A perturbation/close-coupling method for inelastic processes in ion–atom collisions

Jiyun Kuang, Z Chen and C D Lin

Department of Physics, Kansas State University, Manhattan, KS 66506, USA

Abstract. A combined perturbation and close-coupling method is proposed to calculate cross sections for weak inelastic channels in ion–atom collisions. In this method, the time-dependent wavefunction is expanded in terms of basis functions of the dominant channels only, from which the perturbation method is applied to calculate cross sections for the weak channels. The method is applied to calculate probabilities for excitation and charge transfer to the $n = 2$ states in p + H(1s) collisions in the intermediate energy region to check the validity of this approach. Cross sections for excitation to $n = 2$, 3 and 4 levels are obtained and compared to experiment and other theoretical results.

1. Introduction

Theoretical descriptions of electronic transitions in ion–atom collisions have been developed traditionally along two distinct lines. For collisions at high energies, the theory is often formulated based on the perturbation expansion (Macek 1988). On the other hand, the standard approach for collisions in the low to intermediate energy region is the close-coupling method where the strong distortion of the electron cloud in the course of collision is represented by a linear combination of some basis functions (Bransden and McDowell 1992, Fritsch and Lin 1991, Kimura and Lane 1990).

The close-coupling method has been exploited over the last two decades and excellent agreement with experimental results for a large variety of collision systems has been documented (Bransden and McDowell 1992, Fritsch and Lin 1991, Kimura and Lane 1990). The close-coupling method, particularly that employing atomic orbitals on the two collision centres, has been shown to predict not only the total and partial electron capture cross sections for the dominant channels, but also the calculated alignment and other coherence parameters have been shown to be in good agreement with experiments. Despite the success, however, the close-coupling method has not been extensively examined for its usefulness in calculating cross sections for the weak channels. To account for the effect of large channels on the weak channels, in the close-coupling method, basis functions representing both the dominant and the weak channels have to be included simultaneously in the expansion. This makes the size of the basis functions used in the calculation very large and computationally very time consuming. In calculations with large basis set, numerical instability is also easily encountered.

In this paper we propose a combined perturbation/close-coupling method to calculate cross sections for the weak channels in the presence of other dominant channels in ion–atom collisions. Unlike the usual perturbation method where the initial state is only weakly disturbed in the collision, the problems we are concerned with are weak channels in a

collision where the initial state is strongly distorted. We represent this strong distortion of the electron cloud using the standard close-coupling method where only basis functions of the dominant channels are included. We then apply first-order perturbation theory to calculate transition probabilities for the weak channels from this distorted system. The theoretical description of the method is given in section 2. Application of the method to the well studied prototype system of p + H(1s) is given in section 3 to check the validity of this approach. Additional results for the excitation cross sections to $n = 2$, 3 and 4 states are calculated and compared to other close-coupling methods and with available experiments and the results are also shown in section 3. A short summary is given in section 4.

2. Perturbation/close-coupling method (PCC)

The perturbation/close-coupling method is most conveniently formulated starting with the conventional close-coupling method (for a recent review, see Fritsch and Lin 1991). In this method, the time-dependent wavefunction satisfies

$$\left(i\frac{\partial}{\partial t} - H \right) \Psi(r, t) = 0 \tag{1}$$

where the Hamiltonian H

$$H = -\tfrac{1}{2}\nabla_r^2 + V_A(r_A) + V_B(r_B) \tag{2}$$

consists of a kinetic energy operator and effective interaction potentials from the target (A) and from the projectile (B). In the standard close-coupling method, the wavefunction is expanded formally as

$$\Psi(r, t) = \sum_{j=1}^{M} a_j(t)\phi_j(r, t) + \sum_{j=M+1}^{N} c_j(t)\phi_j(r, t) \tag{3}$$

where the total number of basis functions included in the expansion is N. We have separated the first M basis functions on purpose which are the dominant channels from the rest of the $(N - M)$ channels which are the weak channels. In the close-coupling method, all the N basis functions in (3) are treated on an equal footing. The expansion coefficients satisfy a set of coupled differential equations of the form

$$i\sum_{k=1}^{M} S_{jk}(t)\dot{a}_k(t) + i\sum_{k=M+1}^{N} S_{jk}(t)\dot{c}_k(t) = \sum_{k=1}^{M} G_{jk}(t)a_k(t) + \sum_{k=M+1}^{N} G_{jk}(t)c_k(t) \tag{4}$$

with $j = 1, \ldots, M, M + 1, \ldots, N$, and

$$S_{jk}(t) = \langle \phi_j | \phi_k \rangle \qquad G_{jk}(t) = \langle \phi_j | H - i\frac{\partial}{\partial t} | \phi_k \rangle \tag{5}$$

are the overlap matrix element and the interaction matrix element, respectively. The set of N first-order coupled differential equations are solved 'exactly' to obtain transition probability amplitudes to each final state.

   The close-coupling method is most effective for obtaining transition probabilities when dominant channels are considered (Fritsch and Lin 1991, Kimura and Lane 1990). Although

the method has been applied to calculate transition amplitudes for the weak channels, the accuracy and the effectiveness of the method is more questionable.

In the perturbation/close-coupling (PCC) method, the close-coupling calculation is first carried out by including only the dominant channels, the probability amplitudes for the weak channels are then obtained by perturbation theory. As an example, consider the excitation and charge transfer to the $n = 2$ states in p + H(1s) collisions in the 15–100 keV region. Besides the elastic channel, probabilities for charge transfer to the ground state of atomic hydrogen are large. In the standard close-coupling calculations, one would include all the 1s, 2s and 2p states on the two collision centres, resulting in an eight-state calculation. In the PCC method one includes only the two 1s states on the two collision centres in the close-coupling calculation, and probabilities for excitation or electron capture to the $n = 2$ states are solved by perturbation theory. Thus, in the PCC method, instead of solving (3) exactly, we first solve the coupled equations involving the M dominant channels,

$$i \sum_{k=1}^{M} S_{jk}(t)\dot{a}_k(t) = \sum_{k=1}^{M} G_{jk}(t)a_k(t) \tag{6}$$

where $j = 1, \ldots, M$. To obtain the scattering amplitude for a particular weak channel j, we neglect its coupling with other weak channels and only retain its interaction with the M dominant channels. Thus the equation to be solved is

$$i\dot{c}_j(t) = G_{jj}(t)c_j(t) - i\sum_{k=1}^{M} S_{jk}(t)\dot{a}_k(t) + \sum_{k=1}^{M} G_{jk}(t)a_k(t) \tag{7}$$

where j represents a certain weak channel. The first term on the right-hand side of (7) represents the distortion due to the projectile; the last two terms are due to the coupling of the weak state j with all the M dominant channels. The terms involving the overlap matrix elements are due to the non-orthogonality of basis functions from different centres. The above inhomogeneous differential equation can be integrated immediately to obtain the scattering amplitude. Note that (7) becomes identical to the first-order distorted-wave approximation if the summation on the right-hand side includes only the initial state and the amplitude of that state is set at $a_0(t) = 1.0$ for all time.

In ion–atom collisions, most of the weak channels belong to excited states where states within the same hydrogenic manifold are degenerate. It is important to include the coupling among the weak degenerate states in the PCC method in order to get the correct partial cross sections for those degenerate channels. Thus, instead of (7), we solve

$$i\dot{c}_j(t) = \sum_{l=1}^{n} G_{jl}(t)c_l(t) - i\sum_{k=1}^{M} S_{jk}(t)\dot{a}_k(t) + \sum_{k=1}^{M} G_{jk}(t)a_k(t) \tag{8}$$

for $j = 1, \ldots, n$, where n is the number of degenerate substates. The first term on the right-hand side includes the coupling among these weak substates, and the last two terms are the same as in (7). Note that all the weak degenerate states are on the same centre, thus there are no overlap integrals among the weak channels in (8).

The present perturbation/close-coupling method can be considered as an approximation to the standard close-coupling method. In essence, we neglect the coupling among the weak channels unless they are degenerate states within the same centre. Equation (8) can be solved simultaneously for all the degenerate substates in a manifold. Comparing to the standard close-coupling method, the PCC method is greatly simplified. All the matrix elements among the weak channels can be neglected except for one-centre integrals among degenerate substates. Furthermore, only half of the potential matrix $G_{j,k}$ and the overlap matrix $S_{j,k}$ for j belongs to the n weak degenerate channels and k belongs to the M dominant channels need to be calculated.

3. Results and discussion

3.1. Probabilities for excitation and electron capture to n = 2 states

To examine the validity of the PCC approach, we first apply the method to the well studied excitation and electron capture processes to the $n = 2$ excited states in proton–hydrogen atom collisions at 145 keV. The results for excitation to $n = 2$ states are shown in the top part of figure 1 and for electron capture to $n = 2$ states are shown in the bottom part of figure 1. In the full close-coupling calculation, both the $n = 1$ and $n = 2$ atomic states on both collision centres (eight states all together, 8CC) are included and the resulting probabilities are shown as full symbols. In the PCC calculation, we first carry out the close-coupling calculation by including only the 1s orbital on each centre, and excitation to the $n = 2$ states are then calculated by perturbation theory by solving the coupled equations (8) where the degenerate 2s, $2p_0$ and $2p_1$ states are included. The results from such a perturbation calculation are shown as open symbols in figure 1. It is clear that the PCC results are essentially identical to those from the full close-coupling calculation.
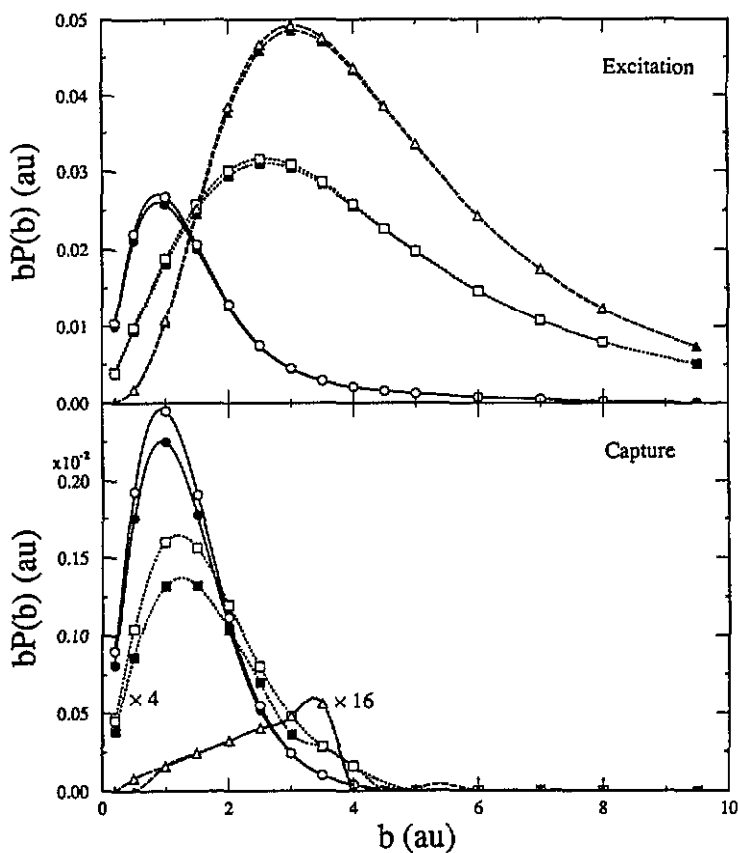

Figure 1. Impact parameter dependence of the probabilities for excitation and electron capture to 2s, $2p_0$ and $2p_1$ states at 145 keV. Full symbols represent the results from eight-state close-coupling (8CC) calculation. Open symbols represent the results from the present perturbation/close-coupling (PCC) calculation. Full, dotted and broken curves denote the 2s, $2p_0$ and $2p_1$ channels, respectively. Note that the probabilities for electron capture to $2p_0$ and $2p_1$ were multiplied by 4 and 16, respectively.

The same procedure can be applied to the electron capture channels. From the same close-coupling results for the amplitudes for the two 1s states, we calculate the probability amplitudes for electron capture to 2s and 2p states. The results are shown in the bottom of figure 1. The agreement with the full close-coupling calculation is also quite satisfactory. Note that the capture probabilities are much smaller, and the probabilities shown for $2p_0$ have been multiplied by 4 and for $2p_1$ by 16. The discrepancies between the close-coupling and the PCC calculation are due to the neglection of the coupling between the $n = 2$ excitation channels and the $n = 2$ electron capture channels. Note that the latter is much smaller and thus the neglection of the coupling with the stronger $n = 2$ excitation channel has some small effects.

We have applied the same perturbation calculations to collision energies at 50 and 25 keV and the results are shown in figures 2 and 3, respectively. The agreement between the two sets of calculations is quite good at 50 keV, and still quite acceptable at 25 keV. For 25 keV, we do not expect such a simple perturbative treatment could give very reasonable results since only two 1s orbitals are included in the close-coupling part for the PCC calculation. In fact, two hydrogenic 1s orbitals are not enough for the low-energy collision, where inclusion of molecular orbitals and/or united orbitals becomes important (Fritsch and Lin 1982).
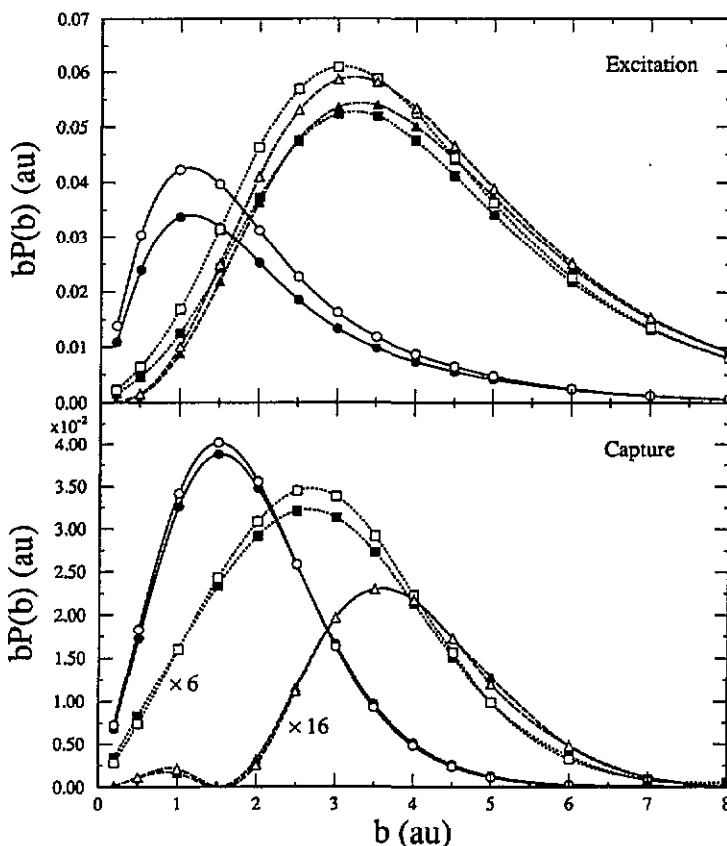

Figure 2. Impact-parameter dependence of the probabilities for excitation and electron capture to 2s, $2p_0$ and $2p_1$ at 50 keV. The notation used is the same as in figure 1.
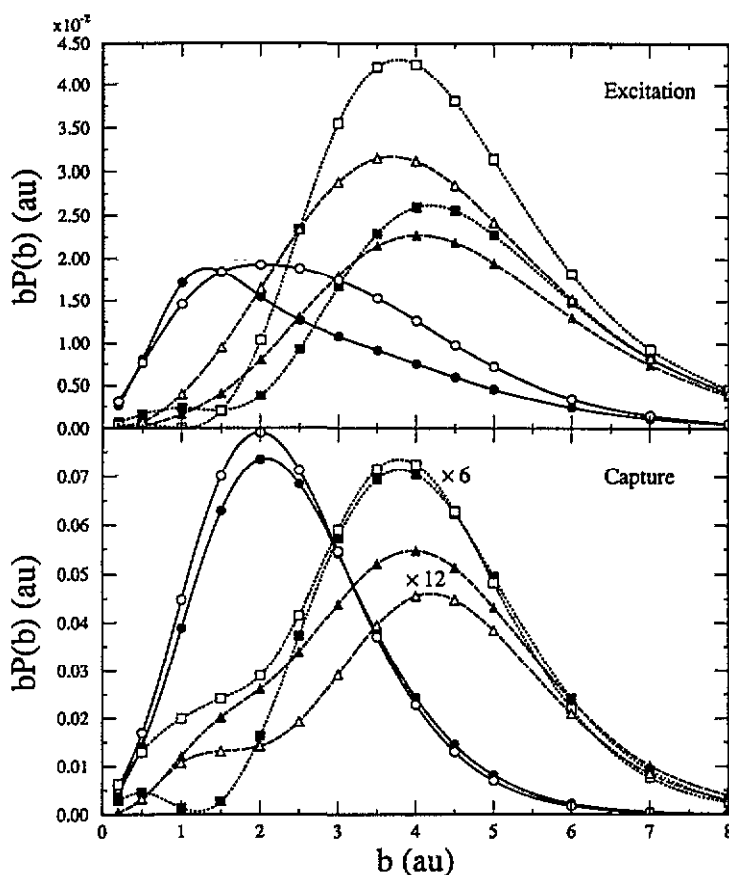
Figure 3. Impact-parameter dependence of the probabilities for excitation and electron capture to 2s, 2p$_0$ and 2p$_1$ at 25 keV. The notation used is the same as in figure 1.

3.2. Total excitation cross section to n = 2 states

We have used the PCC method to obtain total excitation cross sections to H($n = 2$) states and compared the results with several theoretical calculations (Shakeshaft 1978, Ford *et al* 1993) as well as with the experimental data of Park *et al* (1976). The results are shown in the top part of figure 4. Additional theoretical results can be found in the recent article of Slim and Ermolaev (1994). The experimental data of Park *et al* quoted here were normalized to a Born cross section of 6.637×10^{-17} cm^2 at 200 keV as suggested in their original publication. The validity of this normalization is questionable, but the 'converged' theoretical value at this energy from different calculations is still uncertain. The excitation cross sections to the $n = 2$ states at 200 keV calculated by Shakeshaft, by Ford *et al*, and from the present PCC method are 6.04, 6.31 and 6.96, in units of 10^{-17} cm^2, respectively.

In figure 4, the excitation cross sections from the present PCC calculation are shown as open circles. They were obtained by including only 1s orbitals on both collision centres in the close-coupling calculation and the excitation cross sections to the $n = 2$ states are obtained by perturbation theory. Also shown in figure 4 are the results from a full eight-state (1s, 2s, 2p$_0$ and 2p$_1$ on each centre) close-coupling (8CC) calculation, the 70-state close-coupling calculation by Shakeshaft (1978), and the more recent one-centre expansion
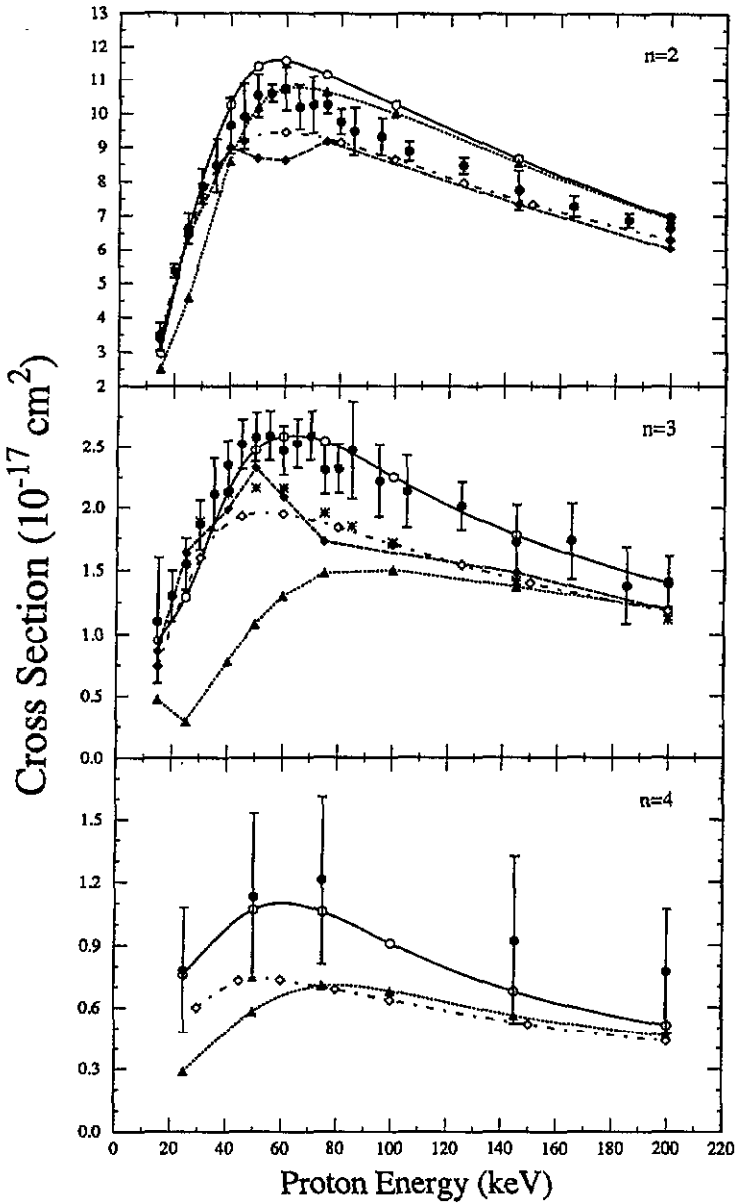
Figure 4. Excitation cross sections to $n = 2$, 3 and 4 levels. The full circles with error bars are the experimental data from Park *et al* (1976). The broken curve with full diamonds is the two-centred Sturmian basis calculation of Shakeshaft (1978). The chain curve with open diamonds is the single-centred expansion calculation of Ford *et al* (1993). For $n = 2$, the full curve with open circles is the present perturbation/close-coupling (PCC) calculation including an 1s on each centre in the close-coupling part. The dotted curve with full triangles is our eight-state close-coupling (8CC) calculation including 1s, 2s, $2p_0$ and $2p_1$ on each centre. For $n = 3$, the asterisks are the results of the asymmetric two-centred expansion of Ermoleav (1991); the dotted curve with full triangles is the present PCC(1) calculation including only a 1s on each centre in the close-coupling part; the full curve with open circles is the present PCC(2) calculation including all the states of $n = 1$ and 2 on each centre in the close-coupling part. For $n = 4$, the dotted curve with full triangles is the present PCC(3) calculation including all the states of $n = 1$ and 2 on each centre in the close-coupling part; the full curve with open circles is the present PCC(4) calculation including all the states of $n = 1$, 2 and 3 on each centre in the close-coupling part.

method of Ford *et al* (1993). It appears that the present PCC results have good overall agreement with the experimental data of Park *et al*.

The better agreement of the present PCC calculation with experiment than the full large-scale close-coupling calculation is surprising. If one regards the present method as an approximation to the full close-coupling calculation, then this better agreement with experiment does not bear any significance. On the other hand, note that the two-centre close-coupling calculation is not a variational method, in that the addition of more basis functions does not guarantee improved results. Furthermore, from the recent results of Slim and Ermolaev (1994) and of Toshima (1994), it appears that close-coupling calculations using a large basis set result in cross sections which do not vary smoothly with the collision energy. This is already true in Shakeshaft's results where the excitation cross section to the $n = 2$ states show a dip at around 60 keV (see figure 4) while the experimental data show no such structure. It was often speculated that the dip is an indication of the lack of convergence in his calculation. However, calculations by Toshima and by Slim and Ermolaev using much larger basis set give a similar non-smooth energy dependence. These results appear to indicate that calculations using large basis set in the AO expansion method are not stable.

3.3. Total excitation cross section to $n = 3$

In the middle part of figure 4, cross sections for excitation to the $n = 3$ level are shown together with the experimental data (Park *et al* 1976) and the results of other theoretical calculations (Shakeshaft 1978, Ford *et al* 1993, Ermolaev 1991). We did two PCC calculations. In PCC(1), we included the two 1s orbitals on either collision centre for the close-coupling calculation part, and then calculated the excitation to the $n = 3$ states by the perturbation method. While in PCC(2), we included the 1s, 2s, $2p_0$ and $2p_1$ on each collision centre for the close-coupling part, and then calculated the excitation to the $n = 3$ states by the perturbation method. As we see from the figure the two PCC results are close to each other at high energies, but differ from each other at low energy. The results from PCC(1) are not satisfactory, especially for energies below 150 keV. The discrepancies between PCC(1) and PCC(2) may be attributed to the mechanism of excitation to the $n = 3$ states in this energy region. In PCC(1), excitation to the $n = 3$ states do not proceed via the intermediate states, while in PCC(2), such a mechanism is included perturbatively. In the lower energy region, excitation to the 3p and 3d states through the 2s and 2p intermediate states is quite large. Failure to include the 2s and 2p orbitals in the close-coupling calculation prevents the formation of 3p and 3d states through the allowed-dipole coupling with the 2s and 2p states.

Note that we could have included the $n = 2$ excitation and charge-transfer channels perturbatively in the PCC(2) calculation for the $n = 3$ excitation probabilities. The results in section 3.2 indicates that the $n = 2$ channels can be obtained by the close-coupling method or by the perturbation method. Inclusion of the $n = 2$ states, even at the perturbation level, does allow the transitions to $n = 3$ via the $n = 2$ intermediate states.

Compared with other theoretical calculations, our results from PCC(2) are in best agreement with the experimental data over the entire 15–200 keV energy range. Note that the experimental data for excitation to the $n = 3$ level were determined by the normalization procedure in which the $n = 2$ states at 200 keV was given by the Born approximation and might have 5–10% additional uncertainty. The calculation by Shakeshaft (1978) displays an erratic energy dependence even though he included 70 basis states in his calculation. Both results of the single-centred calculations by Ford *et al* (1993) and the asymmetric two-centred expansion calculations by Ermolaev (1991) are in good agreement with the

experiment at low energies but not in the high energies. It is of interest to note that the agreement of the PCC results with the experimental ones for excitation to the $n = 3$ level is better than that for excitation to the $n = 2$ level. Similar to the results for $n = 2$, it is too early to draw conclusions that the PCC method is better than the full extensive close-coupling calculations.

3.4. Total excitation cross section to n = 4

Our PCC method can be readily used to calculate excitation cross sections to the higher excited states. In the bottom part of figure 4, the present PCC results for excitation to the $n = 4$ level are plotted, together with the experimental data (Park *et al* 1976) and the results of the theoretical calculation by Ford *et al* (1993). Again, we did two PCC calculations. In PCC(3), we included 1s, 2s, $2p_0$ and $2p_1$ on each collision centre for the close-coupling part, and then calculated the excitation to the $n = 4$ states by the perturbation method. While in PCC(4), we included all the states with $n = 1$, 2 and 3 on each collision centre for the close-coupling part. As we see from the figure, our two PCC results are close to each other at the high energies, but differ a little from each other at low energy. For the same reason as we discussed above, the calculation of PCC(3) excludes the allowed-dipole transition from $n = 3$ to $n = 4$; therefore, its agreement with the data is not so good as PCC(4), but it is acceptable. The results from PCC(4) are converged and in very good agreement with the experimental data over the entire energy range. There is no two-centred close-coupling calculation for excitation to the $n = 4$ level, to the best of our knowledge. There exist two single-centred calculations by Reinhold *et al* (1990) and Ford *et al* (1993). Both results are close to each other, but are somewhat low compared to the Park *et al* experiments. In figure 4, we only plotted the results from Ford *et al* (1993).

In the PCC(4) calculation we have included the $n = 2$ and $n = 3$ states in the close-coupling calculation. However, since the probabilities for exciting these channels are small, they can also be obtained using the perturbation theory . In other words, the amplitudes for excitation (and charge transfer) to $n = 2$ and $n = 3$ as obtained by perturbation theory from the previous subsections can be used in the perturbation calculation for the $n = 4$ states. As a rule of thumb, if the probability of a particular channel is less than 0.01, then the present PCC method can be used to evaluate transition cross section to that state.

3.5. Total electron capture cross sections to 2s and 2p states

The total electron capture cross sections to 2s and 2p states can also be evaluated with the perturbation/close-coupling method. By simply including a 1s orbital on each centre, we can obtain the total electron capture cross sections to 2s and 2p states perturbatively. Our results are given in table 1 along with other theoretical calculations (Shakeshaft 1978, Fritsch and Lin 1982). Our 8CC cross sections are obtained by including $n = 1$ and $n = 2$ states on both collision centres. As we see our perturbation and 8CC results are again close to each other. Very good agreement has been achieved among the different theoretical results for electron capture to 2s. However, obvious deviation exists at low energies (15 and 25 keV) for electron capture to 2p. As already mentioned above, only including 1s orbital on each centre for the close-coupling part is not enough at these energies since molecular orbitals and/or united orbitals are known to be important (Fritsch and Lin 1982) in order to describe low-energy collisions at small impact parameters. The 8CC and the present PCC calculations do not account for this important effect, but the large-scale close-coupling calculations of Shakeshaft and of Fritsch and Lin do include such effects and thus their results are close to each other and are closer to the experimental data.

Table 1. Comparison of theoretical predictions for the total electron capture cross sections (10^{-17} cm^2) to 2s and 2p in the p + H(1s) collision. The PCC and SCC are from the present perturbed close-coupling calculations and the present close-coupling calculations, respectively.

E (keV)	2s				2p			
	PCC	SCC	Sh[a]	FL[b]	PCC	SCC	Sh[a]	FL[b]
15	3.30	2.98	3.41	3.56	0.97	1.69	3.10	3.16
25	3.73	3.57	3.98		1.03	0.99	1.74	
50	1.67	1.64	1.39		0.42	0.40	0.40	
75	0.65	0.62	0.42		0.15	0.14	0.09	

[a] Two-centred Sturmian basis calculations of Shakeshaft (1978).
[b] AO+ calculations of Fritsch and Lin (1982).

4. Summary and conclusions

The perturbation/close-coupling method for treating inelastic processes in ion–atom collisions at intermediate energy is presented and then applied to the collision system of p + H(1s) in the energy range from 15–200 keV. Comparison of the evaluated probabilities for excitation and electron capture to $n = 2$ between the present PCC method and the conventional close-coupling method establishes the validity of this method for calculating excitation and electron capture cross sections of the weak channels.

Our cross sections for excitation to $n = 2$, 3 and 4 levels are in good agreement with the experiment data of Park *et al* (1976). Since the experimental data have very large error bars besides the questionable normalization procedure used, it is hard to evaluate the accuracy of the present method beyond the 10% level. Further experimental work with smaller error bars for the $n = 3$ and 4 levels is needed to assess the accuracy of all the theoretical calculations. However, the results presented prove that the PCC method is very useful in calculating cross sections for the weak channels. Extension of the present method to other collision systems is underway.

Acknowledgments

References

Bransden B H and McDowell M R C 1992 *Charge Exchange and the Theory of ion–atom Collisions* (Oxford: Clarendon)
Ermoleav A M 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** L495–9
Ford A L, Reading J F and Hall K A 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 4537–51
Fritsch W and Lin C D 1982 *Phys. Rev.* A **26** 762–9
—— 1991 *Phys. Rep.* **202** 1–97
Kimura M and Lane N F 1989 *Adv. At. Mol. Opt. Phys.* **26** 79–160
Macek J 1988 *Phys. Rev.* A **37** 2365–77
Park J T, Aldag J E, George J M and Peacher J L 1976 *Phys. Rev.* A **14** 608–14
Reinhold C O, Olson R E and Fritsch W 1990 *Phys. Rev.* A **41** 4837–42
Shakeshaft R 1978 *Phys. Rev.* A **18** 1930–4
Slim H A and Ermolaev A M 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** L203–9
Toshima N 1994 Private communication