

On the dynamical description of K–K charge transfer in highly ionised ion–atom collision systems

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Abstract. We examine the role of electronic relaxation in the description of K–K charge transfer for ion–atom collisions with bare or one-electron projectiles in the intermediate velocity region. Total and differential K–K transfer cross sections for the system $F^{9+} + Si$ are calculated within the coupled-state impact parameter method, starting from a relaxed molecular Hamiltonian and from a frozen two-centre Hamiltonian. By comparing the results of the two molecular expansion calculations with each other and with those of the atomic orbital expansion method, we test the various assumptions about relaxation of passive as well as active electron orbitals in a single-electron molecular orbital picture. A comparison with experimental data favours the description with relaxation in neither active nor passive orbitals for collision energies above 400 keV amu^{-1} .

1. Introduction

Charge transfer is an important process for inner-shell vacancy production in ion–atom collisions with highly ionised projectiles (Richard 1980 and references therein). For incident bare or one-electron ions, much effort has been devoted experimentally to extracting the K–K charge transfer portion from the total target K-shell vacancy production cross sections. Some studies (Randall *et al* 1976, Schuch *et al* 1979) include measurements of differential cross sections. For heavy projectiles at slow or intermediate collision energies where perturbative methods are not applicable, little theoretical information is available about these processes. Briggs (1974) has derived a generalisation of the two-state Demkov–Meyerhof formula for the finite impact parameter two-passage case, but the application of this formula to measured differential cross sections (Schuch *et al* 1979) showed only poor agreement.

Recently, Lin and Tunnell (1980) investigated K–K charge transfer from multi-electron targets to bare or one-electron projectile ions within the semiclassical coupled-state formalism. Retaining in an *atomic* expansion of the time-dependent electronic wavefunction only the two 1s orbitals of the collision partners, they reproduced the experimental total cross sections of Tawara *et al* (1978) for the system $F^{9+} + Si$ quite well at impact velocities v close to the 1s F^{8+} orbital velocity v_e . For smaller collision energies, however, the calculated cross sections tend to overestimate the experimental data considerably, up to a factor of two for the smallest measured energy $E = 400 \text{ keV amu}^{-1}$ ($v/v_e = 0.44$).

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The discrepancies between the experimental data and the results of the two-state atomic expansion method at lower collision energies are not unexpected. In the atomic expansion method used by Lin and Tunnell (1980), the time-dependent electron wavefunction is expressed in terms of travelling atomic orbitals which constitute the 'active' orbitals of the model. These orbitals in turn are constructed from atomic single-particle Hamiltonians, assuming that all the passive electrons remain in their respective initial orbitals throughout the collision encounter. This representation for the time evolution of the electronic system becomes less valid as the collision velocity decreases significantly below $v/v_e \approx 1$. For low energies ($v/v_e \ll 1$) it is usually assumed (Briggs 1976) that the electronic system is described more appropriately as a relaxed system, by choosing a relaxed molecular Hamiltonian and molecular orbitals to represent the evolution of the passive electrons and the active orbitals. In the intermediate velocity region it is not clear which description of the collision dynamics is superior. One may, therefore, ask whether the discrepancy between the experimental data and the cross sections calculated within the atomic model can be explained by the onset of relaxation at lower energies.

In this paper we study K-K charge transfer for the case of $F^{9+} + Si$, starting from the two lowest *molecular* orbitals of the system as the active orbitals. Calculations have been performed with two molecular Hamiltonians representing different assumptions about the relaxation of inner- and outer-shell orbitals. The choice of the Hamiltonians is discussed and the framework of the calculations is laid out in § 2. Section 3 contains the transformation of the potential coupling matrix elements of the atomic expansion method into dynamical couplings between LCAO wavefunctions. Using this transformation, deviations between the cross sections calculated with the molecular and atomic expansions can be analysed more closely. The results of the calculations are given and discussed in § 4.

2. Framework of the MO calculations

To describe a collision encounter within the single-particle molecular orbital (MO) picture, one needs to specify the set of active basis MO to be included explicitly into the dynamical calculation and, for multi-electron systems, the two-centre Hamiltonian representing the dynamics of active and passive electrons. The choice of basis orbitals is usually guided by intuition rather than by quantitative information about the convergence properties of the set. While for the one-electron system $H^+ + H$ the symmetric resonant K-K charge transfer can be described properly with two-orbital expansions over a broad range of velocities (McCarroll 1961, Ferguson 1961), calculations for $H^+ + He^+$ collisions (Winter *et al* 1980) indicate an increased sensitivity of cross sections to the character and size of the basis set for asymmetric systems. The calculations reported here are done with the 1σ and 2σ MO of the system, which should constitute an appropriate basis set at least in the low-energy limit. Several test calculations have been done with an additional $2p\pi$ orbital, but little variation of the calculated cross sections has been observed.

For describing collisions between multi-electron systems in the single-electron approximation, the choice of an appropriate single-particle Hamiltonian constitutes a particularly intricate problem. While the usual molecular model suggests the employment of a molecular Hamiltonian in which all orbitals are relaxed to those of the molecular ground state, for intermediate velocities a more appropriate choice might be

a frozen two-centre Hamiltonian in which all electrons are fixed in their respective atomic orbitals throughout the collision. Since the outer-shell electrons cannot usually be considered as adiabatic, the frozen Hamiltonian of the atomic model might be a better representation, particularly for initially highly ionised collision systems where relaxation of outer-shell electrons changes the screening of inner-shell electrons appreciably. Calculations with this Hamiltonian and with MO as active orbitals reflect the assumption that the outer-shell (passive) orbitals of the system do not relax during the collision encounter while the inner-shell orbitals do relax, though not self-consistently in the Hamiltonian, but as active orbitals. In this work we calculate molecular orbitals and coupling matrix elements separately from a relaxed molecular Hamiltonian and from the frozen two-centre Hamiltonian. By comparing the results of the two calculations presented here with each other and with those of Lin and Tunnell (1980), we assess the importance of assumptions about relaxation of active and passive electron orbitals in the corresponding models.

An effective single-particle molecular Hamiltonian which is to describe the behaviour of the electronic system during the collision encounter should reflect the velocity and orbital dependence of relaxation processes. Recently, Eichler (1978) has shown how self-consistent molecular orbitals can be defined for charge-imbalanced collision systems by introducing a constraint on the solutions of the Hartree-Fock equations. Furthermore, a simple model for simulating this constraint in calculations with an effective Hamiltonian has been discussed and correlation diagrams have been calculated (Eichler *et al* 1979). The relaxation of the collision system towards a state of charge equilibrium, as discussed by Eichler (1978), however, is only one of many possible channels. For the system and the velocities under consideration more probable channels are those involving the transfer or ionisation of only a few outer electrons. Therefore, and in order to avoid the introduction of additional parameters detailing the charge equilibration process, in the present investigation we have adopted the simpler approach of constructing molecular orbitals MO(VSM) from the effective Hamiltonian H_{VSM} of the variable-screening model in the conventional manner (Eichler and Wille 1974, 1975). For the calculation without relaxation in the Hamiltonian, another set of two molecular orbitals MO(HA) has been constructed from the frozen two-centre Hamiltonian of the atomic model, $H_A = T + V_1 + V_2$, where $T + V_i$ ($i = 1, 2$) is the single-particle Hamiltonian describing atom i .

For the two calculations within the molecular model, we have evaluated the dynamical coupling matrix elements and solved the coupled-state equations numerically within the framework and with the methods outlined by Fritsch and Wille (1977). Molecular translational factors of the Schneiderman-Russek type (Schneiderman and Russek 1969) have been employed and Coulomb trajectories have been adopted. The two initial electrons in the 1σ orbital are assumed to move independently of each other during the collision. Starting from an initial occupation amplitude $a_{1\sigma}(t = -\infty; b, v)$ for impact parameter b and impact velocity v , the charge transfer probability per initial $1s$ electron is given by

$$P(b, v) = |a_{2\sigma}(t = +\infty; b, v)|^2 \quad (1)$$

and the single charge transfer cross section as

$$\sigma(v) = 2 \times 2\pi \int_0^\infty db b P(b)(1 - P(b)). \quad (2)$$

Coupled-state calculations are performed for the molecular Hamiltonians with (H_{VSM}) and without (H_{A}) relaxation using the same methods and the same computer code, only that in the latter case the relaxation parameter λ^2 of the variable-screening model (Eichler and Wille 1975) is set to infinity.

3. Comparison of potential couplings and dynamical couplings

It is illustrative to compare the energies and matrix elements of the two present molecular expansions with those of the atomic expansion (Lin and Tunnell 1980). For this purpose the potential coupling matrix elements $H_{ij} = \langle \phi_i^0 | H_{\text{A}} | \phi_j^0 \rangle$ between non-orthogonal time-independent atomic wavefunctions have been transformed to molecular energies and dynamical coupling matrix elements between LCAO wavefunctions, and the comparison has been done in this manner between molecular matrix elements. Defining the transformation from the atomic to the LCAO molecular basis as

$$\begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = \frac{1}{\cos \gamma} \begin{pmatrix} \cos \frac{1}{2}(\chi + \gamma) & \sin \frac{1}{2}(\chi - \gamma) \\ -\sin \frac{1}{2}(\chi + \gamma) & \cos \frac{1}{2}(\chi - \gamma) \end{pmatrix} \begin{pmatrix} \phi_1^0 \\ \phi_2^0 \end{pmatrix} \quad (3)$$

with γ given by the atomic overlap (dependent on the internuclear separation R)

$$\sin \gamma = \langle \phi_1^0 | \phi_2^0 \rangle \quad (4)$$

the mixing angle χ is easily shown to be

$$\tan \chi = \frac{2H_{12} - (H_{11} + H_{22}) \sin \gamma}{(H_{11} - H_{22}) \cos \gamma} \quad (5)$$

the energy separation Δ_{12} of the LCAO molecular orbitals

$$\Delta_{12} = \frac{H_{11} - H_{22}}{\cos \chi \cos \gamma} \quad (6)$$

and the dynamical coupling matrix element[†]

$$\langle \phi_2 | \partial / \partial R | \phi_1 \rangle = \frac{1}{2} d\chi / dR. \quad (7)$$

The transformation equations (3)–(7) from the atomic (diabatic) basis $\{\phi_1^0, \phi_2^0\}$ to the adiabatic basis $\{\phi_1, \phi_2\}$ embody the non-orthogonality of the atomic orbitals explicitly by means of the angle γ , equation (4). The customary form of this transformation assuming orthogonal diabatic states ($\gamma = 0$) (see Child 1978 and references therein) has been applied recently (Fritsch and Wille 1979) to Nikitin's two-state model. Clearly, if translational factors in the basis states are not important, a coupled-state calculation with LCAO molecular orbitals and matrix elements given by equations (6) and (7) gives identical results to those obtained with atomic orbitals and matrix elements H_{ij} since each basis set spans the same Hilbert space for the electronic wavefunction. It should be pointed out that the comparison of dynamical couplings may reveal discrepancies in the various model descriptions of the stationary quasimolecule to a larger or lesser degree depending on the choice of origin for the frame of reference. Since the dynamical calculations within the MO picture are not invariant with respect to a change of coordinate system, one should compare the couplings in the particular coordinate

[†] In deriving equation (7), the origin of the frame of reference is assumed to be the midpoint between the atomic centres. For any other frame of reference, a dipole term has to be added in equation (7).

system chosen for the MO calculations, i.e. the centre-of-mass system which represents the natural choice of an inertial frame on a curved trajectory (for a discussion of translational invariance in straight-line trajectory studies, see Riera and Salin 1976).

4. Results and discussion

Theoretical and experimental single-electron K-K charge transfer cross sections for the system $F^{9+} + Si$ are displayed in figure 1 over the inverse collision velocity. In the velocity region covered by experiments, the results calculated with the molecular Hamiltonian H_{VSM} lie above those of the atomic model (Lin and Tunnell 1980) by a factor of about three. This discrepancy increases for decreasing velocities. The results calculated with molecular orbitals MO(HA) of the frozen Hamiltonian H_A lie roughly midway between the other two. By a test calculation it has been ascertained that the cross sections in figure 1 do not depend sensitively on the choice of the internuclear trajectory. Furthermore, the atomic model calculations of Lin and Tunnell (1980) have been repeated with the atomic potential of Green (see Garvey *et al* 1975 and references therein), and good agreement with their earlier results has been found.

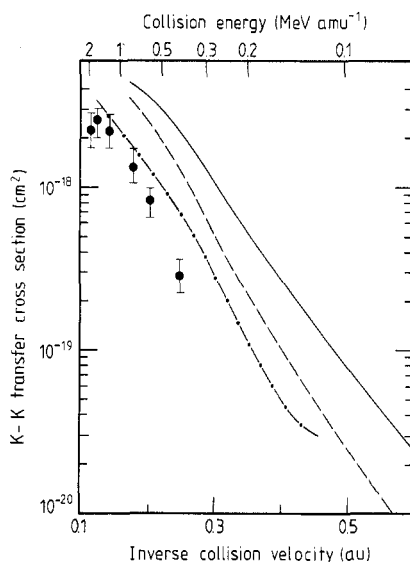


Figure 1. K-K single-electron transfer cross section for $F^{9+} + Si$ collisions. Full curve, calculation with $1\sigma, 2\sigma$ molecular orbitals MO(VSM) of the variable screening model; broken curve, calculation with $1\sigma, 2\sigma$ molecular orbitals MO(AO) of the frozen Hamiltonian H_A ; chain curve, calculation with $1s$ atomic orbitals (Lin and Tunnell 1980); full circles, experimental data of Tawara *et al* (1978).

The calculations within the molecular model and within the atomic expansion method differ from each other mainly in that they represent different choices of the active electron orbitals and of the Hamiltonian describing the dynamics of the passive electrons as well, and in that molecular (Schneiderman and Russek 1969) and atomic (Bates and McCarroll 1958) translational factors, respectively, are adopted. Comparing the studies on charge transfer in $He^{2+} + H$ within the MO picture with molecular

translational factors (Vaaben and Taulbjerg 1979) and with plane-wave translational factors (Winter and Hatton 1980), little sensitivity of their three-state cross sections is observed above the molecular velocity region (about 15% deviation for $0.15 \leq v/v_e \leq 0.45$)[†]. It is, therefore, apparent that it is mainly the different model assumptions about relaxation for both the active and passive electrons, which result in the large discrepancies of the calculated cross sections in figure 1. This fact is clarified and further illustrated in figure 2 by comparing the orbital energy separation Δ_{12} and the couplings in the various models. For internuclear separations $R \geq 0.15$ au, i.e. in the region where the couplings peak, the orbital energy separation calculated from the relaxed Hamiltonian H_{VSM} is smaller than both those calculated from the frozen Hamiltonian H_A , leading to larger cross sections in the calculation with MO(VSM). Figure 2(a) shows that the discrepancy in orbital energies between the models arises mainly from different assumptions about relaxation of passive electrons in the Hamiltonians H_{VSM} and H_A . The two-state LCAO orbital energy separations are even closer to those between molecular orbitals MO(HA) constructed from H_A if in the atomic calculation (Lin and Tunnell 1980) the Herman–Skillman potential is replaced by the potential of Green (Garvey *et al* 1975). The main reason for the pronounced effect of relaxation on the energies is that for highly ionised collision systems relaxation significantly changes the

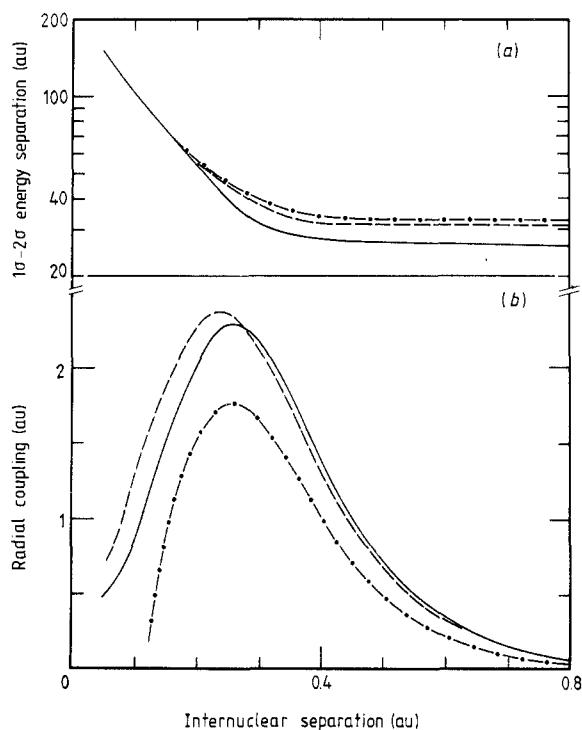


Figure 2. (a) 1σ – 2σ molecular orbital energy separations and (b) radial couplings for the system $\text{F}^{9+} + \text{Si}$. The radial couplings are shown for a frame of reference with the origin at the geometrical centre between the atomic nuclei. For further explanations, see caption to figure 1.

[†] Thorson investigated the system $\text{He}^{2+} + \text{H}$ with two different forms of molecular translational factors and found even better agreement with the results given by Winter and Hatton (1980) (Thorson 1980).

screening of the projectile charge in the Hamiltonian H_{VSM} as the collision partners approach each other, leading to a changed energy shift of the target centred orbital even at large internuclear separations. This long-range relaxation effect does not alter the wavefunctions much as is seen from the similar behaviour of couplings between molecular wavefunctions MO(VSM) and MO(HA) for $R \geq 0.25$ au, cf figure 2(b). The couplings between LCAO wavefunctions are smaller than between molecular wavefunctions MO(VSM) and MO(HA), thus contributing to the smaller cross sections in the atomic model[†]. Since the molecular wavefunctions MO(HA) and the LCAO wavefunctions start from the same frozen Hamiltonian H_A , the discrepancy between the corresponding couplings is attributed to the higher atomic components in a multi-state LCAO decomposition of the molecular wavefunctions MO(HA). These components may be small but their contribution to the couplings may be enhanced by the derivative inherent in the coupling matrix elements.

The calculations within the molecular model can easily be improved by diabatising the 2σ orbital to become a $2p\sigma$ orbital and by including the coupling of this diabatic orbital to the $2p\pi$ orbital. Regardless of whether the $2p\pi$ orbital is considered to be occupied or empty at the onset of the K-K transfer process, i.e., whether the initial conditions are formulated for vacancies or for electrons, the K vacancy production cross section in Si from a three-state calculation with MO(VSM) orbitals is found to be little changed. It is about six per cent larger than the corresponding two-state cross section in figure 1 for impact energies $E = 150 \text{ keV amu}^{-1}$ and 400 keV amu^{-1} .

The impact parameter dependence of the electron transfer probability, equation (1), is displayed in figure 3 for $E = 400 \text{ keV amu}^{-1}$. Characteristically for a two-passage case involving a localised coupling zone, both the calculations with molecular MO(VSM) and with atomic orbitals result in oscillatory transfer probabilities. The maximum and

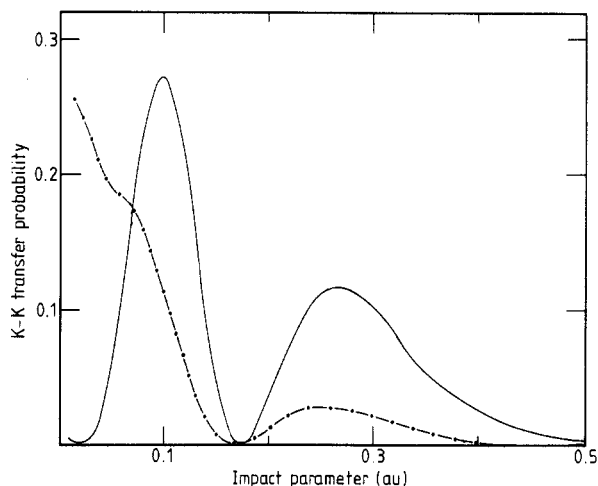


Figure 3. Impact parameter dependence of K-K electron transfer probability for $\text{F}^{9+} + \text{Si}$ collisions at energy $E = 400 \text{ keV amu}^{-1}$. Displayed are the results of calculations with two molecular orbitals MO(VSM) (full curve) and with two atomic 1s orbitals (chain curve).

[†] The discrepancies between the radial couplings in figure 2(b) are slightly diminished if displayed in the centre of mass system which is the coordinate system chosen for the MO calculations. This small effect has no bearing on the discussion in this paragraph.

minimum of the structure around $b = 0.26$ au appears to be only slightly shifted between the two calculations at this energy. As a more distinctive feature, however, the probability distribution of the atomic calculation shows relatively more strength at small impact parameters than the curve of the molecular calculation.

5. Conclusion

Calculated total and differential K-K electron transfer cross sections for the highly ionised collision system $F^{9+} + Si$ have been found to depend critically on the assumptions concerning the dynamics of the orbitals, i.e. assumptions about inner-shell and outer-shell relaxation. We expect this to hold for other asymmetric highly ionised collision systems too, where the onset of relaxation changes the screening of inner-shell orbitals appreciably and where the two lowest molecular orbitals are not sufficiently represented by a linear combination of two 1s atomic orbitals. The experimental data seem to indicate that neither inner- nor outer-shell orbitals relax at the experimentally observed energies. Without more information about the convergence of the two-state expansions, however, the remaining discrepancies between the measured cross sections and those calculated within the atomic model do not allow for more definite statements. On the theoretical side, for intermediate collision energies a more judicious treatment of relaxation effects is warranted, e.g. by including both atomic and relaxed orbitals in the expansion of the time-dependent wavefunction as has been done recently for one-electron systems (Fritsch *et al* 1981, Winter *et al* 1981). Experiments discriminating between different final-state configurations could give information about the behaviour of outer-shell electrons in these collisions. Finally, decisive experimental evidence concerning the validity of the different models could be acquired by measuring the impact parameter dependence of charge transfer, which is much more sensitive to model assumptions than total cross sections.

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