Impact-Parameter Method for Proton–Hydrogen-Atom Collisions. III. The Use of Non-Hydrogenic Expansion Functions in Coupled-State Calculations*

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The boundary condition (at $t \to \infty$) previously shown to be associated with the customary time-dependent Schrödinger equation of the impact-parameter method places a restriction upon the approximate or trial wave functions which are to be used in the usual coupled-state calculations. For the trial wave function to be physically acceptable, it must belong to the class of functions which have the asymptotic form of the exact wave function. This simply means that one must obtain from the coupled-state calculation, approximate transition amplitudes for which the absolute squares are time independent as $t \to \infty$. It is noted that the trial wave function in the six-, eight-, and nine-state Sturmian calculations are not physically acceptable. The trial wave function in the pseudostate calculation of Cheshire, Gallaher, and Taylor is acceptable; however, if one attempted to include an additional pseudostate with the same symmetry as one already in the set, then this trial wave function would not be physically acceptable.

I. INTRODUCTION

The basis for the impact-parameter model customarily used for the calculation of cross sections for proton–hydrogen-atom scattering was given in the first paper of this series.[1] Briefly, the model corresponds to a point charge, denoted here as proton 2, moving along the trajectory

$$\vec{R}_1(t) = \vec{b} + vt\hat{Z},$$

and thereby perturbing hydrogen atom 1. A solution is sought to the time-dependent Schrödinger equation[1]:

$$i\left(\frac{\partial}{\partial t}\right)_{\vec{r}} \psi(\vec{r}, t) = H(\vec{r}, t)\psi(\vec{r}, t),$$

$$H(\vec{r}, t) = -\frac{1}{2}\nabla_{\vec{r}}^2 - \frac{1}{|\vec{r} + \frac{1}{2}\vec{R}_1|} - \frac{1}{|\vec{r} - \frac{1}{2}\vec{R}_1|} + \frac{1}{R_1}, \tag{1}$$

where $\vec{r}$ is the electronic position vector with respect to the midpoint of $\vec{R}_1$. The boundary conditions for Eq. (1) are[1]

$$\psi \sim \phi_i^T e^{-i\epsilon_n t} \quad \text{as } t \to -\infty$$

and

$$\psi \sim \phi_i^T e^{-i\epsilon_n t} + \sum_n A_{ni}\phi_n^T e^{-i\epsilon_n t}$$

$$= \sum_n a_n \phi_n^T e^{-i\epsilon_n t} \quad \text{as } t \to \infty, \tag{2}$$

where $\phi_n^T = T\phi_n$ and T is the unitary translation operator associated with the translation of the origin of the coordinate system from proton 1 to the midpoint of $\vec{R}_1$.[2] The discrete transformed basis vectors ϕ_n^T approach the familiar traveling atomic orbitals[3] as $|t| \to \infty$,[1]

$$\phi_n^T \sim \phi_n(\vec{r}_1)\, e^{-ivx/2}. \tag{3}$$

As previously discussed,[4] the two-centered traveling-orbital expansion provides a very useful scheme by which approximate solutions to Eq. (1) can be developed.[5,6] In this method one constructs a sequence of approximate solutions to Eq. (1) as follows:

$$\psi_N = \sum_{k=1}^{2} \sum_{n=1}^{N} b_{nk}(t)\Phi_{nk}, \quad N = 1, 2, \ldots \tag{4}$$

where[3]

$$\Phi_{nk} = \phi_n(\vec{r}_k)\, e^{\mp ivx/2}\, e^{-i(\epsilon_n + v^2/8)t}$$

$$\equiv \Upsilon_{nk}\, e^{-i(\epsilon_n + v^2/8)t}, \tag{5}$$

and the upper sign applies if $k = 1$, while the lower sign applies if $k = 2$. The unknown coefficients b_{nk} are determined from the set of coupled equations:

$$\left\langle \Phi_{nk} \middle| H - i\frac{\partial}{\partial t} \middle| \psi_N \right\rangle = 0, \; n = 1, 2, \ldots, N, \quad k = 1, 2 \tag{6}$$

with the initial condition

$$b_{nk}(t) \sim \delta_{ni}\,\delta_{k1} \quad \text{as } t \to -\infty.$$

In the Sturmian[7] and pseudostate calculations,[8] approximate wave functions in the form of Eq. (4) were constructed using a finite set of Sturmian functions or pseudofunctions, and Eq. (6) was used to determine the expansion coefficients. It has been suggested that the choice of basis functions

for such calculations is somewhat arbitrary, and computational convenience and flexibility should be the criteria for selection.[6,9,10] However, we will argue that these criteria are not restrictive enough. It is possible in such calculations to obtain transition amplitudes for which the absolute squares do not have limits as $t\to\infty$. We note that the boundary conditions for Eq. (1) place a restriction upon the approximate wave function ψ_N used in a calculation. The calculated transition probabilities must be time independent. This physical requirement is not satisfied by the Sturmian calculations[7]; the approximate wave functions in the six-, eight-, and nine-state Sturmian calculations[7] are not physically acceptable. The pseudostate calculation of Cheshire, Gallaher, and Taylor[8] does meet this physical requirement. However, if one attempted to extend the pseudostate calculation by adding to the basis set another pseudostate of the same symmetry type, a $\bar{4}s$ pseudostate, for example, then the physical requirement would not be satisfied by such calculation.

II. RESTRICTIONS ON EXPANSION FUNCTIONS

By substituting Eq. (4) into Eq. (6), one obtains the following coupled equations for the expansion coefficients:

$$i\sum_{j=1}^{2}\sum_{m=1}^{N} e^{i\epsilon_{nk}t}S_{nkmj}(t)\,e^{-i\epsilon_{mj}t}\left(\frac{d}{dt}\right)b_{mj}(t) = \sum_{j=1}^{2}\sum_{m=1}^{N} e^{i\epsilon_{nk}t}G_{nkmj}(t)\,e^{-i\epsilon_{mj}t}\,b_{mj}(t),$$
$$n=1,2,\ldots,N,\quad k=1,2 \qquad (7)$$

where

$$S_{nkmj}=\langle\Upsilon_{nk}|\Upsilon_{mj}\rangle,$$
$$G_{nkmj}=\left\langle\Upsilon_{nk}\left|H-i\frac{\partial}{\partial t}\right|\Phi_{mj}\right\rangle e^{i(\epsilon_{mj}+v^2/8)t},$$

and Υ_{nk} is defined in Eq. (5). Equation (7) can be written in matrix form as follows:

$$i\frac{d}{dt}\,\underline{b}(t)=\underline{e}^{iEt}\,\underline{S}^{-1}\,\underline{G}\,\underline{e}^{-iEt}\,\underline{b}(t), \qquad (8)$$

where $\underline{b}=\mathrm{Col}\{b_{11},b_{21},\ldots,b_{N1}|b_{12},b_{22},\ldots,b_{N2}\}$ and

$$\underline{e}^{iEt}=(\underline{e}^{-iEt})^{\dagger}=\begin{pmatrix}\underline{W} & \underline{0}\\ \underline{0} & \underline{W}\end{pmatrix},$$

where $\underline{W}$ is an $N\times N$ diagonal matrix with elements $W_{nn}=e^{i\epsilon_n t}$. The matrices $\underline{S}$ and $\underline{G}$ are defined as follows:

$$\underline{S}=\begin{pmatrix}\underline{S}_{11} & \underline{S}_{12}\\ \underline{S}_{21} & \underline{S}_{22}\end{pmatrix},\quad \underline{G}=\begin{pmatrix}\underline{G}_{11} & \underline{G}_{12}\\ \underline{G}_{21} & \underline{G}_{22}\end{pmatrix},$$

where $\underline{S}_{kj}$ and $\underline{G}_{kj}$ are matrices of elements

$$S_{nkmj}=\langle\Upsilon_{nk}|\Upsilon_{mj}\rangle$$

and

$$G_{nkmj}=\left\langle\Upsilon_{nk}\left|H-i\frac{\partial}{\partial t}\right|\Phi_{mj}\right\rangle e^{i(\epsilon_m+v^2/8)t},$$

respectively. In order for ψ_N to be an acceptable trial function, the boundary conditions of Eq. (1) must be satisfied. This implies that

$$b_{nk}(t)\sim\delta_{ni}\,\delta_{k1}\ \text{(for example)}\qquad \text{as } t\to-\infty$$

and

$$b_{nk}(t)\sim b_{nk}\ \text{(a constant)}\qquad \text{as } t\to\infty,$$

since the quantities b_{nk} are interpreted as transition amplitudes.

More precisely, let the vector $\underline{a}=\mathrm{Col}\{a_{11},a_{21},\ldots|a_{12},a_{22},\ldots\}=\mathrm{Col}\{\underline{a}_1|\underline{a}_2\}$ denote a vector of the true transition amplitudes, then according to this approximation scheme,

$$\underline{a}(t)\approx\mathcal{P}(t)\,\underline{b}(t), \qquad (9)$$

where $\mathcal{P}(t)$ is a projection matrix,

$$\mathcal{P}(t)=\begin{pmatrix}\mathcal{P}_{11} & \mathcal{P}_{12}\\ \mathcal{P}_{21} & \mathcal{P}_{22}\end{pmatrix},$$

and $\mathcal{P}_{kj}$ is a matrix of elements:

$$\langle\phi_{nk}^{T}e^{-i\epsilon_n t}|\Phi_{mj}\rangle=e^{-iv^2t/8}\,e^{+i\epsilon_n t}\langle\phi_{nk}^{T}|\Upsilon_{mj}\rangle e^{-i\epsilon_m t}$$
$$=e^{-iv^2t/8}\,e^{i\epsilon_n t}P_{nkmj}\,e^{-i\epsilon_m t},$$

and so Eq. (9) can be written as follows:

$$\underline{a}(t)\approx e^{-iv^2t/8}\,\underline{e}^{iEt}\,\underline{P}\,\underline{e}^{-iEt}\,\underline{b}. \qquad (10)$$

The elements of a_k are ordered so that $1\to 1s$, $2\to 2s$, $3\to 2p_0$, $4\to 2p_1$, $5\to 3s$, etc.

Since the physical states ϕ_{nk}^{T} approach the spatial part of the traveling orbitals Υ_{nk} as $t\to\infty$, $\underline{P}$ has a simple form as $t\to\infty$:

$$\underline{P}\sim\underline{P}_0,$$

where $(\underline{P}_0)_{kj}=0$ and $(\underline{P}_0)_{kk}$ is an infinite matrix with elements all equal to zero, except the first N diagonal terms which are unity. Further, it is well known that the matrix elements of $\underline{G}_{kj}$ vanish in the limit $t\to\infty$, and hence for sufficiently large t, the right-hand side of Eq. (8) can be replaced by zero. That is, for $t>t'$ (where t' is sufficiently large),

$$i\frac{d}{dt}\,\underline{b}(t)\approx 0,$$

and therefore for $t>t'$,

$$\underline{b}_0(t)\approx\underline{b}(t'),$$

where $\underline{b}_0$ is the vector of limiting values of the expansion coefficients obtained in the calculation. Hence from Eq. (10),

$$\underline{a}_0\approx\underline{P}_0\underline{b}_0=e^{-iv^2t/8}\times\mathrm{Col}\{b_{11}(t'),\ldots,b_{N1}(t'),0\ldots|\,b_{12}(t'),\ldots,b_{N2}(t'),0\ldots\},\quad(11)$$

and since the elements of $\underline{b}_0$ are constants, physically acceptable transition probabilities are obtained when the two-centered traveling hydrogenic expansion is used.

Now consider the trial function

$$\Psi_N=\sum_{k=1}^{2}\sum_{k=1}^{N}b_{nk}(t)X_{nk},\quad(12)$$

where

$$X_{nk}=\chi_n(\vec{r}_k)\,e^{\mp ivz/2}\,e^{-i(\alpha_{nk}+v^2/8)t}=\zeta_{nk}\,e^{-i(\alpha_{nk}+v^2/8)t},$$

and where χ_n is some type of orbital such as a pseudostate[8] or Sturmian function[7] and α_{nk} is a phase factor chosen in some arbitrary manner.[7,8] The expansion coefficients are determined from Eq. (8), where of course the elements of $\underline{S}$ and $\underline{G}$ are now

$$S_{nkmj}=\langle\zeta_{nk}|\zeta_{mj}\rangle$$

and

$$G_{nkmj}=\left\langle\zeta_{nk}\left|H-i\frac{\partial}{\partial t}\right|X_{mj}\right\rangle e^{i(\alpha_{mj}+v^2/8)t}$$

and Eq. (8) becomes

$$i\frac{d}{dt}\underline{b}(t)=\underline{e}^{iAt}\underline{S}^{-1}\underline{G}\,\underline{e}^{-iAt}\underline{b}(t),\quad(13)$$

where the matrix $\underline{e}^{iAt}$ is the same as the matrix $\underline{e}^{iEt}$ except that the diagonal elements are $e^{i\alpha_i t}$ instead of $e^{i\epsilon_i t}$. The boundary conditions of Eq. (1) restrict the trial function, Eq. (12), indirectly, since the absolute squares of the expansion coefficients are not interpreted as transition probabilities. From Eq. (9),

$$\underline{a}\approx\mathcal{P}\,\underline{b},\quad(14)$$

where

$$\mathcal{P}=e^{-iv^2t/8}\,\underline{e}^{iEt}\,\underline{P}\,\underline{e}^{-iAt},$$

and in this case the elements of $\underline{P}$ are

$$P_{nkmj}=\langle\phi^T_{nk}|\zeta_{mj}\rangle\sim\langle\Upsilon_{nk}|\zeta_{mj}\rangle.$$

Obviously, the restriction imposed upon ψ_N by the boundary conditions are that the absolute squares of the elements of $\underline{a}$ approach constant values as $t\to\infty$.

For large t the right-hand side of Eq. (13) usually takes the following form:

$$i\frac{d}{dt}\underline{b}_0=\underline{e}^{iAt}(\underline{S}^{-1}\underline{G})_0\,\underline{e}^{-iAt}\underline{b}_0(t)\quad t>t'$$
$$=\underline{e}^{iAt}\underline{K}_0\,\underline{e}^{-iAt}\underline{b}_0(t),\quad(15)$$

where $\underline{K}_0$ is a matrix of constants. With the transformation

$$\underline{B}(t)=\underline{e}^{-iAt}\underline{b}_0(t),\quad(16)$$

Eq. (15) becomes

$$i\frac{d}{dt}\underline{B}(t)=(\underline{A}+\underline{K}_0)\underline{B}(t),\quad(17)$$

where of course $\underline{A}$ is block diagonal, and the blocks are diagonal with elements α_i. Let $\underline{T}$ be a matrix that diagonalizes $(\underline{A}+\underline{K}_0)$[11]; then

$$\underline{T}^{-1}(\underline{A}+\underline{K}_0)\underline{T}=\underline{\Lambda},$$

where $\underline{\Lambda}$ is a diagonal matrix with elements λ_i (the eigenvalues of $\underline{A}+\underline{K}_0$), and if we define

$$\underline{C}(t)=\underline{T}^{-1}\underline{B}(t),\quad(18)$$

then from Eq. (17),

$$i\frac{d}{dt}\underline{C}(t)=\underline{\Lambda}\,\underline{C}(t),\quad t>t'$$

so

$$\underline{C}(t)=\underline{e}^{-i\Lambda(t-t')}\underline{C}(t')$$

and therefore from Eqs. (16) and (18),

$$\underline{b}_0(t)=\underline{e}^{iAt}\underline{T}\,\underline{e}^{-i\Lambda(t-t')}\underline{C}(t').$$

Consequently, Eq. (14) can be written as

$$\underline{a}_0=e^{-iv^2t/8}\,\underline{e}^{iEt}\underline{P}_0\underline{T}\,\underline{e}^{-i\Lambda(t-t')}\underline{C}(t')$$
$$=e^{-iv^2t/8}\,\underline{e}^{iEt}\underline{P}_0\underline{T}\,\underline{e}^{-i\Lambda(t-t')}\,\underline{T}^{-1}\underline{e}^{-iAt'}\underline{b}_0(t'),\quad(19)$$

and the boundary conditions of Eq. (1) impose the condition that the absolute values of the elements of the vector

$$\underline{V}=\underline{e}^{iEt}\underline{P}_0\underline{T}\,\underline{e}^{-i\Lambda(t-t')}\,\underline{T}^{-1}\underline{e}^{-iAt'}\underline{b}_0(t')\quad(20)$$

be time independent.

As an example, consider the four-state Sturmian calculation.[7] The trial function is

$$\Psi_N=\sum_{k=1}^{2}\sum_{n=1}^{4}b_{nk}(t)X_{nk}.$$

The expansion functions X_{nk} have been chosen such that X_{1k} corresponds to a traveling hydrogenic $1s$ orbital, X_{3k} corresponds to a traveling hydrogenic $2p_0$ orbital, X_{4k} corresponds to a traveling hydrogenic $2p_1$ orbital, and in a way X_{2k} can be regarded as a pseudo-$2s$-function. We find

$$\underline{S}_0^{-1}=\underline{I},\quad \underline{K}_0=\underline{G}_0,$$

where $\underline{G}_0$ is block diagonal, and the elements of the blocks are zero except for the (1, 2) element and the (2, 2) element which are

$$G_{12}=-\frac{1}{2}\,\frac{\langle\chi_{1k}|\chi_{2k}\rangle}{1-|\langle\chi_{1k}|\chi_{2k}\rangle|^2}=-\frac{1}{2}\,\frac{S_{12}}{1-|S_{12}|^2},$$

$$G_{22}=\tfrac{1}{2}\,|S_{12}|^2/1-|S_{12}|^2.$$

(The elements of a matrix are labeled by row index first and column index second in this work, and the block index has been suppressed.) We find that $\underline{T}$ is also block diagonal with all elements zero except for unity along the diagonal, and $-S_{12}$ for the (1, 2) element. The matrix $\underline{\Lambda}$ is of course block diagonal, with elements ϵ_1, h_2+G_{22}, ϵ_3, and ϵ_4, respectively. We find that $\underline{P}_0$ is also block diagonal, and the elements of a block are unity along the diagonal; except for the (2, 2) element which is P_{22}, the (1, 2) element which is S_{12}, and the (2, 1) element which is S_{21}. Consequently,

$$\underline{a}_{0k}\approx e^{-iv^2t/8}\begin{bmatrix} b_{1k}(t)+S_{12}\,b_{2k}(t')\,e^{i\alpha_i t'} \\ P_{22}\,b'_{2k}(t')\,e^{i(\epsilon_2-G_{22})t} \\ b_{3k}(t') \\ b_{4k}(t') \\ P_{52}\,b'_{2k}(t')\,e^{i(\epsilon_5-G_{22})t} \\ \vdots \end{bmatrix}, \tag{21}$$

where

$$b'_{ik}(t')=b_{ik}(t')\,e^{iG_{ii}t'}.$$

The trial function in the four-state Sturmian calculation therefore satisfies the boundary conditions of Eq. (1). This, however, is not true for the six-, eight-, or nine-state Sturmian calculations.[7] One finds in these calculations that the absolute square of the amplitudes for the transitions to the higher states of a symmetry class are not independent of time[12]; for example, in the nine-state Sturmian calculation, the transition probabilities corresponding to the transitions

$$1S\to 2S,\ 3S,\ldots$$
$$1S\to 3P,\ 4P,\ldots$$
$$1S\to 4D,\ 5D,\ldots$$
$$\vdots$$

are not physically acceptable, because these approximate transition probabilities are not time independent.

As another example consider the pseudostate calculation of Cheshire, Gallaher, and Taylor.[8] By exactly the same procedure, we find

$$\underline{a}_{0k}\approx e^{-iv^2t/8}\begin{bmatrix} b_{1k}(t') \\ b_{2k}(t') \\ b_{3k}(t') \\ b_{4k}(t') \\ P_{55}\,b'_{5k}(t')\,e^{i(\epsilon_5-\lambda_5)t} \\ P_{66}\,b'_{6k}(t')\,e^{i(\epsilon_6-\lambda_6)t} \\ P_{77}\,b'_{7k}(t')\,e^{i(\epsilon_7-\lambda_7)t} \\ \vdots \end{bmatrix}, \tag{22}$$

and thus the trial function in this pseudostate calculation[8] satisfies the boundary conditions. However, had they included a $\overline{4s}$-pseudo-state in the basis set, which is orthogonal to the other members of the set, the result would have been

$$\underline{a}_{0k}\approx e^{iv^2t/8}\begin{bmatrix} b_{1k}(t') \\ b_{2k}(t') \\ b_{3k}(t') \\ b_{4k}(t') \\ [P_{55}\,\alpha(t)+P_{58}\,\beta(t)]\,e^{i\epsilon_5 t} \\ P_{66}\,b'_{6k}(t')\,e^{i(\epsilon_6-\alpha_6-G_{66})t} \\ P_{77}\,b'_{7k}(t')\,e^{i(\epsilon_7-\alpha_7-G_{77})t} \\ 0 \\ 0 \\ 0 \\ [P_{11,5}\,\alpha(t)+P_{11,8}\,\beta(t)]\,e^{i\epsilon_{11}t} \\ 0 \\ 0 \\ 0 \end{bmatrix}. \tag{23}$$

The quantities $\alpha(t)$ and $\beta(t)$ in the fifth element, the eleventh element, and all other elements corresponding to the amplitudes for transitions to the higher S states oscillate in time with different frequencies. Therefore, such a trial wave function would not be physically acceptable.

We conclude that the four-state Sturmian calculation[7] satisfies the physical requirement imposed upon a calculation by the boundary conditions of Eq. (1), but the six-, eight-, and nine-state Sturmian calculations do not.[7] In addition, we note from Eqs. (22) and (23) that one must exercise care when choosing a basis set which contains pseudostates. In general the basis set must be such that the absolute squares of the

elements of the vector

$$\underline{V} = e^{iEt}\underline{P}_0\underline{T}\, e^{-i\Lambda(t-t')}\underline{T}^{-1}\underline{e}^{-iAt'}\underline{b}_0(t') \qquad (24)$$

be time independent. We suggest that Eq. (24) be added to the set of criteria determining the utility of a basis set.

One could argue that since there are defects in even the two-centered traveling hydrogenic calculations, one could relax the physical requirement imposed upon a calculation by the boundary conditions of Eq. (1). It would only be required that some of the calculated amplitudes lead to physically acceptable transition probabilities. For example, according to this weaker requirement, the $2p$ transition probabilities obtained in the nine-state Sturmian calculation[7] would be acceptable approximate transition probabilities, while the other transition probabilities would not. Such a relaxation of this physical requirement is questionable. The defects in the two-centered traveling hydrogenic calculations are due to the usual truncation error, and the loss of flexibility in the truncated subspace which results from using a two-centered expansion.[4] The defect illustrated by the Sturmian calculations[7] is more serious, however; for it corresponds to transitions continuing to occur between physical states as $t \to \infty$, and of course has no physical significance. It is true that such a defect does not necessarily prevent one from interpreting the squares of those amplitudes which become time independent as transition probabilities, but such an interpretation is questionable.

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