Differential Cross Sections in the Multistate Impact-Parameter Description of Heavy-Particle Collisions

M. R. Flannery and K. J. McCann
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
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Differential cross sections are derived from a multistate impact-parameter treatment of heavy-particle collisions. Various approximations are suggested and their relationship with previous expressions are discussed. The equivalence between the differential cross sections in the impact-parameter and wave versions of the Born approximation is established for elastic and inelastic scattering and is illustrated explicitly for the $1s$, $2s$, $2p_0$, and $2p_{\pm 1}$ excitations of atomic hydrogen by proton and hydrogen-atom impact.

I. INTRODUCTION

Application of the multistate impact-parameter description of heavy-particle collisions has been limited mainly to the evaluation of total inelastic-scattering cross sections. Attention has only recently been focused on the corresponding theoretical differential cross sections. Wilets and Wallace[1] expressed the scattering amplitude $f(\theta)$ as a Fraunhofer integral of the asymptotic transition amplitudes over the impact parameter. Byron[2] and Bransden and Coleman[3] independently derived identical formulas for $f(\theta)$ which differ somewhat from the result of Wilets and Wallace. The relationship between the two formulas is not obvious.

Moreover, a conceptual difficulty arises in that the exact quantum-mechanical expression for $f(\theta)$ involves the electrostatic interaction between the colliding systems averaged over the exact stationary-state wave function satisfying the correct asymptotic boundary condition and the final stationary-state wave function for the isolated atoms. The impact-parameter approach, however, is normally derived from the Dirac method of variation of constants,[4] which is a time-dependent formulation.

In this paper, we will attempt to resolve this conflict and use the multistate description to present yet another expression for $f(\theta)$, which, upon successive approximation, reduces to the results cited above.

Also, the equivalence relationship between the impact-parameter and wave versions of Born's approximation for the *total* cross section has already been established by Crothers and Holt[5] and by McCarroll and Salin.[6] The relationship between the corresponding differential cross sections has been clarified by Byron.[2] An important consequence of the present theory is that both versions of Born's approximation for both elastic and inelastic collisions do yield identical expressions for the differential cross section. This point will be illustrated by the consideration of specific transitions in H^+-$H(1s)$ and $H(1s)$-$H(1s)$ collisions.

II. THEORY

A. Scattering Amplitude and Impact-Parameter Method for Stationary States

In the center-of-mass reference frame, the scattering amplitude for a transition between an initial state i and a final state f of the collision system is

$$f_{if}(\theta,\varphi) = -\frac{1}{4\pi}\frac{2M_{AB}}{\hbar^2}\langle\Psi_f(\vec{k}_f;\vec{r},\vec{R})\,|\,V(\vec{r},\vec{R})\times|\,\Psi_i^+(\vec{k}_i;\vec{r},\vec{R})\rangle_{\vec{r},\vec{R}}\,, \tag{1}$$

in which $V(\vec{r},\vec{R})$ is the instantaneous electrostatic interaction between the two structured collision partners A and B of the system with reduced mass M_{AB}. The composite internal electronic coordinates are denoted by $\vec{r}$ taken relative to the center of mass O of the nuclei with relative separation $\vec{R}$. The angles θ and φ are the spherical angles of the A-B final relative momentum vector $\vec{k}_f$ with polar axis directed along the incident relative momentum $\vec{k}_i$. Equation (1) can be derived either from a time-dependent or a stationary-state treatment of the collision process,[7] but in either description Ψ_f represents the final *stationary* state of the isolated atoms and Ψ_i^+ is the appropriate solution of the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2M_{AB}}\nabla_R^2 + H_e(\vec{r}) + V(\vec{r},\vec{R})\right)\Psi_n^+(\vec{r},\vec{R}) = E_n\Psi_n^+(\vec{r},\vec{R}) \tag{2}$$

subject to the asymptotic boundary condition

$$\Psi_i^+(\vec{r},\vec{R}) \xrightarrow{\text{large } R} \sum_n\left[e^{i\vec{k}_n\cdot\vec{R}_B}\delta_{ni} + f_{in}(\theta,\varphi)\frac{e^{ik_nR_B}}{R_B}\right]\times\varphi_n(\vec{r}_{ai},\vec{r}_{bj})\,. \tag{3}$$

The purely electronic functions φ_n form a complete set of normalized eigenfunctions of the Hamiltonian H_e describing the electronic motion of the isolated atoms with internal energy $\mathcal{E}_n$ and satisfy

$$H_e(\vec{r}_{ai}, \vec{r}_{bj})\varphi_n(\vec{r}_{ai}, \vec{r}_{bj}) = \mathcal{E}_n\varphi_n(\vec{r}_{ai}, \vec{r}_{bj}) , \qquad (4)$$

where $\vec{r}_{ai}$ and $\vec{r}_{bj}$ denote the composite electronic coordinates relative to each respective parent nucleus. The total constant energy E_n in (2) is the sum of the kinetic energy of relative motion $\hbar^2k_n^2/2M_{AB}$ and the energy E_n^e of the electrons relative to O, the center of mass of the nuclei, i.e., $E_n^e = \mathcal{E}_n +$ (the translational kinetic energy of the electrons relative to O). The vector $\vec{R}_B$ specifies the center of mass of the M-electron atom B of mass M_B relative to the center of mass of the N-electron atom A of mass M_A and is given by

$$\vec{R}_B = \vec{R} - \frac{m}{M_A}\sum_{i=1}^{N} \vec{r}_{ai} + \frac{m}{M_B}\sum_{j=1}^{M} \vec{r}_{bj} , \qquad (5)$$

where m is the electronic mass. The plane wave $e^{i\vec{k}_n\cdot\vec{R}_B}$ in the boundary condition (3) therefore contains $e^{i\vec{k}_n\cdot\vec{R}}$ together with phase factors that account for the translational motions of the electrons relative to O. As an aid to further clarity, assume that the collision system contains only one electron. The generalization of the subsequent formulas for excitation of many-electron systems is trivial. Let

$$\Psi_i(\vec{r}, \vec{R}) = e^{i\vec{k}_i\cdot\vec{R}}\chi_i(\vec{r}, \vec{R}) \qquad (6)$$

such that (2) is rewritten as

$$[H_e(\vec{r}) + V]\Psi_i - \frac{\hbar^2}{2M_{AB}}\{e^{i\vec{k}_i\cdot\vec{R}}\nabla_R^2\chi + 2[\vec{\nabla}_R e^{i\vec{k}_i\cdot\vec{R}}]\cdot\vec{\nabla}_R\chi\} = E_i^e\Psi_i(\vec{r}, \vec{R}) . \qquad (7)$$

For heavy-particle collisions, assume (a) that the chief dependence of Ψ_i on $\vec{R}$ is contained in $e^{i\vec{k}_i\cdot\vec{R}}$ such that $\nabla_R^2\chi$ can be neglected, (b) that the relative motion is directed mainly along $\hat{n}$, a unit vector along the Z axis, such that

$$\vec{\nabla}_R e^{i\vec{k}_i\cdot\vec{R}} = k_i\,\hat{n}e^{i\vec{k}_i\cdot\vec{R}} ,$$

and (c) that

$$\nabla_r^2 = \nabla_{r_a}^2 + (m/M_A)\vec{\nabla}_R\cdot\vec{\nabla}_{r_a} \approx \nabla_{r_a}^2 , \qquad (8)$$

such that $H_e(\vec{r}) = H_e(\vec{r}_a)$. With these approximations, (7) becomes

$$[H_e(\vec{r}_A) + V(\vec{r}_a, \vec{R}) - E_i^e]\chi_i(\vec{r}_a, \vec{R}) = i\hbar v_i\left(\frac{\partial\chi_i}{\partial Z}\right)_{\vec{r}\ \text{fixed}} = i\hbar v_i\left[\left(\frac{\partial\chi_i}{\partial Z}\right)_{\vec{r}_a\ \text{fixed}} + \frac{M_{AB}}{M_A}\left(\frac{\partial\chi_i}{\partial z_a}\right)\right] , \qquad (9)$$

where v_i is the incident speed and where[8] the presence of $z_a = \vec{r}_a\cdot\hat{n}$ in (9) results in correct acknowledgment of the electron's translational motion. Further reduction is obtained by the substitution

$$\chi_i(\vec{r}_a, \vec{R}) = \psi_i(\vec{r}_a, \vec{R})e^{i\mathcal{E}_iZ/\hbar v_i}\exp[im(M_{AB}/M_A)v_iz_a/\hbar] \qquad (10)$$

and, since

$$E_i^e = \mathcal{E}_i + \tfrac{1}{2}m(M_{AB}/M_A)v_i^2 ,$$

ψ_i therefore satisfies

$$[H_e(\vec{r}_a) + V(\vec{r}_a, \vec{R})]\psi_i(\vec{r}_a, \vec{R}) = i\hbar v_i\frac{\partial\psi_i}{\partial Z} . \qquad (11)$$

We note, on writing $Z = v_it$, that Eq. (11), which has been derived from a *stationary-state description* of the scattering, is formally identical to the time-dependent Schrödinger equation obtained by considering the motion of the electrons above in a "time-dependent" potential field $V(\vec{r}_a, \vec{R}(t))$ generated by the motion of the nuclei. This procedure would be analogous to the Born-Oppenheimer approximation for the separation of electronic and nuclear motions. For direct excitation, the stationary-state function $\psi_i(\vec{r}_a, \vec{R})$ can be expanded in terms of the isolated atomic functions φ_n in (4) as

$$\psi_i(\vec{r}_a, \vec{R}) = \mathop{\mathrm{S}}_n a_n(\vec{R})\varphi_n(\vec{r}_a)e^{-i\mathcal{E}_nZ/\hbar v_i} \qquad (12)$$

which, on insertion into (11) and with the aid of (4), followed by projection on direct-excitation channel m, yields the following coupled differential equations:

$$\frac{\partial a_m(\vec{R})}{\partial Z} = -\frac{i}{\hbar v_i}\mathop{\mathrm{S}}_n a_n(\vec{R})\langle\varphi_m|V|\varphi_n\rangle_{\vec{r}_a}e^{i\mathcal{E}_{mn}Z/\hbar v_i} , \qquad (13)$$

which when solved subject to the asymptotic condition $a_n(\rho, Z\to-\infty) = \delta_{in}$ provides Ψ_i^+ as a function of $\vec{r}_a$ and $\vec{R}$. Thus, the initial wave function Ψ_i^+ develops in $\vec{R}$ as

$$\Psi_i^+(\vec{r}, \vec{R}) = e^{i\vec{k}_i\cdot\vec{R}}\exp\left[im\left(\frac{M_{AB}}{M_A}\right)\frac{v_iz_a}{\hbar}\right] \times e^{i\mathcal{E}_iZ/\hbar v_i}\psi_i(\vec{r}_a, \vec{R}) \qquad (14)$$

and, as $Z\to-\infty$, reduces to the correct stationary-state incident wave $e^{i\vec{k}_i\cdot\vec{R}_B}\varphi_i(\vec{r}_a)$. The final-state wave function Ψ_f in (1) is the solution of (2) with $V=0$, and is therefore

$$\Psi_f(\vec{r}, \vec{R}) = e^{i\vec{k}_f\cdot\vec{R}}\exp\left[im\left(\frac{M_{AB}}{M_A}\right)\frac{v_fz_a}{\hbar}\right]\varphi_f(\vec{r}_a) . \qquad (15)$$

Hence, with the assumption that the relative speed in the above phase factors is unaffected, i.e.,

$v_i = v_f$, the substitution of (14) and (15) in (1) yields

$$f_{if}(\theta,\varphi) = -\frac{1}{4\pi}\frac{2M_{AB}}{\hbar^2}\int e^{i\vec{K}\cdot\vec{R}} \times\left(\sum_n a_n(\vec{R})\langle\varphi_f(\vec{r}_a)|V(\vec{r}_a,\vec{R})|\varphi_n(\vec{r}_a)\rangle \times e^{i\mathcal{E}_{in}Z/\hbar v_i}\right)d\vec{R}, \quad (16)$$

where $\mathcal{E}_{in} = \mathcal{E}_i - \mathcal{E}_n$ and $\vec{K}$ is the momentum change $\vec{k}_i - \vec{k}_f$. The electrostatic interactions averaged over the electronic motions can be written as[9]

$$\langle\varphi_f|V|\varphi_n\rangle = V_{fn}(R,\Theta)e^{i(m_n-m_f)\Phi}, \quad (17)$$

where m_f is the magnetic quantum number of electronic state f and $\vec{R} \equiv (R,\Theta,\Phi)$. Thus, (13) is

$$\frac{\partial a_m(\vec{R})}{\partial Z} = -\frac{i}{\hbar v_i}\sum_n a_n(Z,\rho,\Phi)V_{mn}(R,\Theta) \times e^{im_{nm}\Phi}e^{i\mathcal{E}_{mn}Z/\hbar v_i}, \quad (18)$$

with $m_{nf} = m_n - m_f$, $\vec{R} = (Z,\rho,\Phi)$ in a cylindrical coordinate frame, and with $a_n(-\infty,\rho,\Phi) = \delta_{in}$ as the boundary condition. Introduction of the phase-independent amplitudes $C_n (\equiv a_n e^{im_{ni}\Phi})$ produces

$$\frac{\partial C_m(\rho,Z)}{\partial Z} = -\frac{i}{\hbar v}\sum_n C_n(\rho,Z)V_{mn}(\rho,Z)e^{i\mathcal{E}_{mn}Z/\hbar v_i}, \quad (19)$$

a set of phase-independent equations capable of numerical solution as functions of ρ and Z. Hence, with the aid of (19) and (16),

$$f_{if}(\theta,\varphi) = -\frac{ik_i}{2\pi}\int e^{i(\vec{K}\cdot\vec{R}+m_{if}\Phi)}e^{i\mathcal{E}_{if}Z/\hbar v_i}\frac{\partial C_f(\rho,Z)}{\partial Z}d\vec{R}, \quad (20)$$

which is the basic formula for the scattering amplitude as determined from the present approach. This formula is essentially identical with that derived by Byron[2] [see Eq. (17b) of his paper]. The generalization of the above equation to excitation in many-electron atomic systems is simple when exchange and transfer of electrons between the two nuclei is neglected.

We note that the above formula is also reproduced when we arbitrarily insert the following fully *time-dependent* initial and final wave functions:

$$\Psi_i^+(\vec{k}_i;\vec{r},\vec{R}(t),t) = \left(\sum_n a_n(t)\varphi_n(\vec{r}_a)e^{-iE_nt/\hbar}\right) \times e^{i\vec{k}_i\cdot\vec{R}-i\hbar k_i^2t/2M_{AB}} \quad (21)$$

and

$$\Psi_f(\vec{k}_i;\vec{r},\vec{R}(t),t) = [\varphi_f(\vec{r}_a)e^{-iE_ft/\hbar}] \times e^{i\vec{k}_f\cdot\vec{R}-i\hbar k_f^2t/2M_{AB}} \quad (22)$$

into the scattering amplitude (1) and use the conservation of energy together with the substitution $Z = v_i t$.

B. Approximations to Scattering Amplitude

Approximation I. The first approximation is based on the fact that for heavy-particle collisions, the Z component of the momentum change can be expanded as

$$K_Z = \vec{K}\cdot\hat{n} = k_i - k_f + 2k_f\sin^2\tfrac{1}{2}\theta \approx k_i - k_f = \frac{\mathcal{E}_{fi}}{\hbar v_i}\left(1+\frac{\mathcal{E}_{fi}}{2M_{AB}v_i^2}+\cdots\right). \quad (23)$$

Hence, the scattering amplitude (20) becomes

$$f_{if}(\theta,\varphi) = -\frac{ik_i}{2\pi}\int e^{i\vec{K}'\cdot\vec{\rho}}[e^{im_{if}\Phi}C_f(\rho,\infty) - \delta_{if}]d\vec{\rho}, \quad (24)$$

where

$$K'^2 = K^2 - K_Z^2 = K^2 - \mathcal{E}_{fi}^2/\hbar^2 v_i^2$$

approximates the square of the momentum change perpendicular to the incident direction, such that $\vec{K}'\cdot\vec{\rho} = K'\rho\cos(\varphi-\Phi)$. Therefore both the Φ and the Z integrations can be performed analytically to yield

$$f_{if}(\theta,\varphi) = -ik_i i^{\Delta}e^{i\Delta\varphi}\int_0^\infty J_\Delta(K'\rho) \times[C_f(\rho,\infty)-\delta_{if}]\rho\, d\rho, \quad (25)$$

where J_Δ are Bessel functions of integral order $\Delta = m_{if}$, the change in magnetic quantum number. The total cross section σ_{if} follows directly from (24) when we write

$$K^2 = k_i^2 + k_f^2 - 2k_ik_f\cos\theta = K'^2 + K_Z^2 \quad (26)$$

to yield

$$\sigma_{if}(k_i) = (k_f/k_i)\int|f_{if}(\theta,\varphi)|^2 d(\cos\theta)\,d\varphi = \frac{1}{4\pi^2}\int_{K'=0}^{[(k_i+k_f)^2-K_Z^2]^{1/2}}\int_{\varphi=0}^{2\pi} e^{i(\vec{\rho}-\vec{\rho}\,')\cdot\vec{K}'}d\vec{K}'\int[e^{i\Delta\Phi}C_f(\rho,\infty)-\delta_{if}]d\vec{\rho} \times\int[e^{-i\Delta\Phi'}C_f^*(\rho',\infty)-\delta_{if}]d\vec{\rho}\,', \quad (27)$$

in which $d\vec{K}'=K'\,dK'\,d\Phi'$ is an element lying entirely in the XY plane. The upper limit to K' in (29) is effectively infinite for heavy particles and hence

$$\sigma_{if}(k_i)=2\pi\int_{\rho=0}^{\infty}|C_f(\rho,\infty)-\delta_{if}|^2\rho\,d\rho \tag{28}$$

in harmony with the prediction from (10) and (12) that $|C_f(\rho,\infty)|^2$ is the probability for excitation at impact parameter ρ, and with Byron.[2] The corresponding probability for elastic collisions is, however, $|C_i|^2+(1-2\,\mathrm{Re}C_i)$ and is not $|C_i|^2$, except of course when $\mathrm{Re}C_i=\frac{1}{2}$, for all ρ, which is an impossibility.

Equation (24) above may be compared to that obtained by Byron[2] [see his Eq. (19)] who used the actual momentum change $k_f\sin\theta$ perpendicular to the incident direction, rather than the XY-component K' used here. For heavy-particle collisions, there is, however, little difference.

Approximation II. This approximation follows from the neglect of $\mathcal{E}_{if}$ in (20) to give

$$f_{if}(\theta,\varphi)=-\frac{ik_i}{2\pi}\int e^{i(\vec{K}\cdot\vec{R}+m_{if}\Phi)}\frac{\partial C_i(\rho,Z)}{\partial Z}d\vec{R}\,. \tag{29}$$

For heavy-particle impacts at high energy, $\vec{K}$ is almost perpendicular to $\hat{n}$ such that

$$\vec{K}\cdot\vec{R}=\vec{K}\cdot\vec{\rho}=K\rho\cos(\theta-\varphi)\,, \tag{30}$$

where K above is taken as the *total* momentum change. Substitution of (30) in (29) yields the expression

$$f_{if}(\theta,\varphi)=-\frac{ik_i}{2\pi}i^{\Delta}e^{i\Delta\varphi}\times\int_0^{\infty}J_{\Delta}(K\rho)\,[C_f(\rho,\infty)-\delta_{if}]\rho\,d\rho\,, \tag{31}$$

which is similar to (25) but with K replacing K'. We note that approximations I and II are identical *only* for elastic collisions. The differences between them will be fully explored for specific inelastic transitions in Sec. II C when we examine the Born wave approximation.

The approximation II, Eq. (31) has also been derived by Bransden and Coleman.[3] However, it is worth pointing out that $f(\theta)$ given by Bransden *et al.*[10] for the excitation of state n by electron impact is valid only then for transitions involving no change in magnetic quantum number (although, for hydrogenic states, $\sum_{l,m}|\Psi_{nlm}|^2$ is, to be sure, spherically symmetric).

Approximation III. On recognizing that $\vec{K}$ is not quite perpendicular to $\vec{k}_i$, we insert the scalar product

$$\vec{K}\cdot\vec{R}=K\rho\cos\tfrac{1}{2}\theta\cos(\varphi-\Phi)+KZ\sin\tfrac{1}{2}\theta \approx K\rho\cos\tfrac{1}{2}\theta\cos(\varphi-\Phi) \tag{32}$$

into (29) and (31) is reproduced except that the argument of the Bessel functions is $K\rho\cos\frac{1}{2}\theta$ instead of $K\rho$ as in approximation II. With $K\approx 2k_i\times\sin\frac{1}{2}\theta$ since $k_i\approx k_f$, then the argument is $k_i\rho\sin\theta$.

Approximation IV. That the Z and Φ integrations in (9) can be achieved in the last two approximations is a direct consequence of the neglect in (32) of $\sin\frac{1}{2}\theta$. A more natural approach, however, is to rotate our initial coordinate frame by $\frac{1}{2}\theta$ about the X axis such that the new Z' axis directed along the vector

$$\hat{n}'=(\vec{k}_i+\vec{k}_f)/|\vec{k}_i+\vec{k}_f|\,, \tag{33}$$

which bisects the initial and final directions and which always ensures that $\vec{K}\cdot\hat{n}=0$ for a given scattering angle θ. Thus, the components of $\vec{R}$ are, in the new (primed) system, given as

$$\begin{bmatrix}\rho'\cos\Phi'\\ \rho\sin\Phi'\\ Z'\end{bmatrix}=\begin{bmatrix}1&0&0\\0&\cos\frac{1}{2}\theta&\sin\frac{1}{2}\theta\\0&-\sin\frac{1}{2}\theta&\cos\frac{1}{2}\theta\end{bmatrix}\begin{bmatrix}\rho\cos\Phi\\ \rho\sin\Phi\\ Z\end{bmatrix} \tag{34}$$

such that (29) reduces exactly,

$$f(\theta,\varphi)=-\frac{ik}{2\pi}\int e^{i\vec{K}\cdot\vec{\rho}'}\frac{\partial a_{if}(Z,\rho,\Phi)}{\partial Z}\times\rho'\,d\rho'\,dZ'\,d\Phi'\,, \tag{35}$$

with a_{if} maintained as functions in the old (unprimed) coordinate system.

To first order, (34) becomes

$$Z'=Z\cos\tfrac{1}{2}\theta,\quad \rho'=\rho\cos\tfrac{1}{2}\theta,\quad \cos\varphi'=\cos\varphi/\cos\tfrac{1}{2}\theta\,, \tag{36}$$

and, by substituting $dZ'=dZ\cos\frac{1}{2}\theta$ in (35), and by proceeding as above, we find

$$f_{if}(\theta,\varphi)=-ik_i\cos^3\tfrac{1}{2}\theta(i\cos\tfrac{1}{2}\theta\,e^{i\varphi})^{\Delta}\times\int_0^{\infty}J_{\Delta}(K\rho\cos\tfrac{1}{2}\theta)[C_{if}(\rho,\infty)-\delta_{if}]\rho\,d\rho\,. \tag{37}$$

If, instead of (36), $Z'=Z$, then a factor $\cos\frac{1}{2}\theta$ disappears from (37). If, in addition, $\phi'\approx\phi$, the $(i\cos\frac{1}{2}\theta\,e^{i\varphi})^{\Delta}$ factor also disappears and the final result is then identical to that of Wilets and Wallace[1] (when $K\approx 2k_i\sin\frac{1}{2}\theta$).

C. Born Version of Scattering Amplitude

By setting $C_n=\delta_{in}$ in the right-hand side of (19), the impact-parameter version of Born's approximation is obtained from (20) to yield

$$f^B_{if}(\theta,\varphi) = -\frac{1}{4\pi}\frac{2M_{AB}}{\hbar^2}\int e^{i\vec{K}\cdot\vec{R}}V_{fi}(\vec{R})\,d\vec{R}\,, \tag{38}$$

the Fourier transform of the coupling interaction, a result identical with the wave version of Born's approximation.

The main advantage of (20) is, of course, its use in a multistate-state treatment, in which the set of coupled differential equations is solved numerically for $C_n(\rho, Z)$. Thus approximation I, Eq. (24), is essential as a first step and involves only the replacement of K_z by $\mathcal{E}_{fi}/\hbar v_i$, which is almost exact for heavy-particle collisions. The Born version of (24), approximation I, is

$$f^B_{if}(\theta,\varphi) = -\frac{1}{4\pi}\frac{2M_{AB}}{\hbar^2}\int e^{i(\vec{K}'\cdot\vec{\rho}+m_{if}\Phi)}\,d\vec{\rho} \times\int V_{fi}(\rho,Z)e^{i\mathcal{E}_{fi}Z/\hbar v_i}\,dZ\,, \tag{39}$$

which when expressed in spherical-polar instead of cylindrical coordinates is equivalent to (38) with $K^2 = K'^2 + \mathcal{E}^2_{fi}/\hbar^2 v_i^2$.

As confirmation of this equivalence in approximation I, consider the following collision processes:

$$H^+ + H(1s) \to H^+ + H(1s, 2s, 2p_{0,\pm1})\,. \tag{40}$$

The appropriate interaction potentials are[11] (in a.u.),

$$V_{1s\,1s}(R) = (1+1/R)e^{-2R}, \quad R^2 = \rho^2 + Z^2 \tag{41a}$$

$$V_{2s\,1s}(\vec{R}) = -\tfrac{2}{27}\sqrt{2}(2+3R)e^{-3R/2} \tag{41b}$$

and

$$V_{2p_0,1s}(\vec{R}) = (Z/R)V_{2p1s}(R)\,,$$
$$V_{2p_{\pm1}1s}(\vec{R}) = (\rho/\sqrt{2}R)V_{2p\,1s}(R)\,, \tag{41c}$$

with

$$V_{2p\,1s}(R) = 4\sqrt{2}\left(\frac{2}{3}\right)^5\left[\frac{1}{R^2} - \left(\frac{1}{R^2} + \frac{3}{2R} + \frac{9}{8} + \frac{27}{64}R\right)e^{-3R/2}\right]. \tag{41d}$$

The inner integral of (39) for these transitions can be expressed in terms of integral Bessel functions K_n of the third kind,[11,12] as

$$\int_{-\infty}^{\infty} V_{1s\,1s}(R)\,dZ = 2[K_0(\gamma\rho) + \rho K_1(\gamma\rho)], \quad \gamma = 2 \tag{42a}$$

$$\int_{-\infty}^{\infty} V_{2s\,1s}(R)\cos\beta Z\,dZ = -\tfrac{8}{27}\sqrt{2}(\alpha^3/A^2)\rho^2 K_2(A\rho), \quad \alpha = \tfrac{3}{2}, \quad A^2 = \alpha^2 + \beta^2 \tag{42b}$$

$$\int_{-\infty}^{\infty} V_{2p\,1s}(R)(Z/R)\sin\beta Z\,dZ = \tfrac{128}{243}\sqrt{2}\beta\{2K_0(\beta\rho) - [2K_0(A\rho) + \tfrac{9}{4}(\rho/A)K_1(A\rho) + \tfrac{27}{32}(\alpha\rho^2/A^2)K_2(A\rho)]\}\,, \tag{42c}$$

$$\int_{-\infty}^{\infty} V_{2p\,1s}(R)(\rho/R)\cos\beta Z\,dZ = \tfrac{256}{243}\{\beta K_1(\beta\rho) - [AK_1(A\rho) + \tfrac{9}{8}\rho K_0(A\rho) + \tfrac{27}{64}\beta(\rho^2/A)K_1(A\rho)]\}\,, \tag{42d}$$

with $\beta = 3/8v_i$ a.u.

The Φ integration in (39) is performed to give

$$f_{if}(\theta,\varphi) = -\frac{2M_{AB}e^2}{\hbar^2}i^{\Delta}e^{i\Delta\varphi}\int_0^{\infty}J_{\Delta}(K'\rho)\rho\,d\rho\int_{-\infty}^{\infty}V_{fi}(\vec{R})e^{i\mathcal{E}_{fi}Z}\,dZ\,, \tag{43}$$

while the ρ integration in the above can be acheived by using the integral formula[12]

$$\int_0^{\infty}\rho^{n+m}K_n(A\rho)J_m(K'\rho)\rho\,d\rho = \frac{2^{n+m}K'^m A^n(n+m)!}{(K'^2+A^2)^{n+m+1}}\,. \tag{44}$$

After some algebraic simplification, the following results for the scattering amplitudes are obtained:

$$f^B_{1s\,1s}(\theta,\varphi) = -\frac{2M_{AB}e^2}{\hbar^2}\frac{K^2+8}{(K^2+4)^2}\,, \tag{45a}$$

$$f^B_{1s\,2s}(\theta,\varphi) = -\frac{2M_{AB}e^2}{\hbar^2}\frac{4\sqrt{2}}{(K^2+\alpha^2)^3}, \quad \alpha = \tfrac{3}{2} \tag{45b}$$

$$f^B_{1s\,2p_0}(\theta,\varphi) = f^B_{1s\,2p}(\theta,\varphi)\cos\delta\,,$$
$$f^B_{1s\,2p_{\pm1}}(\theta,\varphi) = f^B_{1s\,2p}(\theta,\varphi)\sin\delta\,, \tag{45c}$$

where

$$f^B_{1s\,2p}(\theta,\varphi) = -\frac{2M_{AB}e^2}{\hbar^2}\frac{6\sqrt{2}}{K(K^2+\alpha^2)^3}\,, \tag{45d}$$

with $K^2 = K'^2 + \mathcal{E}^2_{fi}/v_i^2$ and $\cos\delta = \hat{K}\hat{n} = K_z/K = \mathcal{E}_{fi}/v_i$. All of these results agree exactly with those obtained from the Born wave formula (38) which can either be evaluated directly using (41) expressed in spherical polar coordinates or alternatively from

$$f_{if}^{\mathrm{BW}}(\theta,\varphi)=-\frac{2M_{AB}e^2}{\hbar^2}\,\frac{\delta_{if}-F_{if}(\vec{K})}{K^2}, \quad (46)$$

where $F_{if}(\vec{K})$ is the form factor

$$\langle\varphi_i(\vec{r}_a)|e^{i\vec{K}\cdot\vec{r}_a}|\varphi_f(\vec{r}_a)\rangle$$

for atomic hydrogen, determined with the atomic axis of quantization taken along $\hat{n}$, the direction of incidence. The equivalence between the two versions of Born's approximation is achieved for approximation I via the fact that $K'^2+A^2=K'^2+K_Z^2+\alpha^2=K^2+\alpha^2$ in the denominator of (44).

The difference between approximations I and II arises essentially from the neglect of $\mathcal{E}_{if}/v_i$ in (20) with the result that K' in (39) is replaced by K. Thus, approximation II yields the Born-wave results only for elastic scattering when $K=K'$, and increases K^2 in (45b) and (45d) by $\mathcal{E}_{fi}^2/v_i^2$. In the limit of high-impact velocities, approximations I and II should therefore agree for inelastic collisions.

Approximations III and IV also neglect $\mathcal{E}_{if}/v_i$ in (20) and attempt thereafter to take fuller account of the direction of $\vec{K}$ (rather than assuming as in approximation II that $\vec{K}$ lies entirely in the XY plane). This procedure leads to K in (45a)–(45d) being replaced by $K\cos\frac{1}{2}\theta$ for both cases and, for IV in addition, to the appearance of an extra multiplicative factor $\cos^3\frac{1}{2}\theta$ for (45a) and (45b) and $\cos^4\frac{1}{2}\theta$ for (45a). Approximations III and IV therefore result in an incorrect angular dependence, becoming worse for the larger scattering angles. Moreover, the resulting errors would be strongly amplified for the case of electron impact.

The basic reason why approximations III and IV are not as good as approximations I and II arises from the fact that, while approximation II essentially neglects K_Z and is thereafter consistent with this neglect, approximations III and IV neglect K_Z initially in (20) and then seek to account for K_Z later by assuming that $\vec{K}$ indeed possesses a Z component.

The following neutral-neutral processes,

$$\mathrm{H}(1s)+\mathrm{H}(1s)\to\mathrm{H}(1s)+\mathrm{H}(1s,2s,2p_0,2p_{\pm1}), \quad (47)$$

have also been explored in both Born versions. The appropriate interaction potentials have already been given.[9,12] For the elastic case,

$$\int_{-\infty}^{\infty}V_{1s1s}(\vec{R})\,dZ=2[K_0(2\rho)+\rho K_1(2\rho)-\tfrac{1}{2}\rho^2K_2(2\rho)-\tfrac{1}{6}\rho^3K_3(2\rho)], \quad (48)$$

and the integrals for the inelastic case are also known.[12] The subsequent ρ integrations can also be performed analytically, and approximation I then yielded precisely the Born-wave values deduced from the customary formula,

$$f_{if}^{\mathrm{BW}}(\theta,\varphi)=\frac{2M_{AB}e^2}{\hbar^2}\,\frac{[1-F_{1s1s}(K)][\delta_{if}-F_{if}(\vec{K})]}{K^2}, \quad (49)$$

for H-H impacts.

Finally, as another example, assume that some reaction is assumed to proceed (with unit probability) only for collisions with impact parameter $\rho\le R_0$, a reaction radius. Then the resulting integrations in (25) can be performed analytically in terms of Bessel and Lommel functions. For the case with $\Delta=0$, the scattering amplitude is simply (with $a_i=0$, $a_f=1$ for $\rho\le R_0$, and $a_i=1$, $a_{if}=0$ otherwise)

$$f_{if}(\theta,\varphi)=-ik_iR_0J_1(KR_0)/K$$
$$=-f_{ii}(\theta,\varphi)\to-\tfrac{1}{2}k_iR_0^2 \quad (50)$$

for small $K\approx 2k_i\sin\frac{1}{2}\theta$. Both the elastic and inelastic differential cross sections are therefore peaked at small scattering angles θ, with magnitude $\frac{1}{4}k_i^2R_0^4$, and have angular spread $(k_iR_0)^{-1}$. Hence, little error is introduced by setting

$$\sigma_{if}=2\pi\int_0^{\pi}|f_{if}|^2\,d(\cos\theta)$$
$$=2\pi R_0^2\int_0^{\infty}[J_1(k_iR_0\theta)]^2\frac{d\theta}{\theta}$$
$$=\pi R_0^2=\sigma_{ii} \quad (51)$$

as predicted elsewhere[13] for collisions with a total absorbing sphere in the limit of large incident momentum k_i. The total cross section for both elastic and inelastic scattering is therefore

$$\sigma=\sigma_{ii}+\sigma_{if}=2\pi R_0^2$$
$$=(4\pi/k_i)\,\mathrm{Im}f_{ii}(\theta=0) \quad (52)$$

in harmony with the optical theorem.

In conclusion, a basic expression (20) for the scattering amplitude $f(\theta)$ has been simply derived. The Born version of (20) is identical to the Born-wave result of $f^{\mathrm{BW}}(\theta)$. When a multistate description is used, several approximations are explored and are presented in decreasing order of effectiveness [as determined by the comparison of the corresponding Born versions with $f^{\mathrm{BW}}(\theta)$]. The Born version of the "best" approximation I agrees with $f^{\mathrm{BW}}(\theta)$ in the heavy-particle limit, i.e., when $K_Z=\mathcal{E}_{fi}/v_i$. The possible elaboration of this approximation to electron-atom collisions is of interest. The relationship of these approximations with those previously derived[1-3] is probed.

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