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Collision amplitudes shorn of first Born terms

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We present a procedure to subtract the contribution of the first Born approximation from "exact" transition amplitudes of projectile plus target collision complexes. Following this preliminary step, only a small set of amplitudes requires accurate calculation, these amplitudes are labeled by low values of angular momentum and are invariant under coordinate rotations.

I. INTRODUCTION

Collisions of a charged particle with an atom or molecule may result from a projectile approach with impact parameter b comparable to, or much larger than, atomic radii. Large impact parameters b imply a large geometrical effective target (πb^2) and a weak interaction which would afford adequate evaluation of a cross section in the Born approximation. More accurate calculations are instead required for small impact parameters, especially at low collision velocities. The analytic compactness of the Born cross-section formula, however, makes it desirable to represent the effect of collisions with low impact parameter as a departure from the Born evaluation rather than as the result of a wholly separate treatment.[1] This paper presents a general procedure to this end.

The compact form of a Born treatment represents the transition amplitude in a collision as a function of the momentum $\hbar\mathbf{q}$ transferred from the projectile to the target, where

$$\mathbf{q}=\mathbf{k}_i-\mathbf{k}_f \tag{1}$$

is the difference of the initial and final wave vectors of the projectile. This amplitude is represented by[2]

$$\langle E_fJ_fM_f\mathbf{k}_f|\mathbf{T}^B|E_iJ_iM_i\mathbf{k}_i\rangle = \frac{me^2}{2\pi^2}\frac{\sqrt{k_ik_f}}{\hbar^2q^2} \times\left\langle E_fJ_fM_f\left|\sum_\alpha z_\alpha \exp(i\mathbf{q}\cdot\mathbf{r}_\alpha)\right|E_iJ_iM_i\right\rangle , \tag{2}$$

where E, J, and M characterize the target states before (i) and after (f) the collision, and $(z_\alpha,\mathbf{r}_\alpha)$ indicate the charge and position of the αth particle in the target. The matrix element in (2) constitutes the Fourier transform of the electric charge distribution associated with the target's transition $i\rightarrow f$. The coefficients of (2) stem from the Fourier expansion of the Coulomb field generated by the projectile's transition between plane-wave states $(\mathbf{k}_i,\mathbf{k}_f)$ normalized per unit energy (Sec. 4.3.2 of Ref. 3).

A corresponding amplitude $\mathbf{T}^{\rm ex}$ calculated accurately for low impact parameters is instead usually represented in a base of angular momentum eigenstates of both target and projectile,

$$\langle E_fJ_fM_f,k_fl_fm_f|\mathbf{T}^{\rm ex}|E_iJ_iM_i,k_il_im_i\rangle . \tag{3}$$

Representing $\mathbf{T}^{\rm ex}$ as a departure from $\mathbf{T}^B$, i.e., as

$$\mathbf{T}^{\rm ex}=\mathbf{T}^B+(\mathbf{T}^{\rm ex}-\mathbf{T}^B) , \tag{4}$$

requires us then to cast both $\mathbf{T}^B$ and $\mathbf{T}^{\rm ex}$ in the same base.

Note at the outset that the interaction between projectile and target is invariant under rotations of coordinates. The basic forms of $\mathbf{T}^B$ and $\mathbf{T}^{\rm ex}$ should be similarly invariant but their initial representations (2) and (3) are not. An invariant form of (3) is readily extracted by replacing the separate pairs of magnetic quantum numbers (M_i,m_i) and (M_f,m_f) by their sum $M=M_i+m_i=M_f+m_f$, which is conserved in the collision. Accordingly we transform (3) by addition coefficients for the vector angular momenta of the collision complex, $\mathbf{J}=\mathbf{J}_i+\mathbf{l}_i=\mathbf{J}_f+\mathbf{l}_f$, namely, $\langle JM|J_fM_f,l_fm_f\rangle$ and a conjugate, writing

$$\langle E_fk_f(J_fl_f)J|\mathbf{T}^{\rm ex}|E_ik_i(J_il_i)J\rangle = \sum_{M_f,m_f,M_i,m_i}\langle JM|J_fM_f,l_fm_f\rangle \times\langle E_fJ_fM_f,k_fl_fm_f|\mathbf{T}^{\rm ex}|E_iJ_iM_i,k_il_im_i\rangle\langle J_iM_i,l_im_i|JM\rangle . \tag{5}$$

Note that this basic matrix element (5) is diagonal in J and explicitly independent of M, i.e., of reference coordinates, as desired.

We shall here represent $\mathbf{T}^B$ in the base of (5) as a superposition of terms in the base of (2). We understand that the seemingly straightforward task of achieving this goal in suitable and general form has been hampered previously by analytical complications, due to the use of different representations in Eq. (2) for target and projectile states, namely, angular momentum eigenstates for the target and momentum eigenstates for the projectile. This difference stems from the fact that a collision amounts, in the first Born approximation, to an elementary transfer of momentum $\hbar\mathbf{q}$ from projectile to target. Constructing a *frame transformation* that would recast (2) in the base of (3) with minimum loss of compactness and transparency has required many steps of trial and error.

Note that the Born matrix element on the right of (2) depends only on the magnitude of $\mathbf{q}$, regardless of the magnitudes and directions of $\mathbf{k}_i$ and $\mathbf{k}_f$. (Indeed, experimental verification of this independence is a familiar test of the Born approximation.[2]) In our problem the magnitudes k_i and k_f are specified as input parameters of the matrix element (3) but the angle between $\hat{\mathbf{k}}_i$ and $\hat{\mathbf{k}}_f$ is not. [Integrations over this angle, at constant (k_i,k_f), amount to integrations over the magnitude of $\mathbf{q}$]. Accordingly the matrix element on the left of (2) should be indicated more explicitly as $\langle E_fJ_fM_f,k_f\hat{\mathbf{k}}_f|\mathbf{T}^B|E_iJ_iM_i,k_i\hat{\mathbf{k}}_i\rangle$. Our goal of recasting this matrix in a form congruent to (3) requires us then to split off its dependence on the directions $(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)$, replacing them with corresponding orbital and magnetic quantum numbers. This will be achieved formally by the double expansion

$$\langle E_fJ_fM_f\mathbf{k}_f|\mathbf{T}^B|E_iJ_iM_i\mathbf{k}_i\rangle=\sum_{l_f,m_f}\sum_{l_i,m_i}\langle\hat{\mathbf{k}}_f|l_fm_f\rangle\langle E_fJ_fM_f,k_fl_fm_f|\mathbf{T}^B|E_iJ_iM_i,k_il_im_i\rangle\langle l_im_i|\hat{\mathbf{k}}_i\rangle\ , \tag{6}$$

whose transformation coefficients are defined as

$$\langle\hat{\mathbf{k}}_f|l_fm_f\rangle=i^{-l_f}Y_{l_fm_f}(\hat{\mathbf{k}}_f),\langle l_im_i|\hat{\mathbf{k}}_i\rangle=i^{l_i}Y^*_{l_im_i}(\hat{\mathbf{k}}_i)\ , \tag{6$'$}$$

by Eq. (4.7) of Ref. 3. The frame transformation we seek amounts thus to casting the expression on the right of (2) as an explicit function of $\{k_f,\hat{\mathbf{k}}_f,k_i,\hat{\mathbf{k}}_i\}$ rather than as a simple function of $\mathbf{q}=\mathbf{k}_i-\mathbf{k}_f$.

Different bases are used for target and projectile in (2) because the Born approximation deals with the elementary process of momentum transfer $\hbar\mathbf{q}$ from projectile to target. An exact calculation deals instead with the transient complex formed by projectile and target; it is treated in a single base and leaves invariant the angular momentum $\mathbf{J}$ of the complex in an arbitrary frame about its center of mass. The connection between the two frames is carried out in Sec. II. It will be applied in Sec. III, for purposes of illustration, to the elementary collisions $e+H$ for which (2) is known in fully analytical form. Final comments are presented in Sec. IV.

II. FRAME TRANSFORMATIONS

The transformation of the operator $\mathbf{T}^B$ from its representation (2) to a frame congruent with (5) is mediated by the *angular momentum* $\mathbf{j}_t$ *transferred* from projectile to target. It articulates in several steps, namely,

(a) Analysis of $\mathbf{T}^B$ into contributions labeled by a quantum number j_t.

(b) Separation of $\mathbf{T}^B$'s dependence on target and projectile variables.

(c) Expansion of $\mathbf{T}^B$ into harmonics (6$'$) of $\hat{\mathbf{k}}_f$ and $\hat{\mathbf{k}}_i$.

(d) Transformation of $\mathbf{T}^B$ from the frame of (3) to that of (5).

A. Expansion into partial waves

The matrix element in Eq. (2) is called the "form factor" of the target's transition from its initial state to its final state, as indicated by

$$F_{fi}(\mathbf{q})=\left\langle E_fJ_fM_f\left|\sum_\alpha z_\alpha\exp(i\mathbf{q}\cdot\mathbf{r}_\alpha)\right|E_iJ_iM_i\right\rangle\ . \tag{7}$$

Real and imaginary parts of this expression are readily identified in the expansion of its exponential into powers of $\mathbf{q}\cdot\mathbf{r}_\alpha$. The even-power terms are real and of even parity under the inversion $\mathbf{r}_\alpha\to-\mathbf{r}_\alpha$; parity conservation restricts their contributions to transitions $i\to f$ that conserve parity. The odd-power terms are instead imaginary and contribute only to parity-changing transitions.

A more compact and instructive analysis of contributions to the form factor emerges from the familiar expansion of its exponential into partial waves,

$$F_{fi}=\left\langle E_fJ_fM_f\left|\sum_\alpha z_\alpha\sum_{j_t}i^{j_t}(2j_t+1)P_{j_t}(\hat{\mathbf{q}}\cdot\hat{\mathbf{r}}_\alpha)j_{j_t}(qr_\alpha)\right|E_iJ_iM_i\right\rangle \tag{8}$$

$$=\left\langle E_fJ_fM_f\left|\sum_\alpha z_\alpha\sum_{j_t,m_t}i^{j_t}4\pi Y^*_{j_tm_t}(\hat{\mathbf{q}})Y_{j_tm_t}(\hat{\mathbf{r}}_\alpha)j_{j_t}(qr_\alpha)\right|E_iJ_iM_i\right\rangle\ , \tag{8$'$}$$

where P_{j_t} is a Legendre polynomial of degree j_t and j_{j_t} indicates the spherical Bessel function of order j_t. Here the factor i^{j_t} shows that the terms with even (odd) values of j_t are real (imaginary), the factor $P_{j_t}(\hat{\mathbf{q}}\cdot\hat{\mathbf{r}}_\alpha)$ selects even (odd) values of j_t according to the equal (opposite) parity of the target states (f,i). Moreover the factor $Y_{j_tm_t}(\hat{\mathbf{r}}_\alpha)$ in

(8′) amounts to a 2^{j_t}-pole operator which changes the target's angular momentum J_i to J_f in accordance to the vector operator equation

$$\mathbf{J}_f-\mathbf{J}_i=\mathbf{j}_t=\mathbf{l}_i-\mathbf{l}_f \ . \tag{9}$$

The component of this equation along the polar axis yields the corresponding relation among the magnetic quantum numbers of Eq. (3)

$$M_f=m_t+M_i, m_f+m_t=m_i \ . \tag{9′}$$

These relations illustrate how the angular momentum $\mathbf{j}_t$ is transferred from projectile to target in the (Born approximation) collision process.

Equation (8) restricts the value of j_t, through the triangular condition

$$J_i+J_f \geq j_t \geq |J_i-J_f| \ , \tag{10}$$

to a range set by the specified values of J_i and J_f. This condition usually enhances the importance of the expansion (8) by reducing the number of its terms to a *very few*, with low j_t, in collisions that do not disrupt the target structure completely. The opposite limit implies a large momentum transfer $q \gg 1$ a.u., in which case the collision resolves into separate binary interactions of the projectile with individual electrons and is made unlikely by the prefactor of (2) $\propto 1/q^2$. (Note, incidentally, that effects of exchange between an incident electron and atomic electrons could be included in the first Born approximation correctly only in the limit of binary collisions; here we exclude them in this approximation, viewing them instead as an essential ingredient of $\mathbf{T}^{\text{ex}}-\mathbf{T}^B$.)

Returning, finally, to the restriction placed by parity conservation on the expansions of the form factor, we note its simple representation in terms of the parities (P_f,P_i) of the states (f,i) and the values of j_t,

$$P_iP_f=(-1)^{j_t}=(-1)^{l_f-l_i} \tag{11}$$

Let us also mention that a second set of "magnetic" form factors becomes relevant in high energy collisions where the interaction between projectile and target *currents* is no longer negligible and yields a parity selection rule opposite to (11); their contribution will *not* be considered hereafter.

B. Separation of variables

The expansion (8′) of $P_{j_t}(\hat{\mathbf{q}}\cdot\hat{\mathbf{r}}_\alpha)$ into products of harmonics $Y^*_{j_tm_t}(\hat{\mathbf{q}})Y_{j_tm_t}(\hat{\mathbf{r}}_\alpha)$ has initiated the process of factoring out the dependence of $F_{fi}(\mathbf{q})$ on $\mathbf{q}=\mathbf{k}_i-\mathbf{k}_f$ and on target variables. The harmonic $Y^*_{j_tm_t}(\hat{\mathbf{q}})$ can also be factored out of the matrix element in (8′). Paralleling this separation we shall also factor out the dependence of $F_{fi}(\mathbf{q})$ on magnetic quantum numbers, which depend on the coordinate axis, from invariant functions.

The next step in this process represents $F_{fi}(\mathbf{q})$ through the Wigner-Eckart theorem

$$F_{fi}(\mathbf{q})=\sum_{j_t m_t} i^{j_t}Y^*_{j_tm_t}(\hat{\mathbf{q}})\langle J_fM_f|j_tm_t,J_iM_i\rangle G_{fi}(j_t,q) \ , \tag{12}$$

in terms of the Wigner coefficient that depends on $\{M_f,m_t,M_i\}$ and of the invariant

$$G_{fi}(j_t,q)=4\pi\frac{\langle E_fJ_f\mu|\sum_\alpha z_\alpha Y_{j_t0}(\hat{\mathbf{r}}_\alpha)j_{j_t}(qr_\alpha)|E_iJ_i\mu\rangle}{\langle J_f\mu|j_t0,J_i\mu\rangle} \ . \tag{12′}$$

The arbitrary value of μ in (12′) can be set to 0 if J_i is an integer or to $\frac{1}{2}$ if half integer, as indicated by

$$\mu=\tfrac{1}{2}\sin^2 J_i\pi \ . \tag{12″}$$

The new factor G_{fi} still depends on the projectile momenta $(\mathbf{k}_f,\mathbf{k}_i)$, though only through their scalar combination $\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i$ in the expression of $\mathbf{q}$. This combination will be separated from G_{fi} later through expansion in Legendre polynomials $P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)$. However, a part of the dependence of G_{fi} on $\mathbf{q}$ can be separated readily through the following factorization of the Bessel function,

$$j_{j_t}(qr_\alpha)=(qr_\alpha)^{j_t}\hat{j}_{j_t}(qr_\alpha) \ , \tag{13}$$

whose modified Bessel function $\hat{j}_{j_t}$ is represented by a series in *even* powers of qr_α and remains finite at $qr_\alpha=0$. The factor q^{j_t} of (13) can be taken out of G_{fi} and combined with the harmonic $Y^*_{j_tm_t}(\hat{\mathbf{q}})$ of (11) to form a harmonic polynomial $|\mathbf{k}_i-\mathbf{k}_f|^{j_t}Y^*_{j_tm_t}(\hat{\mathbf{q}})$ in the components of $(\mathbf{k}_f,\mathbf{k}_i)$. The factor $r_\alpha^{j_t}$ combines similarly with $Y_{j_t0}(\hat{\mathbf{r}}_\alpha)$ in (12′) to form the axially symmetric polynomial $z_\alpha r_j^{j_t}Y_{j_t0}(\mathbf{r}_\alpha)$ in the components of $\mathbf{r}_\alpha$, which represents the 2^{j_t}*-pole moment* of the target's charge density at $\mathbf{r}_\alpha$. The radial oscillations, of the remaining factor of (13), $\hat{j}_{j_t}(qr_\alpha)$, modulate this multipole moment, whereby the modified coefficient

$$\hat{G}_{fi}(j_t,q)=\frac{G_{fi}(j_t,q)}{4\pi q^{j_t}}=\frac{\langle E_fJ_f\mu|\sum_\alpha z_\alpha r_\alpha^{j_t}Y_{j_t0}(\hat{\mathbf{r}}_\alpha)\hat{j}_{j_t}(qr_\alpha)|E_iJ_i\mu\rangle}{\langle J_f\mu|j_t0,J_i\mu\rangle} \tag{14}$$

represents the 2^{j_t}-pole moment of the modulated charge density of the target's transition $i\rightarrow f$. It is this 2^{j_t}-pole moment $\hat{G}_{fi}(j_t,q)$—more precisely, its ratio to the factor q^2 in the denominator of (2)—which remains to be expanded into polynomials $P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)$ to separate out the variables $(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)$. We thus set

$$q^{-2}\hat{G}_{fi}(j_t,q)=\sum_L \tfrac{1}{2}(2L+1)H_{fi}(j_t,L,k_f,k_i)\times P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)\ , \tag{15}$$

whose coefficients

$$H_{fi}(j_t,L,k_f,k_i)=\int_{-1}^{+1}d(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)q^{-2}\hat{G}_{fi}(j_t,q)P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i) \tag{16}$$

remain to be evaluated numerically as discussed in Sec. III. The desired dependence of $\mathbf{T}^B$ on the projectile directions $(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)$ is thus represented by expansion into polynomial factors

$$|\mathbf{k}_i-\mathbf{k}_f|^{j_t}Y^*_{j_tm_t}(\hat{\mathbf{q}})P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)\ . \tag{17}$$

A special note applies to "monopole" transitions, with $j_t=0$. In this case, no contribution accrues to (14) from the zeroth order term of the expansion of $\hat{j}_0$ into powers of $(qr)^2$, owing to orthogonality of the i and f states with $E_f\neq E_i$ and $J_f=J_i$. Proportionality of the matrix element to q^2 cancels the q^{-2} factor in (16).

C. T^B expansion into harmonics of $(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)$

The expansion of T^B into harmonics of the directions $\hat{\mathbf{k}}_f$ and $\hat{\mathbf{k}}_i$ must be carried out separately for each term of the earlier expansions with indices j_t and L. Since the function (17) transforms under coordinate rotations as a bra $\langle j_tm_t|$, the expansion we seek should consist of appropriate superpositions of products of Y_{lm} functions of $\hat{\mathbf{k}}_f$ and $\hat{\mathbf{k}}_i$. The transformation properties of each of these functions are specified by Eq. (6) and (6′), to ensure that the coefficient of each product shall transform just as the matrix element (3) of $\mathbf{T}^{\mathrm{ex}}$. That is, the base products shall have the form

$$Y_{l_fm_f}(\hat{\mathbf{k}}_f)Y^*_{l_im_i}(\hat{\mathbf{k}}_i)\ . \tag{18}$$

The appropriate superposition coefficient consists of two factors, namely, a vector addition coefficient for a product that transforms as a bra, and the factor $(-1)^{m_f}$ that transforms $Y_{l_fm_f}$ into $Y^*_{l_f,-m_f}$. The resulting harmonic function of the pair $(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)$ is

$$\mathcal{Y}^*_{l_fl_i,j_tm_t}(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)=\sum_{m_f,m_i}\langle j_tm_t|l_f,-m_f,l_im_i\rangle\times(-1)^{m_f}Y_{l_fm_f}(\hat{\mathbf{k}}_f)Y^*_{l_im_i}(\hat{\mathbf{k}}_i)\ . \tag{19}$$

Consider now that the expression (17) consists of two factors, one of which transforms as $\langle j_tm_t|$ while P_L is invariant. We perform then its expansion in two steps. The first step consists of expanding the first term of (17), $|\mathbf{k}_i-\mathbf{k}_f|^{j_t}Y^*_{j_tm_t}(\hat{\mathbf{q}})$, which can be cast as a polynomial of degree of j_t in the components of $\mathbf{k}_f$ and $\mathbf{k}_i$ and whose expansion into terms of degree $k_f^lk_i^{j_t-l}$ is known[4] to be

$$q^{j_t}Y^*_{j_tm_t}(\hat{\mathbf{q}})=\sum_{l=0}^{j_t}\left[\frac{4\pi(2j_t+1)!}{(2l+1)![2(j_t-l)+1]!}\right]^{1/2}\times(-1)^{j_t-l}k_f^lk_i^{j_t-l}\mathcal{Y}^*_{l,j_t-l,j_tm_t}(\hat{\mathbf{k}}_f,\hat{\mathbf{k}}_i)\ . \tag{20}$$

Note that the index pair (l_f,l_i) of (19) has been replaced here by the pair (l,j_t-l) each of which is $\leq j_t$ in accordance with the degree of the initial expression.

The second step consists now of expanding the product of the functions $\mathcal{Y}^*_{l,j_t-l,j_tm_t}$ on the right of (20) and of $P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)$ into functions (19). The indices (l_f,l_i) are now restricted only by the triangular relations among (l,L,l_f) and (j_t-l,L,l_i), where the values of L are only restricted by the convergence of the coefficients $H_{fi}(j_t,L,k_f,k_i)$ as $L\rightarrow\infty$. The coefficients of this expansion are identified by inspection as matrix elements familiar in spectroscopy,[5] namely,

$$\langle l,j_t-l,j_t,m_t|P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)|l_fl_ij_tm_t\rangle=(-1)^{l+l_i+j_t}\frac{4\pi}{2L+1}\begin{Bmatrix}j_t & j_t-l & l\\ L & l_f & l_i\end{Bmatrix}\langle l\|Y_{l_f}\|L\rangle\langle j_t-l\|Y_{l_i}\|L\rangle\ , \tag{21}$$

where

$$\langle l\|Y_{l_f}\|L\rangle=(-1)^l\left[\frac{(2l+1)(2L+1)(2l_f+1)}{4\pi}\right]^{1/2}\begin{pmatrix}l & L & l_f\\ 0 & 0 & 0\end{pmatrix}\ . \tag{21′}$$

Combination of (20) and (21) yields now the expansion of (17) in two-variable harmonics (19),

$$|\mathbf{k}_i-\mathbf{k}_f|^{j_t}Y^*_{j_tm_t}(\hat{\mathbf{q}})P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)=\frac{4\pi}{2L+1}\sum_{l_f,l_i}X(j_t,L,l_f,l_i,k_f,k_i)\mathcal{Y}^*_{l_fl_ij_tm_t}(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)\ , \tag{22}$$

with the coefficient

$$X(j_t,L,l_f,l_i,k_f,k_i)=(-1)^{l_i}k_i^{j_t}\sum_{l=0}^{j_t}\left[\frac{4\pi(2j_t+1)!}{(2l+1)![2(j_t-l)+1]!}\right]^{1/2}\langle l\|Y_L\|l_f\rangle\langle j_t-l\|Y_L\|l_i\rangle\begin{Bmatrix}l & j_t-l & j_t\\ l_i & l_f & L\end{Bmatrix}\left[\frac{k_f}{k_i}\right]^l\ . \tag{22′}$$

Note that this expansion involves only algebraic properties of projectile variables whereby its coefficients (22′) can be evaluated without reference to target properties.

Our final goal here is to expand functions of $(\hat{k}_f,\hat{k}_i)$ into products of separate harmonics of their two arguments, analogous to (6′), whose expansion coefficients will be cast as matrix elements $\langle l_f m_f| \cdots |l_i m_i\rangle$ akin to those on the right of (6). This goal is reached by transcribing (22), recalling the expression (19) of $\mathcal{Y}^*$ as a product of harmonics, in the form

$$|\mathbf{k}_i-\mathbf{k}_f|^{j_t} Y^*_{j_t m_t}(\hat{\mathbf{q}}) P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_f)=\sum_{l_f,m_f,l_i,m_i}\langle\hat{\mathbf{k}}_f|l_f m_f\rangle\langle l_f m_f||\mathbf{k}_i-\mathbf{k}_f|^{j_t}Y^*_{j_t m_t}(\hat{\mathbf{q}})P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)|l_i m_i\rangle\langle l_i m_i|\hat{\mathbf{k}}_i\rangle\;, \tag{23}$$

with

$$\langle l_f m_f||\mathbf{k}_i-\mathbf{k}_f|^{j_t}Y^*_{j_t m_t}(\hat{\mathbf{q}})P_L(\hat{\mathbf{k}}_f\cdot\hat{\mathbf{k}}_i)|l_i m_i\rangle=i^{l_f-l_i}\frac{4\pi}{2L+1}X(j_t,L,l_f,l_i,k_f,k_i)\langle j_t m_t|l_f,-m_f,l_i m_i\rangle(-1)^{m_f}\;. \tag{23′}$$

The matrix element of $\mathbf{T}^B$ on the right of (6), congruent with the matrix element (3) of $\mathbf{T}^{\text{ex}}$, can now be constructed as a linear combination of matrix elements (23′) with coefficients drawn from the previous equations (2), (12), (14), and (15). The result is

$$\langle E_f J_f M_f,k_f l_f m_f|\mathbf{T}^B|E_i J_i M_i,k_i l_i m_i\rangle=\frac{4me^2}{\hbar^2}\sqrt{k_f k_i}\sum_{L=0}^{\infty}\sum_{j_t}(-1)^{(1/2)(j_t+l_f-l_i)}H_{fi}(j_t,L,k_f,k_i)X(j_t,L,l_f,l_i,k_f,k_i)$$
$$\times\sum_{m_t}\langle J_f M_f|j_t m_t J_i M_i\rangle\langle j_t m_t|l_f,-m_f,l_i m_i\rangle(-1)^{m_f}\;. \tag{24}$$

A few remarks may illustrate Eq. (24): Its first factors derive from (2), the $\sum_L$ from (15) and the $\sum_{j_t m_t}$ from (12). The imaginary factors from (12) and (33′) yield the real factor ±1 owing to the parity Eq. (11). The coefficient H_{fi} is a target property, whose convergence at high L depends mainly on the factor q^{-2} in (16). The coefficient X has been discussed below (22′). The quantum numbers (l_f,m_f) appear in different positions on the left and right of (24), namely, in a bra on the left and in a ket on the right. The difference originates from the implied use of the relation $\mathbf{j}_t=\mathbf{l}_i-\mathbf{l}_f$ in (19) and of $\mathbf{J}_f=\mathbf{J}_i+\mathbf{j}_t$ in (12), and is rectified by the identity

$$\sum_{m_t}\langle J_f M_f|j_t m_t,J_i M_i\rangle\langle j_t m_t|l_f,-m_f,l_i m_i\rangle(-1)^{m_f}=(-1)^{l_f}\left[\frac{2j_t+1}{2l_i+1}\right]^{1/2}\sum_{m_t}\langle J_f M_f|j_t m_t,J_i M_i\rangle\langle l_f m_f,j_t m_t|l_i m_i\rangle\;, \tag{24′}$$

whose last factor represents $\mathbf{l}_i=\mathbf{j}_t+\mathbf{l}_f$. An interpretation of the $\sum_{m_t}$ on the right will emerge below.

D. Invariant form of T^B

The invariant form of $\mathbf{T}^B$, congruent with (5), results at this point by applying the transformation on the right of (5) to the expressions $\sum_{m_t}\ldots$ on the right of (24). The combination of these expressions mirrors the recoupling of three angular momenta

$$\mathbf{J}=\mathbf{J}_f+\mathbf{l}_f=(\mathbf{J}_i+\mathbf{j}_t)+\mathbf{l}_f=\mathbf{J}_i+(\mathbf{l}_f+\mathbf{j}_t)=\mathbf{J}_i+\mathbf{l}_i=\mathbf{J}\;, \tag{25}$$

represented by a well-known formula in terms of a 6j-coefficient.[6] It reads

$$\langle(j_t J_i)J_f l_f,JM|J_i(l_f j_t)l_i,JM\rangle=\sum_{M_f,m_f,M_i,m_i}\langle JM|J_f M_f,l_f m_f\rangle\langle J_f M_f|j_t m_t,J_i M_i\rangle\langle l_f m_f,j_t m_t|l_i m_i\rangle\langle J_i M_i,l_i m_i|JM\rangle$$
$$=(-1)^{(j_t+J_i+J+l_f)}[(2J_f+1)(2l_i+1)]^{1/2}\begin{Bmatrix}J_i & J_f & j_t\\ l_f & l_i & J\end{Bmatrix}\;. \tag{26}$$

Equations (24), (24′), and (26) combine now into the desired expression of $\mathbf{T}^B$,

$$\langle E_f k_f(J_f l_f)J|\mathbf{T}^B|E_i k_i(J_i l_i)J\rangle$$
$$=\frac{4me^2}{\hbar^2}\sqrt{k_f k_i}\sum_{L=0}^{\infty}\sum_{j_t=|J_i-J_f|}^{J_i+J_f}(-1)^{J_i+J+(1/2)(j_t+l_i-l_f)}[(2J_f+1)(2j_t+1)]^{1/2}$$
$$\times H_{fi}(j_t,L,k_f,k_i)X(j_t,L,l_f,l_i,k_f,k_i)\begin{Bmatrix}J_i & J_f & j_t\\ l_f & l_i & J\end{Bmatrix}\;. \tag{27}$$

As noted earlier all the target's dynamical properties are incorporated in the coefficients H_{fi} of (27), to be studied in Sec. III. The remainder of (27) consists of explicit algebraic functions of (k_f, k_i) and of angular momentum quantum numbers. Notably these numbers consist of two subsets with different restrictions: Triangular conditions restrict the magnitudes of the subsets $\{J_i, J_f, j_t, l, j_t - l\}$ in accordance with the usually low values of (J_f, J_i); the upper rows of the $6j$ coefficients in (22′) and (27) include *only* elements of this subset. The remaining subset $\{l_f, l_i, L, J\}$ is similarly restricted to values close to that of L and occurs in the lower rows of the $6j$ coefficients. The magnitude of L itself is limited only by the convergence of H_{fi} as L increases, as noted above. The dependence of the $6j$'s on a large L has been discussed in the literature.[7]

The physical dimensions of the several factors of the $\mathbf{T}^B$ expression (27) may be noted: $\mathbf{T}^B$ itself is dimensionless as are both the matrix element and its coefficient in (2). The coefficient H_{fi} has the dimensions of $(\text{length})^{j_t+2}$, being an integral over a dimensionless variable of the 2^{j_t}-pole moment $\hat{G}_{fi}$ multiplied by the inverse square wave number q^{-2}. The X coefficient has the dimensions $(\text{length})^{-j_t}$ of its factor $k_i^{j_t}$. The prefactor of the $\sum_{L=0}^{\infty}$ cancels the residual dimensions.

III. PARAMETER $H_{fi}(j_t, L, k_f, k_i)$

This parameter is defined by (16) and earlier equations as a superposition of matrix elements (2) of $\mathbf{T}^B$ with different magnitudes of the momentum transfer $\mathbf{q}$, a superposition anticipated in Sec. I. The integration variable of (16), $\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_i$, is included in the parameter

$$\begin{aligned} q^2 &= |\mathbf{k}_i - \mathbf{k}_f|^2 \\ &= (k_i - k_f)^2 + 2k_i k_f (1 - \hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_i) \\ &= 2(\bar{k}^2 - \delta\bar{k}^2) \left[(1 - \hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_i) + \frac{\delta\bar{k}^2}{2(\bar{k}^2 - \delta\bar{k}^2)} \right], \end{aligned} \tag{28}$$

where

$$\begin{aligned} \bar{k} &= \tfrac{1}{2}(k_i + k_f), \\ \frac{\delta\bar{k}}{\bar{k}} &= \frac{k_i - k_f}{k_i + k_f} \xrightarrow[\delta\bar{k}/\bar{k} \ll 1]{} \frac{1}{2} \frac{E_i - E_f}{E_i + E_f}. \end{aligned} \tag{28′}$$

This parameter occurs both in the denominator of the integrand of (16) and in the factor $\hat{G}_{fi}(j_t, q)$ through the expansion of the function

$$\hat{j}_{j_t}(qr) = \sum_{\nu=0}^{\infty} \frac{(-q^2 r^2/2)^\nu}{\nu! [2(\nu + j_t) + 1]!!} \tag{29}$$

in the matrix element of (14). The integral (16) could thus be evaluated analytically for each term of the series (29), but its net value would not be readily assessed owing to the alternating sign of those terms. Indeed, the radius of the series of integrals may prove insufficient.[8] We shall then report here an example of numerical evaluation, prefacing it by a qualitative discussion.

The oscillating function (29), $j_{j_t}(qr)/(qr)^{j_t}$, converges as $(qr)^{-(j_t+1)}$ when $qr \to \infty$ and is further multiplied in the matrix element of (14) by the exponentially converging 2^{j_t}-pole density of the $i \to f$ transition. The $\nu = 0$ term of the expansion (29), which becomes very large as $\hat{\mathbf{k}}_f \cdot \hat{\mathbf{k}}_i \to 1$, determines thus the behavior of the coefficient $H_{fi}(j_t, L, k_f, k_i)$ at large L, which we shall indicate as H_L for brevity. This term fails to contribute, however, for $j_t = 0$ as noted as the end of Sec. II B. Its contribution to H_L is represented by

$$\begin{aligned} H_L^{(0)} &= \frac{\langle E_f J_f | \sum_\alpha z_\alpha r_\alpha^{j_t} | E_i J_i \rangle}{k_i k_f} Q_L \left[\frac{1 + (\delta\bar{k}/k)^2}{1 - (\delta\bar{k}/k)^2} \right] \\ &\xrightarrow[\bar{k}/\delta\bar{k} > L \gg 1]{\delta\bar{k}/\bar{k} \ll 1} \frac{1}{\bar{k}^2} \left\langle E_f J_f \left| \sum_\alpha z_\alpha r_\alpha^{j_t} \right| E_i J_i \right\rangle \\ &\quad \times \ln \left[\frac{2}{L} \frac{E_i + E_f}{E_i - E_f} \right], \end{aligned} \tag{30}$$

where Q_L is the Lth Legendre function of the second kind. The upper limit of L in the last expression is set by the use of an approximation form of Q_L; we have in fact $Q_L(z) \to 0$ (as $L \to \infty$) at constant $z > 1$ whereas the logarithmic approximation to Q_L in (30) becomes negative for $L > \bar{k}/\delta\bar{k}$. Our interest in the approximate form lies in its showing that $\bar{k}^2 H_L^{(0)}$ depends mainly on $\bar{k}/\delta\bar{k}L$ in the intermediate range of this parameter, and vanishes as $L \to \infty$ for given $\bar{k}$ and $\delta\bar{k}$.

For purposes of illustration we have evaluated H_L numerically for a few transitions of the H atom whose form factor has an analytic expression as a function of q^2.[9] The resulting values are plotted in Fig. 1, with the scales sug-

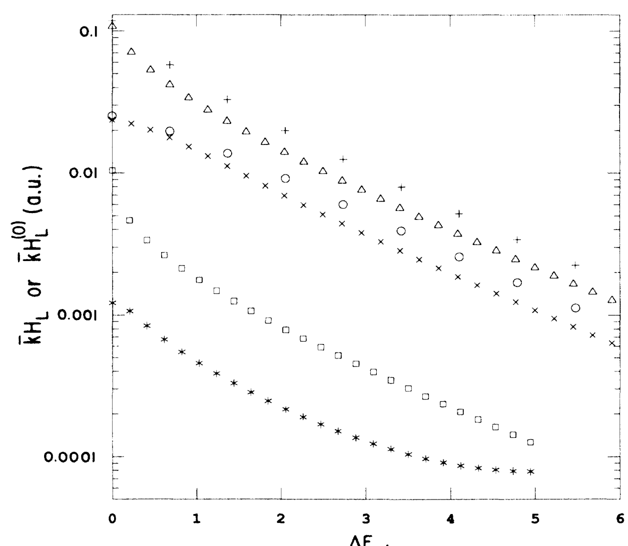

FIG. 1. Values of $H_{fi}(j_t, L, k_f, k_i)$ for $1s \to 2p$ transitions in atomic H. Notations are as in Sec. III. H_L: ○, $E_i = 20$ eV; ×, $E_i = 50$ eV, ∗, $E_i = 500$ eV. $H_L^{(0)}$: +, $E_i = 20$ eV; △, $E_i = 50$ eV; □, $E_i = 500$ eV. For $1s \to np$, $H_L \propto n^{-3}$. (For the physical dimension of H_{fi} see text at end of Sec. II). Note how the scale adjustments of abscissas and ordinates condense the data into similar curves.

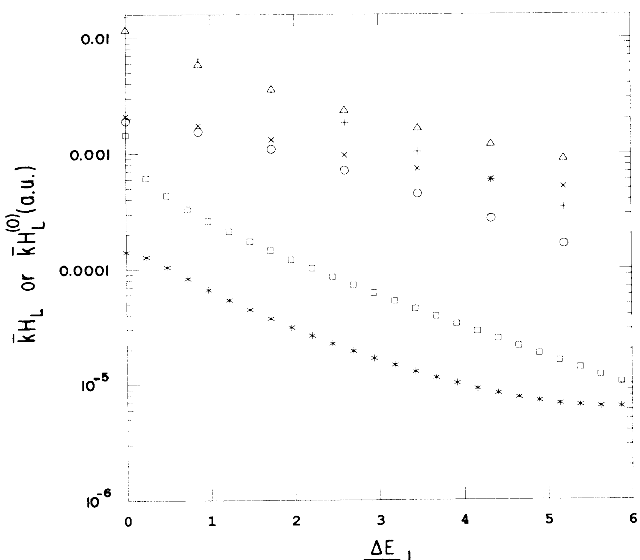

FIG. 2. Values of $H_{fi}(j_t, L, k_f, k_i)$ for $1s \rightarrow 3d$; notations as in Fig. 1.

gested by the analysis of $H_L^{(0)}$, except that it proves more practical to plot $\bar{k}H_L$ rather than $\bar{k}^2 H_L$. The low values of the ratio $H_L/H_L^{(0)}$ reflect the partial cancellations resulting from the sum in Eq. (29). The lower values of H_L for the quadrupole transition $1s \rightarrow 3d$ are shown in Fig. 2.

IV. FINAL REMARKS

Equation (27) represents $\mathbf{T}^B$, the first Born contribution to a collision amplitude, in the same frame as was used in Eq. (5) for the "exact" amplitude $\mathbf{T}^{\text{ex}}$, thus completing the task outlined in Sec. I. As anticipated in Sec. I, the expression (27) of $\mathbf{T}^B$ amounts to a superposition of the familiar Born approximation matrix elements (2), which are included in the coefficients $H_{fi}(j_t, L, k_f, k_i)$ through their definition (16) and through the earlier relations (14), (12′), (8), and (7). Subtraction of (27) from (5) defines a set of collision amplitudes

$$\langle E_f k_f (J_f l_f) J | \mathbf{T}^{\text{ex}} - \mathbf{T}^B | E_i k_i (J_i l_i) J \rangle$$

whose magnitude converges to zero rapidly as J increases, thus restricting the scope of "exact" calculations of the target plus projectile complex.

Sample calculations of inelastic collisions of slow electrons with atoms are planned within this limited scope, by the same R-matrix procedure that has yielded input data for spectroscopic applications.[10] These data consist essentially of scattering eigenphases and eigenvectors, which yield spectroscopic information by multichannel quantum-defect techniques on the one hand and collision data on the other hand. Making their link to collisions practicable was the primary motivation of the present paper.

An incidental benefit accrues to the analysis of collisions from the introduction of the angular momentum transfer $\mathbf{j}_t$ in our treatment [Eq. (9)]. Even though the explicit dependence of $\mathbf{T}^B$ on the momentum transfer $\mathbf{q}$ has been transformed away in Sec. II, we are aware that the direction $\hat{\mathbf{q}}$ of target recoil has been seen to provide a convenient coordinate axis for the study of collisions regardless of its relevance to the Born approximation.[11] In this context we note that the invariance of $\mathbf{T}^B$ in Eq. (2) under rotations about $\hat{\mathbf{q}}$ implies $M_f = M_i$ in the $\hat{\mathbf{q}}$ frame together with the restriction of the $\sum_{m_t}$ to $m_t = 0$ in (8′), (23′), and following equations. Nonzero elements of the transition matrix with $m_t \neq 0$ in this frame are accordingly a signature of the contributions of $\mathbf{T}^{\text{ex}} - \mathbf{T}^{\text{B}}$. There are only a few such contributions, in general, owing to the restriction (9). Their relevance to the multipole transitions of the collision target is represented by Eq. (11) and following of Ref. 12.

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