J. Phys. B: At. Mol. Phys. **15** (1982) 1255–1268. Printed in Great Britain

Close-coupling calculations for inelastic processes in intermediate energy ion–atom collisions

W Fritsch† and C D Lin‡

† Bereich Kern- und Strahlenphysik, Hahn-Meitner-Institut für Kernforschung Berlin GmbH, D-1000 Berlin 39, West Germany.

‡ Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA.

Received 5 November 1981, in final form 21 December 1981

Abstract. A modified two-centre atomic orbital expansion is proposed for close-coupling calculations of inelastic electronic processes in ion–atom collisions at intermediate energy, and electron transfer cross sections are calculated for $H^+ + H$ and $He^+ + H^+$ collisions. For close collisions, the inclusion of united-atom orbitals in the expansion is shown to be essential for reproducing experimental data as well as earlier calculations based on multi-state molecular orbital or other pseudostate expansions. The convergence of two-state atomic orbital expansion calculations for KK charge transfer is assessed for various asymmetries of the collision system. It is argued that the present expansion is convenient and fast converging over a broad range of collision energies, particularly for close collisions. In another application, K-shell excitation in $Ne^+ + O$ collisions is modelled. At low collision velocities, no deviations from the predictions of $2p\pi$–$2p\sigma$ molecular orbital studies are found even with extended basis sets.

1. Introduction

Inelastic electronic processes in ion–atom collisions are of wide fundamental and practical interest for a multitude of collision systems under various kinematic conditions. For near-symmetric collision systems or not-too-fast collisions, the semiclassical close-coupling method is well established as the standard method for describing electron excitation or transfer. Ever since the pioneering work of Ferguson (1961) and McCarroll (1961), molecular orbital (MO) or atomic orbital (AO) expansions have been employed when the collision velocity v was regarded as, respectively, small against or comparable with the mean electron velocity v_e in the initial or final atomic orbitals. Furthermore, in a single-electron description of multi-electron systems, relaxed or frozen two-centre Hamiltonians have been chosen in studies based on, respectively, MO or AO expansions (Briggs 1976, Fritsch *et al* 1981a, and references in these works). No standard treatment of the time evolution of the colliding system has emerged yet in the intermediate velocity region, i.e. when the collision is too fast for a predominantly quasi-molecular development of the system, but too slow for approximating the transient quasi-stationary states of the collision system by undistorted atomic orbitals. Often, the molecular or atomic model has been extended beyond their respective range of applicability ($v/v_e \ll 1$ or $v/v_e \simeq 1$) without *a priori* justification. Specific atomic expansion schemes have been devised for the symmetric $H^+ + H$ collision system in the intermediate energy region, usually through modelling the molecular binding effect by adding suitable pseudostates at the two collision centres

0022-3700/82/081255+14$02.00 © 1982 The Institute of Physics

(Gallaher and Wilets 1968, Cheshire *et al* 1970) or at a third centre (Anderson *et al* 1974, Antal *et al* 1975). Recently, a perturbation approach for the intermediate energy region has been presented (Ryufuku and Watanabe 1978, 1979). This method, however, has been questioned (Bransden *et al* 1980, Eichler 1981) since seemingly important perturbation terms have been left out.

In this paper we present and test a two-centre pseudostate atomic orbital expansion specifically designed for the intermediate velocity region. It has been noted early for the $H^+ + H$ system (Wilets and Gallaher 1966) that the failure of AO expansions at low velocities is due to the poor representation of united-atom (UA) orbitals even by the full *bound* spectrum of the separated atoms (SA). On the other hand, a large-scale MO expansion calculation for the intermediate energy region is not only inconvenient but also physically inappropriate. Therefore, we introduce a *two-centre* AO expansion with orbitals of both separated atoms and the united atom such that frozen (AO) as well as relaxed (MO) electronic orbitals are properly represented at small and large internuclear separations. Within the Hilbert space spanned by this expansion, the system is then free to develop along atomic orbitals at higher velocities or along tighter bound orbitals at lower velocities. In fact, we will show for an example that the static correlation diagram of the collision system is well reproduced with an expansion of this kind and that results of dynamical calculations are close to those from MO expansions even in the low-velocity MO region.

The expansion model put forward in this paper rests on similar ideas as the three-centre atomic expansion model first described by Anderson *et al* (1974) in which UA orbitals are positioned at the centre of charge of the colliding nuclei. At first sight, UA orbitals travelling with the collision centres seem to be at variance with basic MO model ideas and with the observation of MO x-rays being emitted from the centre-of-mass system (Meyerhof *et al* 1975). For slow collisions, however, details of translational effects might be of minor importance for representing the evolution of the electronic charge distribution if only long-range couplings are avoided. At higher velocities, in turn, where molecular binding effects subside UA orbitals moving with the collision centres might provide an even better representation of couplings to SA continua than can be provided in the three-centre expansion†. Positioning the basis orbitals at only two centres results, of course, in a major simplification of the computational effort since only two-centre integrals have to be calculated and, after a few modifications, conventional AO expansion codes can be used.

For the same reason of convenience, simple plane-wave translation factors (Bates and McCarroll 1958) are attached to all orbitals as is the standard procedure in investigations employing AO expansion schemes at higher energies. Different kinds of translation factors have been used in low-energy MO studies (see, e.g. Vaaben and Taulbjerg (1981), Crothers and Hughes (1979), Kimura and Thorson (1981) and references therein). The comparison of low-energy cross sections presented here with those based on MO expansions indicates that, in the present model, the electron translational effect is sufficiently represented, at least in all cases considered but one, where various MO studies lead to conflicting results among themselves (cf § 3.2).

The pseudostate atomic expansion method proposed here will be applied at first to charge transfer in the benchmark system $H^+ + H$. For this collision system, the present expansion is different from that of Cheshire *et al* (1970) mainly in that here

† The UA orbitals provide some representation of the SA continua in so far as (1) the energy expectation values of the SA Hamiltonians between UA orbitals are usually positive, and (2) the projection of UA orbitals to the space of SA continua is of considerable norm.

the pseudostates of the expansion are the actual UA (He^+) orbitals instead of some approximations to He^+ orbitals in the work of Cheshire *et al* (1970). Then we progress to discuss electron transfer in the collision system $H^+ + He^+$ which lately has evolved into a testing ground for different models since calculated cross sections are rather model sensitive and experiments are available (Winter 1981 and references therein). Finally we will demonstrate that the present expansion is capable of describing K excitation (or 2p–1s vacancy transfer) in near-symmetric multi-electron collision systems, i.e. the process understood within the MO picture by considering the $2p\pi$–$2p\sigma$ coupling mechanism.

Some details of the model and of the calculations are given in § 2. Results of calculations extending from the AO expansion velocity region down into the MO region are given in § 3 and compared with other calculations and with experiments. Convergence properties of the expansions are studied here, too. Section 4 contains a few concluding remarks.

2. Framework of the calculations

The calculation of electron transfer probabilities and cross sections within the semiclassical close-coupling method starts from defining the two-centre pseudostate atomic orbital basis, henceforth denoted as AO+ basis†. Physical arguments have to be invoked for choosing a set of SA and UA orbitals as small as possible but such that it still leads to near-converged results. For low collision velocities, the set of initial and final SA orbitals has to be complemented by those UA orbitals suggested by the system's molecular correlation diagram. For higher velocities, additional SA orbitals will be needed to act as intermediate steps in the inelastic process and, moreover, UA orbitals will be needed not only for representing remaining binding effects but also for representing SA continua. Clearly, it is within the aim of the present paper to provide some experience in defining appropriate AO+ basis sets.

The various basis sets used in this work are listed in table 1(*a*) for the $H^+ + H$ and $H^+ + He^+$ charge transfer calculations and in table 1(*b*) for the calculations of K

Table 1. Basis sets used in (*a*) charge transfer calculations and in (*b*) calculations of K excitation in $Ne^+ + O$ collisions. Listed are the orbitals at a given collision centre.

	Set	SA orbitals	UA orbitals
(*a*)	16 AO+	1s 2s 2p	1s 2s 2p
	10 AO+	1s	1s 2s 2p
	8 AO+	1s	1s 2p
	6 AO+	1s	1s 2s
	4 AO+	1s	1s
	8 AO	1s 2s 2p	—
	2 AO	1s	—
	22 AO+	1s 2s 2p	1s 2s 2p 3d
(*b*)	10 AO+	1s 2p	2p
	6 AO+	1s	2p

† The present model has been proposed and preliminary results have been reported in an earlier communication (Fritsch *et al* 1981b).

vacancy production in $Ne^+ + O$ collisions. In the charge transfer study, the largest basis set for most of the calculations (16 AO+) was taken to consist of the SA and UA 1s, 2s and 2p orbitals around each centre, thus overlapping with the full basis set (8 AO) of a recent conventional AO calculation (Bransden and Noble 1981, see also Winter 1981) and including in addition those UA orbitals to which the lowest MO correlate for one-electron systems Z_1, Z_2, $1/2 \leqslant Z_1/Z_2 \leqslant 2$. Smaller basis sets were taken in order to test the convergence of the results and the relative importance of various basis orbitals, in particular the importance of including UA orbitals in contrast to including higher SA orbitals in a conventional AO expansion. In another convergence test for the calculation of 2s electron transfer in $H^+ + H$ collisions, the 16 AO+ set was complemented by 3d UA orbitals (22 AO+ basis) which are needed for an improved representation of the low-lying $3d\sigma_g$ MO.

As an illustration of how well the various basis sets of table 1(*a*) are able to represent the static quasi-molecule, figure 1 shows part of the molecular correlation diagram for the system $H^+ + He^+$, calculated by diagonalising the two-centre Hamiltonian in the space spanned by those sets and with molecular eigenfunctions of the Hamiltonian. By their very construction, both AO+ and conventional AO expansions reproduce the lowest MO of the correlation diagram in the limit of internuclear separations $R \to \infty$, but only the AO+ expansions do so for $R \to 0$. Figure 1 shows that the inclusion of SA 2s and 2p orbitals in the 8 AO expansion causes only little improvement of the $1s\sigma$ energy over that calculated from the simple 2 AO expansion while the $2p\sigma$ energy is notably lowered. Inclusion of the tighter bound UA 1s orbital in the 4 AO+ expansion results already in an excellent reproduction of the $1s\sigma$ curve while adding another UA 2s and 2p orbitals (10 AO+) leads to a very good representation of the $2p\sigma$ MO and to a fair representation of the $2s\sigma$ MO at least for smaller internuclear separations. Finally, including both SA and UA 1s, 2s and 2p orbitals (16

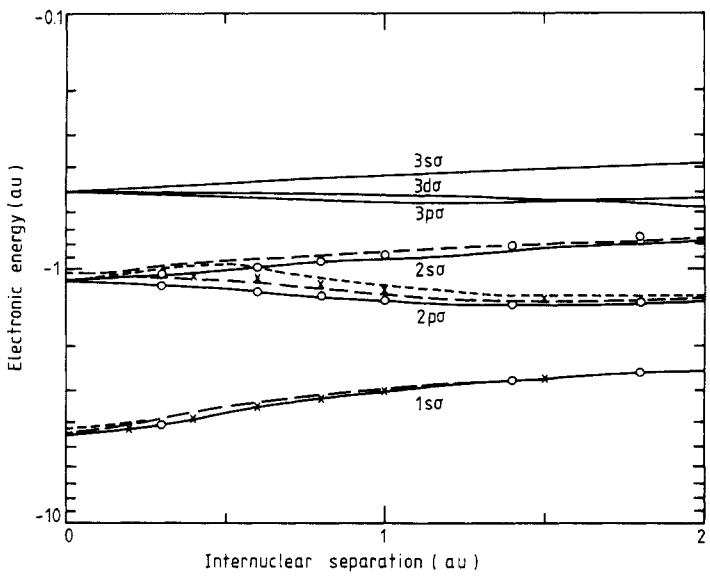

Figure 1. Lowest σ states of the correlation diagram for the $(H+He)^{2+}$ system. ——, exact MO curves. Approximations: — —, 8 AO; – – –, 2 AO; ×, 4 AO+; ○, 10 AO+ expansion.

AO+) leads to molecular 1sσ, 2pσ and 2sσ energies deviating from the exact values by less than 1%. Of course, all these deviations are only representative for similar deviations between non-diagonal coupling matrix elements. There is, therefore, no need to consider possible error compensating effects through the taking of energy differences in the coupled equations. After all, only actual dynamical close-coupling calculations can show quantitatively how well the static quasi-molecule needs to be represented for deriving sufficiently reliable cross sections at a given collision energy.

For the calculation of K vacancy production in $Ne^+ + O$ collisions, we have closely followed the one-electron MO description of Taulbjerg *et al* (1976). The Ne and O atomic orbitals are constructed from effective nuclear charges $Z = 9$ and $Z = 7$, respectively, and, correspondingly, the UA orbitals from a UA nuclear charge $Z = 16$. The largest basis set (10 AO+, see table 1(*b*)) contains the initial (vacancy) Ne 2p orbitals and final O 1s orbital as well as UA 2p orbitals as representatives of 2pσ and 2pπ MO at small internuclear separations. In addition, Ne 1s and O 2p orbitals are needed to represent the lowest MO of this near-symmetric collision system at small and intermediate internuclear separations properly. In a second basis set of 6 AO+, the SA 2p orbitals were left out and the initial vacancy was put into the UA $2p_x$ orbital instead in order to simulate a feature of the customary MO description in which the initial vacancy is forced into the 2pπ orbital and its development studied only within moderate internuclear separations†.

Having defined a basis set, the subset of orbitals around each centre is orthogonalised by diagonalising the respective SA Hamiltonian within the subset, thus ensuring a convenient formulation of the initial condition and the ready extraction of transition probabilities. Then the evaluation of potential coupling matrix elements with plane-wave translation factors is straightforward (McCarroll 1961). The atomic centres are assumed to move on straight-line trajectories. The coupled-state equations are solved numerically by variable-step-size Runge–Kutta integration. Probabilities are calculated for transitions into individual SA orbitals around both centres as well as into 'all' bound states by projecting out the bound-state components (up to principal quantum number $n = 6$) of the pseudostates.

3. Results and discussion

3.1. Charge transfer calculations

Electron transfer cross sections from 16 AO+ close-coupling calculations are displayed and compared with other calculations and with experiments in figure 2. Shown are cross sections for KK transfer and for transfer into all bound states for collision systems $H^+ + H$, $H^+ + He^+$ and for a collision system with intermediate charge ratio, $H^+ + Z_2^{(Z_2-1)+}$ with $Z_2 = 1.5$, in the H^+ impact energy range $E(H) = 1.5$–150 keV. The data is shown over the inverse collision velocity such as to particularly expand the intermediate- and low-energy region, and such that a first-order, classically forbidden process is reflected in a straight line at low velocities (Child 1978). An approximate

$$\exp(-\text{constant}/v)$$

behaviour at low energies is actually seen in figure 2 for the asymmetric collision systems while the resonant KK transfer in $H^+ + H$ collisions shows its well known ever increasing

† The scattering plane is taken to be the x–z plane with the initial velocity along the (space fixed) z direction.

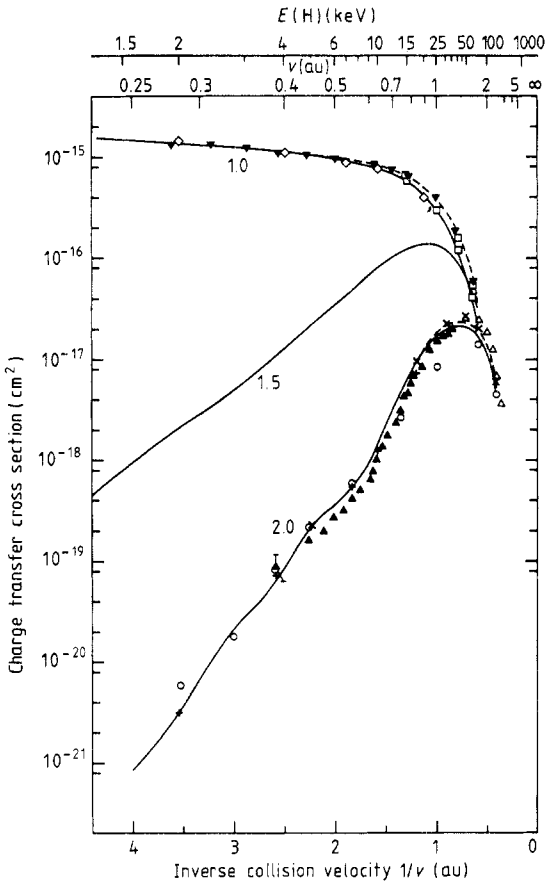

Figure 2. Cross sections for KK charge transfer (K) and for charge transfer into all bound states (Σ) in $H^+ + Z_2^{(Z_2-1)+}$ collisions, $Z_2 = 1$, 1.5, 2, over the inverse collision velocity. Theory: ——, 16 AO+ (K), this work; – – –, 16 AO+ (Σ), this work; +, 10 MO (K) (Winter *et al* 1980); ×, 24 Sturmian (Σ) (Winter 1981); ○, 8 AO (Σ) (Bransden and Noble 1981); ◇, 14 pseudostates (K) (Cheshire *et al* 1970); □, 70 pseudostates (K) (Shakeshaft 1978). Experiments (all Σ): ▼, McClure (1966); ▲, Peart *et al* (1977); △, Angel *et al* (1978).

trend for decreasing collision velocities. The oscillatory structure in the low-energy cross sections of figure 2, slightly visible for the $Z_2/Z_1 = 1.5$ collision system but quite prominent for $H^+ + He^+$, is probably a multichannel effect. For $H^+ + He^+$ collisions, the $He^+(n = 2)$ excitation cross section is of the same order of magnitude as that for KK charge transfer even for the lowest energies shown in figure 2 and the corresponding channels are likely to interfere at small internuclear separations. We note that for a given charge ratio Z_2/Z_1 the calculated transition probabilities and cross sections scale with the parameter Z_1 in the same way as derived for MO calculations by Taulbjerg *et al* (1975), see equations (17) and (18) of their work. The collision system with $Z_2/Z_1 = 1.5$, therefore, is representative for a $He^{2+} + Li^{2+}$ collision system or for others as far as they are approximated by two effective nuclear charges Z_A, Z_B, $Z_A/Z_B = 1.5$, with the same initial conditions.

For the symmetric collision system $H^+ + H$, the calculated transfer cross sections are seen to agree well with experiment (McClure 1966) and with other calculations

based on pseudostate expansions (Cheshire *et al* 1970, Shakeshaft 1978). This agreement, of course, is due to the fact that the dominant resonant KK transfer process in $H^+ + H$ collisions occurs over a broad range of impact parameters. For decreasing velocities, increasingly distant collision encounters contribute to the total transfer cross section such that the initial and final atomic 1s orbitals already give a fair representation of the time-dependent electronic wavefunction in 1s–1s transitions. The theoretical models are subjected to a much more sensitive test when applied to excitation or transfer processes into $n = 2$ states (Morgan *et al* 1973). In figure 3,

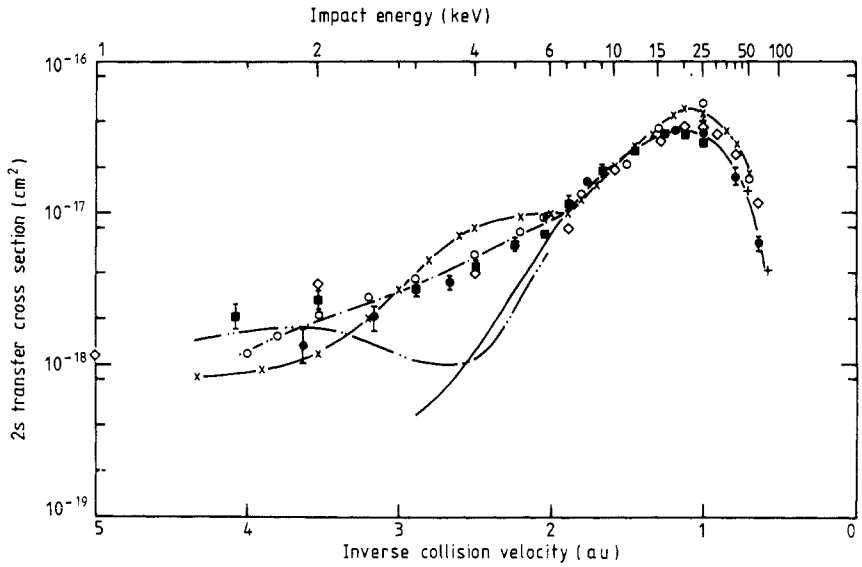

Figure 3. Cross sections for transfer into 2s orbitals in $H^+ + H$ collisions over the inverse collision velocity. Theory: —×—, 16 AO+, this work; ○, 22 AO+, this work; ◇, 14 pseudostates (Cheshire *et al* 1970); +, 70 pseudostates (Shakeshaft 1978); —·—, MO (Kimura and Thorson 1981); —··—, MO (Crothers and Hughes 1979). Experiment: ——, curve drawn through data points of Bayfield (1969); ■, Hill *et al* (1979); ●, Morgan *et al* (1980).

various calculated and measured 2s transfer cross sections in $H^+ + H$ collisions are depicted over the inverse collision velocity. On the low-velocity side, the experimental data of Hill *et al* (1979) and of Morgan *et al* (1980) are seen to be in fair agreement with a recent MO calculation by Kimura and Thorson (1981), while the earlier measurement of Bayfield (1969) and the MO investigation of Crothers and Hughes (1979) result in smaller or structured cross sections†. The 2s transfer cross sections from the 16 AO+ expansion oscillate around the curve calculated by Kimura and Thorson (1981) and, similarly, the points due to Cheshire *et al* (1970) are scattered around that curve. The cross sections calculated by Kimura and Thorson are, however, closely reproduced in the 22 AO+ calculation which allows for an improved representation of the $3d\sigma_g$ MO, cf table 1(*a*). Convergence tests with even larger basis sets (involving UA 3s, 3p, 4f orbitals) have proven this close agreement to be significant rather than accidental, and another publication will be devoted to this and other

† The quoted MO calculations employ different sophisticated forms of molecular translation factors. For a detailed comparison of the two calculations, see the discussion in Kimura and Thorson (1981).

transition processes into $n = 2$ states. The mutual agreement (within 30%) between the more recent experimental data, the MO results of Kimura and Thorson and those calculated with the 22 AO+ expansion is remarkable in view of the circumstance that 2s transfer is actually a small process in comparison with 1s and 2p transfer at low collision energies (Morgan *et al* 1973), and that different basis sets and different translation factors are used in the two calculations. On the other hand, the large discrepancy between all of these data and the MO cross sections calculated by Crothers and Hughes (1979) is not understood at this point. For a test, Kimura and Thorson (1981) have solved the coupled equations (to first order in velocity only) with the published matrix elements of Crothers and Hughes but did not succeed in reproducing the 2s transfer curve of Crothers and Hughes even qualitatively, although they did so for the inelastic 2p process. For the 2s transfer process, they rather obtained cross sections lying 30–40% above their own curve, i.e. roughly qualitative agreement with their own calculated cross sections. Further work is needed to understand fully the large deviation between the cross sections reported by Crothers and Hughes and those from the other calculations.

On the higher velocity side, $v \geqslant 0.8$ au in figure 3, the measured 2s transfer cross sections are all close to each other and well reproduced by Shakeshaft's (1978) calculation using 70 pseudostates. The calculation of Cheshire *et al* (1970) overestimates the experimental cross sections and even more so do the 16 AO+ or 22 AO+ expansion calculations. It seems rather likely that an inclusion of SA $n = 3$ orbitals and some better representation of the SA continua would improve the convergence of the AO+ results but this is outside the scope of the present paper.

For $H^+ + He^+$ collisions, the calculated total transfer cross sections are rather sensitive to details of theoretical models, cf figure 2. The cross sections derived from the 16 AO+ expansion are in excellent agreement with the 10 MO result of Winter *et al* (1980) from the lowest velocities up to $v \simeq 0.55$ au. For higher velocities, they rather follow the results of the 24-state Sturmian expansion (Winter 1981) with a maximum deviation of 10% at about the peak energy. It seems to be significant that both the present results and those of the Sturmian expansion reproduce the shape of the experimental data of Peart *et al* (1977) rather closely while they overestimate its absolute values by about 40% which is much more than the quoted experimental absolute uncertainty of 7%. On the other hand, the data of Angel *et al* (1978) at higher energies are up to 30% larger than the calculated ones. While these discrepancies cannot be explained fully convincingly at this point, the similar structure of calculated and measured cross sections for the low energies suggests a larger experimental error than assumed by Peart *et al* (1977).

Figure 2 also includes the $H^+ + He^+$ transfer cross sections calculated with an 8 AO expansion (Bransden and Noble 1981)†. It appears that they deviate from the 16 AO+ or Sturmian results appreciably near the peaking velocity where a conventional atomic expansion calculation is better justified than in other velocity regions. For lower energies, the agreement with the calculations based on 16 AO+, MO or Sturmian expansions is generally fairly good. This fair agreement is, however, partly accidental as illustrated by the impact-parameter-weighted KK transition probabilities $bP_{KK}(b)$ in figure 4. For $v = 0.283$ au, figure 4(*a*), the curves from the 16 AO+, 10 MO and 8 AO calculations all show three oscillations over impact parameter, but the 8 AO

† Our code has been employed to calculate the transfer cross sections labelled 8 AO below $v = 0.38$ au and all 8 AO impact-parameter-dependent transition probabilities shown in this work.

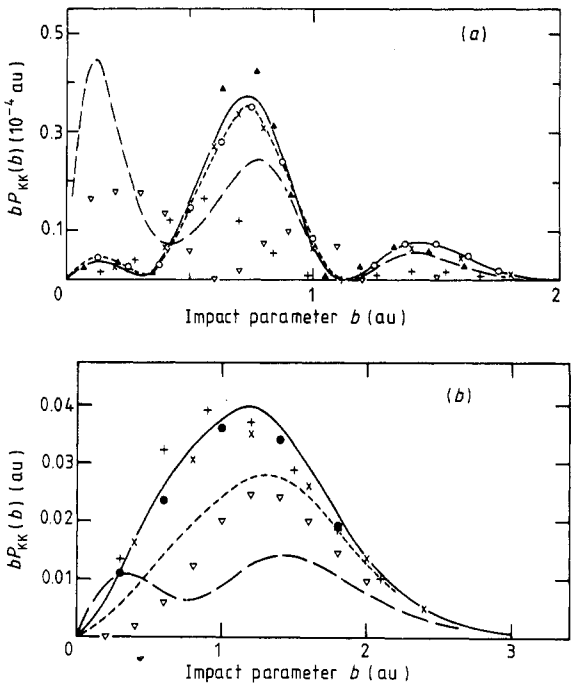

Figure 4. Impact-parameter-weighted KK transition probabilities over impact parameter for $H^+ + He^+$ collisions at (*a*) $v = 0.283$ au and (*b*) $v = 0.837$ au collision velocity. Shown are results from close-coupling calculations with different basis sets: ——, 16 AO+; – – –, 10 MO (Winter *et al* 1980); — —, 8 AO; ×, 10 AO+; +, 8 AO+; ▲, 6 AO+; ▽, 4 AO+; ●, 24 Sturmian expansion (Winter 1981).

curve vastly overestimates the transition at small impact parameters and underestimates to a lesser extent the transitions in the medium and large impact parameter region, leading to an integrated KK cross section close to that from the 16 AO+ or 10 MO expansion ($\sigma_{KK} = 3.4, 3.3, 3.2 \times 10^{-19}$ cm^2 in, respectively, the 8 AO, 16 AO+, 10 MO calculations). Finally, an unrealistic high L capture cross section contribution from small impact parameter collisions results in the comparatively high 8 AO capture cross section into all bound states, see figure 2. At the higher velocity $v = 0.837$ au, figure 4(*b*), the weighted transition probability from the 8 AO expansion shows a spurious structure not seen in any AO+, MO or Sturmian calculation, and too little strength even at large impact parameters. At this velocity, the addition of only UA 1s orbitals to the initial and final 1s orbitals in the 4 AO+ calculation gives results closer to those of the 16 AO+ expansion than does the 8 AO calculation and, as likewise for the lower velocity, the inclusion of UA 1s, 2s and 2p orbitals in the 10 AO+ calculation is by far superior to alternatively including the corresponding SA orbitals in the 8 AO calculation. Among those UA orbitals, inclusion of 2s orbitals appears to be far more important than that of 2p orbitals at the lower velocity, cf the 6 AO+ and 8 AO+ results in figure 4(*a*), thus reversing the usual observation in MO studies for near-symmetric systems that the 2sσ orbital is less important than 2pσ and 2pπ orbitals.

Furthermore, figure 4(*a*) illustrates that for lower velocities the 16 AO+ and the 10 MO expansions give almost identical results not only for total cross sections, cf

figure 2, but also for KK transition probabilities. The calculated cross sections or transition probabilities can, therefore, be regarded as converged to within a few per cent, the 16 AO+ expansion as capable of describing the time evolution of the $H^+ + He^+$ electronic system even in the velocity region associated with MO expansions. For higher velocities, figure 4(*b*) demonstrates a similar agreement between transition probabilities from 16 AO+ and 24 Sturmian expansions while the 10 MO expansion gives smaller results. This again suggests a high degree of convergence of both the 16 AO+ and the 24 Sturmian expansion and confirms the conjecture of Winter (1981) that the 10 MO expansion (Winter *et al* 1980) may lack continuum MO contributions for convergence at higher velocities.

Further information about the convergence of the present expansion for $H^+ + He^+$ collisions is given in figure 5. It shows total KK transfer cross sections from n AO+ expansions, $n = 4, 6, 8, 10$, normalised to the 16 AO+ results, over the inverse collision velocity. As already discussed earlier for the transition probabilities at two velocities, the inclusion of SA 2s, 2p orbitals in the 16 AO+ expansion is seen to be of little relevance for the KK transfer cross sections below $v \simeq 1$ au (cf 16 AO+ and 10 AO+ points) while the presence of UA 1s, 2s and 2p orbitals is rather essential (cf 16 AO+ and 8 AO points), among the latter particularly the UA 2s orbital. For higher velocities $v > 1$ au, the 16 AO+ and 10 AO+ results start to deviate from each other. Since there discrepancies with the Sturmian results show up, cf figure 2, the convergence of the calculated cross sections is not secured as firmly as for $v \leqslant 1$ au. For better convergence, additional pseudostates for representing the SA continua may be needed here.

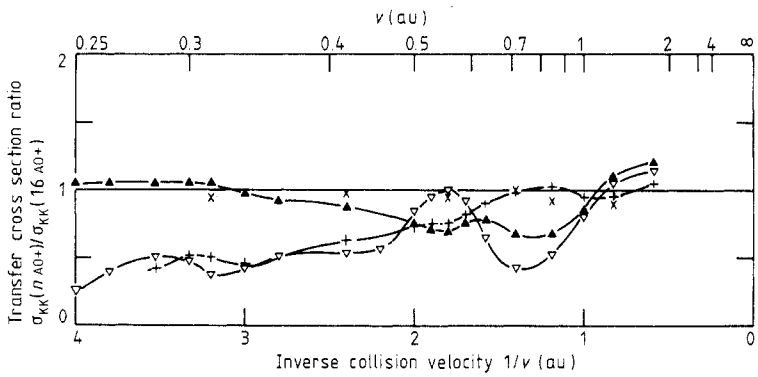

Figure 5. KK transfer cross sections in $H^+ + He^+$ collisions from n AO+ expansion calculations, $n = 4, 6, 8, 10$, over the inverse collision velocity. Results are normalised to the cross sections from 16 AO+ calculations. ×, 10 AO+; +, 8 AO+; ▲, 6 AO+; ▽, 4 AO+ expansion.

Figure 6 depicts KK charge transfer cross sections from 2 AO expansions, normalised to the corresponding 16 AO+ cross sections, for collision systems $H^+ + H$, $H^+ + He^+$ and $H^+ + Z_2^{(Z_2-1)+}$, $Z_2 = 1.5$. This graph is intended to draw attention to the effect of the symmetry of the system to the reliability of two-state AO calculations. It shows that for the symmetric $H^+ + H$ system the 2 AO expansion already gives quite reasonable integrated cross sections for low velocities up to moderately high velocities $v \leqslant 0.7$ au, due to the dominance of distant collision encounters, while the result of 2 AO calculations for $H^+ + He^+$ oscillate around the converged 16 AO+ results with

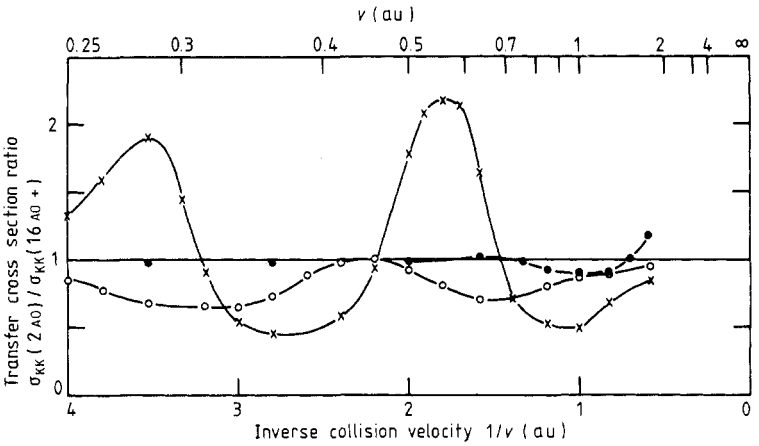

Figure 6. KK transfer cross sections in $H^+ + Z_2^{(Z_2-1)+}$ collisions from 2 AO expansion calculations over the inverse collision velocity. Results are normalised to the cross sections from 16 AO+ close-coupling calculations. Points marked ●, ○, × indicate results of calculations with, respectively, $Z_2 = 1, 1.5, 2$.

a relative ratio of up to a factor of two. Calculations with 2 AO expansions for the system with the intermediate charge ratio $Z_2/Z_1 = 1.5$ give results with an accuracy between that for the other two collision systems. From figure 6 we conjecture that 2 AO expansions for near-symmetric multi-electron systems should give fairly accurate results even well below the peaking velocity region, thus confirming earlier observations (see e.g. Lin and Tunnell 1980).

3.2. 2p–1s vacancy transfer calculations

In figure 7, calculated O 1s vacancy production probabilities in $Ne^+ + O$ collisions are displayed over the scaled impact parameter $v^{-1/3}b$ for Ne impact energy $E = 385$ keV ($v = 0.878$ au). Taulbjerg *et al* (1976) have shown in their $2p\pi$–$2p\sigma$ rotational coupling study that, within the 2 MO model, the transition probability over $v^{-1/3}b$ is a universal curve for all velocities provided (i) the energy separation and the coupling matrix are approximated by the first non-vanishing term in their respective expansions in powers of the internuclear separation, and (ii) the colliding partners move on straight-line trajectories. This universal curve is shown in figure 7 together with the results of the AO+ calculations. The probabilities from the 10 AO+ and from the 6 AO+ calculations agree very well with each other indicating an almost complete transition of the vacancy from the initial Ne $2p_x$ orbital into the UA $2p_x$ orbital before the transition into the UA $2p_z$ orbital takes place at small internuclear separations, i.e. almost complete relaxation of the electronic wavefunction along molecular orbitals†. The probabilities based on AO+ expansion calculations, in turn, are extremely close to the universal curve given by Taulbjerg *et al* (1976) particularly at small impact parameters for which assumption (i) is most valid. At larger impact parameters, the AO+ curves rather follow the MO curve calculated with the exact

† Calculations with the initial vacancy set into the Ne $2p_z$ orbital result in much smaller transition probabilities than those shown in figure 7.

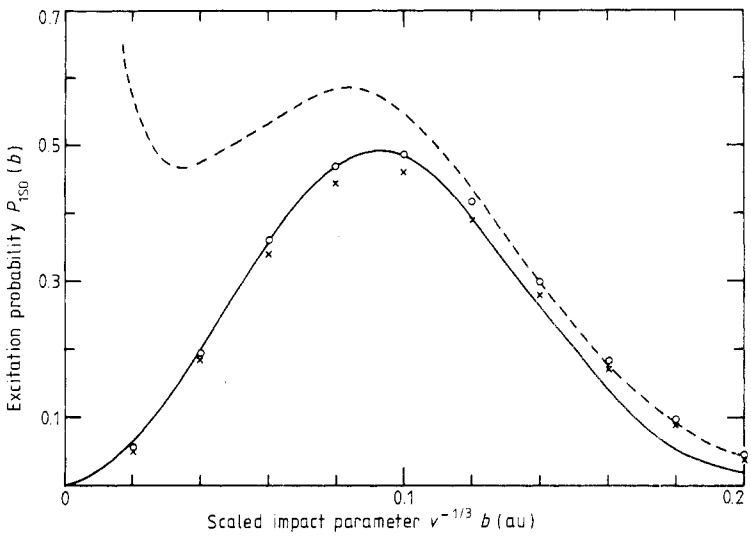

Figure 7. K excitation probability over scaled impact parameter for $Ne^+ + O$ collisions. Solutions of close-coupling equations with straight-line trajectories: ——, schematic $2p\pi$–$2p\sigma$ model, universal curve (Taulbjerg *et al* 1976); ○, 10 AO+; ×, 6 AO+ expansion. Solution with curved trajectories: – – –, exact $2p\pi$–$2p\sigma$ model (Taulbjerg *et al* 1976). All probabilities but those of the universal curve are calculated for Ne impact energy $E = 385$ keV.

form of MO energies and matrix elements and with a curved-line trajectory (Taulbjerg *et al* 1976). For these larger impact parameters, of course, the curvature of the trajectory does not have much effect.

Further vacancy transition probabilities have been calculated for various collision velocities $0.5 \leq v \leq 5$ au. In the velocity range $v \leq 1$ au, the calculated probabilities over the scaled impact parameter essentially coincide with the points shown in figure 7 for $v = 0.878$ au. At higher velocities, they start to drop in absolute magnitude below the low-velocity quasi-universal AO+ curve (up to a suppression by a factor 1/5 for $v = 5$ au) while still approximately retaining their shape for a given velocity. At the same time, transitions into (partially initially vacant) O 2p orbitals and into the (initially vacant) pseudostates increase to an extent that no quantitative statement about an actual physical system can be derived at this point for higher velocities. Clearly, a more sophisticated treatment is needed, involving a departure from the single-electron description and more realistic 2p atomic wavefunctions. We note that a similar need would arise in a multi-state MO model.

An attempt has been made to shed light on the question how couplings to higher orbitals may influence the results of the calculations. In experiments, the valley between the 'adiabatic' and the 'kinematic' peak in the 1s excitation curve is observed to be much weaker than in the calculations† or even filled in (Luz *et al* 1979 and references therein). In the calculations reported here, a straight-line internuclear trajectory is assumed and, therefore, the kinematic peak does not occur. If, however,

† By including couplings to the $3p\sigma$ orbital, Vaaben and Taulbjerg (1978) calculated a 1s excitation curve in perfect agreement with experiment. This agreement was lost, however, in a full four-state ($2p\sigma$–$2p\pi$–$3p\sigma$–$3p\pi$) calculation.

couplings to higher orbitals have some effect in curved-line trajectory calculations it is well conceivable that they should show up as a pronounced shoulder in the straight-line trajectory description. In a test study at $E = 385$ keV, we have complemented the 10 AO+ basis by the six 3s, 3p, 3d UA orbitals centred around the Ne nucleus. Starting with an electron in the O 1s orbital, the calculated probabilities for transitions into Ne 2p orbitals are little changed from those of the time-reversed 10 AO+ description, and the population of other orbitals is observed to be negligible. This result is unlikely to depend on details like the exact orbital binding energies. We conclude that, in a single-electron MO description, couplings to orbitals correlating to UA $n = 3$ orbitals should not be important at least for small impact parameters and in straight-line trajectory studies. No conclusion, however, can be drawn about effects in multi-electron studies. When the presence of more than one electron and vacancy in the system is handled properly, contributions could be important e.g. from those initial configurations in which the dominant Ne $2p_x$–O 1s transition is blocked by an initial electron in the Ne $2p_x$ orbital.

4. Conclusions

The modified atomic orbital expansion AO+ introduced in this paper has been shown to be a practical and effective alternative to MO or other pseudostate expansions in ion–atom collisions. Since the AO+ basis contains both SA and UA atomic orbitals it is capable of describing the time development of the electronic wavefunction for both distant and close collisions. An attractive feature of the present expansion compared with other pseudostate expansion sets is that it contains the relevant physical orbitals directly. As a trade-off, the calculation of matrix elements can be more costly in terms of computer time than with some other pseudostate expansions, e.g. an expansion in Sturmian functions. The present expansion is conveniently enlarged for more complex situations. When raising or lowering the collision velocity, the selection of additional orbitals in the basis set is guided by physical considerations. In describing multi-electron systems, complications like the avoided crossings in MO studies do not occur.

As applications, charge transfer cross sections for $H^+ + H$ and for $H^+ + He^+$ collisions and K excitation in $Ne^+ + O$ collisions have been studied. Suitable AO+ basis sets are found to be equivalent to MO expansions down to small adiabaticity ratios, for the particularly model sensitive collision system $H^+ + He^+$ down to $v/v_e(H) = 0.28$ ($v/v_e(He) = 0.14$) for a ten-state AO+ expansion. For adiabaticity ratios $v/v_e \geqslant 0.63$, this expansion is found to be superior to a ten-state MO expansion. The inclusion of UA orbitals is demonstrated to be distinctly more important than that of the corresponding SA orbitals in an ordinary AO expansion at all velocities.

Much work remains to be done. For the calculation of realistic low-energy differential cross sections directly comparable with experiment, curved trajectories should be implemented. For a detailed treatment of collisions between multi-electron atoms, complex Hamiltonians have to be taken into account as has been done previously in two-state atomic expansion studies. Furthermore, multi-electron transitions have to be allowed for, too. However, even in the absence of fully converged, time consuming AO+ calculations for complex collision systems, AO+ case studies for simplified representative one-electron systems may already rule out or point to the importance of selected effects in more involved investigations.

Acknowledgments

We gratefully acknowledge discussions with T G Winter about aspects of his and of our works. WF appreciates the warm hospitality extended to him during his leave at the Physics Department of Kansas State University where the present work was taken up. This work is supported in part by the US Department of Energy, Division of Chemical Sciences. CDL is also supported in part by the Alfred P Sloan Foundation.

References

Anderson D G M, Antal M J and McElroy M B 1974 *J. Phys. B: At. Mol. Phys.* **7** L118–21
Angel G C, Sewell E C, Dunn K F and Gilbody H B 1978 *J. Phys. B: At. Mol. Phys.* **11** L297–300
Antal M J, Anderson D G M and McElroy M B 1975 *J. Phys. B: At. Mol. Phys.* **8** 1513–21
Bates D R and McCarroll R 1958 *Proc. R. Soc.* A **245** 175–83
Bayfield J E 1969 *Phys. Rev.* **185** 105–12
Bransden B H, Newby C W and Noble C J 1980 *J. Phys. B: At. Mol. Phys.* **13** 4245–55
Bransden B H and Noble C J 1981 *J. Phys. B: At. Mol. Phys.* **14** 1849–56
Briggs J S 1976 *Rep. Prog. Phys.* **39** 217–89
Cheshire I M, Gallaher D F and Taylor A J 1970 *J. Phys. B: At. Mol. Phys.* **3** 813–32
Child M S 1978 *Advances in Atomic and Molecular Physics* vol 14 (New York: Academic) pp 225–80
Crothers D S F and Hughes J G 1979 *Phil. Trans. R. Soc.* A **292** 539–61
Eichler J K M 1981 *Phys. Rev.* A **23** 498–509
Ferguson A 1961 *Proc. R. Soc.* A **264** 540–6
Fritsch W, Lin C D and Tunnell L N 1981a *J. Phys. B: At. Mol. Phys.* **14** 2681–9
—— 1981b *IEEE Trans. Nucl. Sci.* **NS-28** 1146–8
Gallaher D F and Wilets L 1968 *Phys. Rev.* **169** 139–49
Hill J, Geddes J and Gilbody H B 1979 *J. Phys. B: At. Mol. Phys.* **12** L341–4
Kimura M and Thorson W R 1981 *Phys. Rev.* A **24** 1780–92
Lin C D and Tunnell L N 1980 *Phys. Rev.* A **22** 76–85
Luz N, Sackmann S and Lutz H O 1979 *J. Phys. B: At. Mol. Phys.* **12** 1973–93
McCarroll R 1961 *Proc. R. Soc.* A **264** 547–57
McClure G W 1966 *Phys. Rev.* **148** 47–54
Meyerhof W E, Saylor T K and Anholt R 1975 *Phys. Rev.* A **12** 2641–3
Morgan T J, Geddes J and Gilbody H B 1973 *J. Phys. B: At. Mol. Phys.* **6** 2118–38
Morgan T J, Stone J and Mayo R 1980 *Phys. Rev.* A **22** 1460–6
Peart B, Grey R and Dolder K T 1977 *J. Phys. B: At. Mol. Phys.* **10** 2675–82
Ryufuku H and Watanabe T 1978 *Phys. Rev.* A **18** 2005–15
—— 1979 *Phys. Rev.* A **20** 1828–37
Shakeshaft R 1978 *Phys. Rev.* A **18** 1930–4
Taulbjerg K, Briggs J S and Vaaben J 1976 *J. Phys. B: At. Mol. Phys.* **9** 1351–71
Taulbjerg K, Vaaben J and Fastrup B 1975 *Phys. Rev.* A **12** 2325–32
Vaaben J and Taulbjerg K 1978 *Nordic Spring Symposium on Atomic Inner-Shell Phenomena, Geilo, Norway* vol 1, ed J M Hansteen and R Gundersen pp 23–33
—— 1981 *J. Phys. B: At. Mol. Phys.* **14** 1815–26
Wilets L and Gallaher D F 1966 *Phys. Rev.* **147** 13–20
Winter T G 1981 to be published
Winter T G, Hatton G J and Lane N F 1980 *Phys. Rev.* A **22** 930–6