

## Atomic-orbital expansion study for the (quasi-)two-electron collision systems $O^{6+} + He$ and $C^{6+} + He$

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**Abstract.** The atomic-orbital expansion method within the close-coupling scheme is extended to two-electron collision systems. Coupling matrix elements are evaluated with full account of electron exchange and translation. Results are presented for one-electron capture in the (quasi-)two-electron systems  $O^{6+} + He$  and  $C^{6+} + He$  in the energy range 0.5–40 keV amu<sup>-1</sup> where a one-electron potential model description fails. Calculated total transfer cross sections agree very well with experiment. A comparison of subshell cross sections indicates about the same degree of convergence of the calculations as has been reached in analogous calculations for (quasi-)one-electron systems of comparable complexity.

### 1. Introduction

The description of electron transfer in (quasi-)one-electron ion-atom collision systems has improved much in accuracy, reliability and effectiveness in recent years. For collision energies that allow a classical treatment of the nuclear motion, the time-dependent Schrödinger equation for the electronic motion has been solved exactly within various preselected spaces of basis functions (close-coupling method), and the results compare favourably with experimental data over generally two orders of magnitude in collision energy. In fact, the theoretical determination of total transfer cross sections has been reduced to mere routine work with existing methods and codes while the calculation of small partial transfer cross sections still requires careful consideration of the transfer process and of competing physical channels<sup>†</sup>. One of the more impressive demonstrations of the convergence between theory and experiment in this field is the recent experimental confirmation (Ciric *et al* 1985) of predicted (Fritsch and Lin 1984a) partial transfer cross sections in  $C^{4+} + H$  and  $O^{6+} + H$  collisions, as well as the close agreement of measured total capture and line emission cross sections in  $C^{6+}$ ,  $N^{7+} + H$  and  $O^{8+} + H$  collisions (Dijkkamp *et al* 1985a, Meyer *et al* 1985, 1986) with results of close-coupling studies (Green *et al* 1982, Shipsey *et al* 1983, Fritsch and Lin 1984b). All these works also verify the long standing assertion that for *distant* collisions the concepts of both molecular-orbital (MO) and atomic-orbital

<sup>†</sup> The latest controversy about electron transfer in  $H^+ + Na$  collisions (cf the discussion by Fritsch (1984)) seems to be settled now with the realisation that calculations done for this system in the early 1980s are insufficient or numerically incorrect (Allan 1986, Flower 1985, Kimura 1985, Shingal *et al* 1985, 1986).

(AO) expansion schemes are equally appropriate for describing electron transfer over a wide range of collision energies (Lin 1978), leaving the choice of basis functions within the close-coupling method a matter of numerical convenience. Modifications of the AO expansion method have been introduced for its use in *close* or slow collisions (Fritsch and Lin 1982), and have been applied to a number of cases, see e.g. the report by Fritsch and Lin (1984c). Other less frequently used expansion schemes are also referred to there.

In this paper we discuss the extension of the AO expansion scheme within the close-coupling method to (quasi-)two-electron systems, and present calculated cross sections for one-electron transfer in  $O^{6+} + He$  and  $C^{6+} + He$  collisions in the energy range 0.5–40 keV amu<sup>-1</sup>. There have already been pioneering investigations of charge transfer within two-electron versions of the AO expansion scheme. As early as 1965, Green *et al* set up and solved an atomic two-state expansion model for the  $H^+ + He$  system. Some ten years later, Winter and Lin (1974) applied a many-state expansion to the same system, using the approximation that exchange coupling terms can be neglected. The formulation and numerical techniques which are presented here are distinguished from those used in earlier works in that they are quite general and allow for an easy, straightforward inclusion of channels with high quantum numbers  $n$  and  $l$  as they occur in highly ionised collision systems, essentially by upgrading existing one-electron AO expansion codes. Furthermore, our formulation avoids any approximation in the evaluation of coupling matrix elements as they have been justified in very recent work on  $He^+ + Li$  collisions at higher energies (Bransden *et al* 1984).

The collision systems  $O^{6+} + He$  and  $C^{6+} + He$  have been chosen as first applications of the formalism in this paper since they are at the same time complex and simple enough for our purpose: (i) the electron correlation in the He atom is important enough to make a one-electron potential approach inadequate, but also weak enough to allow for a representation of the ground-state wavefunction by a simple optimised product wavefunction; (ii) double-electron capture channels are not important; (iii) the dominant electronic process is one-electron capture into the  $n = 3$  projectile orbitals at large internuclear separations where the AO expansion model is known to be particularly well applicable. Finally, recent experimental data ( $O^{6+} + He$ ) and theoretical results ( $C^{6+} + He$ ) allow for a comparative discussion not only of the calculated total transfer cross sections but even of the more sensitive subshell cross sections.

Other models have been devised which also include explicitly the interelectronic interaction in the description of two-electron collision systems since the early 1980s. Harel and Salin (1980) have included this interaction between one-electron molecular orbitals but have neglected the effect of orbital translation. Kimura *et al* (1983) have included the translation effect, and we will make a comparison with the results of their MO formulation for  $C^{6+} + He$  later on. The time-dependent Hartree-Fock approach has been applied (Stich *et al* 1983, Sandhya Devi and Garcia 1984) to systems which develop close to their molecular ground state. That method is probably less attractive for the systems considered in this work. Other more specialised model calculations which usually neglect either the electron translation or the exchange effect are numerous and are not further discussed here.

In the following section, we summarise the atomic-orbital expansion model in its form for two-electron systems. A third section deals with the numerical calculation of matrix elements in the AO expansion model. Section 4 contains the application to the collision systems  $O^{6+} + He$  and  $C^{6+} + He$ . In § 5 we conclude with an assessment of the results and of their implication for future studies.

## 2. Theory: the atomic-orbital expansion scheme with two-electron configurations

For one-electron systems, the atomic-orbital expansion method has been frequently described in the literature (see, e.g., McDowell and Coleman 1970). Here we give in short form its extension to (quasi-)two-electron systems. Atomic units are used throughout this paper if not explicitly stated otherwise.

Let us assume that the two atomic collision centres A and B move on some classical trajectory with velocities  $v_A$  and  $v_B$ , respectively. Let us furthermore assume that the electronic motion during the collision is sufficiently well represented by a superposition of a finite number of two-electron configurations  $\Phi_n(\mathbf{r}_1, \mathbf{r}_2)$  in which, for fixed channel number  $n$ , each electron moves along with either centre A or B ( $\mathbf{r}_j$  denotes the coordinate of electron  $j$ ,  $j = 1, 2$ , in the centre-of-mass system). We then start from the decomposition of the time-dependent two-electron wavefunction  $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$  into this set of configurations  $\Phi_n$ ,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_n a_n(t) \Phi_n(\mathbf{r}_1, \mathbf{r}_2) \chi_n(t) \quad (1)$$

with time-dependent occupation amplitudes  $a_n(t)$  and a phase factor

$$\chi_n(t) = \exp \left[ -i \left( E_n t + \int^t T_n(t') dt' \right) \right] \quad (2)$$

which contains the asymptotic electronic binding energy in configuration  $n$ ,

$$E_n = \lim_{t \rightarrow \infty} \langle \Phi_n | H_{el} | \Phi_n \rangle \quad (3)$$

and a classical kinetic energy term  $T_n(t)$  associated with the motion of the electrons with their respective centre. Then if the two electrons of configuration  $n$  are attached to different centres,

$$T_n = \frac{1}{2} v_A^2 + \frac{1}{2} v_B^2. \quad (4)$$

In equation (1), spin functions have been suppressed for simplicity. For the collision systems considered in this paper, the spin degrees of freedom have been included by imposing proper symmetry conditions on the configurations  $\Phi_n$ .

In equation (3),  $H_{el}$  consists of the Hamiltonians  $H_0(j)$  of electron  $j$ ,  $j = 1, 2$ , with respect to both centres A and B, and the interelectronic interaction  $V_{12}$ ,

$$H_{el} = H_0(1) + H_0(2) + V_{12} \quad (5)$$

$$V_{12} = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}. \quad (6)$$

Each basis configuration  $\Phi_n$  is either of one-centre type or of two-centre type with appropriate translational factors attached to them. In the simplest case they are symmetrised products of travelling one-electron orbitals, e.g. if the two electrons are attached to different centres,

$$\Phi_n(\mathbf{r}_1, \mathbf{r}_2) = P^\pm [\phi_{1n}(\mathbf{r}_1^A) \exp(i\mathbf{v}_A \cdot \mathbf{r}_1) \phi_{2n}(\mathbf{r}_2^B) \exp(i\mathbf{v}_B \cdot \mathbf{r}_2)] \quad (7)$$

where  $\phi_{in}(\mathbf{r}_j^c)$  is the  $i$ th ( $i = 1, 2$ ) function in configuration  $\Phi_n$ , describing electron  $j$  with its coordinate  $\mathbf{r}_j^c$  measured from the atomic centre  $c$  ( $c = A, B$ ), and the operator  $P^\pm$  is the Pauli (anti-)symmetrisation operator according to spin triplet (singlet) conditions. We note that the configuration functions  $\Phi_n(\mathbf{r}_1, \mathbf{r}_2)$  still depend on time through the movement of the collision centres, i.e. through the travelling electronic coordinates  $\mathbf{r}_j^c$  and, for curved-line trajectories, through the velocities  $v_c$  of the centre  $c$ .

In full analogy to the well known close-coupling method for one-electron problems, the decomposition (1) is inserted into the time-dependent Schrödinger equation for two electrons, leading to coupled differential equations for the occupation amplitudes  $a_n(t)$ ,

$$i \sum_k N_{nk} \dot{a}_k = \sum_k M_{nk} a_k \quad (8)$$

with overlap matrix elements

$$N_{nk} = \langle \Phi_n \chi_n | \Phi_k \chi_k \rangle \quad (9)$$

and potential coupling matrix elements

$$M_{nk} = \langle \Phi_n \chi_n | H_{el} - i \partial / \partial t | \Phi_k \chi_k \rangle. \quad (10)$$

Starting from the two-electron Hamiltonian  $H_{el}$  for a given two-electron system, or from a model two-electron Hamiltonian for a quasi-two-electron system, the matrix elements (9) and (10) are calculated on a time mesh along the internuclear trajectory, using methods to be discussed in the next section. With these matrix elements, the coupled equations (8) are solved numerically with a variable step size Runge-Kutta procedure, beginning from the initial condition at large negative times where only one configuration  $\Phi_i$  is occupied, up to large positive times where the amplitudes  $a_n(t)$  stabilise and where they represent probability amplitudes for the occupation of some final physical states as well as pseudostates. The physical interpretation of  $a_n(t \rightarrow \pm\infty)$ , of course, depends on a meaningful choice of configurations  $\Phi_n$  and favours a basis set  $\{\Phi_n\}$  which is orthogonal in the limit  $t \rightarrow \pm\infty$  (for small times  $t$ , the configurations  $\Phi_n$  of two-centre type are not even normalised). As for the interpretation of the population of pseudostates as a measure of ionisation events, we refer the reader to works by Fritsch and Lin (1982, 1983) and by Mukoyama *et al* (1985).

From the absolute squares of probability amplitudes at  $t \rightarrow \infty$ , partial inelastic cross sections are formed as usual by integrating over the impact parameter plane, and total transfer cross sections are calculated by summing the partial cross sections of all transfer channels  $n$  which are included in the basis set.

### 3. Calculation of matrix elements

For the determination of the time-dependent occupation amplitudes  $a_n(t)$ , equation (8), it is essential to calculate the matrix elements (9) and (10) in an efficient way. As far as these are composed of matrix elements of one-particle operators between products of travelling atomic orbitals, equation (7), they can clearly be calculated with the methods used in AO expansion studies for one-electron systems. In particular, the overlap matrix (9) and the one-electron operator part of the coupling matrix (10) can be easily calculated on a curved-line trajectory by combining equations (3)–(5) in the work of Fritsch (1982) and by using well known calculational techniques which go back to early studies with AO expansions (McCarroll 1961). In this section, we concentrate on the evaluation of matrix elements of the two-electron operator  $V_{12}$ , equation (6), between basis configurations  $\Phi_n$ , i.e. on the evaluation of expressions like

$$I_{nk}(t) = \int d^3 r_1 d^3 r_2 \omega_{1nk}(\mathbf{r}_1 t) V_{12} \omega_{2nk}(\mathbf{r}_2 t) \quad (11)$$

in which the atomic product functions  $\omega_{ink}$  are of the form

$$\omega_{ink}(\mathbf{r}_i t) = \phi_{in}^*(\mathbf{r}_i) \phi_{ik}(\mathbf{r}_i) \exp[i(\mathbf{v}_B - \mathbf{v}_A) \cdot \mathbf{r}_i] \quad (12)$$

if  $\Phi_{in}$  ( $\Phi_{ik}$ ) moves with centre A (B), and suitably modified otherwise. In equation (12), the atomic product functions  $\omega$  depend only on the coordinate of electron  $i$ ,  $r_i$ , as well as on time or internuclear separation  $R$ . If the electrons in all single-electron orbitals  $\phi_{ij}$  ( $j = n, k, i = 1, 2$ ) were positioned at the same centre or would not travel the correlation term (11) could be calculated with a number of efficient methods known in atomic- or molecular-structure physics. For the collision case for which the translational factor part in equation (12) is non-trivial, we have chosen to generalise expressions given by Mehler and Rüdénberg (1969), which seemed to be well suited for implementation into an existing AO expansion code for one-electron systems. Starting from equation (11), we introduce the Neumann expansion for  $V_{12}$  in elliptical coordinates  $\xi_i, \eta_i, \phi_i$  of the electrons  $i, i = 1, 2$ . Then, after some elementary algebra (Mehler and Rüdénberg 1969) we arrive at the following expression for the basic integral  $I_{nk}$ :

$$I_{nk}(t) = (4/R) \sum_{lm} \int_1^\infty dx f_{lm}^1(xt) f_{lm}^2(xt) \quad (13)$$

where

$$f_{lm}^i(xt) = \frac{1}{(x^2 - 1)^{1/2} P_l^{|m|}(x)} \int_1^x d\xi_i P_l^{|m|}(\xi_i) \Omega_{lm}^i(\xi_i t) \quad i = 1, 2 \quad (14)$$

and

$$\Omega_{lm}^i(\xi t) = (R/2)^3 \int_{-1}^1 d\eta \int_0^{2\pi} d\phi (\xi^2 - \eta^2) \mathcal{Y}_{lm}(\eta\phi) \omega_{ink}(\mathbf{r}t). \quad (15)$$

In equation (15), the real spherical harmonics  $\mathcal{Y}_{lm}$ ,

$$\mathcal{Y}_{lm}(\eta\phi) = \left( \frac{2l+1}{1+\delta_{m0}} \frac{(1-|m|)!}{(1+|m|)!} \right)^{1/2} P_l^{|m|}(\eta) \begin{cases} \cos |m|\phi & \text{for } m \geq 0 \\ \sin |m|\phi & \text{for } m < 0 \end{cases} \quad (16)$$

are used, and  $P_l^m(u)$  denotes the associated Legendre function of the first kind.

As  $f_{00}^i(x = \infty, t)$  is simply the overlap integral between one-electron atomic-orbital functions including translational factors, it is clear that  $f_{lm}^i(x = \infty, t)$ , equation (14), can be easily evaluated with the same methods and with similar computational investment as those matrix elements which are used in calculations for one-electron problems. In particular, one or even two of the integrations in equation (15) may be solved in closed form while the  $\xi$  integration in equation (14) is solved numerically on a  $\xi$  mesh such that  $f_{lm}^i(x, t)$  is also available for all  $x \geq 1$ . Accordingly, for the evaluation of  $I_{nk}$ , equation (13), only one integral needs to be solved in addition to those to which one is accustomed in one-electron problems while the sum over  $0 \leq l < \infty$  and  $-l \leq m \leq l$  (which might appear to be as awkward as another two integrations) can usually be cut off after a few terms for a given requirement of accuracy for  $I_{nk}$ . In this way, i.e. if  $I_{nk}$  and the full matrix element, equation (10), are evaluated to an accuracy of four decimal places,  $l_{\max}$  can be kept safely below 12 and in most cases well below that figure. The only exceptions are constituted by certain couplings at large separations  $R$ , i.e. when the translational factors cancel (e.g.  $\langle \phi_{1s}^A(\mathbf{r}_1) \phi_{1s}^B(\mathbf{r}_2) | V_{12} | \phi_{1s}^A(\mathbf{r}_1) \phi_{1s}^B(\mathbf{r}_2) \rangle$ ). Those cases would require very large values of  $l_{\max}$  in the sum of equation (13). Therefore, they are evaluated separately with the customary multipole expansion of  $V_{12}$  in spherical coordinates where the range of  $l$  values is limited by triangular relations of  $l$  with the respective orbital angular momenta of atomic orbitals at either collision centre.

The expressions given in this and in the preceding section reduce to expressions given by Green *et al* (1965) if used in conjunction with their model description of the  $H^+ + He$  system. Before moving on to the more involved systems considered here we have ascertained that in actual numerical calculations the results of Green *et al* are recovered. Furthermore, some of the calculated matrix elements could be compared with results which were computed independently by Sabourin (1985).

#### 4. Model study for the collision systems $O^{6+} + He$ and $C^{6+} + He$

In the following, we apply the theory as outlined above to the (quasi-)two-electron systems  $O^{6+} + He$  and  $C^{6+} + He$  and compare with experimental data and with the results of a previous study within the molecular-orbital (MO) model. These systems are particularly attractive for a first test of the two-electron atomic-orbital formalism as they primarily involve *distant* collisions in which a number of  $l$  orbitals in higher  $n$  shells ( $n = 3, 4$ ) are populated. Thus AO-type expansions can be expected to show their particular strength here. Furthermore, in the energy region studied here, the correlation between the two electrons in the ground state of He makes a one-electron potential model for these systems less reliable. Indeed, it will be shown below that results from a one-electron AO description with a simple He potential from the literature do not agree with experiment.

##### 4.1. Formulation of the model

The collision systems  $O^{6+} + He$  and  $C^{6+} + He$  are expected to behave very similarly in the intermediate energy range. The two electrons in the K shell of oxygen can be safely considered as inert in collisions. From a discussion based on the energy diagrams it is clear that one-electron capture into the projectile  $n = 3$  shell is the dominant process (see the work by Kimura and Olson (1984) for  $C^{6+} + He$ ), and this is confirmed by experiment for  $O^{6+} + He$  (Dijkkamp *et al* 1985b). The different cores of the  $O^{6+}$  and  $C^{6+}$  projectiles will at best affect the total transfer cross sections at low energies but may well influence the  $l$  distribution of transfer at all energies under consideration. The  $O^{6+}$  core is represented by the potential

$$V_{O^{6+}}(r) = -\frac{6}{r} - \frac{2}{r} \exp(-2\alpha r)(1 + 2\alpha r + 2\alpha^2 r^2) \quad (17)$$

with  $\alpha = 8.4$ , which is the summed potential of the nucleus and of two electrons in scaled 1s orbitals. As final states for both collision systems we have taken the antisymmetrised product states  $|n_p l_p\rangle |1s He^+\rangle$  where the projectile states  $|n_p l_p\rangle$  include all  $n_p = 3, 4$  orbitals and the 2s orbital. For  $O^{6+}$  projectiles these are constructed by diagonalising the  $O^{6+}$  Hamiltonian within the space of the 2s and the  $n_p = 3, 4$  hydrogenic orbitals with effective charges  $Z_p = 6$  (the 2s orbital has been taken in order to improve the 3s and 4s energies in the diagonalisation process). With the choice of potential (17), the deviation of the model 3s(4s) $O^{6+}$  energy from the Hartree-Fock values (Lindgaard and Nielsen 1977) is thus 0.0053 (0.0080) au, i.e. small compared with the binding energy gain in the collision of about 1.33 au for  $n = 3$ . These deviations become even smaller with increasing  $l > 0$ . By starting with the same hydrogenic basis set for both collision systems, of course, we have to calculate the matrix elements of  $V_{12}$  only once for both collision systems.

The AO basis consists of the 17 two-electron configurations given above as well as a representation of the He ground state by an antisymmetrised product of hydrogenic 1s states with effective charges 2.183 and 1.188. The total electronic binding energy from that representation is  $-2.8757$  au and thus only 0.028 au above the experimental value. The representation of the He ground state could be improved by adding further components into a configuration wavefunction, e.g. the remaining deviation of the binding energy from experiment could be halved by adding just one appropriate  $|2p(Z_1)2p(Z_2)\rangle$  component, but this was not done in the present collision study. In another restriction of this study, it is assumed in the basis that in the energy range under consideration, 0.5–40 keV amu<sup>-1</sup>, the target is always left in its ground state after collision. Furthermore, double capture channels and molecular corrections are not included. Certainly the representation of relevant adiabatic quasimolecular states by the chosen basis could be improved by adding tighter-bound atomic orbitals, cf works by Fritsch and Lin (1982, 1984c), but this was not done here in order to keep the model description as simple as possible.

Straight-line internuclear trajectories are employed in the calculations above 1 keV amu<sup>-1</sup> impact energy. At and below that energy Coulomb trajectories are employed, associated with two moving point-like nuclear charges of  $Z_p = 6$  and  $Z_t = 1$ . While the choice of  $Z_p$  is not considered to be critical, this might not be true for  $Z_t$ . The choice  $Z_t = 1$  is of course only correct in the outgoing transfer channels at large separations. However, it represents a compromise between other possible more extreme choices of 0 or 2.

#### 4.2. Results and discussion

Calculated total and partial transfer cross sections in O<sup>6+</sup> + He and C<sup>6+</sup> + He collisions are listed in tables 1 and 2, respectively. As expected, the projectile  $n = 3$  shells are populated dominantly in both collision systems. At higher energies, however, transfer becomes less selective and transfer into  $n = 4$  orbitals gains strength. At energies above 2 keV amu<sup>-1</sup>, the cross sections for population of the  $n = 3$  and 4 shells, and hence also the total transfer cross sections, are about the same in both systems while, below that energy, the cross sections for the C<sup>6+</sup> + He system are distinctly smaller than those for the O<sup>6+</sup> + He system. Not surprisingly, the  $l$ -subshell cross sections depend somewhat more strongly on details of the collision system, except at the highest energy point where they seem to tend towards their statistical relative ratio.

Table 2 also contains, in the last column, total transfer cross sections in C<sup>6+</sup> + He collisions from a *one*-electron potential model. In this model, which is analogous to the ones used by us earlier, cf e.g. Fritsch and Lin (1984a), the one-electron initial and final configurations are the 1s He and the  $n = 3, 4$  C<sup>5+</sup> orbitals, and the model potential representing the He core is taken from the study by Opradolce *et al* (1983). Although, in the latter paper it was concluded that the potential model description gives a satisfactory transfer cross section in the special case of Ar<sup>6+</sup> + He collisions, it turns out to be quite unsatisfactory for the case C<sup>6+</sup> + He (as well as for O<sup>6+</sup> + He), particularly at low energy, both with respect to the two-electron description and to experiment (see below). It is only at higher energies, i.e. when the collision velocity is larger than the electronic orbital velocity, that the 'spectator' electron may be assumed as frozen in its initial orbital during the collision. Of course, with a reduced claim on the accuracy of results, the one-electron model may seem acceptable at the higher energies of the present study, too.

**Table 1.** Calculated total transfer cross sections  $\sigma_{\text{tot}}$ , partial transfer cross sections  $\sigma_n$  for population of the projectile principal shell  $n$ , and  $l$ -subshell partial cross sections  $\sigma_{nl}$  in  $\text{O}^{6+} + \text{He}$  collisions at impact energies  $E$ . Cross sections are in  $10^{-16} \text{ cm}^2$ , energies in  $\text{keV amu}^{-1}$ .

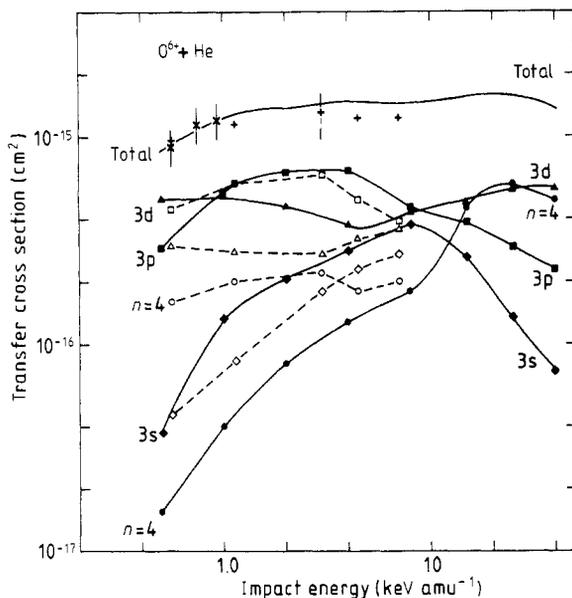
$E$	$\sigma_{\text{tot}}$	$n$	$\sigma_n$	$\sigma_{n0}$	$\sigma_{n1}$	$\sigma_{n2}$	$\sigma_{n3}$
0.5	8.5	3	8.32	0.37	2.94	5.00	
		4	0.15	0.03	0.04	0.06	0.03
1	12.4	3	12.0	1.33	5.41	5.27	
		4	0.40	0.03	0.10	0.21	0.06
2	13.6	3	12.8	2.06	6.68	4.11	
		4	0.80	0.08	0.14	0.41	0.17
4	14.7	3	13.4	2.81	6.83	3.78	
		4	1.26	0.09	0.18	0.45	0.54
8	14.4	3	12.6	3.78	4.47	4.36	
		4	1.76	0.11	0.23	0.54	0.89
15	15.8	3	11.3	2.64	3.85	4.82	
		4	4.55	0.20	0.41	1.56	2.38
25	15.6	3	9.93	1.35	2.92	5.66	
		4	5.66	0.09	0.62	1.14	3.81
40	13.6	3	8.65	0.74	2.28	5.62	
		4	4.93	0.12	0.51	0.97	3.34

**Table 2.** Calculated total transfer cross sections  $\sigma_{\text{tot}}$ , partial transfer cross sections  $\sigma_n$  for population of the projectile principal shell  $n$ , and  $l$ -subshell partial cross sections  $\sigma_{nl}$  in  $\text{C}^{6+} + \text{He}$  collisions at impact energies  $E$ , from this two-electron study. The last column ( $\sigma_{1e}$ ) shows results from a study based on a one-electron potential model. Cross sections are in  $10^{-16} \text{ cm}^2$ , energies in  $\text{keV amu}^{-1}$ .

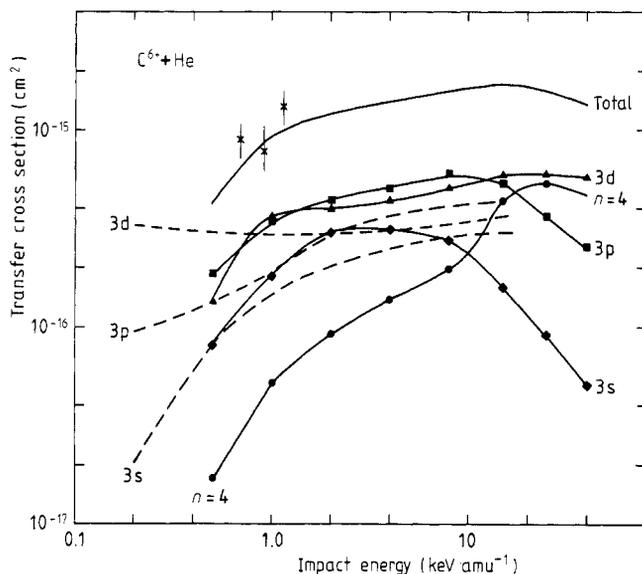
$E$	$\sigma_{\text{tot}}$	$n$	$\sigma_n$	$\sigma_{n0}$	$\sigma_{n1}$	$\sigma_{n2}$	$\sigma_{n3}$	$\sigma_{1e}$
0.5	4.2	3	4.0	0.80	1.87	1.35		15.3
		4	0.17	0.02	0.02	0.07	0.06	
1	9.3	3	8.8	1.81	3.59	3.61		
		4	0.52	0.07	0.19	0.20	0.06	
2	12.4	3	11.4	3.07	4.40	3.97		23.5
		4	0.92	0.13	0.23	0.38	0.18	
4	14.0	3	12.6	3.09	5.10	4.43		
		4	1.38	0.08	0.22	0.52	0.56	
8	15.8	3	13.9	2.74	6.01	5.12		
		4	1.96	0.05	0.28	0.58	1.05	
15	17.3	3	12.9	1.58	5.35	5.93		
		4	4.39	0.13	0.38	1.28	2.61	
25	15.8	3	10.6	0.91	3.61	6.04		18.2
		4	5.28	0.09	0.50	1.10	3.59	
40	13.6	3	8.85	0.51	2.55	5.79		16.5
		4	4.70	0.09	0.44	0.96	3.21	

In figure 1, calculated partial and total transfer cross sections for the  $O^{6+} + He$  system are compared with experimental data from the optical measurements by Dijkkamp *et al* (1985b) and with the charge state analysis measurements by Iwai *et al* (1982). The calculated total transfer cross sections are in excellent agreement with both sets of experimental data. For the  $n = 3$  partial transfer cross sections, there are some quantitative discrepancies between experimental data (estimated uncertainties are of the order of 30%) and the calculation, although the more general energy dependences of those partial cross sections agree well. Particularly, the measured 3d population at low energies is larger than the corresponding result from this work. From the figure, the discrepancy between the published measured and calculated  $n = 4$  partial transfer cross sections seems to be most serious. However, the optical measurements of the corresponding lines are less certain than assumed at the time of the publication of the experimental paper (Dijkkamp 1985). Actually, from the molecular energy diagram (see the one for  $C^{6+} + He$  collisions (Kimura and Olson 1984)) we expect that the  $n = 4$  partial cross sections should drop rapidly with decreasing energy.

In figure 2, calculated total and partial transfer cross sections for the  $C^{6+} + He$  system are compared with experimental data by Iwai *et al* (1982) and with the results of a theoretical study based on the molecular orbital (MO) picture (Kimura and Olson 1984). The calculated total transfer cross sections of this work are in rather striking agreement with the measurements at low energies where they do depend on particular features of the system, cf figure 1 for the  $O^{6+} + He$  system. The partial transfer cross sections for the  $n = 3$  shell from the two calculations agree only qualitatively. At higher energies, the MO results are probably less reliable since they are derived without the



**Figure 1.** Energy dependence of total and partial one-electron capture cross sections in  $O^{6+} + He$  collisions. Full curves link results of this work; full diamonds, squares, triangles and circles denote calculated partial cross sections for transfer into 3s, 3p, 3d and all  $n = 4$  projectile states, respectively. Open symbols linked by broken curves denote corresponding results measured by Dijkkamp *et al* (1985b). Measured total transfer cross sections are by Iwai *et al* (1982) ( $\times$ ) and by Dijkkamp *et al* (1985b) ( $+$ ).



**Figure 2.** Total and partial one-electron capture cross sections in  $C^{6+} + He$  collisions. Full curves and symbols denote results of this work as explained in the caption of figure 1, broken curves the results of the MO study by Kimura and Olson (1984). Measured total transfer cross sections are by Iwai *et al* (1982) ( $\times$ ).

$n = 4$  capture channels and since, in the MO study, matrix elements are calculated only to first order in the collision velocity. At low energies, the partial cross sections from the MO study combine to an almost flat total transfer cross section which seems to be less in agreement with experimental evidence and with expectation, but which certainly is not excluded by the data.

The striking difference in magnitude between total transfer cross sections in low-energy  $O^{6+} + He$  and  $C^{6+} + He$  collisions, as borne out in this investigation and in experiment, makes an explanation by physical arguments desirable. Unfortunately, such arguments are not easy to find without a detailed discussion. In test calculations at  $0.5 \text{ keV amu}^{-1}$  with straight-line trajectories the difference in question recurs, hence it is not due to the different trajectories chosen for the two systems. However, it is known from a theoretical study for the (quasi-)one-electron systems  $X^{6+} + H$  (Larsen and Taulbjerg 1984) that an understanding of the core effect requires a discussion of wavefunctions or matrix elements and not only of energies. We do not pursue this discussion for the systems under investigation here, as it would be tedious and would involve much repetition of arguments put forward by Larsen and Taulbjerg. We note that for the system  $X^{6+} + H$  a pronounced effect of the electronic core in slow collisions, similar in magnitude to the effect pointed out here, has been documented in experiments over a large range of projectile atomic numbers  $X$  (Crandall *et al* 1980).

## 5. Conclusions

In this work we present an extension of the atomic-orbital expansion method to two-electron systems. The extension of the formalism is very straightforward, and the evaluation of the interelectronic matrix element requires one integration in addition

to those integrations which are performed in the case of one-electron systems. The additional integration causes an increase by a factor of about ten in the computing time required for studies in the two-electron formulation. However, for collision systems with two (almost equivalent) electrons outside a presumably frozen core, a *one*-electron model in the intermediate energy region is in general unsatisfactory, and this is clearly seen for the example of  $O^{6+} + He$  and  $C^{6+} + He$  collisions in this work. In turn, one-electron transfer cross sections from the *two*-electron formalism are in good agreement with experiment for both systems. Remaining discrepancies with experiment, i.e. discrepancies between partial transfer cross sections, may be partly due to limitations of the model calculations but also due to problems in the difficult experiment, as indicated above. The limitations which seemed acceptable in this study are primarily (i) the representation of the He ground state by a simple antisymmetrised product wavefunction, (ii) the exclusion of excited He or  $He^+$  configurations, (iii) the exclusion of double-capture channels, and (iv) the exclusion of molecular binding effects in this study. At energies below some  $0.5 \text{ keV amu}^{-1}$  limitations (i) and (iv) as well as trajectory effects would make results less reliable, and so would limitation (ii) as well as higher transfer channels beyond the  $n = 3$  and 4 channels at energies greatly above  $25 \text{ keV amu}^{-1}$ . In the intermediate energy regime, however, it seems that the two-electron formalism represents the actual physical situation as well as the one-electron AO formalism does for analogous one-electron systems, cf the works on  $C^{4+} + H$  by Fritsch and Lin (1984a) and by Ciric *et al* (1985).

There are certainly large challenges ahead for the two-electron AO expansion method, i.e. when any of the limitations of this study cannot be reasonably maintained. Highly correlated target atoms like  $H^-$  will require the inclusion of configuration interaction wavefunctions, more symmetric systems may involve significant molecular binding effects at low energy, and in some systems there will be important double-capture or even doubly-excited channels or other correlated processes. The present study may be taken as an indication that the AO expansion model provides techniques of addressing all these problems. Only future investigations will show what precision can be achieved in practice for complex two-electron problems. After completion of this paper, a two-state AO expansion study on  $H(2s)$  formation in  $H(1s) + H(1s)$  collisions appeared (McLaughlin and Bell 1985). The formalism developed in that paper is very close to that used here. Their results demonstrate the power of a consistent AO expansion description at low to intermediate energies if compared with other descriptions which imply additional approximations.

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### References

- Allan R J 1986 *J. Phys. B: At. Mol. Phys.* **19** 321-34  
Brandsen B H, Ermolaev A M and Shingal R 1984 *J. Phys. B: At. Mol. Phys.* **17** 4515-21

- Ciric D, Dijkkamp D, Vlieg E and de Heer F J 1985 *J. Phys. B: At. Mol. Phys.* **18** L17-22
- Crandall D H, Phaneuf R A and Meyer F W 1980 *Phys. Rev. A* **22** 379-87
- Dijkkamp D 1985 private communication
- Dijkkamp D, Ciric D and de Heer F J 1985a *Phys. Rev. Lett.* **54** 1004-7
- Dijkkamp D, Gordeev Yu S, Brazuk A, Drentje A G and de Heer F J 1985b *J. Phys. B: At. Mol. Phys.* **18** 737-56
- Flower D R 1985 private communication
- Fritsch W 1982 *J. Phys. B: At. Mol. Phys.* **15** L389-93
- 1984 *Phys. Rev. A* **30** 1135-8
- Fritsch W and Lin C D 1982 *J. Phys. B: At. Mol. Phys.* **15** 1255-68
- 1983 *Proc. 13th Int. Conf. on Physics of Electronic and Atomic Collisions (Berlin)* ed J Eichler *et al* (Amsterdam: North-Holland) Abstracts p 502
- 1984a *J. Phys. B: At. Mol. Phys.* **17** 3271-8
- 1984b *Phys. Rev. A* **29** 3039-51
- 1984c *Proc. 13th Int. Conf. on Electronic and Atomic Collisions (Berlin) 1983* ed J Eichler *et al* (Amsterdam: North-Holland) Invited papers pp 331-42
- Green T A, Shipsey E J and Browne J C 1982 *Phys. Rev. A* **25** 1364-73
- Green T A, Stanley H E and Chiang Y-C 1965 *Helv. Phys. Acta* **38** 109-24
- Harel C and Salin A 1980 *J. Phys. B: At. Mol. Phys.* **13** 785-98
- Iwai T, Kaneko Y, Kimura M, Kobayashi N, Ohtani S, Okuno K, Tagaki S, Tawara H and Tsurubuchi S 1982 *Phys. Rev. A* **26** 105-15
- Kimura M 1985 private communication
- Kimura M and Olson R E 1984 *J. Phys. B: At. Mol. Phys.* **17** L713-9
- Kimura M, Sato H and Olson R E 1983 *Phys. Rev. A* **28** 2085-90
- Larsen O G and Taulbjerg K 1984 *J. Phys. B: At. Mol. Phys.* **17** 4523-42
- Lin C D 1978 *J. Phys. B: At. Mol. Phys.* **11** L185-90
- Lindgaard A and Nielsen S E 1977 *At. Data Nucl. Data Tables* **19** 522-633
- McCarroll R 1961 *Proc. R. Soc. A* **264** 547-57
- McDowell M R C and Coleman J P 1970 *An Introduction to the Theory of Ion-Atom Collisions* (Amsterdam: North-Holland)
- McLaughlin B M and Bell K L 1985 *J. Phys. B: At. Mol. Phys.* **18** L771-8
- Mehler E L and Rüdénberg K 1969 *J. Chem. Phys.* **50** 2575-80
- Meyer F W, Howald A M, Havener C C and Phaneuf R A 1985 *Proc. 14th Int. Conf. on Physics of Electronic and Atomic Collisions (Palo Alto) 1985* (Amsterdam: North-Holland) p 491 and to be published
- 1986 *Phys. Rev. A* **32** 3310-8
- Mukoyama T, Lin C D and Fritsch W 1985 *Phys. Rev. A* **32** 2490-3
- Opradolce L, Valiron P and McCarroll R 1983 *J. Phys. B: At. Mol. Phys.* **16** 2017-28
- Sabourin T 1985 private communication
- Sandhya Devi K R and Garcia J D 1984 *Phys. Rev. A* **30** 600-3
- Shingal R, Bransden B H, Emolaev A M, Flower D R, Newby C W and Noble C J 1986 *J. Phys. B: At. Mol. Phys.* **19** 309-20
- Shingal R, Newby C W, Noble C J, Flower D R and Bransden B H 1985 *Proc. 14th Int. Conf. on Physics of Electronic and Atomic Collisions (Palo Alto)* (Amsterdam: North-Holland) Abstracts p 494
- Shipsey E J, Green T A and Browne J C 1983 *Phys. Rev. A* **27** 821-32
- Stich W, Lüdde H J and Dreizler R M 1983 *Phys. Lett.* **99A** 41-5
- Winter T G and Lin C C 1974 *Phys. Rev. A* **10** 2141-55