_j(N,N';\hat{K})K^{2j} \tag{5}$$

can be made for small K. The unit vector $\hat{K}$ orients the momentum transfer vector $\vec{K}$ in the space-fixed coordinate system. Assuming the transition $N\rightarrow N'$ involves a fixed, and bounded, excitation energy ΔE, the Bethe cross section is easily shown to be (see, for example, the Appendix of the first article cited in Ref. 1 or Ref. 17)

$$Q(N,N')=4V^{-2}\int d\Phi[A_1(N,N';\hat{K})\ln V+B(N,N';\hat{K})]+O(\Delta E/V^4),\quad \text{as } V\rightarrow\infty. \tag{6}$$

Here A_1 is related to the dipole moment associated with the transition and

$$B(N,N';\hat{K})=-A_1(N,N';\hat{K})\ln\Delta E+\int_0^1 dK\,K^{-3}\{|E(N,N';\vec{K})|^2-K^2A_1(N,N';\hat{K})\}+\int_1^{\infty}dK\,K^{-3}|E(N,N';\vec{K})|^2. \tag{7}$$

As indicated by Eq. (6), the Bethe cross section is an asymptotic expansion of the Born cross section which includes terms like $O(V^{-2})$ for large V.

The motivation for writing the cross section in the asymptotic form of Eq. (6) is the importance of small momentum transfers K for certain scattering events. The expansion used in Eq. (5) allows us to add and subtract the most important term for small K, A_1K^2, from the square of the Born matrix element Eq. (4). The dipole matrix element is thereby isolated and Eq. (6) clearly displays the importance of A_1 for large V. The relationship between electron scattering and optical transitions for dipole-allowed events is also made clear by Eq. (6). In the event $N\rightarrow N'$ represents a dipole forbidden event $A_1\equiv 0$; however, the above equations and the following analysis are still correct.

Equations (5)–(7) represent the Bethe cross section and are nothing more than a generalization to molecules of the matrix elements occurring in Miller and Platzman's work[17] on atomic target systems.[13] However, it is worth emphasizing the compact nature of Eq. (6) for the total cross section, due to the fact that A_1 and B are independent of the collision velocity V, and the importance of reducing computational effort so one can give appropriate attention to the large number of degrees of freedom signified by N and N'.

Further progress with Eqs. (5)–(7) depends on the success of the Born-Oppenheimer approximation. In addition, we specialize the discussion to targets consisting of diatomic molecular systems. This is not necessary but it does simplify the notation while maintaining the more important properties of general molecular targets. The Born-Oppenheimer function is written as[18]

$$\Psi(N)=\psi_n(\cdots\vec{r}_j\cdots;\vec{R})F_\omega(\vec{R}). \tag{8}$$

The symbol n signifies the set of quantum numbers necessary to completely describe an eigenstate of the electronic Hamiltonian resulting from the BO approximation. The symbol ω has the same meaning with respect to the Hamiltonian for the relative motion of the nuclei. The function ψ_n describes the electronic motion in the state n for some value of the internuclear vector, $\vec{R}=\vec{\rho}_1-\vec{\rho}_2$, and F_ω describes the internuclear motion.

Substituting Eq. (8) into Eq. (4)

$$E(n\omega, n'\omega'; \vec{K}) = \int d\vec{R}\, F^*_{\omega'}(\vec{R})\, \epsilon(\vec{K}, \vec{R})\, F_\omega(\vec{R}) \tag{9}$$

is found, where

$$\epsilon(\vec{K}, \vec{R}) \equiv \int d\tau\, \psi^*_{n'}(\cdots \vec{r}_j \cdots ; \vec{R})\left[\textstyle\sum_j \exp(i\vec{K}\cdot\vec{r}_j) - \sum_i Z_i \exp(i\vec{K}\cdot\vec{\rho}_i)\right]\psi_n(\cdots \vec{r}_j \cdots ; \vec{R}) \tag{10}$$

and the volume element $d\tau$ stands for all electronic degrees of freedom, including spin. The relationship

$$A_1(n\omega, n'\omega'; \hat{\vec{K}}) = \left|\int d\vec{R}\, F^*_{\omega'}(\vec{R})\, D(\hat{K}, \vec{R})\, F_\omega(\vec{R})\right|^2, \tag{11}$$

where

$$D(\hat{K}, \vec{R}) \equiv \int d\tau\, \psi^*_{n'}(\cdots \vec{r}_j \cdots ; \vec{R})\left[\textstyle\sum_j (i\vec{K}\cdot\vec{r}_j) - \sum_i Z_i (i\hat{K}\cdot\vec{\rho}_i)\right]\psi_n(\cdots \vec{r}_j \cdots ; \vec{R}), \tag{12}$$

follows from Eq. (5), Eq. (9), and the orthonormal properties of the molecular functions having the form of Eq. (8). Substituting Eqs. (9) and (11) into Eq. (7) provides the definition of B when the form of the molecular eigenfunction is given by Eq. (8). Equation (10) is the analog to the electronic Born matrix element found for atomic targets. Note the relationship

$$\lim_{K\to 0} K^{-2}|\epsilon(\vec{K}, \vec{R})|^2 = |D(\hat{K}, \vec{R})|^2, \quad \text{when} \quad n \neq n'. \tag{13}$$

We now proceed to develop the closure cross section for the case in which electronic excitation has taken place, $n \neq n'$. Hence the resulting asymptotic closure cross section will be for exciting the target from the initial state $n\omega$ to the totality of states for nuclear motion ω' in the final electronic state n'. The assumed form for the molecular eigenfunctions, Eq. (8), gives rise to the closure property

$$\sum_{\lambda'}^{s} F^*_{\lambda'}(\vec{R}')F_{\lambda'}(\vec{R}) + \int d\vec{k}\, F^*_{\vec{k}}(\vec{R}')F_{\vec{k}}(\vec{R}) = \delta(\vec{R} - \vec{R}'), \tag{14}$$

which results from completeness of the vibrational and rotational eigenfunctions in the state n'. The quantity ω' has been replaced by λ' for the discrete states and by $\vec{k}$ for the continuum states. In general, λ' could have an infinite number of values, but for diatomic molecules the sum is known to consist of a finite number; this is implied by the presence of the letter s over the summation sign. The range of the magnitude of $\vec{k}$ is from zero to infinity. The implication of Eq. (8) is that the functions F_ω are solutions to a second-order partial differential equation where the potential occurring in that equation is the fixed nuclear electronic eigenvalues either with or without the addition of the so-called adiabatic correction terms. Summing the asymptotic cross section, Eq. (6), over all λ' and $\vec{k}$ reduces to just the consideration of the coefficients A_1 and B and the function $O(\Delta E/V^4)$. Using the notational convention

$$\left\{\sum_{\lambda'}^{s} + \int d\vec{k}\right\} A_1(n\omega, n'\omega'; \hat{K}) = A_1(n\omega, n'; \hat{K}) \tag{15}$$

and similarly for other functions, the equalities

$$A_1(n\omega, n'; \hat{K}) = \int d\vec{R}\, |F_\omega(\vec{R})|^2\, |D(\hat{K}, \vec{R})|^2 \tag{16}$$

and

$$\begin{aligned} B(n\omega, n'; \hat{K}) = {} & \int d\vec{R}\, |F_\omega(\vec{R})|^2 \Big\{ \int_0^1 dK\,K^{-3}\left[|\epsilon(\vec{K}, \vec{R})|^2 - K^2|D(\hat{K}, \vec{R})|^2\right] \\ & + \int_1^\infty dK\,K^{-3}|\epsilon(\vec{K}, \vec{R})|^2 \Big\} - \Big\{\sum_{\lambda'}^{s} + \int d\vec{k}\Big\} A_1(n\omega, n'\omega'; \hat{K}) \ln\Delta E \end{aligned} \tag{17}$$

are easily established. The asymptotic closure cross section is

$$\Big\{\sum_{\lambda'}^{s} + \int d\vec{k}\Big\}\, 4V^{-2}\int d\Phi\left[A_1(N, N', \hat{K})\ln V + B(N, N', \hat{K})\right] \equiv \tilde{Q}(n\omega, n') = 4V^{-2}\int d\Phi\left[A_1(n\omega, n'; \hat{K})\ln V + B(n\omega, n'; \hat{K})\right]. \tag{18}$$

It is extremely important to note that it is not possible to state that $\tilde{Q}$ is an asymptotic expansion from the analysis that leads to Eq. (6). This is most easily seen by observing that it was necessary to fix the excitation energy ΔE at a finite value to give meaning to the function $O(\Delta E/V^4)$ appearing in Eq. (6) and that the use of the closure relationship, Eq. (14), requires the range of ΔE to include infinity. Section III contains a detailed discussion of this point. The additional analysis given in Sec. IV proves that

$$\Big[\sum_{\lambda'}^{s}+\int_0^{\infty}k^2dk\int d\Omega(\hat{k})\Big]\Big\{4V^{-2}\int d\Phi[A_1(N,N';\hat{K})\ln V+B(N,N,\hat{K})]\Big\}$$
$$-\Big[\sum_{\lambda'}^{s}+\int_0^{k^*}k^2dk\int d\Omega(\hat{k})\Big]Q(N,N')=o(\ln V/V^{2+\gamma}) \tag{19}$$

as V becomes large, with $\gamma>0$, provided that s is finite, that Eq. (5) is valid, that $\Delta E>0$, and that $|E(N,N';\vec{K})|^2$ can be bounded by a certain function. (This function is given in Sec. IV.) In Eq. (19) k is the magnitude of the momentum associated with the energy above the dissociation limit of the n' electronic state, k^* is the maximum value of k allowed by energy conservation, and $d\Omega(\hat{k})$ is the element of solid angle for $\vec{k}$.

The meaning of Eq. (19) can be stated in the following way. The quantity $\tilde{Q}(n\omega,n')$ defines two terms in an asymptotic expansion of the result of summing $Q(N,N')$ over all modes of nuclear motion in the final electronic state allowed by energy conservation. This follows from A_1 being a coefficient for the term $O(\ln V/V^2)$, B being a coefficient for the term $O(V^{-2})$, and Eq. (19), which shows that the next term is $o(V^{-2})$ as V becomes large.[12] Hence our claim for Eq. (18) is established. It seems likely that higher terms in this asymptotic expansion could be found, but this point is not explored here.

The asymptotic expansion of closure over the Born cross section seems to give similar results no matter what degrees of freedom are being considered, as long as the closure property can be justified. Note the close resemblance between the asymptotic expansion found here for closure over $Q(N,N')$ and σ_{tot} of Ref. 13. The connection with Bethe's work[11] is more difficult because of his specialization to hydrogenic targets and additional approximations.[16] We will attempt to amplify this relationship to closure over electronic degrees of freedom by indicating how the analysis given below can be used to prove that σ_{tot} is also an asymptotic expansion.

III. THE CLOSURE ARGUMENT

The relationship between the excitation energy ΔE and the initial and final states must be given. If the initial eigenenergy is $E(N)$ and the energy of a discrete state of nuclear motion in the n' electronic state is $E(n'\lambda')$ then

$$\Delta E(\lambda')\equiv E(n'\lambda')-E(N)>0 \tag{20}$$

defines the excitation energy. If the state of nuclear motion in n' is in the continuum, a dissociating state, and the energy between $E(N)$ and the dissociation limit of the state n' is $I(>0)$, then

$$\Delta E(k)=I+k^2/2m>0 \tag{21}$$

is the energy difference. The quantity m is the reduced mass of the target and $k^2/2m$ is the kinetic energy of the dissociating fragments with respect to the center of mass of the target.

Equation (6) can be written as

$$\tilde{Q}(N,n'\omega')-Q(N,n'\omega')=O(\Delta E(\omega')/V^4), \tag{22}$$

where

$$\tilde{Q}(N,n'\omega')=4V^{-2}\int d\Phi\,\Big\{A_1(N,n'\omega';\hat{K})\int_{\Delta E(\omega')/V}^{1}dK\,K^{-1}+\int_0^1 dK\,K^{-3}[|E(N,n'\omega';\vec{K})|^2-K^2A_1(N,n'\omega';\hat{K})]$$
$$+\int_1^{\infty}dK\,K^{-3}|E(N,n'\omega';\vec{K})|^2\Big\}. \tag{23}$$

From the definition of I, the relationship $I\geqslant\Delta E(\lambda')$ is obvious. Hence if we sum Eq. (22) over all λ',

$$\sum_{\lambda'}^{s}[\tilde{Q}(N,n'\lambda')-Q(N,n'\lambda')]=O(I/V^4),\qquad \text{as } V\to\infty, \tag{24}$$

follows from the properties of order relations,[12] provided s is finite. This proves the statement made in Sec. II that the asymptotic expansion for the sum of $Q(N,N')$ over λ' is given by the sum of $\tilde{Q}(N,N)$ over λ'.

A similar argument can be given for the sum over discrete electronic states. In this case, the sum is over n', with fixed rotation-vibration modes, and I is interpreted as the ionization energy. Since n' has an infinite range, we presume there exists a finite n^* such that

$$\tilde{Q}(N, n'\lambda') - Q(N, n'\lambda') = (n')^{-1-a}[\tilde{Q}(N, n^*\lambda') - Q(N, n^*\lambda')] \tag{25}$$

is true for all $n' > n^*$, where $a > 0$. A bound similar to Eq. (24) can then be established for the sum of Eq. (22) over all discrete n'. Note that $\Delta E > 0$ is required for the existence of $Q(N, N')$ if $A_1(N, N'; \hat{K}) \neq 0$. Hence the term $n' = n$ must be omitted from the n' sum. [Equation (25) corresponds to the n^{-3} law for hydrogenic systems if $a = 2$.]

Integrating Eq. (22) over all $\vec{k}$,

$$\int_0^\infty k^2 dk \int d\Omega(\hat{k}) \{\tilde{Q}(N, n'\vec{k}) - Q(N, n'\vec{k})\} = O\{4\pi V^{-4} \int_0^\infty k^2 dk \Delta E(k)\} \tag{26}$$

for large V, results from the property of order relations.[12] The integral in the order relation is divergent; see Eq. (21) for the definition of $\Delta E(k)$. This is certainly correct, but it does not allow the conclusion that $\tilde{Q}(N, n')$ is asymptotic to $Q(N, n')$ for large V. The asymptotic property of $\tilde{Q}(N, n')$ is developed in Sec. IV. If one identifies k with the magnitude of the momentum of the ionized electron(s) and notes the discussion in the preceding paragraph, a result identical to Eq. (26) can be established for the integration over the continuum of the target electrons.

We close this section with one further remark: For some value of V there is a maximum value k^* such that $Q(N, n'\vec{k})$ is zero for all $k > k^*$. The quantity k^* is determined from the condition $K_0 = K_1$, which is a statement of energy conservation. The magnitude of the initial momentum is $k_i = |\mu\vec{V}/\hbar|$, where μ is the reduced mass of the target plus incident electron and $\vec{V}$ is the initial collision velocity. As mentioned in Sec. II, μ is approximated by the electron mass and atomic units are being used, hence $k_i = V$. From the usual definitions,[19]

$$k_f^2 = V^2 - 2\Delta E(k), \quad K_0 = k_i - k_f, \quad \text{and} \quad K_1 = k_i + k_f.$$

Hence energy conservation requires $k_f = 0$, and from Eq. (21) we find $k^* = [m(V^2 - 2I)]^{1/2}$. From the above comments, the left side of Eq. (26) can be rewritten as

$$\int_0^\infty k^2 dk \int d\Omega(\hat{k}) \{\tilde{Q}(N, n'\vec{k}) - Q(N, n'\vec{k})\} = \int_0^\infty dk[\int d\Omega(\hat{k}) k^2 \tilde{Q}(N, n'\vec{k})] - \int_0^{k^*} dk[\int d\Omega(\hat{k}) k^2 Q(N, n'\vec{k})]. \tag{27}$$

This form for the integral over k is introduced for the sake of convenience in the following section. Since we are interested in the behavior of the Born cross section for large V, it is tacitly assumed that V is such that no values of λ' are forbidden by energy conservation requirements.

IV. PROOF THAT $\tilde{Q}(N,n')$ IS ASYMPTOTIC TO $Q(N,n')$

If $\tilde{Q}(N, n')$ is to be two terms in an asymptotic expansion of $Q(N, n')$ it is necessary[12] to prove that the difference in Eq. (26) behaves like $o(V^{-2})$ for large V. The analysis given in Sec. III gave a much weaker result; the asymptotic character of $\tilde{Q}(N, n')$ is established in this section by further analysis of Eq. (26). An adaptation of a technique used to solve a slightly different problem[20] will be used.

To simplify the notation, the definitions

$$f(K, k) \equiv \int d\Phi \int d\Omega(\hat{k}) k^2 K^{-3} |E(N, n'\vec{k}; \vec{K})|^2, \qquad A_1(k) \equiv k^2 \int d\Phi \int d\Omega(\hat{k}) A_1(N, n\vec{k}; \hat{K})$$

are introduced. From Eq. (3),

$$\int_0^{k^*} k^2 dk \int d\Omega(\hat{k}) Q(N, n'\vec{k}) = 4V^{-2} \int_0^{k^*} dk \int_{K_0}^{K_1} dK f(K, k), \tag{28}$$

and from Eq. (23),

$$\int_0^\infty k^2 dk \int d\Omega(\hat{k}) \tilde{Q}(N, n'\vec{k}) = 4V^{-2} \int_0^\infty dk \{A_1(k) \int_{\Delta E(k)/V}^1 dK K^{-1} + \int_0^1 dK[f(K, k) - A_1(k) K^{-1}] + \int_1^\infty dK f(K, k)\}, \tag{29}$$

are easily established from the above definitions.

It will be shown that

$$\int_0^\infty dk[\int d\Omega(\hat{k}) k^2 \tilde{Q}(N, n'\vec{k})] - \int_0^{k^*} dk[\int d\Omega(\vec{k}) k^2 Q(N, n'\vec{k})] = o(V^{-2}) \tag{30}$$

as V becomes large, provided the expansion in Eq. (5) has a finite radius of convergence around $K = 0$, and that the (finite positive) numbers A, B, and C, which are independent of K and k, exist such that

$$A_1(k) \leqslant A, \qquad k \leqslant 1, \tag{31}$$

$$\leqslant Ak^{-\alpha}, \qquad k \geqslant 1, \tag{32}$$

$$|f(K,k) - A_1(k)K^{-1}| \leqslant BK, \qquad k \leqslant 1, \quad K \leqslant 1, \tag{33}$$

$$\leqslant BKk^{-\alpha}, \qquad k \geqslant 1, \quad K \leqslant 1, \tag{34}$$

$$f(K,k) \leqslant CK^{-\beta}, \qquad k \leqslant 1, \quad K \geqslant 1, \tag{35}$$

$$\leqslant CK^{-\beta}k^{-\alpha}, \qquad k \geqslant 1, \quad K \geqslant 1. \tag{36}$$

The small K behavior is chosen to be consistent with Eq. (5) and the small k behavior is simply that $A_1(k)$ and $f(K,k)$ be bounded from above. The condition that the Bethe cross section be asymptotic to the Born cross section for a given excitation event, Eq. (6), requires $\beta > 1$. If the Born cross section for all continuum events is to have an asymptotic expansion like the Bethe cross section, $\alpha > 1$ is necessary. Hence the condition $\alpha > 1$ and $\beta > 1$ are employed in the following analysis. From these conditions and Eqs. (31)–(36),

$$|f(K,k) - A_1(k)K^{-1}| \leqslant (C+A)K^{-1}k^{-\alpha}, \quad k \geqslant 1, \quad K \geqslant 1, \tag{37}$$

can be deduced.

An outline of the proof of Eq. (30), using the conditions stated by Eqs. (31)–(36), follows. From Eqs. (28), (29), and (30)

$$\int_0^\infty dk[\int d\Omega(\hat{k})k^2\tilde{Q}(N,n'\vec{k})] - \int_0^{k^*} dk[\int d\Omega(\hat{k})k^2 Q(N,n'\vec{k})] = 4V^{-2}[E_a + E_b + E_c] \tag{38}$$

can be written if

$$E_a = \int_0^{k^\dagger} dk\{A_1(k)\ln[VK_0/\Delta E(k)] + \int_0^{K_0} dK[f(K,k) - A_1(k)K^{-1}] + \int_{K_1}^\infty dKf(K,k)\}, \tag{39}$$

$$E_b = \int_{k^\dagger}^{k^*} dk\{A_1(k)\ln[VK_0/\Delta E(k)] + \int_0^{K_0} dK[f(K,k) - A_1(k)K^{-1}] + \int_{K_1}^\infty dKf(K,k)\}, \tag{40}$$

and

$$E_c = \int_{k^*}^\infty dk\{\int_0^{\Delta E(k)/V} dK[f(K,k) - A_1(k)K^{-1}] + \int_{\Delta E(k)/V}^\infty dKf(K,k)\}. \tag{41}$$

The quantity $k^\dagger$ has been introduced for computational convenience and is the value of k such that $K_0 = 1$. From the energy conservation conditions given near the end of Sec. III,

$$k^\dagger = [m(2V - 2I - 1)]^{1/2}.$$

Choosing $\frac{1}{2}(\alpha - 1) = \beta - 1 = \gamma > 0$, the relationships

$$E_a = O(V^{-\gamma}), \tag{42}$$

$$E_b = O(V^{-\gamma}\ln V), \tag{43}$$

and
$$E_c = O(V^{-2\gamma}\ln V), \tag{44}$$

as V becomes large, will be established. Hence

$$\int_0^\infty dk[\int d\Omega(\hat{k})k^2\tilde{Q}(N,n'\vec{k})] - \int_0^{k^*} dk[\int d\Omega(\hat{k})k^2 Q(N,n'\vec{k})] = O(V^{-2-\gamma}\ln V) \tag{45}$$

as V becomes large. This establishes Eq. (30) and shows that $\tilde{Q}(N,n')$ is asymptotic to $Q(N,n')$. A sharper result than Eq. (45) may be possible but, since we only require Eq. (30), there is no need to investigate this point.

Proof of Eq. (42): From Eq. (39) we see that $0 \leqslant k \leqslant k^\dagger$ is required where $k^\dagger = [m(2V - 2I - 1)]^{1/2}$. With this restriction $2\Delta E < V^2$ for $V > 1$. Hence

$$K_0 = k_i - k_f = V - (V^2 - 2\Delta E)^{1/2} = \Delta E/V + \Delta E^2/(2V^3) + \Delta E^3/(2V^5) + \dots \tag{46}$$

and $$K_1 = k_i + k_f = 2V - \Delta E/V - \Delta E^2/(2V^3) - \Delta E^3/(2V^5) - \cdots \tag{47}$$

are absolutely and uniformly convergent series. From the first term of Eq. (39) and Eqs. (31) and (32)

$$\int_0^{k^\dagger} dk\, A_1(k)\ln[VK_0/\Delta E(k)] \leqslant A\int_0^1 dk\ln[VK_0/\Delta E(k)] + A\int_1^{k^\dagger} dk\, k^{-\alpha}\ln[VK_0/\Delta E(k)]. \tag{48}$$

Substituting for K_0 from Eq. (46), expansion of the logarithmic function and term by term integration of the resulting series gives

$$\int_0^{k^\dagger} dk\, A_1(k)\ln[VK_0/\Delta E(k)] = O(V^{-\frac{1}{2}(1+\alpha)}), \quad \text{as } V\to\infty . \tag{49}$$

The second term of Eq. (39) is

$$\left| \int_0^{k^\dagger} dk \int_0^{K_0} dK[f(K,k) - A_1(k)K^{-1}]\right| \leqslant B\int_0^1 dk \int_0^{K_0} dKK + B\int_1^{k^\dagger} dk\, k^{-\alpha}\int_0^{K_0} dKK, \tag{50}$$

where Eqs. (33) and (34) have been used. Integration of Eq. (50) is elementary if Eq. (46) is used and

$$\left| \int_0^{k^\dagger} dk \int_0^{K_0} dK[f(K,k) - A_1(k)K^{-1}]\right| = O(V^{\frac{1}{2}(1-\alpha)}), \quad \text{as } V\to\infty , \tag{51}$$

results. Using Eqs. (35) and (36), the last term of Eq. (39) becomes

$$\int_0^{k^\dagger} dk \int_{K_1}^\infty dK f(K,k) \leqslant C\int_0^1 dk \int_{K_1}^\infty dK K^{-\beta} + C\int_1^{k^\dagger} dk\, k^{-\alpha}\int_{K_1}^\infty dK K^{-\beta}. \tag{52}$$

Using Eq. (47) it is a simple matter to establish

$$\int_0^{k^\dagger} dk \int_{K_1}^\infty dK f(K,k) = O(V^{1-\beta}), \quad \text{as } V\to\infty , \tag{53}$$

from Eq. (52).

Proof of Eq. (43): First, the ranges of integration in Eq. (40) are increased. For $k^\dagger \leqslant k \leqslant k^*$, with $k^\dagger = [2m(V - I - \frac{1}{2})]^{1/2}$ and $k^* = [m(V^2 - 2I)]^{1/2}$,

$$\Delta E(k)/V \geqslant (V - \tfrac{1}{2})/V. \tag{54}$$

Since k^* is the value of k that makes $k_f = 0$, it follows that

$$K_0 = k_i - k_f \leqslant k_i = V \tag{55}$$

for this range of k. Similarly,

$$K_1 = k_i + k_f \geqslant k_i = V. \tag{56}$$

From Eqs. (40) and (54)–(56)

$$E_b \leqslant \int_{k^\dagger}^{k^*} dk\, \{A_1(k)\ln[V^2/(V - \tfrac{1}{2})] + \int_0^V dK|f(K,k) - A_1(k)K^{-1}| + \int_V^\infty dK f(K,k)\} . \tag{57}$$

The integrals over dk and dK are now uncoupled. Use of Eqs. (32), (37), (34), and (36) quickly result in

$$E_b = O(V^{\frac{1}{2}(1-\alpha)}\ln V), \quad \text{as } V\to\infty . \tag{58}$$

Proof of Eq. (44): From Eq. (41),

$$E_c \leqslant \int_{k^*}^\infty dk k^{-\alpha}\{B\int_0^1 dKK + (C+A)\int_1^{\Delta E(k)/V} dK K^{-1} + C\int_{\Delta E(k)/V}^\infty dK K^{-\beta}\} \tag{59}$$

follows from Eqs. (34), (36), and (37). The limit $\Delta E(k)/V$ in the last integral of Eq. (59) can be replaced by $(V - \frac{1}{2})/V$, but further simplification is not possible. Careful but elementary evaluation of Eq. (59) yields

$$E_c = O(V^{1-\alpha}\ln V), \quad \text{as } V\to\infty . \tag{60}$$

The only conditions placed on α and β were that they be greater than unity. We are then free to make the choice $\frac{1}{2}(\alpha - 1) = \beta - 1 = \gamma > 0$. From this and Eqs. (49), (53), and (60), Eqs. (42), (43), and (44) are established. This finishes the proof of Eq. (30).

V. CONCLUSIONS

The sum of the Born cross section over all rotational-vibrational states of the final electronic state, which are allowed by energy conservation, was shown to be given asymptotically to $O(V^{-2})$ by the sum of the Bethe cross section over the complete set of rotational-vibrational eigenfunctions. The only approximation needed in addition to the first Born approximation was the Born-Oppenheimer separation of nuclear and electronic variables. The proof does require the number of final discrete rotational-vibrational states to be finite, $\Delta E > 0$, a certain upper bound on $|E(N, n'\vec{k}; \vec{K})|^2$, and the existence of an expansion of $|E(N, n'\vec{k}; \vec{K})|^2$ around $K = 0$ with a first term involving the power K^2. A method for treating a case with an infinite number of final discrete states was given. The bounding function, discussed in Sec. IV, seems to introduce only very weak requirements on the Born matrix element for continuum events. Hence the asymptotic property of the closure sum over the Bethe cross section is a fairly general result. In particular, the case of closure over electronic degrees of freedom was discussed.

It proved possible to simplify all but one of the matrix elements defining $\tilde{Q}(n\omega, n')$ without further approximation by use of the closure relation. See Eqs. (16) and (17). Although these equations are left in an abstract form, we contend that $\tilde{Q}(n\omega, n')$ is a very practical cross section to evaluate. Excluding the last term of Eq. (17), the only data required are just those necessary to evaluate the old closure approximation cross section; that is, the electronic matrix element $|\epsilon(\vec{K}, \vec{R})|^2$ and the initial rotational-vibrational function $F_\omega(\vec{R})$. This exceptional term requires, in addition, the final state functions $F_{\omega'}(\vec{R})$ for the evaluation of $A_1(n\omega, n'\omega'; \hat{K})$. See Eq. (11). However, A_1 is a dipole matrix element, which is considerably easier to treat than $|E(NN'; \vec{K})|^2$. These points are made much more graphic by the specific example treated in the following paper.

One more useful characteristic of the asymptotic closure cross section should be mentioned. If the cross section for any part of the spectrum of $F_{\omega'}(\vec{R})$ is known, the cross section for the remaining part of the spectrum can be found by subtraction from the asymptotic closure cross section. This property will prove extremely useful in the following paper, where it becomes necessary to separate the discrete and continuum contributions for electron excitation of the $1s\sigma_g$-$2p\sigma_u$ transition in H_2^+.

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Improvement in the First Born Theory of Electron Scattering by Molecular Systems. II. Example of the $1s\sigma_g$-$2p\sigma_u$ Transition in H_2^+[†]

James M. Peek and Thomas A. Green

Sandia Laboratories, Albuquerque, New Mexico 87115

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The asymptotic closure cross section, derived in I of this series, is calculated for the $1s\sigma_g$-$2p\sigma_u$ excitation of H_2^+ by fast electrons. These data are compared with earlier treatments of this system which were based on a less rigorous theory. The earlier data are observed to be surprisingly accurate. The Bethe cross section for exciting discrete vibrational modes in the $2p\sigma_u$ orbital of H_2^+ is calculated. This cross section is then used, along with the asymptotic closure cross section, to generate the Bethe cross section for all continuum modes of nuclear motion in the $2p\sigma_u$ orbital of H_2^+. Two approximations are considered for this partitioning of the asymptotic closure cross section and they are not found to be, in general, very useful.

I. INTRODUCTION

The problem of electron-molecule scattering in first Born theory was discussed in the preceding paper[1] with the intention of developing a formula both convenient for computation and as free of additional approximations as is possible. The result, see Eqs. (16)–(18) of I, was somewhat specialized. First, the one additional assumption of the Born-Oppenheimer separation of nuclear and electronic variables was necessary. In addition, the cross section applied only to the sum of all rotational-vibrational modes in the final electronic state which could not be the same as the initial electronic state. Finally, the cross section is two terms in an asymptotic expansion of the first Born cross section for large magnitudes of the initial collision velocity V.

The "asymptotic closure cross section," as it was called in I, is applied here to the specific example of the $1s\sigma_g$-$2p\sigma_u$ transition in H_2^+. A large quantity of literature has already appeared on this particular system[2-7] and our purpose is not to add more but to display the advantages, as well as the disadvantages, of this approach. The hydrogen molecule ion is especially suited for this exercise since theoretical details of its structure are either well known or accessible through relatively simple numerical processes. Hence our goal of evaluating the first Born cross section without further approximation is most easily attained for this target. Experimental studies[8] of this system have also provided motivation for developing the present approach. They have demonstrated beyond doubt that the proton production cross section depends strongly on the initial vibrational-state population.[8] Since highly excited initial vibrational states are involved, assumptions similar to those leading to the Franck-Condon theory of optical transitions[9] will not be useful. We feel the present approach is especially suited for this situation and, by a careful documentation of this example, hope to stimulate interest in the effects of rotational-vibrational excitation on various other collisional phenomena.

Section II contains an analysis of the asymptotic closure cross section for the $1s\sigma_g$-$2p\sigma_u$ transition in H_2^+. The cross section is evaluated for all initial vibrational states ν with zero-rotational angular momentum L.

Much of the earlier theoretical work was based on the old closure theory discussed in I. Briefly, this approximation consists of summing the Born cross section over the complete set of rotational-