Impact-Parameter Method for Proton–Hydrogen-Atom Collisions. II. The Coupled-State Calculation, and Convergence of the Two-Centered Traveling Hydrogenic Expansion*

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Several calculational procedures for generating approximate solutions to the time-dependent Schrödinger equation of the impact-parameter model are discussed in this work. It is emphasized that in these calculational procedures a trial wave function is selected from a definite class of functions the class of functions which have the asymptotic form of the exact wave function and then some property satisfied by the exact wave function is used to fix the trial wave function. The customary set of coupled equations can be obtained by requiring that the Schrödinger equation be satisfied in the subspace defined by the basis set used to express the trial wave function. Recently, it has been popular to show that these coupled equations follow by making certain functionals stationary. It is shown, however, that these functionals are not stationary about the exact solution for the variations represented by available trial wave functions which, as they must, reflect our ignorance of the exact nature of the true wave function. In this work, a functional related to the norm of the exact wave function is given, and this functional is shown to be stationary about the exact wave function for the variations represented by available trial wave functions. A calculational procedure based upon the stationary property of this functional is given by which variational parameters in a trial wave function can be determined. If these parameters are taken to be time-varying nuclear charges in the basis functions, one obtains the equations given by Cheshire. Finally, the question of convergence of the two-centered traveling hydrogenic orbital expansion is considered. We conclude that the two-centered expansion does not provide a scheme by which a sequence of approximate wave functions can be generated that converges to the exact wave function. However, it appears from the comparison of the approximate cross sections obtained in two-, four-, eight-, and 14-state calculations that the cross sections for the 1s exchange reaction and possibly for the 2s transitions may be tending to limiting values.

I. INTRODUCTION

The time-dependent impact-parameter model used to study high-energy proton–hydrogen-atom scattering has been examined in the first paper of this series.[1] Specifically, it is found that there are two equivalent Schrödinger time representations in which to describe the model system of a hydrogen atom being perturbed by a moving point charge.[1] Since the boundary conditions associated with the second Schrödinger equation would be difficult to apply, we shall consider in this work only the first equation [Eq. (23) of paper I], which is[1]

$$i\frac{\partial}{\partial t}\psi = [h_1 + V_1(t)]\psi, \tag{1}$$

where

$$h_1 = -\tfrac{1}{2}\nabla_{\vec{r}_1}^2 - 1/r_1,$$

$$V_1(t) = 1/R_1(t) - 1/|\vec{r}_1 - \vec{R}_1(t)|.$$

The vectors $\vec{r}_1$ and $\vec{R}_1(t)$ denote the positions of the electron and proton 2 with respect to proton 1.

The boundary conditions associated with Eq. (1) are from Eq. (23a) of paper I[1]:

$$\psi \sim \phi_{i1} e^{-i\epsilon_{i1}t} \quad \text{as } t \to -\infty \tag{2}$$

and

$$\psi \sim \phi_{i1} e^{-i\epsilon_{i1}t} + \sum_{n1} A_{n1i1}\phi_{n1} e^{-i\epsilon_{n1}t} \equiv \sum_{n1} a_{n1i1}\phi_{n1} e^{-i\epsilon_{n1}t} \quad \text{as } t \to \infty,$$

where ϕ_{n1} is an eigenvector of h_1, with eigenvalue ϵ_{n1}, ϕ_{i1} is the initial state of the system, and A_{n1i1} is the amplitude for the transition from the state ϕ_{i1} to the state ϕ_{n1} induced by the perturbation V_1. The index denoting the identity of the proton which is the nucleus of the hydrogen atom will be suppressed in what follows when the meaning is clear.

Equation (1) is customarily written in the coordinate system with origin at the midpoint of $\vec{R}_1$; transforming Eq. (1), we obtained[1]

$$i\left(\frac{\partial}{\partial t}\right)_T \psi^T(t) = (h^T + V^T)\psi^T, \tag{3}$$

where

$$h^T = T h_1 T^\dagger = -\tfrac{1}{2}\nabla_{\vec{r}}^2 - 1/|\vec{r} + \tfrac{1}{2}\vec{R}(t)|\,,$$

$$V^T = T V_1 T^\dagger = 1/R_1 - 1/|\vec{r} - \tfrac{1}{2}\vec{R}_1|\,,$$

$$\left(\frac{\partial}{\partial t}\right)_T = T\frac{\partial}{\partial t}T^\dagger = \left(\frac{\partial}{\partial t}\right)_{\vec{r}}\,,$$

and where $\vec{r}$ is the position of the electron with respect to the midpoint of $\vec{R}_1$. The operator T is the unitary translation operator associated with the transformation of coordinates.[2] The boundary conditions associated with Eq. (3) are[1]

$$\psi^T \sim \phi_i^T e^{-i\epsilon_i t} \quad \text{as } t \to -\infty \tag{4}$$

and

$$\psi^T \sim \phi_i^T e^{-i\epsilon_i t} + \sum_n A_{ni}\,\phi_n^T e^{-i\epsilon_n t} \quad \text{as } t \to \infty\,,$$

where

$$\phi_n^T = T\phi_n\,, \tag{5}$$

and it was shown that the discrete transformed orbitals ϕ_n^T approach the spacial part of the familiar traveling atomic orbitals[3] as $|t| \to \infty$[1]:

$$\phi_n^T \sim \phi_n(\mathbf{r}_1)e^{-ivs/2}\,. \tag{6}$$

It has not been possible to obtain the exact solution of Eq. (1) or (3). Instead, several calculational procedures have been developed by which approximate solutions can be obtained.[4] By construction, these methods correspond to generating approximate wave functions in a subspace of the complete Hilbert space, and therefore only approximations to the set of exact transition amplitudes, shown in Eq. (2) or (4), can be obtained. In this work, we take the point of view that it is inconsistent not to recognize this fact, and calculational procedures based upon the tacit assumption that the error between the exact and trial wave function vanishes as $|t| \to \infty$ are inconsistent and arbitrary.

Since one must necessarily deal with the continuum, an expansion in the basis $\{\phi_n\}$ or $\{\phi_n^T\}$ is really a formal expansion; and since an account of the continuum is necessary, the approximation obtained by neglecting the contribution from the continuum would not be expected to be good. Consequently, one must turn to other approximation schemes. We consider the very successful scheme provided by the two-centered traveling-orbital expansion.[3-9] Wilets and Gallaher[8] concluded that the two-centered traveling hydrogenic orbital expansion is converging very slowly, while Rapp and Dinwiddie[9] concluded that the convergence, at least for the 1*s* exchange and 2*s* cross sections, appears fairly rapid. The question of convergence is considered in this work. There has been an attempt to show that this approximation scheme is variational in nature by showing that the coupled equations follow by requiring that a certain functional be stationary.[4,10-14] This variational nature has then been cited as the justification for using as a trial wave function a time-dependent linear combination of (i) arbitrary exponentials,[8] (ii) traveling Sturmian functions,[8,12] (iii) traveling hydrogenic functions with time-varying nuclear charges,[8,13,14] and (iv) a combination of atomic and molecular traveling orbitals.[11] However, in some of this work, it is possible to obtain transition amplitudes which do not have limits as $t \to \infty$,[12] and in one case it is not possible to obtain an unique solution because the coupled equations become redundant.[11] Obviously, these defects suggest that the variational justification for this approximation scheme is more restrictive than previously realized. In this work, we examine the variational nature of the calculation, and conclude that the justification is not variational in the implied sense.[4,10-14] That is, in the sense that one determines that a functional is stationary about the exact wave function for variations in unknown quantities, in this case not only the shape of the wave function in the strong-interaction region, but also the transition amplitudes; and then uses the stationary property of the functional to fix the unknown parameters in the trial function. We show that the functional assumed to be stationary in previous work[4,10-14] is not in fact stationary about the true solution for the type of variation represented by available trial functions which, as they must, reflect our ignorance of the exact nature of the true wave function. A functional is given in this work which is stationary about the true wave function for all variations that maintain the asymptotic form of the exact wave function, and the relationship between a calculational procedure based upon the stationary property of this functional and the Euler-Lagrange[13,14] procedure is demonstrated.

II. APPROXIMATION METHODS

A. Variation Methods

Consider the functional

$$I(\chi) = \int_{-\infty}^{\infty} dt \langle \chi | h + V - i\frac{\partial}{\partial t} | \chi \rangle\,, \tag{7}$$

which is defined on the class of functions $[\chi]$. For χ to belong to the class $[\chi]$ it must have the asymptotic behavior

$$\chi \sim \phi_i\, e^{-i\epsilon_i t} \qquad \text{as } t \to -\infty \tag{8}$$

and

$$\chi \sim \sum_n c_n \phi_n\, e^{-i\epsilon_n t} \quad \text{as } t \to \infty\,,$$

where ϕ_n and ϵ_n are, respectively, eigenvectors and eigenvalues of h, the hydrogen-atom Hamiltonian, and c_n are arbitrary coefficients. The first-order variation of I due to a variation in χ about ψ is

$$\delta I(\psi) = \int_{-\infty}^{\infty} dt \langle \psi | h + V - i\frac{\partial}{\partial t} | \delta\psi \rangle \ . \tag{9}$$

The variation is subject to Eq. (8), but is otherwise arbitrary; therefore from Eqs. (2) and (8),

$$\delta\psi \sim 0 \qquad \text{as } t \to -\infty$$

and

$$\delta\psi \sim \sum_n \delta a_n \phi_n e^{-i\epsilon_n t} \quad \text{as } t \to \infty , \tag{10}$$

where, of course, δa_n is the error in the approximate transition amplitude c_n. Using the fact that h and V are Hermitean operators, and integrating Eq. (9) by parts, we find

$$\delta I(\psi) = -i\sum_n a_n^* \delta a_n \ . \tag{11}$$

Note that the functional I, shown in Eq. (7), is the functional[15] assumed by others[4,10-14] to be stationary. As shown by Eq. (11), this functional is stationary only if it is defined on the class of functions which have the exact form of the true wave function as $t \to \infty$; in this case $\delta a_n \to 0$ as $t \to \infty$. Such a class of functions is very abstract, and available trial functions, which reflect our ignorance of the exact nature of the true wave function, do not belong to this class.

We define the functional

$$J(\chi) = I(\chi) - I(\chi)^* ;$$

then

$$\delta J(\psi) = -i\delta\left(\sum_n |a_n|^2\right),$$

and hence the functional

$$N(\chi) = -iJ(\chi) + \sum_n c_n^*(\chi) c_n(\chi) \tag{12}$$

is stationary for a variation in χ about ψ subject to Eq. (10). For $\chi = \psi$,

$$N(\psi) = \sum_n a_n^* a_n = 1$$

since

$$J(\psi) = 0 ,$$

and therefore $N(\chi)$ is a functional which in some way expresses the fact that the norm of ψ is stationary for the types of variations implied by Eq. (10). In addition, it can also be shown that

$$N(\psi) = -iJ(\chi) + \sum_n^N |c_n|^2 = N(\chi) = 1 , \tag{13}$$

and thus the functional $N(\chi)$ is not only stationary about the value of one, but all higher-order variations also vanish.

Consider an approximate or trial vector $\chi = \psi_N$ located in a selected subspace H_N spanned by the basis set $\{\phi_n\}$: We take H_N to be the closed linear envelope of the set of vectors ϕ_n, $n = 1, 2 \ldots, N$. The basis set may include continuum eigenvectors, but we will not distinguish these vectors from the discrete vectors. The trial vector can be expressed as follows[16]:

$$\psi_N = \sum_{n=1}^{N} c_n(t) \phi_n e^{-i\epsilon_n t} , \tag{14}$$

and the problem is to determine the set of functions $c_n(t)$ such that ψ_N approximates ψ. In essence, we assume the subspace H_N that we have selected is a good choice[17]; if so then ψ is contained in it, and

$$\delta N = 0 , \tag{15}$$

$$J = 0 , \tag{16}$$

$$I = 0 , \tag{17}$$

for some vector in the form of Eq. (14), and the problem is to determine this vector. However, since each function $c_n(t)$ is expected to represent in the limit $t \to \infty$ a possible transition amplitude, Eq. (15) is trivially satisfied and thus of no use in fixing the set of functions $\{c_n(t)\}$. If we require that[18]

$$\langle \phi_n | h + V - i\frac{\partial}{\partial t} | \psi_N \rangle = 0, \ n = 1, 2, \ldots, N , \tag{18}$$

then both Eqs. (16) and (17) are satisfied in the subspace H_N. Equation (18) is the usual set of close-coupled equations one attempts to solve.[18] The particular set of functions $\{c_n(t)\}$ determined by solving Eq. (18) will be denoted as $\{b_n(t)\}$ in order to distinguish them from other sets determined by some other method.

Suppose that in addition to the N-linear parameters $c_n(t)$, the trial function also depends on one or several additional parameters ξ (for example, the parameters ξ could be nuclear charges in the basis functions which are allowed to vary with time, subject to the condition that they approach unity as $|t| \to \infty$[13,14]); then from Eq. (13),

$$N(\xi) = -iJ(\xi) + \sum_{n=1} |c_n(\xi)|^2 = 1 \tag{19}$$

and

$$\left(\frac{\partial N}{\partial \xi}\right) d\xi = -i\left(\frac{\partial J}{\partial \xi}\right) d\xi + \frac{\partial}{\partial \xi}\left(\sum_{n=1}^{N} |c_n|^2\right) d\xi = 0 . \tag{20}$$

Equations (19) and (20) are rigorously true, and can be viewed as constraints upon any calculational procedure.

A calculation procedure could be as follows: One requires that the Schrödinger equation be satisfied in the subspace H_N, then

$$I[\psi_N(\xi)] = 0 . \tag{21}$$

Equation (21) coupled with Eq. (20) forms an isoperimetric problem; we find from Eq. (20),

$$\lambda\left(\frac{\partial I}{\partial \xi}\right) d\xi = 0 ,$$

where λ is a Lagrange multiplier. Since λ is arbitrary, we obtain

$$\left(\frac{\partial I}{\partial \xi}\right) d\xi = 0 ,$$

which yields an Euler-Lagrange equation for ξ:

$$\frac{\partial}{\partial \xi}\langle \psi_N | h + V - i\frac{\partial}{\partial t} | \psi_N \rangle - \frac{d}{dt}\left(\frac{\partial}{\partial \dot{\xi}}\langle \psi_N | h + V - i\frac{\partial}{\partial t} | \psi_N \rangle\right) = 0 . \tag{22}$$

As previously discussed, Eq. (21) yields the N-coupled equations for the N-linear parameters $c_n(t)$. Equation (22) yields equations for the parameters ξ. It should be noted that Eqs. (21) and (22) are the equations obtained by Cheshire[13] and by McCarroll, Piacentini, and Salin[14] in the calculational procedure based upon the assumption that the functional I is the stationary about the exact solutions for variations belonging to the class $[\chi]$.

Finally it should be noted that the functionals I, J, and N are invariant under the transformation which moves the origin of the coordinate system from proton 1 to the midpoint of $\vec{R}_1(t)$ as long as the functionals are defined on the transformed class $\chi^T = T\chi$, where T is the unitary translation operator.

B. One-Centered Expansion

It is well known that the one-centered approximation method of Eqs. (14)–(18) provides a method for constructing a convergent sequence of approximate wave functions ψ_N. The sequence converges not only in the weak sense,[19] but also in the strong sense,[19] i.e.,

$$\| \psi - \psi_N \| \to 0, \qquad N \to \infty$$

since from Eq. (13)[19,20]

$$\| \psi_N \| = \| \psi \| = 1. \tag{23}$$

However, it is interesting to note that Eq. (23) also shows that ψ_N is not necessarily the best approximation to ψ in the subspace H_N.[21] If ψ is decomposed as follows:

$$\psi = \psi^N + \delta\psi^N ,$$

where ψ^N is the projection of ψ in H_N, and $\delta\psi^N$ is a vector in the orthogonal complement to H_N; then

$$\| \psi - \psi_N \| = \| \delta\psi_N \| + \| \delta\psi^N \| .$$

The error vector in H_N, $\| \delta\psi_N \|$, is not necessarily zero, since

$$\| \psi^N - \psi_N \| \geq \| \psi_N \| - \| \psi^N \| \geq 0 ,$$

since

$$\| \psi_N \| = \sum_{n=1}^{N} |b_n|^2 = 1 ,$$

while

$$\| \psi^N \| = \sum_{n=1}^{N} |a_n|^2 \leq 1 .$$

C. Two-Centered Expansion

In the first paper of this series it was shown that although it is sufficient to solve Eq. (1) in order to obtain the amplitudes for both excitation and charge exchange, it is necessary in any expansion in terms of the eigenvectors of the unperturbed Hamiltonian h_1 to explicitly account for the continuum of h_1, since the information needed to obtain the amplitudes for charge exchange is contained in the continuum.[1] Therefore, one cannot construct a good approximate vector ψ_N in the subspace H_N which is spanned by a set of discrete eigenvectors of h_1, and so the one-centered approximation scheme is not a practical approximation method.

Consider the approximate vector

$$\psi_N = b_{i1}(t)\phi_{i1} e^{-i\epsilon_{i1}t} + b_{n2}(t)\phi_{n2} e^{-i\epsilon_{n2}t} , \tag{24}$$

where ϕ_{i1} is the eigenvector of h_1 which describes the initial state, and ϕ_{n2} is an eigenvector of h_2, the Hamiltonian for the hydrogen atom for which proton 2 is the nucleus. The approximate vector can be written as

$$\psi_N = b_{i1}(t)\phi_{i1} e^{-i\epsilon_{i1}t} + \sum_{n1} \langle \phi_{n1} | \phi_{n2} \rangle \; e^{i(\epsilon_{n1} - \epsilon_{n2})t} b_{n2}(t) \; \phi_{n1} e^{-i\epsilon_{n1}t}$$

$$= \sum_{n1} B_{n1}(t)\phi_{n1} e^{-i\epsilon_{n1}t} ,$$

so if the functions $B_{n1}(t)$ approach a limiting value as $t\to\infty$, $\psi_N\epsilon[\chi]$ and the subspace H_N is defined as the closed linear envelope formed by the set ϕ_{i1} and ϕ_{n1} such that $\langle\phi_{n1}|\phi_{n2}\rangle\neq 0$. Therefore, by including a discrete eigenvector of h_2, the subspace has been increased from H_i (spanned by ϕ_{i1}) to H_N, where H_N contains a continuum. If we write H_N as

$$H_N=\sum_n \oplus H_n ,$$

then initially the vector ψ_N is located in H_i; as the perturbation acts, projections build up in all of H_N; and finally as $t\to\infty$, ψ_N is located in the subspace of H_N:

$$H_N'=H_i\oplus \sum_{n:c\,tn} \oplus H_n ,$$

which is just the subspace of H (the complete space) in which the rearranged state ϕ_{n2} and ϕ_i are located.

However, one should note that this approximation scheme is very different from the procedure based upon the one-centered expansion. Consider the ratio of the projections of ψ into the two subspaces H_n and $H_{n'}$, where n and n' are continuum indices; we have:

$$R=|a_n/a_{n'}| .$$

The same ratio for the approximate wave function determined from the one-centered approximation scheme is

$$R=|b_n/b_{n'}| ,$$

while from the two-centered approximation scheme it is

$$R=|\langle\phi_{n1}|\phi_{n2}\rangle/\langle\phi_{n'1}|\phi_{n2}\rangle| . \qquad (25)$$

Now, the absolute value of $a_n(b_n)$ is independent of the absolute value of $a_{n'}(b_{n'})$, except for the relationship expressing probability conservation; while Eq. (25) shows that in the two-centered approximation scheme these amplitudes are dependent. The two-centered expansion has provided the continuum needed to describe the rearranged state, but a certain amount of flexibility in this subspace has been lost; and hence, there is an error in the calculated charge-exchange amplitudes besides the usual truncation error incurred by the use of the one-centered approximation scheme.

This process cannot be continued.[22] A tacit assumption in Eq. (24) is that ϕ_{n2} describes a rearranged state so that b_{n2} has a limit as $t\to\infty$. This is of course not true; the electron in a rearranged state *in this representation* must have a linear momentum which is not accounted for by the second term of Eq. (24) (remember that ϕ_{n2} is an eigenvector of a different representation, and in that representation it is a possible final state of the system). However, it has been possible to solve the coupled equations, and the absolute square of b_{n2} has a limit, and it has been interpreted as the transition probability for charge exchange. If we attempted to continue to add more basis functions to Eq. (24), then not only would the functions b_{nk} not have limits, but also the absolute squares would not have limits; and hence it would be impossible to interpret these quantities as transition probabilities.[22] A similar problem is encountered in a pseudostate or Sturmian calculation, and will be discussed in the third paper of this series.

D. Two-Centered Traveling-Orbital Expansion

Consider the transformed functional

$$I(\chi^T)=\int_{-\infty}^{\infty} dt\left\langle\chi^T\left|h^T+V^T-i\left(\frac{\partial}{\partial t}\right)_T\right|\chi^T\right\rangle=I(\chi) .$$

The set $\{\phi_n^T\}$ forms a basis for the system. Transforming the set $\{\phi_{n2}\}$, we obtain

$$\phi_{n2}^T=T^\dagger\phi_{n2}$$

and the set $\{\phi_{n2}^T\}$ also forms a basis for the system. In addition, the basis functions from either set have the same origin of the coordinate system; hence in the two-centered expansion

$$\psi_N=\sum_{k=1}^{2}\sum_{n=1}^{N} b_{nk}(t)\phi_{nk}^T e^{-i\epsilon_n t} \qquad (26)$$

the functions $b_{nk}(t)$ determined from the coupled equations will have limits as $t\to\infty$, and can be interpreted as transition probabilities. In addition, since the transformed basis functions approach the spacial part of the traveling atomic orbitals, a possible trial function could be written as follows:

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

which is the customary two-centered traveling-orbital expansion.

The above discussion concerning the two-state approximation in the two-centered method would of course be unchanged for the case of the two-centered traveling-orbital expansion. Now consider the vector:

$$\psi_{N'}=\sum_{k=1}^{2}\sum_{n=1}^{2} b_{nk}(t)\Phi_{nk} .$$

It could be that the subspace selected by the above expansion, $H_{N'}$,

$\{H_{N'}: \phi_{11}^T, \phi_{21}^T,$ and all ϕ_{n1}^T such that

$$\langle \phi_{n1}^T | \phi_{12}^T \rangle \text{ or } \langle \phi_{n1}^T | \phi_{22}^T \rangle \neq 0\}$$

is really not different from H_N,

$$H_{N'} \subseteq H_N,$$

where H_N is, of course,

$$\{H_N: \phi_{11}^T \text{ and all } \phi_{n1}^T \text{ such that } \langle \phi_{n1}^T | \phi_{12}^T \rangle \neq 0\}.$$

For example, suppose that ϕ_{12}^T and ϕ_{22}^T are the transformed 1s and 2s orbitals, then the number of eigenvectors of h_1^T which overlap with ϕ_{12}^T is not likely different from the number that overlap with ϕ_{22}^T. However, the set of functions $\{b_{nk}; n=1, N\}$ determined by requiring that

$$\left\langle \Phi_{n1} \left| h^T + V^T - i\left(\frac{\partial}{\partial t}\right)_T \right| \psi_N \right\rangle = 0, \qquad n=1, N$$

$$\left\langle \Phi_{n2} \left| h^T + V^T - i\left(\frac{\partial}{\partial t}\right)_T \right| \psi_N \right\rangle = 0, \qquad n=1, N$$

would in general yield different values for the transition probabilities for $N=2$ than for $N=1$; for consider the ratio of the absolute value of the projections in H_n and $H_{n'}$:

$$R = \left| \frac{\langle \phi_{n1}^T | \phi_{12}^T \rangle e^{i(\epsilon_{n1}-\epsilon_{12})t} b_{12}(t) + \langle \phi_{n1}^T | \phi_{22}^T \rangle e^{i(\epsilon_{n1}-\epsilon_{22})t} b_{22}(t)}{\langle \phi_{n'1}^T | \phi_{12}^T \rangle e^{i(\epsilon_{n'1}-\epsilon_{12})t} b_{12}(t) + \langle \phi_{n'1}^T | \phi_{22}^T \rangle e^{i(\epsilon_{n'1}-\epsilon_{22})t} b_{22}(t)} \right|.$$

Therefore, even if the addition of two more states has not increased the size of the subspace, it has provided for increased flexibility in the subspace. Consequently, for a trial vector of the form of Eq. (26), an increase in N provides in general for an increase in the size of the subspace, and for an increase in flexibility in the subspace needed to describe rearrangement.

One could ask if this approximation scheme provides a procedure for obtaining a converging sequence of transition probabilities or cross sections. More precisely, one could ask if the cross sections determined from this process converge to the exact value of the cross section, or if this is not true do the numerical values of the cross sections determined in this process converge to a definite value? Consider the first question. If we proceed to the limit $N \to \infty$ (again this is meant

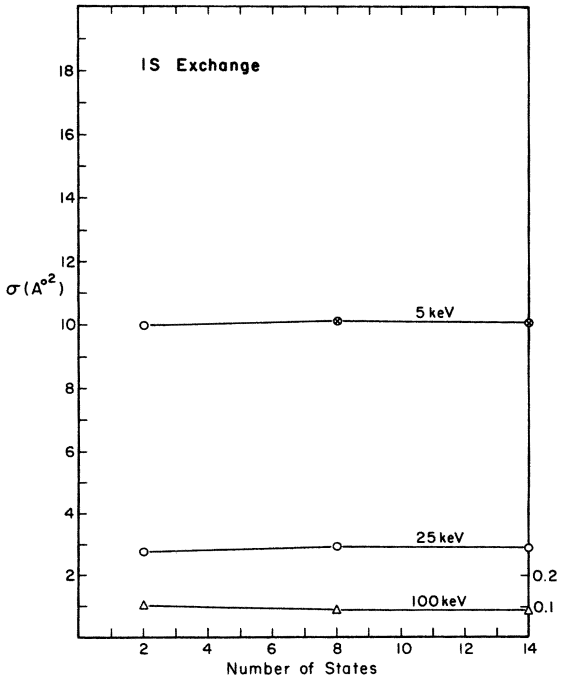

FIG. 1. Cross sections for the 1s-exchange reaction vs the number of states used in coupled-state calculations. Points ⊗ have been calculated by linear interpolation in Tables II, III, and IV of Ref. (9).

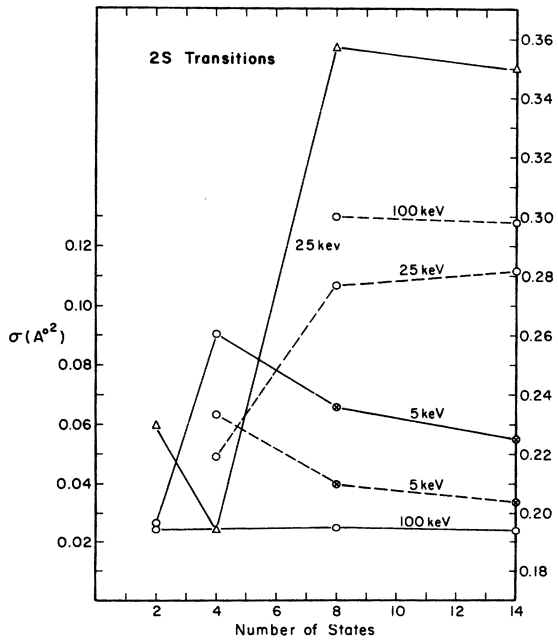

FIG. 2. Cross sections for the 2s reactions vs the number of states used in coupled-state calculations. The solid curve is for the 2s-exchange process, while the dashed curve is for the 2s-excitation process. The left vertical scale is to be used for points ○ and ⊗; points ⊗ have been calculated by linear interpolation in Tables II, III, and IV of Ref. 9; while right vertical scale is to be used for points △.

symbolically), we are constructing sequence of subspaces which cover the complete space H; i.e.

$$\lim_{N\to\infty} H_N \subseteq H,$$

and thus we are assured that ψ is located in the space that we have constructed. However, as we pass to the limit, the set of coupled equations become redundant, and cannot be solved uniquely. Therefore, this approximation scheme does not provide a procedure for constructing a sequence of vectors ψ_N that converges to ψ.

Further, we expect that this is more than just an "in-principle" argument. The set of coupled equations can be written in matrix form as follows:

$$i\underline{S}\frac{d}{dt}\underline{b} = \underline{G}\underline{b}, \tag{27}$$

where $\underline{b}$ is a vector of elements b_{nk}, $\underline{S}$ is an overlap matrix and $\underline{G}$ is a matrix of interaction elements. To solve Eq. (27) one must invert $\underline{S}$; and since only numbers of finite length can be used in most numerical computations, we would expect that as the size of the basis set is increased, the $\underline{S}$ matrix would tend to become singular, and Eq. (27) could not be solved uniquely.

The second question can only be investigated heuristically: One attempts to determine from the various calculations the convergence of the cross sections, and consequently there cannot be an unequivocal answer. In Fig. 1, the cross sections for the $1s$-exchange reaction obtained in the two state approximation,[5] the eight-state approximation,[9] and the 14-state approximation[9] are compared graphically. Obviously, either the $1s$-exchange cross section has converged within a reasonable tolerance to a definite value, or the values are converging so slowly that it would probably be impossible to calculate the limiting value by this procedure. In Fig. 2, the cross sections for the $2s$ transitions obtained in a two-state approximation,[6] a four-state approximation,[7] an eight-state approximation,[9] and the 14-state approximation are compared graphically. We note that the convergence is not uniform. For the cross section at 100 keV, we again note that either the value has converged for all practical purposes, or it would be virtually impossible to calculate the limiting value by this procedure.

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