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Comprehensive convergence study of TCAO close-coupling method for the excitation and ionization in keV H^+–H collisions

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Abstract. Convergence of the two-centre atomic orbital (TCAO) close-coupling calculations for the excitation and ionization of atomic hydrogen by keV proton impact is carefully examined using various large basis sets on each centre. It is shown that reliable cross sections for the weak channels can only be obtained with a large number of basis states on the target and a limited number of bound states on the projectile. Cross sections for excitation to 2ℓ, 3ℓ, 4ℓ and 5ℓ states and for ionization are presented and compared to available experimental data and to other theoretical calculations.

1. Introduction

The two-centre atomic orbital (TCAO) close-coupling method was initiated by Bates and McCarroll (1958) and developed by Wilets and Gallaher (1966) and Cheshire *et al* (1970). Since the 1970s, this method has been extensively exploited for studying ion–atom collisions in the intermediate impact energy region (for recent reviews, see Bransden and McDowell 1992, Fritsch and Lin 1991). For the intermediate impact energy where the velocity of the projectile is of the same order as that of the active target electron, excitation, capture and ionization processes are of comparable importance. This makes the TCAO close-coupling method a natural choice to account for the dynamic two-centre nature of the collision process. However, the convergence of the TCAO close coupling method around the peak region poses a great challenge to the method itself and has not been fully addressed until very recently (Kuang and Lin 1996a, to be referred to as paper I). In this paper, we continue our study of the convergence of TCAO close-coupling calculations for the excitation and ionization of atomic hydrogen by keV protons with various large basis sets on each centre.

In the traditional TCAO close-coupling calculations (Bransden and McDowell 1992, Fritsch and Lin 1991), it is common to employ both atomic bound states and positive-energy pseudo-states on each collision centre. This type of symmetric TCAO method has been used to obtain cross sections for the dominant channels in various collision systems. However, it has been noticed recently by Slim and Ermolaev (1994), Kuang *et al* (1994), Lin (1994) and Toshima (1994) that large-size symmetric TCAO close-coupling calculations fail

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to produce the smooth cross sections with impact energy for the weak channels. Moreover, the calculated excitation cross sections and the derived photon polarization parameters from the large basis set calculations (Shakeshaft 1978, Slim and Ermolaev 1994, Toshima 1994) show pronounced oscillatory structures which are not present in the experimental data (Park *et al* 1976, Detleffsen *et al* 1994, Werner and Schartner 1996). As we have demonstrated in paper I, the structures in these calculations are attributed to the simultaneous use of the short-range pseudo-continuum states on both collision centres. That is, the symmetric TCAO calculations with a large number of pseudostates on both centres are incapable of achieving converged cross sections for ionization and for excitation to high lying states. The underlying problem that lies in TCAO calculations is that the range of interaction among the bound states and the ionization states on the two centres is truncated, due to the representation of true continuum states by short-range pseudostates.

In paper I, we proposed the so-called BBC close-coupling scheme, an asymmetric TCAO close-coupling method, in which pseudostates are placed only at one centre. This method allows us to obtain reliable cross sections for transition to the highly excited states that are located on the same centre as the pseudostates. For example, excitation cross sections can be evaluated using the BBC-T close-coupling method, where all the pseudostates are on the target centre, while electron capture cross sections can be evaluated with the BBC-P close-coupling method where all the pseudostates are on the projectile centre. With 76 states ($n \leqslant 4 +$ pseudo-states) on the projectile and 20 bound states ($n \leqslant 4$) on the target (BBC-P), our calculated capture cross sections vary smoothly with the impact energy in the keV region. With the same 76 states on the target and 20 bound states on the projectile (BBC-T), the evaluated excitation cross sections to 2ℓ and 3ℓ states vary smoothly with the impact energy above 50 keV. However, the evaluated cross sections to the weak channels, e.g. for excitation to 2s, 3s and 3d states and for ionization, still have some structure around 30 keV, i.e. near the peak region. Although structures in the total cross sections are not uncommon for ion–atom collisions, they occur only for collisions at lower energies where the projectile velocity is less than the orbiting velocity of the active target electron. For collisions at intermediate or high energies, the collision time is short and there is no known mechanism which is expected to produce structures in total cross sections. While the calculations in paper I produce smooth total cross sections above 50 keV impact energy, we tend to believe that the structures near 30 keV seen in that calculation are the consequence of lack of convergence of the bases used. In this paper we further enlarge the base set to confirm that the results above 50 keV from the present calculation agree with those in paper I and that the structures near 30 keV are now removed with the new base set.

2. Basis sets and TCAO close-coupling method

Recently, we have developed a new general TCAO close-coupling code based on the use of an even-tempered basis set (Reeves 1963). Each function in such a basis set consists of an exponential multiplied by a solid spherical harmonic, i.e. a spherical harmonic multiplied by r^l. A set of even-tempered basis functions is thus defined as

$$\chi_{klm}(\boldsymbol{r}) = N_l(\zeta_k)\mathrm{e}^{-\zeta_k r}\mathcal{Y}_{lm}(\boldsymbol{r}) \qquad \mathcal{Y}_{lm}(\boldsymbol{r}) = r^l Y_{lm}(\hat{\boldsymbol{r}}) \tag{1}$$

where $N_l(\zeta_k)$ is a normalization constant, and the orbital exponents, ζ_k, are taken to form a geometric sequence $\zeta_k = \alpha\beta^k$, $k = 1, 2, \ldots, N$, where the two parameters α and β can be determined by energy minimization. The atomic states used for the TCAO close-coupling

method are then expanded in terms of the even-tempered basis functions as

$$\phi_{nlm}(\boldsymbol{r}) = \sum_k c_{nk}\chi_{klm}(\boldsymbol{r}) = \sum_k c_{nk}N_l(\zeta_k)\mathrm{e}^{-\zeta_k r}\mathcal{Y}_{lm}(\boldsymbol{r}) \tag{2}$$

where the linear coefficients c_{nk} can be readily determined by diagonalizing the single-centred atomic Hamiltonian.

We shall summarize several advantages associated with the use of an even-tempered basis set. First, it has only two parameters, α and β; therefore, we can easily perform the energy optimization over α and β. Secondly, a large basis set can be efficiently generated and eventually a complete set can be reached in the limits $\alpha \to 0$, $\beta \to 1$ and $\beta^N \to \infty$ as $N \to \infty$. Thirdly, an even-tempered basis set on a single centre cannot become linearly dependent if $\beta > 1$. Finally, and most importantly, all the matrix elements required for the TCAO close coupling method with plane-wave electronic translational factors can be evaluated in a very efficient way when the even-tempered basis set is used, since only one-dimensional numerical integration is needed and the integrand consists only of known elementary functions.

Within the semiclassical impact parameter approximation, the essence of the TCAO close-coupling method is to expand the time-dependent wavefunction $\Psi(\boldsymbol{r}, t)$ in terms of bound atomic orbitals plus continuum states (BBC expansion) with plane-wave electronic translational factors, i.e.

$$\Psi(\boldsymbol{r}, t) = \sum_i a_i(t)\phi_i^A(\boldsymbol{r}, t) + \sum_j b_j(t)\phi_j^B(\boldsymbol{r}, t) + \sum_k c_k(t)\phi_k^C(\boldsymbol{r}, t) \tag{3}$$

where we have explicitly distinguished the set of continuum states $\{\phi_k^C(\boldsymbol{r}, t)\}$ from the two sets of bound states $\{\phi_i^A(\boldsymbol{r}, t)\}$ and $\{\phi_j^B(\boldsymbol{r}, t)\}$ on centre A and centre B, respectively. The actual continuum states for the ion–atom collision system need not be associated with a specific centre (either target or projectile). It is conceptually clear that there is only one set of continuum states—either centred on the target or the projectile. The transition amplitudes $\{a_i, b_j, c_k\}$ are obtained through the standard procedure by solving the first order coupled ordinary differential equations (Brankin *et al* 1992) with the proper initial condition.

Mathematically, one may consider the present BBC close-coupling method as an extension of the 'one and a half centred expansion' (OHCE) by Reading *et al* (1981) and the asymmetric close-coupling calculation by Ermolaev (1990). It should be noted that the emphasis of the latter two methods is based on the ease in performing calculations. In contrast, we are mainly concerned with the formal convergence property of the close-coupling method. Since we are interested in excitation and ionization cross sections in this paper, the pseudo-states will be placed on the target only. In order to study convergence, we have devised three sets of target states: the first set has 76 atomic states with $\ell \leqslant 3$, which is the same as in paper I; the second set consists of 134 atomic states with $\ell \leqslant 4$ (table 1); the third set is made up of 174 atomic states with $\ell \leqslant 5$ (table 2). Note that the second and third sets have the same components for $\ell \leqslant 3$. Extensive convergence tests were carried out using these sets on the target and a varying number of bound states ($n \leqslant 4$) on the projectile. Throughout this paper, we will use the notation pxHy to represent a basis set. This notation means that there are x states on the projectile (proton) and y states on the target (H atom). The numerical aspects of the present work are the same as in paper I.

Table 1. Even-tempered basis functions used to generate the bound and pseudo-continuum states of atomic hydrogen up to 134 states in total. The eigen-energies (au) were obtained from diagonalizing the atomic Hamiltonian of the single centre.

s	p	d	f	g
−0.500 00				
−0.125 00	−0.125 00			
−0.055 56	−0.055 55	−0.055 56		
−0.031 25	−0.031 25	−0.031 25	−0.031 25	
−0.019 99	−0.019 98	−0.019 96	−0.019 99	−0.020 00
−0.013 82	−0.013 54	−0.013 25	−0.013 74	
−0.009 71				
0.008 18	0.006 60	0.006 26	0.002 90	0.003 21
0.111 77	0.122 82	0.131 68	0.090 93	0.167 79
0.428 10	0.475 00	0.542 12	0.375 59	0.978 99
1.264 62	1.408 65	1.744 75	1.213 56	4.549 36
3.374 03	3.795 12	5.169 59	3.645 20	19.891 55
8.758 60	9.940 50	15.096 04	11.083 10	
23.600 06	26.610 47			

$\alpha = 0.035$, $\beta = 1.440$, $N = 16$ for s,
$\alpha = 0.051$, $\beta = 1.500$, $N = 14$ for p,
$\alpha = 0.049$, $\beta = 1.600$, $N = 12$ for d,
$\alpha = 0.065$, $\beta = 1.600$, $N = 10$ for f,
$\alpha = 0.100$, $\beta = 2.000$, $N = 7$ for g.

3. Results and discussion

3.1. Convergence test of excitation cross sections with 76 states on the target

It is shown in paper I that the evaluated cross sections for excitation to 2s, 3s and 3d and for ionization with the basis set p20H76 have some structure around 30 keV. Therefore, we first compare the excitation cross sections to these channels calculated with the basis sets pxH76, where $x = 0, 1, 4, 10$ and 20. For $x = 0$, it is simply a single-centre close coupling calculation. For $x = 1$, there is a 1s state present on the projectile. For $x = 4$, the four states on the projectile are 1s, 2s, $2p_0$ and $2p_1$. For $x = 10$, the ten states on the projectile are all the bound states up to $n = 3$. And finally for $x = 20$, all 20 bound states up to $n = 4$ are present on the projectile. As in paper I, we only compare our results with those obtained by Ford *et al* (1993) using the single-centred AO expansion to make the figures more readable, since only their excitation cross sections are claimed to be converged within a few per cent over the entire energy region from 15 to 200 keV. Most other previous TCAO close-coupling calculations (see Slim and Ermolaev 1994) lack the necessary convergence test. Note that we have extended our calculations down to 5 keV, where Ford *et al* (1993) failed to obtain converged results with their single-centred AO expansion.

Our calculated excitation cross sections to 2s, 3s and 3d with the basis sets pxH76 are presented in figure 1, along with those obtained by Ford *et al* (1993). As it is expected, the single-centre close-coupling calculation (p0H76) failed to converge at low energies. This is not surprising since the number of bases used in our calculation is less than one-third of that (273 for $\ell \leqslant 5$) used by Ford *et al* (1993). The low-energy behaviour can be dramatically improved by including the 1s state on the projectile. With the basis set p1H76, we can actually predict the minimum position (around 10 keV) of the excitation cross section to 2s which is due to the two competing mechanisms of rotational and radial coupling when

Table 2. Even-tempered basis functions used to generate the bound and pseudo-continuum states of atomic hydrogen up to 174 states in total. The eigen-energies (au) were obtained from diagonalizing the atomic Hamiltonian of the single centre.

s	p	d	f	g	h
−0.500 00					
−0.125 00	−0.125 00				
−0.055 56	−0.055 55	−0.055 56			
−0.031 25	−0.031 25	−0.031 25	−0.031 25		
−0.019 99	−0.019 98	−0.019 96	−0.019 99	−0.019 97	
−0.013 82	−0.013 54	−0.013 25	−0.013 74	−0.013 85	−0.013 89
−0.009 71					
0.008 18	0.006 60	0.006 26	0.002 90	0.002 05	0.008 21
0.111 77	0.122 82	0.131 68	0.090 93	0.075 53	0.204 80
0.428 10	0.475 00	0.542 12	0.375 59	0.318 78	1.375 71
1.264 62	1.408 65	1.744 75	1.213 56	1.053 22	7.648 57
3.374 03	3.795 12	5.169 59	3.645 20	3.219 33	
8.758 60	9.940 50	15.096 04	11.083 10	9.833 00	
23.600 06	26.610 47				

$\alpha = 0.035$, $\beta = 1.440$, $N = 16$ for s,
$\alpha = 0.051$, $\beta = 1.500$, $N = 14$ for p,
$\alpha = 0.049$, $\beta = 1.600$, $N = 12$ for d,
$\alpha = 0.065$, $\beta = 1.600$, $N = 10$ for f,
$\alpha = 0.085$, $\beta = 1.635$, $N = 9$ for g,
$\alpha = 0.075$, $\beta = 2.222$, $N = 6$ for h.

viewed from the molecular picture (Fritsch and Lin 1982). Our results from the p1H76 basis set agree well with those of Ford *et al* (1993) over the entire energy range. These results show no structure and vary smoothly with the impact energy. We consider our calculation with p1H76 to be more accurate than the asymmetric close-coupling calculation (not shown in figure 1) with p1H50 by Ermolaev (1990).

Figure 1 also contains results from the p4H76 calculation (shown as plus symbols). Notice that the increased basis does not improve the results. Moreover, the resulting excitation cross sections to 2s, 3s and 3d appear to have a shoulder around 30 keV. There is no known physical mechanism to support such a shoulder structure around this energy range. Neither the single-centred calculation by Ford *et al* (1993) nor the present asymmetric two-centred p1H76 calculation have any structure. Therefore, we think the structure is artificial. Adding more projectile-centred bound states in the expansion, say p10H76 and p20H76, makes the shoulder even more prominent. Note that excitation to 2s, 3s and 3d is much weaker than excitation to 2p and 3p and at energies near 30 keV where the projectile velocity nearly matches the velocity of the electron in the target. It seems that excitation cross sections to the weaker channels are more sensitive to the basis set used in the close-coupling expansion, especially around the peak region. This might suggest that the basis sets (p4H76, p10H76 and p20H76) have certain deficiencies. In other words, the TCAO close-coupling method may not be reliable for weak channel calculations when the basis size is blindly increased. We have checked the product of all eigenvalues of the overlap matrix at small impact parameters, which we think is a measure of the linear dependence. We found that the product is generally larger than 0.01; therefore, the two-centre basis set used in the present calculation is linearly independent and the shoulder structure cannot be caused by linear dependence of the basis set.

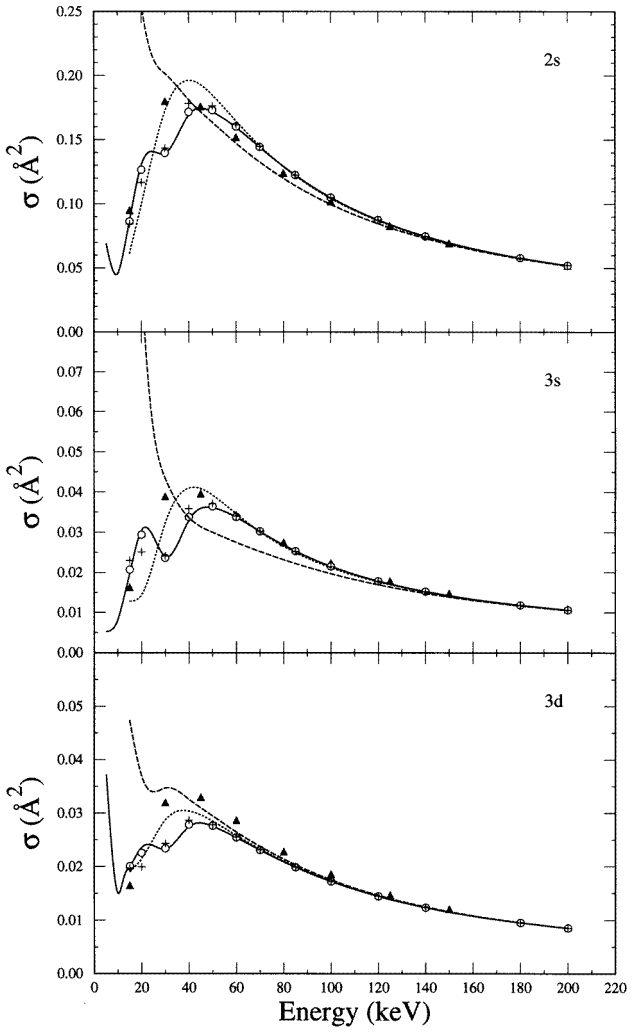

Figure 1. Excitation cross sections to 2s, 3s and 3d. Curves are obtained with cubic spline interpolation through the calculated points (symbols); full triangles, Ford *et al* (1993); broken curve, present p0H76; dotted curve, present p1H76; circles, present p4H76; +, present p10H76; full curve, present p20H76.

3.2. Convergence test of excitation cross sections with 1s state on the projectile

In order to see whether or not our asymmetric two-centred (p1Hy) close coupling calculation is still reliable as the number of target-centred bases is enlarged, we compared the calculated excitation cross sections to 2s, 3s and 3d with the basis sets p1H76, p1H134 and p1H174 in figure 2. Our largest single-centred calculation, p0H174, and the calculation by Ford *et al* (1993) are also shown. Note that the number of radial components for each ℓ in our basis set H174 differs from that in the calculation by Ford *et al* (1993), although we have as many angular momentum components ($\ell \leqslant 5$) as they do. For excitation to 2p and 3p (not shown), the present single-centred calculation p0H174 is almost the same as that by Ford *et al* (1993). For excitation to these weak channels, our calculation with p0H174 differs

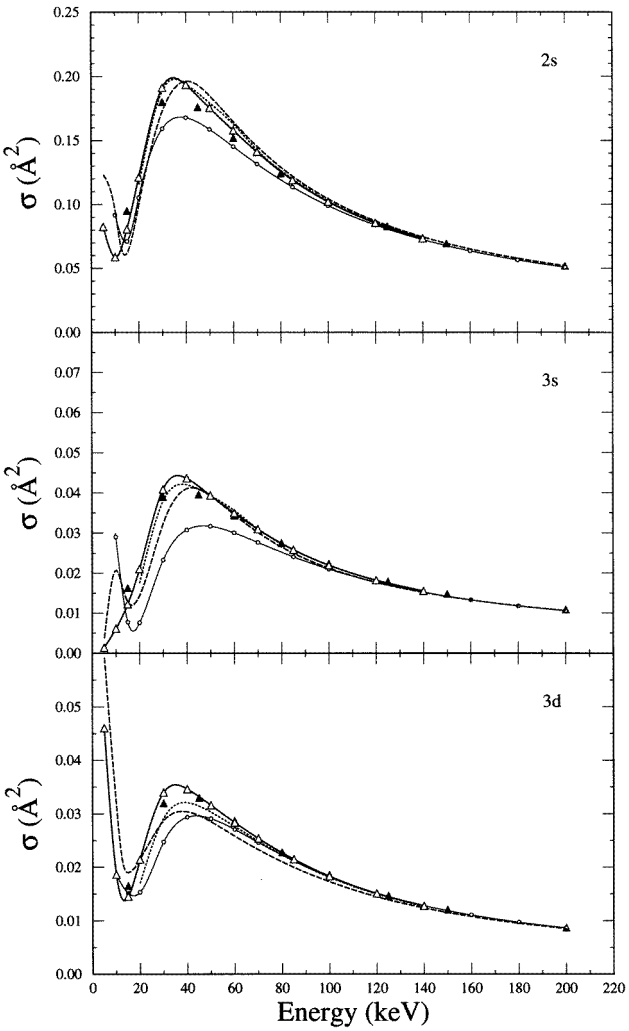

Figure 2. Excitation cross sections to 2s, 3s and 3d. Curves are obtained with the same interpolation as in figure 1; full triangles, Ford *et al* (1993); thin full curve with small circles, present p0H174; broken curve, present p1H76; dotted curve, present p1H134; full curve with open triangles, present p1H174.

slightly from theirs around the peak region.

The slow convergence of the single-centred expansion is significantly improved by adding a projectile-centred 1s orbital, i.e. the basis set p1Hy. As we see from the figures, all asymmetric close coupling (p1Hy) and the single-centred calculations are able to produce smooth excitation cross sections over the impact energy range from 20 to 200 keV. The overall agreement among these calculations is very good. The improvement from p1H76 to p1H174 is not very significant, which means the basis set p1H76 is 'complete' to some extent, while the basis set p0H174 has not yet converged as far as excitation to the weak channels is concerned. Nevertheless, the basis set p1H174 gives the best agreement with the single-centred calculation by Ford *et al* (1993). It is hard to say whether our p1H174 calculations produce better excitation cross sections than their single-centred calculations

do without more precise measurements. Notice that the asymmetric basis set (p1Hy) is still valid below 15 keV where the single-centred basis set fails.

3.3. Convergence test of excitation cross sections with 174 states on the target

Although the present asymmetric close-coupling calculations with the basis set p1H174 can give good excitation cross sections, we cannot extract accurate ionization cross sections from such calculations because electron capture cross sections to $n = 2, 3$ states are not negligible and they are not included in the basis set. We can of course extract the so-called electron removal cross sections, which are the sum of capture cross sections to 1s and cross sections to all pseudo-states. In order to extract ionization cross sections, we need to add more bound states on the projectile centre to allow a better representation of capture channels. We have performed two sets of asymmetric close-coupling calculations with the basis sets p10H174 and p20H174. The calculated excitation cross sections are shown in figure 3. Since excitation cross sections to 2ℓ and 3ℓ obtained with the basis set p10H174 are almost identical to those evaluated with the basis set p20H174, the former have been omitted from the figures. The similarity in these calculations is understandable because capture cross sections to 4ℓ states are very small compared to the $n \leqslant 3$ capture cross sections.

Unlike the previous close-coupling calculation with the basis set p20H76, where a shoulder appeared in the excitation cross sections to 2s, 3s and 3d respectively (see figure 1), the calculation with the basis set p20H174 only displayed a slight plateau around 40 keV in the excitation cross sections to 2s and 3s. The plateau structure may still imply deficiency of the basis set p20H174 and thus the deficiency of the TCAO close-coupling method when too many states are presented on the projectile centre. Beyond the peak region, the difference in the excitation cross sections for p1H174 and p20H174 calculations is quite small. Nevertheless, the calculation with p1H174 gives slightly smoother excitation cross sections. Both calculations are considered to be converged within a few per cent except near the peak region of the 2s and 3s excitation cross sections. However, the asymmetric close-coupling calculation with the basis set p20H174 allows us to extract the ionization cross section (see section 3.4). It is interesting to compare the two calculations with the basis sets p20H76 and p20H174. Both include the same projectile-centre states; however, the former has an obvious shoulder structure around 30 keV in the excitation cross sections to the weak channels, while the latter only has a flat peak in the same region. This immediately implies that the shoulder structure in the p20H76 calculation is an artifact of the basis set. We have also performed calculations with the basis set p20H134 (not shown), and the evaluated cross sections are very close to those obtained with p20H174.

On the top frame of figure 3, we have included the most recent measurement for 2s excitation cross sections by Higgins *et al* (1996). The experiment was based on the observation of Lyman alpha emission. The experimental data display a smooth energy dependence of 2s excitation cross sections. However, the 30% uncertainty in the experimental normalization procedure precludes any possibility of drawing definite conclusions regarding the convergence tests in the present calculation.

3.4. Convergence test of ionization cross sections

As mentioned above, we can readily extract total ionization cross sections with the asymmetric close-coupling calculations using the basis set p20Hy. The calculated ionization cross sections are shown in figure 4, together with our previous BBC-P type close-coupling

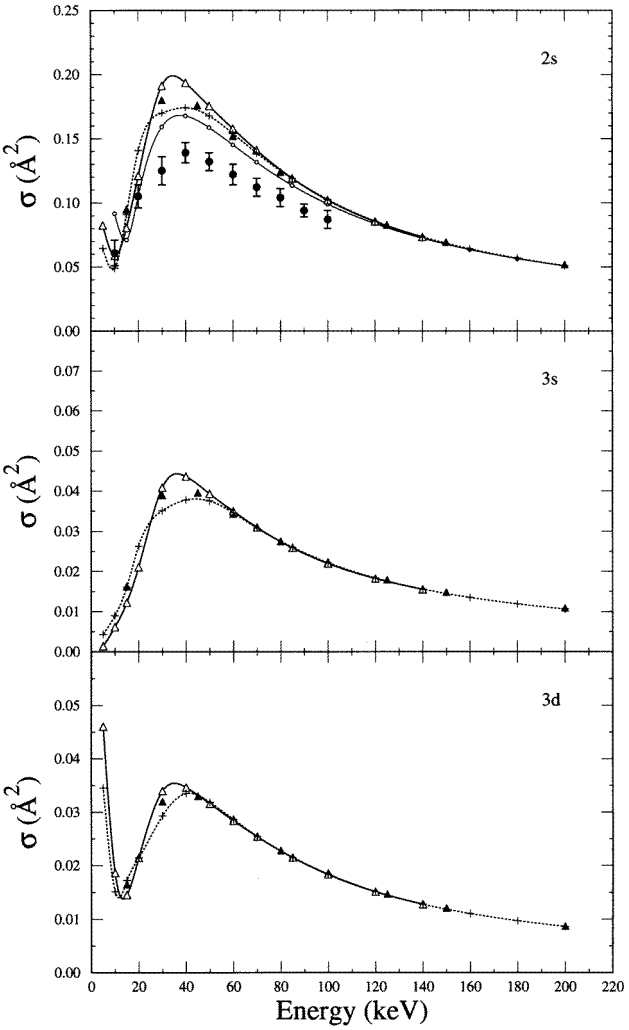

Figure 3. Excitation cross sections to 2s, 3s and 3d. Curves are obtained with interpolation; full triangles, Ford *et al* (1993); full curve with open triangles, present p1H174; dotted curve with +, present p20H174; full circles, experimental data by Higgins *et al* (1996).

calculation with basis set p76H20 (paper I) and the experimental data by Shah and Gilbody (1981) and Shah *et al* (1987). All the previous symmetric close-coupling calculations (Shakeshaft 1978, Toshima 1993) tend to overestimate the ionization cross section near the experimental peak region and are omitted from the figure, see paper I. For impact energies below 25 keV, the ionization cross sections from the p76H20 and p20Hy basis sets are clearly converged.

For impact energies above 80 keV, all asymmetric close-coupling calculations with basis sets p20Hy are converged; however, around the experimental peak region, the convergence is very sensitive to the basis set. The calculation with the set p20H76 appears to have a shoulder around 40 keV. This situation is readily improved with the basis set p20H134, but we can still see a very slight structure. Using the p20H174 set, we eventually obtain smooth

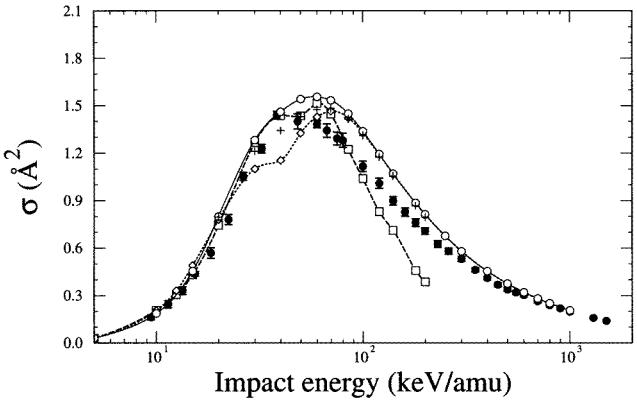

Figure 4. Ionization cross sections. Curves are obtained with interpolation; broken curve, previous p76H20 (paper I); dotted curve, previous p20H76; full curve, present p20H174; +, present p20H134; full circles, experimental data by Shah and Gilbody (1981) and Shah *et al* (1987).

ionization cross sections. Note that the evaluated ionization cross sections with p20H174 agree very well with those obtained using p76H20 up to 40 keV. The difference between these two calculations occurs above 40 keV because the basis set p76H20 only works for low energy impact where the continuum states are close to the projectile centre. Our converged ionization cross section differs from the experimental data above 50 keV. The difference reaches a maximum around 80 keV and then decreases with increasing impact energy. As can seen from the present study, converged ionization cross sections can be obtained using target-centred pseudostates in the asymmetric two-centre close-coupling calculation over the entire impact energy range.

3.5. Comparison of evaluated excitation cross sections with experiments

There are a number of experimental measurements for protons colliding with ground-state hydrogen atoms in the impact energy region studied here. The first direct experimental measurement was carried out by Park *et al* (1976) using energy-loss spectroscopy. They obtained total excitation cross sections to $n = 2, 3, 4$. Very recently, Detleffsen *et al* (1994) determined excitation cross sections to np levels ($n = 2 \ldots 6$) using the optical method. These experimental results are compared with the present calculation using the p20H174 base set as well as with the calculation by Ford *et al* (1993) in figures 5 and 6. In figure 5, the 2p excitation cross section has been multiplied by 0.8 to avoid overcrowding with the total $n = 2$ excitation cross sections. For the total and np excitation cross sections, the calculations with basis sets p1H174 and p20H174 differ little from each other. Note that we have renormalized the Park *et al* (1976) data to our calculation (0.629 Å^2 for excitation cross section to $n = 2$ at 200 keV), since their original data were normalized to the Born value (0.664 Å^2), which is not correct at this energy. The renormalization was done by multiplying all original experimental numbers for excitation to $n = 2, 3, 4$ (Park *et al* 1976) by a common factor of 0.947. For $n = 2$ excitation, good agreement between the present results and the experiment is shown in figure 5. By comparison, the measurement of Detleffsen *et al* (1994) appears to have overestimated the 2p excitation cross section.

For excitation to 3p, the present calculation is in good agreement with the calculation of Ford *et al* (1976) as well as with the experiment by Detleffsen *et al* (1994). However,

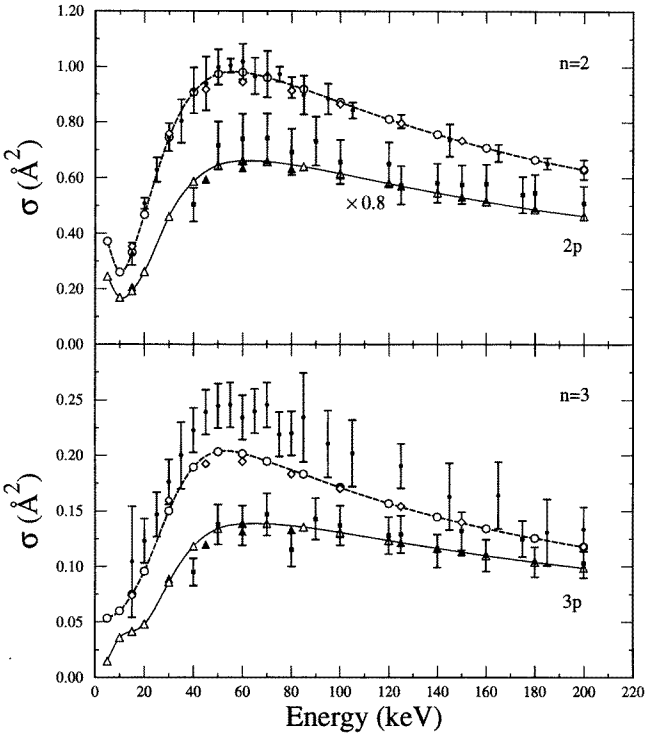

Figure 5. Excitation cross sections to 2p, 3p, and $n = 2, 3$. Full triangles and open diamonds, Ford *et al* (1993); full curve with open triangles and broken curve with open circles, present p20H174; full squares, experiment by Detleffsen *et al* (1994); full circles, experiment by Park *et al* (1976).

for the total excitation cross section to $n = 3$, the experimental data by Park *et al* (1976) lay a little bit above our calculation and those of Ford *et al* (1993). For excitation to $n = 4$, the experimental data by Park *et al* (1976) carry big error bars. The two theoretical calculations, which agree with each other, just touched the lower end of the error bars, as shown in figure 6. For excitation to 4p, the agreement between the theoretical results and the experimental data by Detleffsen *et al* (1994) is quite good. To the best of our knowledge, there is no close-coupling calculation for excitation to $n = 5$. Our calculation is compared to the only available measurement by Detleffsen *et al* (1994) in the lower part of figure 6. Although the experimental data are for excitation to 5p, they are closer to our total excitation cross sections to $n = 5$. We think more work is needed from both theory and experiment in determining the accurate excitation cross sections to such high lying states.

As in paper I, we can derive Balmer H_α polarization fractions from the present asymmetric close-coupling calculations. The results obtained with the basis set p20H174 are plotted in figure 7 together with our previous BBC-T close-coupling calculation with basis set p20H76, as well as the experimental data (Werner and Schartner 1996). Since the polarization fraction depends on the excitation cross sections to individual m sublevels, the experimental measurement provides a critical test of various theoretical studies. It was shown in paper I that all the symmetric close-coupling calculations displayed pronounced oscillatory structure which is absent in the experiment. Therefore, all previous symmetric close-coupling calculations are omitted from the figure. The two asymmetric close-coupling

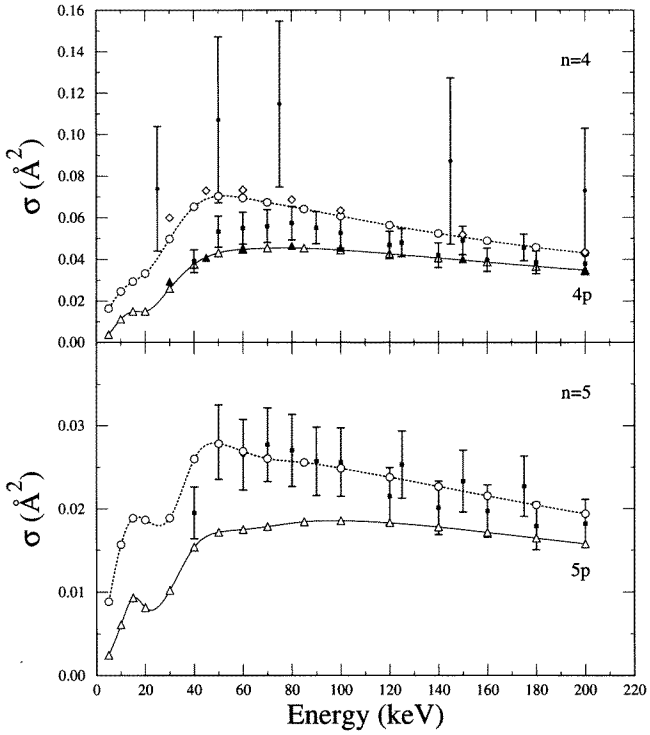

Figure 6. Excitation cross sections to 4p, 5p, and $n = 4, 5$. The same notation is used as in figure 5.

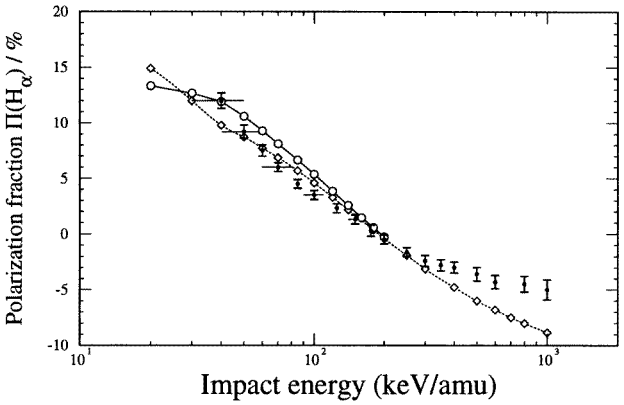

Figure 7. Polarization fraction of Balmer H_α induced by proton impact. Full curve with circles, present p20H174; dotted curve with diamonds, previous p20H76; full circles, experiment by Werner and Schartner (1996).

calculations with basis sets p20H76 and p20H174 predict smooth Balmer H_α polarization fractions, and are in good agreement with experimental data at impact energies below 300 keV. The slight difference between the two calculations vanishes with increasing impact energies. The discrepancy between the present close-coupling calculation and the experiment at impact energies above 300 keV remains to be understood. Since our results are also close

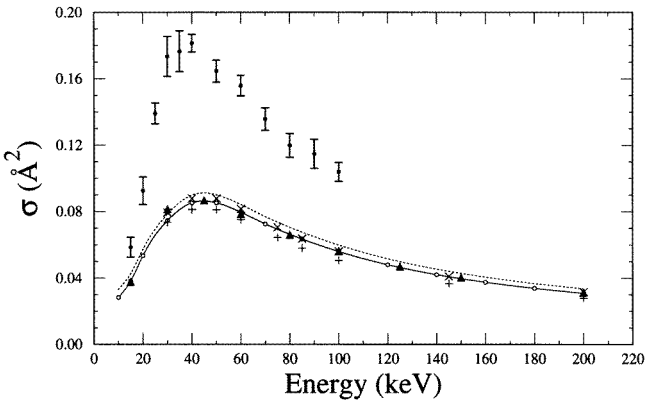

Figure 8. Cross sections for Balmer alpha emission from direct target excitation. Full curve with circles, present p20H174; dotted curve, cascade correction included from present p20H174; +, asymmetric calculation by Ermolaev (1991); ×, cascade correction included from Ermolaev (1991); full triangles, Ford *et al* (1993); full circles, experiment by Donnelly *et al* (1991).

to those from the Born approximation at these energies, we believe both calculations are reliable for impact energies above 300 keV.

The total cross sections for Balmer alpha emission from direct target excitation can also be obtained from the present calculations. Our results are presented in figure 8 and compared to other theoretical calculations (Ermolaev 1991, Ford *et al* 1993) as well as with the experiment of Donnelly *et al* (1991). The symmetric close-coupling calculation by Slim (1993) was not shown because of the artificial structure around the peak region. Since we have calculated excitation cross sections to 4ℓ and 5ℓ states directly, we also determined the cascade correction from these levels. All three theoretical calculations presented in figure 8 agree very well with each other. The disagreement (about a factor of two) between the experiment of Donnelly *et al* (1991) and the theory still exists. Considering that the present calculation as well as the calculation of Ford *et al* (1993) appear to have converged, further experiments for Balmer alpha emission are called for in order to resolve this discrepancy.

4. Summary and conclusions

In this paper we have carried out extensive convergence studies for the two-centre atomic orbital close-coupling method for keV protons colliding with atomic hydrogen. In agreement with our previous study, we again found that reliable excitation and ionization cross sections can only be calculated with the asymmetric TCAO close-coupling method. This method requires a large number of basis states on the target and a limited number of bound states on the projectile. The transition cross sections thus obtained show a smooth dependence with impact energy over the entire keV region. The results appear to be variational in that the evaluated results are improved uniformly as more target states are added. Caution must be taken as more projectile-centred states are added to the TCAO close-coupling expansion. However, a certain number of projectile-centre states are necessary in order to extract reliable ionization cross sections. Some balance may be exercised when performing TCAO close-coupling calculations. The results obtained with the various basis sets are considered to be converged within a few per cent level beyond the peak region.

The present study disclosed the extreme difficulty in obtaining converged cross sections around the peak region, especially for the weak channels. We found that a sufficiently large basis set with large angular momenta is necessary and the TCAO close-coupling method is still likely to fail. This point has not been appreciated in the past. Although the single-centre expansion by Ford *et al* (1993) can produce rather reliable excitation and ionization results, a very large basis set is needed in order to obtain converged results at low impact energies. However, the present asymmetric TCAO close-coupling method is able to calculate individual excitation and ionization cross sections to the same accuracy with a smaller basis set, and to obtain reasonably accurate capture cross sections at the same time. Although these points are based on our sample study for the $p + H(1s)$ system (all the data reported here are available upon request via E-mail), we expect the conclusion is applicable to other systems, for example, collisions between multiply charged ions and light atoms. We have applied the present method to alpha particles colliding with hydrogen atoms (Kuang and Lin 1996b) and the conclusion is consistent with the present study.

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