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LETTER TO THE EDITOR

Subshell electron capture cross sections of argon atoms by protons

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Abstract. We have developed a non-perturbative *ab initio* theory for evaluating electron transfer cross sections from the individual subshells of multi-electron atoms by heavy projectile in the keV/amu to the MeV/amu energy region. By employing a two-state two-centre atomic eigenfunction expansion and an independent-electron approximation with a realistic Herman–Skillman potential for the target atom, we have calculated the charge transfer cross sections from the individual subshells of argon atoms by protons. The results for partial and total capture cross sections are compared with other theoretical calculations and experimental data. It is concluded that experimental partial capture cross sections from individual subshells are desirable for a more stringent test of the charge transfer theory.

Electron transfer is an important process in ion–atom collisions; it is fundamental to the understanding and the control of plasmas. Over the years experimentalists have studied the transfer of electrons in a variety of ion–atom collisions over a wide range of energies. A great deal of experimental data has been accumulated (Betz 1972, Tawara and Russek 1973), but the corresponding theoretical investigations have been scarce. Except at very low collision energies where the quasi-molecular approach is appropriate, there have been very few theoretical attempts to understand charge-exchange processes in the keV/amu to MeV/amu collision energy region for multi-electron ion–atom collisions.

Existing theoretical study of electron-transfer processes in the keV/amu to MeV/amu energy region for multi-electron ion–atom collisions (Mapleton 1968, Shevelko 1978) has been limited to the simple Oppenheimer (1928), Brinkman and Kramers (1930) (OBK) approximation. However, the validity of these calculations is questionable. Firstly, it has never been established that the OBK approximation is a valid first-order theory for charge transfer. (A more careful examination of the various first-order theories for charge transfer was given recently by Lin *et al* (1978).) Secondly, for most systems of practical interest the capture probabilities are not small and first-order perturbation theory is not expected to be valid.

According to the Massey's criterion, electron capture from an atomic subshell peaks at energies where the projectile velocity is nearly identical to the orbital velocity of the subshell. For a given multi-electron ion–atom collision, the electron transfer cross section is dominated by the capture from the outer subshell at low energies, but the contribution from inner subshells becomes more and more important with increasing energies. It is desirable to investigate, both theoretically and experimentally, the

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contribution of each individual subshell to the total electron capture cross section as a function of projectile's energies.

More elaborate theoretical studies of charge transfer in the keV/amu to MeV/amu energy region are available in the literature (Mapleton 1972, Bransden 1972, Basu *et al* 1978) for simple atomic systems based upon the atomic eigenfunction expansion method originally proposed by Bates (1958), but the generalisation of the method to multi-electron systems is hampered by two complications. Firstly, the region of validity of the method is not well established: for the simple p–H collision system, it has been shown that the convergence of the expansion with respect to the number of atomic basis functions is slow and continuum functions have to be included. Since continuum functions are inconvenient to handle, Sturmian functions (Gallaher and Wilet 1968, Shakeshaft 1976) and pseudo-states (Cheshire *et al* 1970) were introduced in the atomic basis expansion by earlier workers; however, these methods cannot be conveniently generalised to other systems. Secondly, for collisions like p + He, He^{2+} + He and He^{+} + He, atomic eigenfunctions including all the electrons in the collision systems are used in the expansion (Winter and Lin 1975). Generalisations of the method to multi-electron ion–atom collisions by including all the electrons in the collision system is obviously too complicated to study the general behaviour of electron transfer collisions.

Recently Lin *et al* (1978) have examined the region of validity of the truncated atomic-expansion method. It was concluded that the method is adequate for describing collisions at energies where the projectile velocity matches the orbital electron velocity, i.e. in the energy region where the non-resonant capture cross section peaks. By using an independent-electron approximation and a simple atomic Coulomb potential for K-shell electrons, the truncated two-state two-centre atomic-expansion method has been applied to calculate electron capture from the K shell of multi-electron atoms by protons and by other heavy bare projectiles. The results of these calculations are in harmony with experimental data in the energy region where the model is expected to be valid.

In this communication, we extend the atomic-expansion method to electron capture from outer subshells of multi-electron atoms for collision energies in the keV/amu to MeV/amu region. In order to describe the outer subshells properly within the independent-electron approximation, a realistic atomic potential for the multi-electron target atom has to be employed. Using a Hartree–Fock–Slater potential to describe the target atom, we compute electron transfer cross sections from the various subshells of Ar atoms within the two-state two-centre atomic-expansion method in an extended energy region. The total and partial electron transfer cross sections from individual subshells are computed. The total cross sections are shown to be in harmony with experimental data. The partial cross sections are presented for stimulating future experimental studies.

In the atomic-expansion method, the transfer of a single active electron e from the target A to the projectile B is treated mathematically by solving the time-dependent Schrödinger equation

$$\left(H_e - i\frac{\partial}{\partial t}\right)\psi(\boldsymbol{r}, t) = 0 \tag{1}$$

by expanding the electronic wavefunction $\psi(\boldsymbol{r}, t)$ in terms of travelling atomic eigenfunctions of the (A + e) and (B + e) systems. In the independent-electron approximation, the active electron is under the influence of the potential $V_A(r_A)$ before the capture

and of $V_B(r_B)$ after the capture, where $r_A(r_B)$ is the distance of the electron from the target (projectile); and the total electronic Hamiltonian of the active electron is approximated as

$$H_e = -\tfrac{1}{2}\nabla^2 + V_A(r_A) + V_B(r_B). \tag{2}$$

Atomic units are used in (1) and (2), and the rest of this paper. In the truncated two-state two-centre atomic-expansion method, $\psi(\boldsymbol{r}, t)$ is expressed as

$$\begin{aligned}\psi(\boldsymbol{r}, t) = {} & a(t)\phi_A(\boldsymbol{r}_A)\exp[-i(\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{r} + \tfrac{1}{8}v^2 t + \epsilon_A t)] \\ & + b(t)\phi_B(\boldsymbol{r}_B)\exp[-i(-\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{r} + \tfrac{1}{8}v^2 t + \epsilon_B t)]\end{aligned} \tag{3}$$

i.e. by expanding in terms of the initial state ϕ_A and the final state ϕ_B, where $\phi_A(\phi_B)$ is the atomic eigenstate of the electron in the potential $V_A(V_B)$, with eigenenergy $\epsilon_A(\epsilon_B)$; and $\boldsymbol{r}$ is the position of the electron measured with respect to the midpoint of the internuclear axis. The velocity-dependent phase factors in (3) are introduced to preserve translational invariance (Bates 1958). By substituting (3) into (1), a set of coupled equations for $\{a(t), b(t)\}$ are obtained. These equations are solved numerically for each impact parameter ρ and each impact energy E, with initial conditions $a(-\infty) = 1$ and $b(-\infty) = 0$; the capture probability for each impact parameter ρ is $P(\rho) = |b(+\infty)|^2$. The total single-electron capture cross sections from the two ns electrons, say, are obtained by

$$\sigma = 2\pi \int_0^\infty 2P(1-P)\rho \, d\rho.$$

In this initial study we investigate the charge transfer collisions of argon atoms with protons. Because the first ionisation energy of argon atoms (15·6 eV) is nearly in resonance with the ground-state binding energy of the hydrogen atom (13·6 eV), electron capture is dominated by the capture of outer-shell electrons of the target to the ground state of the projectile. Capture to excited states of the projectile is less probable because of larger energy defects. At higher collision energies, capture from inner subshells is expected to be more important, but capture to the excited states can again be neglected.

For protons colliding with multi-electron atoms, the potentials in (2) are chosen to be $V_B = -1/r_B$, $V_A = V_{HS}$, where V_{HS} is the numerical atomic Herman–Skillman (1963) potential for the target. This potential, which is identical to the Hartree–Fock–Slater potential with a cut-off introduced by Latter (1955), has been shown to be very useful in predicting the gross features of photoionisation cross sections of atoms. For the present study, it is inconvenient to use the numerical potential V_{HS} and numerical wavefunctions. We thus fit the numerical potential to an analytical form

$$V_{HS} = -\frac{1}{r}[1 + (Z-1)\,e^{-\lambda r}(1 + a_1 r + a_2 r^2 + a_3 r^3)] \tag{4}$$

where Z is the nuclear charge of the target. Except for the exponential damping term, this potential is similar to that used by McEnnan *et al* (1976), the damping term being needed to represent the large-r region properly. The form (4) is chosen mainly so that the matrix elements in the coupled equations can be reduced to a tractable one-dimensional numerical integration. Details of the numerical method will be presented elsewhere.

For bare projectiles, the basis functions ϕ_B and eigenenergy ϵ_B are exactly known, but ϕ_A and ϵ_A for the target have to be calculated from V_{HS}. To obtain ϕ_A and ϵ_A, we expand ϕ_A as

$$\phi_A = \sum_i c_i u_i \tag{5}$$

where $u_i = N_i r^{n_i - 1} e^{-\lambda_i r}$ are the Slater basis functions used in the analytic Hartree–Fock wavefunctions and the parameters are tabulated in Clementi and Roetti (1974). The coefficients c_i and eigenvalue ϵ_A are obtained by solving the Schrödinger equation with V_{HS} as given in (4). The coefficients c_i and eigenvalue ϵ_A are found to differ only slightly from the values given by Clementi and Roetti (1974).

The results for the theoretical electron capture cross sections from the various subshells of Ar atoms by protons are shown in figure 1. Also shown are the available experimental data. The theoretical values are the calculated capture cross sections from the subshells of Ar atoms to the final 1s state of hydrogen atoms. For the capture from np ($n = 2, 3$) subshells, two-state calculations have been done separately for np_x and np_z states (the y axis is chosen to be perpendicular to the collision plane and the z axis is along the direction of the velocity vector v; thus there is no np_y state contribution) at each E and ρ, and the two results are added to give the np capture cross sections. In figure 1 the experimental total capture cross sections (Tawara and

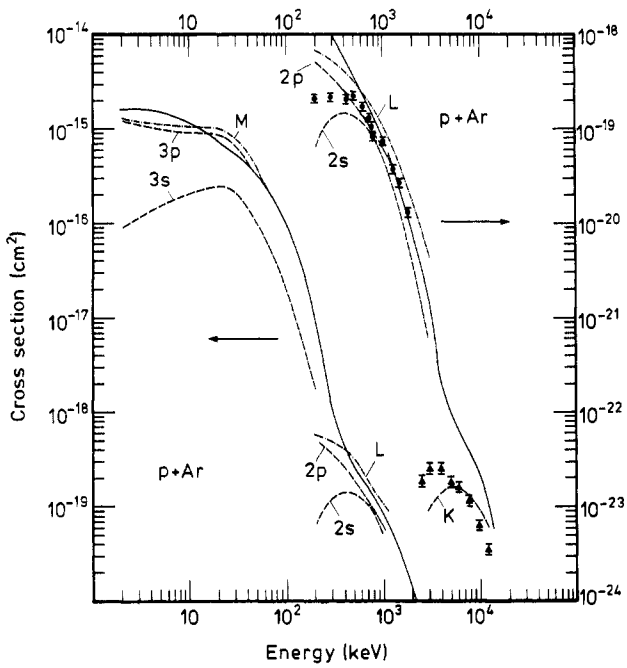

Figure 1. Total and partial electron capture cross sections of argon by protons. The total experimental cross sections, shown as full curves, are obtained from the compilation of Tawara and Russek. Calculated partial capture cross sections from each subshell are shown by broken curves. The total theoretical M- and L-shell cross sections are shown as chain curves. Experimental L- and K-shell capture cross sections are from Rødbro *et al* (1979) and Macdonald *et al* (1974), respectively.

Russek 1973) are shown in a full curve for proton energies ranging from 2 keV to 12 MeV where the capture cross section drops from 10^{-15} to 10^{-24} cm^2.

In comparing the total electron capture cross sections, we note from figure 1 that over the energy region 2 keV $< E <$ 200 keV, the total capture is dominated by the transfer of electrons from the M shell. The agreement between theoretical and experimental values is good, though the shape at lower energies is not very well reproduced. We have calculated both the M-shell and L-shell capture cross sections at $E = 200$ keV. At this energy, the M-shell capture cross section is still an order of magnitude greater than the calculated L-shell capture cross section. However, at the next calculated energy point $E = 400$ keV, L-shell capture becomes important. In the energy region from 400 keV to 12 MeV, capture from the L shell dominates the total capture cross sections even in the energy region where the K-shell capture cross section peaks (~6 MeV); however we expect that K-shell capture will eventually take over at higher energies. In figure 1, we also show the calculated L-shell capture cross sections in the energy region from 200 keV to 3 MeV. The L-shell capture cross sections do not reproduce the total capture cross sections in the 300–500 keV region. However, if the M-shell contribution (obtained by extrapolation from the calculations at $E < 200$ keV) is added to the L-shell values, then there is good agreement between theoretical and experimental *total* cross sections. However, the theoretical L-shell capture cross sections at $E = 3$ MeV appear to be too high, a feature which can probably be attributed to the breakdown of the present model at high energies.

There are no experimental partial 3s- and 3p-subshell capture cross sections for comparison with the present calculations. In the calculation shown in figure 1, there is no inter-shell correlation included in the theoretical method, but the importance of inter-shell correlation for Ar 3s subshell is well recognised from the photoionisation studies (Lin 1974, Amusia and Cherepkov 1975), where the 3s partial photoionisation cross sections are shown to behave *qualitatively* differently if the inter-shell correlation (with the 3p subshell) is included—as confirmed by experiments. It is interesting to see if the experimental 3s capture cross sections show any qualitative deviation from the prediction of figure 1, thus permitting us to assess the importance of many-electron correlation effects in electron capture. For the capture from the L shell, there are some experimental data from Rødbro *et al* (1979) in the energy region 200 keV–2·0 MeV. The agreement between the calculations and their data is reasonable at higher energies, though there is about a factor of two discrepancy at lower energies. For the capture from the K shell, there are experimental data from Macdonald *et al* (1974) for comparison. The theoretical values given in the figure are calculated using V_{HS}; they differ only slightly (less than 20%) from the previous calculations (Lin *et al* 1978) where a Coulomb potential was used. There is still a noticeable discrepancy between the theory and experiment in the low-energy region. This discrepancy could be due to the inter-shell coupling; it could also be due to the inadequacy of the two-state atomic-expansion method for very asymmetric collisions. Further investigations have to be done to resolve the origin of this difference.

In figure 1 we did not extend the M-shell capture calculations beyond 200 keV, nor beyond 3 MeV for the L-shell capture calculations. It is known that the two-state approximation is not adequate for capture at higher velocities (in comparison with the orbital electron velocity before the capture). In the higher energy region, the continuum distorted-wave approximation is probably more suitable (Belkic *et al* 1979).

We also mention that capture of electrons from the L and K shells of argon by protons has been investigated recently by Ford *et al* (1979a, b) using an atomic

eigenfunction expansion centred around the target atom. Because the expansion is around the target atom only, a large basis set is needed in order to achieve comparable accuracy as compared with our two-state two-centre atomic-expansion method.

In conclusion, we have performed some initial investigations of electron capture cross sections from the subshells of argon atoms by protons. The gross feature of total experimental capture cross sections is well reproduced by the present theoretical model. Experimental partial capture cross sections are desirable for a more detailed assessment of the theoretical collision model and of the importance of intershell electron correlation for charge transfer processes.

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