Convergence and completeness of the pseudostate expansion for proton-hydrogen collisions in two-center close-coupling calculations

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The completeness and convergence of the pseudostate representation of continuum states are studied for ionization of atomic hydrogen by proton impact within the framework of the two-center atomic-orbital close-coupling method. Three types of two-center expansions are compared: Pseudocontinuum states are used (a) both on the target and on the projectile, (b) only on the target, and (c) only on the projectile. Satisfactorily consistent ionization cross sections are obtained for the three expansions at intermediate energies, though the latter two show much slower convergence. This implies that pseudocontinuum states on a center can complement the states on another center to some extent even though they are localized. Expansion (c) fails to converge at high energies within a realistic CPU time, while both treatments (b) and (c) reveal a deficiency arising from the lack of symmetry at low energies below a few keV. The converged theoretical ionization cross sections are larger than the available experimental data by 20% at a collision energy of 50 keV. [S1050-2947(99)00303-0]

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I. INTRODUCTION

It is a standard procedure to use square-integrable pseudocontinuum states [1,2] for the representation of ionization channels in the two-center close-coupling calculations [3] because real continuum states, which have finite overlap with bound states on the opposite center even in the limit of infinite separation, give rise to an essential difficulty in the interpretation of transition probabilities after the collision has finished. The close-coupling formalism is based on the variational principle [2,4] so that the addition of a new basis function should always lead to improvement of the trial wave function and hence we expect that the usage of pseudocontinuum states on both the centers is a better description than the usage only on a single center. Despite this expectation, the two-center atomic-orbital close-coupling formalism possesses inherent problems even for the simplest system of $p+\mathrm{H}(1s)$.

One problem is the instability of individual excitation and capture cross sections that occurs when pseudocontinuum states are used on both centers [5]. Kuang and Lin [6] attributed the instability to the simultaneous use of pseudocontinuum states on the two centers and proposed to use them only on one center following the work of Slim and Ermolaev [5]. Their interpretation, however, was unable to clarify the following nature of the cross sections. When pseudocontinuum states are used only on the target, excitation cross sections are stable and well behaved, but capture cross sections remain unstable. If one uses pseudocontinuum states only on the projectile instead, excitation cross sections become unstable. It is not possible to make both excitation and capture cross sections stable simultaneously by this prescription. Another embarrassing point is that their ionization cross section for $p+\mathrm{H}(1s)$ collisions seems to have converged to a different value from the cross section of the full two-center calculations. Furthermore, both of the two theoretical ionization cross sections disagree with the measured values [7,8] around a collision energy of 50 keV, where the ionization cross sections take their maximum values.

Toshima [9] showed that the unphysical oscillatory structures of the cross sections as a function of energy is caused by a strong coupling between bound and pseudocontinuum states belonging to different centers. The discreteness of the pseudocontinuum states enhances the coupling excessively when the momentum matching occurs with a bound state. As evidence of this interpretation it was demonstrated that the spurious structure tends to be less prominent as the density of the pseudocontinuum states becomes higher since the couplings with adjacent pseudocontinuum states averages the coupling with the matched state. This interpretation also clarifies why only excitation cross sections are stable if pseudocontinuum states are used only on the target. The significance of the strong coupling induced by the momentum matching had been recognized before by Reading *et al.* [10] in their charge-transfer calculations based on a single-center expansion. They proposed another procedure to remedy the difficulty arising from the discreteness of the pseudocontinuum states. In their *method of deltas*, the average is taken over each energy interval between adjacent pseudocontinuum states.

Mathematically, atomic eigenstates on a single center can form a complete set and we do not need any continuum state on another center for the representation of an ionization process. Simultaneous usage of wave functions on different centers may bring about an unfavorable problem of overcompleteness. This is not the case for the practical numerical calculations, in which we can use a limited, too small to be called complete, number of basis functions for the expansion. The addition of basis functions to another center accelerates the convergence of the expansion drastically, as has been often demonstrated in the calculations of quantum chemistry. When the collision velocity is smaller than the typical orbital velocity of the active bound electrons, the electronic state during the collision can be simulated well by an adiabatic molecular orbital. It is generally recognized that

a single-center expansion of a diatomic-molecule electronic wave function is not satisfactory unless one uses a huge number of basis functions. In addition, usage of pseudocontinuum states only on one center violates the reflection symmetry of the wave function for symmetric systems such as $p+\mathrm{H}(1s)$.

In this paper we study the convergence problem of the two-center expansion for the pseudostate representation in the semiclassical impact parameter close-coupling formalism. Three types of expansions are used to see quantitatively the completeness of the pseudocontinuum states: the full two-center expansion (a) in which pseudocontinuum states are used on both the centers and the reduced two-center expansions (b) and (c) in which pseudocontinuum states are used only on the target or on the projectile, respectively, similarly to Kuang and Lin [6]. To supplement the calculations we also make a comparison with the single-center expansion, which was recently revived by Ford *et al.* [11]. Atomic units are used unless otherwise stated.

II. NUMERICAL METHOD

The numerical procedure of the present close-coupling method is the same as the one used in previous papers [12,13]. The relative motion of the heavy particles is described classically by a rectilinear trajectory with a constant velocity v in the impact-parameter representation. The time-dependent two-center electronic wave function is expanded in a standard way as

$$\Psi(\mathbf{r},t)=\sum_{i=1}^{N_T} a_i(t)\psi_i^T(\mathbf{r}_T,t)+\sum_{i=N_T+1}^{N} a_i(t)\psi_i^P(\mathbf{r}_P,t), \tag{1}$$

where $\psi_i^T(\mathbf{r}_T,t)$ and $\psi_i^P(\mathbf{r}_P,t)$ are the target and the projectile atomic orbital with appropriate electron translation factors attached and $\mathbf{r}_T$, $\mathbf{r}_P$, and $\mathbf{r}$ are the electron coordinates measured from the target nucleus, the projectile nucleus, and the coordinate origin, respectively. The quantization axis of the atomic states is chosen to be perpendicular to the collision plane so that the set of wave functions with quantum numbers $\ell+m$ even is decoupled from the set with $\ell+m$ odd. The initial state being the ground state with $\ell=m=0$, we couple only the states with $\ell+m$ even. The eigenfunctions of each center are further expanded in terms of the Gaussian-type orbital (GTO) basis functions as

$$\varphi_{nlm}(\mathbf{r})=\sum_{\nu} c_\nu^{n\ell} e^{-\alpha_\nu r^2} r^\ell Y_{\ell m}(\hat{r}), \tag{2}$$

where the nonlinear parameters α_ν are generated as a modified geometrical progression and the coefficients $c_\nu^{n\ell}$ are determined so as to diagonalize the atomic Hamiltonian of the target and the projectile. It is not essential for the present study whether the basis functions are constructed from the Gaussian or the Slater orbitals. Although the bound states are also represented approximately as a linear combination of GTOs, the energy eigenvalues are accurate enough to regard the states as exact.

Substitution of the wave function (1) into the scattering Schrödinger equation gives coupled differential equations, which are solved numerically at each impact parameter with sufficient care to keep the overall numerical inaccuracy confined to cross sections smaller than 10^{-3} after integrating the transition probabilities over the impact parameters. In order to achieve this level as a whole, the inaccuracy in each step has to be much smaller than the total standard. For instance, since all the integrals associated with the coupling matrix elements are obtained analytically owing to the advantage of the GTO representation, the accuracy of the matrix elements is always better than ten digits. The differential equations are solved by the Runge-Kutta-Verner method with 10^{-6} accuracy.

TABLE I. Ionization cross sections in cm^2 for $p+\mathrm{H}(1s)$ at 50 keV.

E (keV)	T161P161	T197P197	T289P289
1	5.220×10^{-20}	5.161×10^{-20}	
2	3.681×10^{-19}		
4	2.603×10^{-18}	2.630×10^{-18}	
7	9.831×10^{-18}		
15	4.471×10^{-17}	4.548×10^{-17}	
25	1.087×10^{-16}	1.097×10^{-16}	1.074×10^{-16}
35	1.558×10^{-16}	1.570×10^{-16}	
50	1.782×10^{-16}	1.787×10^{-16}	1.778×10^{-16}
75	1.634×10^{-16}	1.638×10^{-16}	
100	1.395×10^{-16}	1.396×10^{-16}	1.376×10^{-16}
150	1.032×10^{-16}	1.036×10^{-16}	
200	7.612×10^{-17}	7.750×10^{-17}	
400	4.085×10^{-17}	4.108×10^{-17}	
800	2.277×10^{-17}	2.288×10^{-17}	

III. RESULTS

Hereinafter we classify the basis functions by the number of states on each center. For instance, T197P50 denotes that it contains 197 states on the target and 50 states on the projectile. We have the following cases.

(a) *Full two-center expansion*. The present author has reported some calculations of the full two-center expansion for proton-hydrogen collisions in previous papers. Among them the largest basis set, though ionization cross sections are not shown in the paper, is T161P161, which consists of 50 bound states and 111 pseudocontinuum states with $\ell\leqslant4$ on each center [9]. To see whether the contribution of $\ell=5$ states is small enough, calculations are done adding 36 h states on each center (T197P197). The ionization cross sections of the two basis sets are compared in Table I. The difference is about 1% at the lowest energy of 1 keV and decreases as the collision energy increases. At 50 keV, where the ionization cross sections become largest, the difference is less than 0.3%. As a further check of the convergence for making the energy spacings between adjacent pseudocontinuum states smaller, even larger basis set T289P289 calculations are executed at three energies near the cross-section maximum point and the cross sections are also shown in Table I. This set contains 112 bound states and 177 pseudocontinuum states on each center and all the energy levels are shown in Table II. The cross sections of T289P289 are close

TABLE II. Energy levels of the 289 basis functions.

$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$	$\ell=5$	$\ell=6$
−0.5000						
−0.1250	−0.1250					
−0.0555	−0.0555	−0.0555				
−0.0312	−0.0312	−0.0312	−0.0312			
−0.0200	−0.0200	−0.0200	−0.0200	−0.0200		
−0.0139	−0.0139	−0.0139	−0.0139	−0.0139	−0.0139	
−0.0102	−0.0102	−0.0102	−0.0102	−0.0102	−0.0102	−0.0102
−0.0078	−0.0078	−0.0078	−0.0078	−0.0078	−0.0078	−0.0078
0.0067	0.0040	0.0099	0.0124	0.0149	0.0113	0.0047
0.0247	0.0188	0.0391	0.0508	0.0653	0.0603	0.0417
0.0603	0.0487	0.1041	0.1422	0.1994	0.2059	0.1672
0.1281	0.1063	0.2413	0.3515	0.5477	0.6322	0.5864
0.2539	0.2138	0.5249	0.8268	1.4569	1.8999	2.0244
0.4837	0.4114	1.1086	1.9127	3.8763		
0.8991	0.7713	1.3375	4.4284			
1.6451	1.4260	2.3158				
2.9814	2.6201	4.8373				
5.3774	4.8119					

to those of T197P197. We have also compared the transition probabilities of the three sets as a function of the impact parameter and verified that they are hardly distinguishable in a plotted figure.

(b) *Pseudocontinuum states only on the target*. At first the pseudocontinuum states on the projectile are removed from the basis sets that were used for the full two-center calculations before. Generally, the ionization cross sections obtained are smaller than those of the full two-center calculations by 10–15 % at a peak energy of 50 keV, in agreement with the results of Kuang and Lin [6]. For example, the T197P56 basis set gives 1.548×10^{-16} cm^2. However, we realized that the ionization cross sections increase further, though rather slowly, if we add more pseudocontinuum states on the target; the previous calculations did not achieve convergence. It is important to notice that we need large-angular-momentum states to make the expansion converged if we use the pseudocontinuum states only on a single center. In Table III we show how the ionization cross section at a collision energy 50 keV increases for an increasing maximum number of the angular momentum. At higher energies the contribution of the large-angular-momentum components becomes less important and we can obtain more easily cross sections consistent with the full two-center calculations. The largest calculations T462P20, which includes 35 bound states with $n=1-5$ and 427 pseudocontinuum states with $\ell=0-8$ on the target and 20 bound states with $n=1-4$ on the projectile, requires much longer CPU time than T161P161. If we add the $n=5$ bound states on the projectile (T462P35) to make the number of the bound states on each center equal, the CPU time becomes even longer, twice longer than that of T462P20. An interesting feature we found is that the convergence is improved and accelerated if we add a small number of pseudocontinuum states on the projectile.

(c) *Pseudocontinuum states only on the projectile*. The convergence behavior is similar to case (b) at low energies. When the collision energy is not higher than 50 keV, nearly the same number of pseudocontinuum states are needed for convergence as in case (b). Namely, T20P462 calculations give ionization cross sections similar to T462P20 at low energies. If we add some pseudocontinuum states on the target the convergence is also improved greatly. The different nature from expansion (b) is that the convergence becomes quickly worse at high energies. When the projectile velocity is much larger than the average velocity of the target initial bound electron, only high-lying pseudocontinuum states matching in momentum with the target initial state can be excited and the distribution of the partial cross sections tends to spread to larger angular momenta.

We compare the transition probabilities of the five calculations, T462P20, T197P69, T197P197, T69P197, and T20P462 at 50 keV, where the 69-state set consists of 40 bound states of $\ell=0-3$ and 29 continuum states of $\ell=0-1$. Figure 1 shows three of them. We do not present the probabilities of T462P20 and T20P462 there since they are almost identical to the total ionization probabilities of the other three calculations. Integrated ionization cross

TABLE III. Ionization cross sections of expansion (b) in cm^2 for $p+\mathrm{H}(1s)$ at 50 keV. Pseudocontinuum states are included only on the target center.

$\ell_{\max}$	Basis function	Ionization cross section
5	T197P56	1.548×10^{-16}
6	T218P20	1.574×10^{-16}
	T361P20	1.642×10^{-16}
7	T258P20	1.616×10^{-16}
	T283P20	1.650×10^{-16}
	T399P20	1.711×10^{-16}
8	T417P20	1.713×10^{-16}
	T440P20	1.719×10^{-16}
	T462P20	1.733×10^{-16}

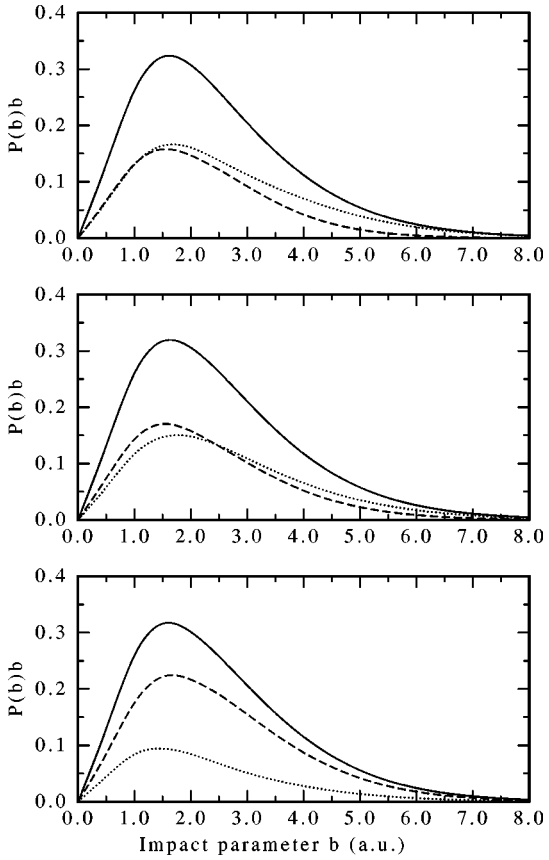

FIG. 1. Ionization probabilities as a function of the impact parameter b at a collision energy of 50 keV. b is in atomic units. Dotted lines and dashed lines are the components of the ionization to the target and to the projectile pseudocontinuum states, respectively, and solid lines are the total sum. The figures are for T197P69, T197P197, and T69P197 in order from top to bottom.

sections of the five basis sets are 1.733×10^{-16}, 1.761×10^{-16}, 1.787×10^{-16}, 1.752×10^{-16}, and 1.748×10^{-16} cm^2, respectively. We see that only the partition of the ionization into the two centers changes, keeping the total sum of the ionization probabilities nearly invariant. This implies that the physical interpretation of ionization to the target or to the projectile continua is insignificant, as it is for the real continuum states that spread over both centers. When the collision energy is not high, the ionized electron encounters both nuclei while leaving their Coulomb forces. Such a continuum state possesses more or less a two-center character and thus the single-center expansion based on square-integrable functions does not work effectively. High-angular-momentum partial waves are required if we try to expand a localized distribution in terms of wave functions of a different center. The distribution of partial cross sections at 50 keV are plotted as a function of angular momentum ℓ in Fig. 2. It is clearly demonstrated that the distribution extends to larger angular momenta when we expand the electronic wave function only by single-center pseudocontinuum states. In Table IV all the energy levels of the largest 462-state basis set are shown. As easily recognized, the state densities of $\ell\geq3$ are chosen to be higher than those of the 289-state basis set. A high density for $\ell\geq3$ is needed to get good convergence for expansions (b) and (c).

As the collision energy increases the effective interaction

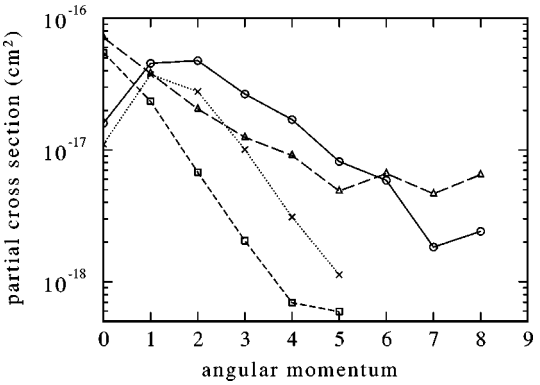

FIG. 2. Distribution of partial ionization cross sections as a function of the angular momentum at a collision energy of 50 keV. The solid line with circles is for T462P20 and the long-dashed line with triangles is for T20P462. The dotted line with crosses and the short-dashed line with squares are, respectively, the target-center and the projectile-center components of T197P197 calculations.

time between the projectile and the electron becomes short and the wave functions of the electron tends to show a single-center nature around the target. The distribution centered on the target corresponds to a wave packet moving with a velocity v if it is described in the projectile frame. Only high-lying pseudocontinuum states on the projectile can represent such a wave packet at high energies. Since the energy spacings between discretized continuum states become larger as the energy eigenvalue increases as shown in Tables II and IV, it quickly becomes difficult to represent the target-centered continuum states only by the projectile pseudocontinuum states.

Before and after the collision the target and the projectile atoms are separated far from each other so that the overlap of localized wave functions of different centers is negligibly small. In this situation all the basis functions are orthogonal and none of them can be replaced by other members. The fact that the same ionization probabilities and cross sections are obtained at low and intermediate energies whichever center the pseudocontinuum states are placed on indicates that the ionization is determined in a confined region where wave functions on different centers have a sizable overlap with or linear dependence on each other. This is also the reason why reliable ionization cross sections can be obtained using square-integrable pseudocontinuum states.

Some of present theoretical ionization cross sections are compared with measured values [7,8] in Fig. 3. All the two-center calculations show satisfactory mutual agreement below 200 keV. T20P462 underestimates the ionization cross section above 200 keV and quickly becomes worse as the collision energy increases because this basis set does not contain abundantly high-lying continuum states that are required for the momentum matching. At 400 keV the ionization cross section of T20P462 is 4.272×10^{-18} cm^2, which is smaller than the other theoretical values by one order of magnitude. If we add high-lying matching states to it, the ionization cross section increases to 3.156×10^{-17}. Although the value is improved drastically, it is still smaller than the other theoretical values. For better agreement we need basis functions of larger angular momenta $\ell>8$. In T462P0 the same pseudocontinuum states are used as in the two-center

TABLE IV. Energy levels of the 462 basis functions.

$\ell=0$	$\ell=1$	$\ell=2$	$\ell=3$	$\ell=4$	$\ell=5$	$\ell=6$	$\ell=7$	$\ell=8$
−0.5000								
−0.1250	−0.1250							
−0.0555	−0.0555	−0.0555						
−0.0312	−0.0312	−0.0312	−0.0312					
−0.0200	−0.0200	−0.0200	−0.0200	−0.0200				
0.0020	0.0041	0.0041	0.0037	0.0021	0.0086	0.0046	0.0032	0.0093
0.0415	0.0162	0.0235	0.0157	0.0134	0.0229	0.0163	0.0172	0.0316
0.1404	0.0247	0.0273	0.0336	0.0310	0.0455	0.0352	0.0464	0.0855
0.3764	0.0617	0.0732	0.0605	0.0586	0.0821	0.0668	0.1107	0.2228
0.9205	0.1280	0.1631	0.1010	0.1024	0.1422	0.1210	0.2581	0.5892
2.1517	0.2460	0.3382	0.1626	0.1732	0.2424	0.2157	0.6089	1.6176
4.9205	0.4557	1.3569	0.2571	0.2884	0.4120	0.3847	1.4784	4.6985
11.175	0.8287	2.7067	0.4032	0.4782	0.7027	0.6916		
	1.4955	5.4446	0.6310	0.7945	1.2084	1.2608		
	2.6966	11.105	0.9887	1.3280	2.1021	2.3418		
	4.8815		1.5559	2.2394	3.7095			
	8.9036		2.4633	3.8187				
			3.9300					

calculations (T462P20). The single-center calculations give overestimated cross sections below 100 keV and the disagreement with other theoretical cross sections becomes more serious as the collision energy decreases. This tendency was reported by Ford *et al.* [11] before. When projectile states are not included in the basis set at all, the target continuum states try to compensate for the projectile wave functions. Ford *et al.* claimed that their ionization cross section should be regarded as an electron-removal cross section that contains both ionization and electron capture. We show in Fig. 4 the electron-removal probability of the single-center calculations at 1 keV. For comparison we also show the electron-capture probabilities of the two-center calculations T197P197. Evidently, the ionization (electron-removal) probability of the single-center calculation bears a close resemblance to that of the electron capture of the two-center calculation, though the absolute values are rather different. The shape of the ionization probability curve of T197P197 is singly peaked and quite different from the other two both in

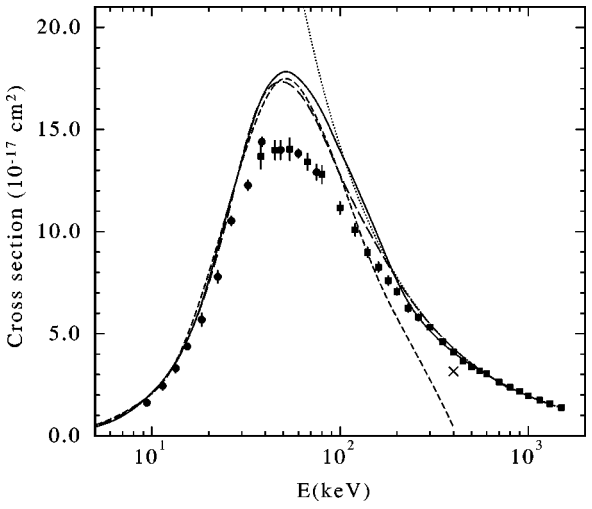

FIG. 3. Ionization cross sections for $p+\mathrm{H}(1s)$ collisions. Theoretical cross sections: solid line, T161P161; long-dashed line, T462P20; short-dashed line, T20P462; dotted line, single-center calculations of T462P0; cross, T20P496 in which matching-energy states for 400 keV are added to T20P462. Experiment: solid squares and solid circles with error bars are from Shah and Gilbody [7] and Shah *et al.* [8], respectively.

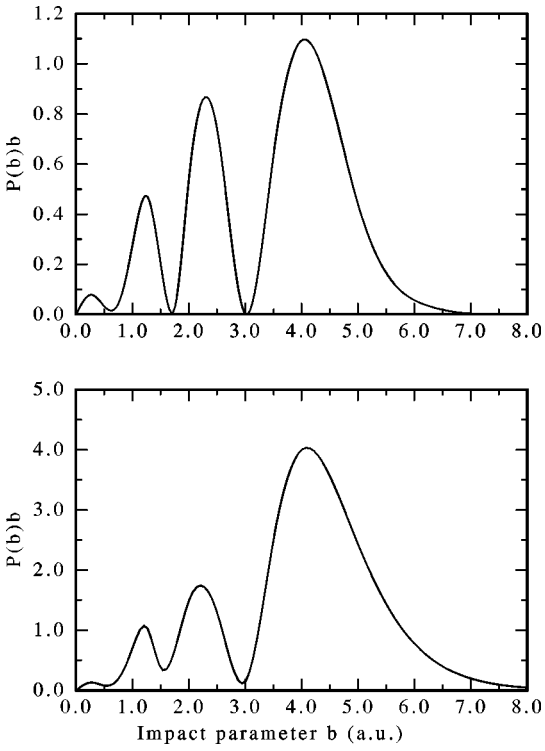

FIG. 4. Top: ionization (electron removal) probability of the single-center calculation of T462P0. b is in atomic units. Bottom: electron capture probability of the two-center calculation T197P197. Both are for a collision energy of 1 keV.

TABLE V. Excitation and capture cross sections of T197P197 in cm^2 for $p+H(1s)$ at low energies.

E (keV)	Cross section	$2s$	$2p$	$3s$	$3p$	$3d$
1	excitation	4.863×10^{-19}	2.281×10^{-17}	1.944×10^{-20}	2.479×10^{-19}	2.113×10^{-19}
	capture	4.741×10^{-19}	2.286×10^{-17}	2.065×10^{-20}	2.463×10^{-19}	2.096×10^{-19}
4	excitation	5.064×10^{-18}	3.258×10^{-17}	1.457×10^{-19}	1.249×10^{-18}	2.257×10^{-18}
	capture	4.525×10^{-18}	2.644×10^{-17}	6.199×10^{-20}	1.393×10^{-18}	2.040×10^{-18}

shape and in magnitude. Since the real ionization probability is several orders of magnitude smaller than the electron-capture probability, it does not affect the shape of the electron-removal probability of the single-center expansion. From this comparison we see that the target pseudocontinuum states can also simulate projectile bound states.

Near the peak position of 50 keV, all the two-center calculations are well converged. Nevertheless, the theoretical cross sections are generally larger than the measured values [7,8] by 20% there. It is not easy to specify the cause of this disagreement from the theoretical side. We just state that the measurements are not absolute but the cross sections are normalized to the Born cross section at a high energy. We should comment also on a fact that some previous close-coupling calculations showed better agreement with the measurements. If we use an insufficient number of pseudocontinuum states, the ionization cross sections are generally underestimated and we happen to see better agreement. For instance, if we truncate the expansion (b) at $\ell=5$ as we do for T197P56, the ionization cross section obtained becomes much closer to the measurements.

Toshima [12] pointed out that the contribution of the projectile pseudocontinuum is not negligible even at the MeV region and explicit inclusion of those states in the two-center close-coupling basis set makes the ionization cross section larger than the Born cross sections. We also confirmed this finding in the present calculations. However, ionization cross sections are dependent on the choice of projectile pseudocontinuum states. If one of the eigenenergies of the projectile pseudocontinuum states is located near the matching energy, the contribution of the projectile continua is drastically enhanced and the population of the target continua is also increased through a back coupling. As a result, the total ionization cross exceeds that of the Born approximation by 10% or so at 1 MeV. If all the pseudocontinuum states stay far away from the matching energy, the obtained ionization cross section is smaller than the Born cross section. For example, the matching energy is 16 a.u. for $E=800$ keV. Since the highest eigenenergy of the basis set of T161P161 (see [9]) is 3.54 a.u., the momentum matching does not occur for this basis set at 800 keV and as a result the ionization cross section does not exceed the Born cross section, 2.4 $\times10^{-17}$ cm^2. As discussed by Toshima [9], the discreteness, which is more prominent for high-lying pseudocontinuum states, may enhance the population of the matching projectile continuum states excessively. Although the ionization cross sections are probably overestimated when momentum matching occurs with target bound states, it is still an open question whether the real ionization cross section is larger or smaller than the Born cross section at high energies.

We have been mainly interested in the ionization cross sections so far. There is one important thing to note about the symmetry between the excitation and the capture cross sections. When the collision energy is low enough to neglect the electron translation factor, the excitation cross section to a target state with quantum numbers (n,ℓ,m) should be equal to the capture cross section to the projectile state with the same quantum numbers. At such a low energy, the electronic state is well approximated by the molecular orbital of H_2^+. The initial state $H(1s)$ is expressed as a sum of $1s\sigma$ and $2p\sigma$ states with equal weights $1/\sqrt{2}$. The lowest state $1s\sigma$ departs from other molecular states quickly as the internuclear distance R decreases while the $2p\sigma$ state increases and tends to correlate to other excited states [2]. Since the energy differences between the $1s\sigma$ state and the others are very large, $1s\sigma$ contributes little to transitions to excited molecular states and only the other counterpart $2p\sigma$ can induce transitions. The target and the projectile ground states are equally populated in the $2p\sigma$ molecular state so that transition probabilities to a target state and a projectile state with the same quantum numbers (n,ℓ,m) become equal. We can see this tendency clearly in Table V in which excitation and capture cross sections at low energies are compared for the basis set T197P197. However, if we use an asymmetric basis set, the symmetry is inevitably broken to some extent. In place of T462P20 we here use T462P35, which contains an equal number of bound states on each center, to see the effect arising only from the asymmetry of the continuum states. As shown in Table VI, the asymmetry is more serious for smaller cross sections. If we use pseudocontinuum states only on the target, we can get more easily stable excitation cross sections at intermediate collision energies, but the symmetry breaking instead introduces inconsistency to the rela-

TABLE VI. Excitation and capture cross sections of T462P35 in cm^2 for $p+H(1s)$ at low energies.

E (keV)	Cross section	$2s$	$2p$	$3s$	$3p$	$3d$
1	excitation	4.162×10^{-19}	2.280×10^{-17}	1.930×10^{-20}	1.849×10^{-19}	2.180×10^{-19}
	capture	5.102×10^{-19}	2.299×10^{-17}	2.621×10^{-20}	1.811×10^{-19}	2.050×10^{-19}
4	excitation	5.389×10^{-18}	3.234×10^{-17}	1.581×10^{-19}	1.316×10^{-18}	2.286×10^{-18}
	capture	4.504×10^{-18}	2.712×10^{-17}	6.803×10^{-20}	1.403×10^{-18}	1.982×10^{-18}

tion between the excitation and capture cross sections. When a pair of cross sections differ from each other by a large amount, at least one of them is incorrect.

In the close-coupling formalism all the states used for the expansion are fully coupled so that an error arising from the broken symmetry between excitation and capture cross sections may introduce an unfavorable effect to the ionization cross sections. The symmetry of the molecular pseudocontinuum states constructed from asymmetric basis functions is also broken. However, it is rather difficult to estimate quantitatively how large the effect is on the ionization cross sections. Further investigation is needed for the influence of the broken symmetry on the ionization processes.

IV. SUMMARY

Three types of two-center expansions are investigated by performing large-scale close-coupling calculations for proton-hydrogen collisions. The basis functions are increased until convergence is achieved and satisfactorily consistent ionization cross sections are obtained for the three expansions in the energy region below 200 keV. The pseudocontinuum states constructed from the square-integrable functions by the diagonalization of atomic Hamiltonians can be regarded as complete for the description of the ionization process in this energy region. The expansion in which the pseudocontinuum states are used only on the projectile fails to converge at high energies within a realistic CPU time. On the other hand, at the low-energy region below a few keV, the symmetry between the excitation and capture cross sections is broken if we use pseudocontinuum states only on one center. The full two-center expansion achieves convergence most easily and hence the required CPU time is much shorter than that of the other two expansions.

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[1] W. Fritsch and C.D. Lin, Phys. Rep. **202**, 1 (1991).
[2] B.H. Bransden and M.R.C. McDowell, *Charge Exchange and the Theory of Ion-Atom Collisions* (Clarendon, Oxford, 1992).
[3] D.F. Gallaher and L. Wilets, Phys. Rev. **169**, 139 (1968); R.S. Shakeshaft, Phys. Rev. A **14**, 1626 (1976); K. Fujiwara and N. Toshima, J. Phys. Soc. Jpn. **52**, 4118 (1983); N. Toshima and J. Eichler, Phys. Rev. A **40**, 125 (1989).
[4] Yu.N. Demkov, *Variational Principles in the Theory of Collisions* (Pergamon, Oxford, 1963).
[5] H.A. Slim and A.M. Ermolaev, J. Phys. B **27**, L203 (1994).
[6] J. Kuang and C.D. Lin, J. Phys. B **29**, 1207 (1996); **29**, 5443 (1996); **30**, 101 (1997).
[7] M.B. Shah and H.B. Gilbody, J. Phys. B **14**, 2361 (1981).
[8] M.B. Shah, D.S. Elliott, and H.B. Gilbody, J. Phys. B **20**, 2481 (1987).
[9] N. Toshima, J. Phys. B **30**, L131 (1997).
[10] J.F. Reading, A.L. Ford, G.L. Swafford, and A. Fitchard, Phys. Rev. A **20**, 130 (1979); J.F. Reading and A.L. Ford, J. Phys. B **12**, 1367 (1979).
[11] A.L. Ford, J.F. Reading, and K.A. Hall, J. Phys. B **26**, 4537 (1993); **26**, 4553 (1993).
[12] N. Toshima, J. Phys. B **25**, L635 (1992); Phys. Lett. A **175**, 133 (1993).
[13] N. Toshima, Phys. Rev. A **50**, 3940 (1994).