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LETTER TO THE EDITOR

Electron capture for ion–atom collisions at intermediate energies†

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Abstract. A simple two-state two-centre atomic expansion method is introduced to obtain electron-capture cross sections for ion–atom collisions at intermediate energies where the projectile velocity is comparable to the characteristic orbital velocity of the electrons. The non-perturbative *ab initio* theory is shown to be capable of predicting inner-shell electron-capture cross sections in accord with experiments. No semi-empirical corrections are required in the present approach. The region of validity of the method is also discussed.

The transfer of bound electrons from target atoms to heavy projectiles is an important process for inner-shell vacancy production during ion–atom collisions, particularly in the case of highly charged incident ions (Richard 1975).

For collisions in which the velocity of the projectile V_p is much smaller than the characteristic orbital velocity V_{el} of the active electron, considerable understanding of the electron-transfer mechanism has been achieved in the past decade based upon the molecular orbital (MO) model (Fano and Lichten 1965). Recently, the MO model has been applied (Briggs and Macek 1972, Briggs 1976, Taulbjerg *et al* 1976) in the calculation of K-shell vacancy production cross sections in symmetric and near symmetric ion–atom collisions. For slow collisions ($V_p \ll V_{el}$), their calculations are in good accord with experimental results. For collisions at higher velocities $V_p \gtrsim V_{el}$, the basic assumption of the MO model that the collision complex forms a quasi-molecule is no longer valid. In particular, the transfer of an L vacancy to K vacancy will no longer be dominated by the $2p\pi$–$2p\sigma$ rotational coupling; at higher collision energies vacancy transfer through a direct Coulomb ionisation mechanism is more important (Fastrup *et al* 1974).

For direct excitations and ionisations at high energies, it is well known that the predictions of the plane-wave Born approximation (PWBA) and its variants are in good agreement with experiments, particularly when the binding-energy correction is included (Basbas *et al* 1973). The problem of charge transfer is, however, not adequately described by the PWBA. This inadequacy is twofold. On the one hand, it has been shown that the second Born term dominates the first Born term at high energies (Bransden 1972, Mapleton 1972). On the other hand, because of the non-orthogonality of initial and final states, there is no unique form of the first

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Born theory in the case of charge transfer and the different forms give different results.

Disregarding the question of the validity of the first Born theory, a straightforward derivation of the plane-wave first Born amplitude for charge transfer involves an internuclear potential. For direct process, the internuclear potential does not contribute to the transition amplitude. In the charge-transfer problem, however, the internuclear term provides a non-zero contribution. This undesirable feature led to the OBK approximation (Oppenheimer 1928, Brinkman and Kramers 1930) in which the internuclear potential is not included in the first Born amplitude. On the other hand, others (Bates and Dalgarno 1952, Jackson and Schiff 1953) argued in favour of retaining it.

By treating the non-orthogonality of the initial and final states appropriately, it has been shown (Bates 1958) that an additional term due to orthogonalisation is introduced into the usual first Born transition amplitude. This term resembles the internuclear interaction potential for the proton–hydrogen-atom system, but as shown elsewhere (Lin *et al* 1978) this term takes the form Z_B/R asymptotically at large R rather than the form of the internuclear potential $Z_A Z_B/R$, where Z_A and Z_B are the charges of the target nucleus and the projectile, respectively, and R is the internuclear separation. In the last few years, it becomes apparent that a straightforward generalisation of the Jackson–Schiff approximation gives unphysical results if the full internuclear potential is included in calculating the electron-capture cross sections from multi-electron atoms (Halpern and Law 1975, Band 1976). On the other hand, calculations of capture cross sections based upon orthogonalising the final state to the initial state are in much better agreement with experiments than the OBK or the Jackson–Schiff approximations.

For highly charged incident heavy ions, the electron-capture cross sections are large when the projectile velocity is near the characteristic orbital velocity of the electrons to be captured. In particular, the capture process dominates over the direct ionisation process for target vacancy production for near symmetric systems. For these systems, the perturbation theory is not likely to work because of the large capture probabilities. Nevertheless, the OBK approximation has been widely used in the literature to 'explain' experimental results. Often a semi-empirical correction (Lapicki and Losonsky 1976) has to be introduced into the theoretical calculations in order to achieve any reasonable comparison.

In this letter, we show that the two-centre atomic expansion method originally proposed by Bates can predict accurate electron-capture cross sections for fast ion–atom collisions in the energy region where $V_p \simeq V_{el}$. We will point out that while it is still impossible to give a simple theoretical description for electron capture at high energies ($V_p \gg V_{el}$) (Belkić and McCarroll 1976), the medium energy region ($V_p \simeq V_{el}$), where the capture cross sections peaks, can be easily obtained with reasonable accuracy.

We will employ the single-electron approximation by considering the active electron to be captured only. The active electron is treated as moving in a two-centre nuclear field with effective charges Z_A of the target and Z_B of the projectile. The wavefunction $\Psi(r, t)$ of the active electron satisfies the time-dependent Schrödinger equation,

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

where

$$H_e = -\tfrac{1}{2}\nabla_r^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B}. \tag{2}$$

(Atomic units are used in this paper unless otherwise indicated.)

In equation (2), r_A, r_B and r are the distances of the electron from the target, the projectile and the midpoint of the internuclear axis. To solve equation (1), we expand $\Psi(r, t)$ in terms of travelling atomic basis functions of the target and the projectile. By making a truncated expansion, we write

$$\Psi(r, t) = a(t)\psi_A(r_A)\exp[-i(\tfrac{1}{2}v.r + \tfrac{1}{8}v^2t + E_A t)] + b(t)\psi_B(r_B)\exp[-i(-\tfrac{1}{2}v.r + \tfrac{1}{8}v^2t + E_B t)] \tag{3}$$

where $\psi_A(\psi_B)$ is the eigenfunction of the active electron in the initial(final) state with energy $E_A(E_B)$. The velocity-dependent phase factors are introduced into equation (3) to ensure translational invariance.

By substituting equation (3) into equation (1), a set of coupled first-order differential equations for $a(t)$ and $b(t)$ are obtained. By solving these equations numerically for each energy E and each impact parameter ρ, the probability $P(\rho)$ for capture is $P(\rho) = |b(+\infty)|^2$. The total capture cross section per target electron is obtained from

$$\sigma = 2\pi \int_0^\infty \rho P(\rho)\, d\rho. \tag{4}$$

We have applied this method to compute the total capture cross sections for several ion–atom collisions, with the results shown in table 1. In table 1, we list the calculated K-shell electron-capture cross sections per electron from the K shell of the target. The experimental data are deduced from several sources (Woods *et al* 1976, Winters *et al* 1973†, Hopkins *et al* 1976a,b), either using $\frac{1}{2}(\sigma^0 - \sigma^2)$ or $\sigma^0 - \sigma^1$, where σ^0, σ^1 and σ^2 are the measured *total ionisation* cross sections of the target atoms due to a bare nucleus, hydrogen-like and helium-like projectiles at the same energies. Thus, direct Coulomb ionisation cross sections and capture cross sections to excited states of the projectiles are subtracted from the total cross sections in this technique. The errors introduced by this approximation is not significant since direct Coulomb ionisation cross sections are much smaller compared with the capture cross sections for projectiles with K-shell vacancies, particularly for nearly symmetric systems.

In this calculation, the effective charge Z_B for the projectile is the charge for the bare nucleus, the effective charge Z_A for the target is chosen to be $Z_A = Z - \frac{5}{16}$, where Z is the charge of the target nucleus. The experimental K-shell ionisation energy is used for E_A and $E_B = -\frac{1}{2}Z_B^2$. By choosing the experimental energy E_A and charge Z_A separately, the unitarity condition of the two-state calculation is not enforced.

In table 1, we see that the calculated and experimental capture cross sections are in very good agreement for the systems we have studied. This agreement is satisfactory in view of the simplicity of the present approach. It is appropriate to comment on other *ab initio* calculations in comparison with the present one. For example, the OBK results for the systems considered in table 1 are usually about ten times

† All values multiplied by 1·34 on recommendation by JRM due to normalisation error.

Table 1. K–K electron-capture cross sections per target electron (in 10^{-20} cm^2). Experimental data are obtained from $\frac{1}{2}(\sigma^0 - \sigma^2)$ except the one indicated by an asterisk which is obtained from $(\sigma^1 - \sigma^2)$.

Projectile + target	Energy (MeV)	V/V_K†	σ_{CAL}	σ_{EXP}‡
N^{7+} + Ne	14	0·79	368	355[a]
	19	0·92	343	350
O^{8+} + Ne	24	0·96	368	435
	30	1·08	269	330
	35	1·17	195	300*
F^{9+} + Ne	20	0·81	516	440
	25	0·90	440	430
	30	1·00	360	410
C^{6+} + Ar	12·6	0·42	1·30	1·79[b]
	19·0	0·52	2·52	2·34
	22·6	0·57	5·40	5·83
N^{7+} + Ar	14·7	0·42	5·1	3·2
	26·3	0·56	12·6	13·2
F^{9+} + Ar	20	0·42	25·2	9·7[c]
	30	0·52	32·4	29·0
	36	0·57	45·6	30·4
	46	0·64	52·8	47·7
	56	0·71	48·8	53·6
	66	0·77	40·8	48·8
	76	0·82	39·6	44·3
F^{9+} + Kr	46	0·30	7·4 (−2)	1·0 (−2)
	56	0·33	7·9 (−2)	3·7 (−2)
	66	0·36	7·5 (−2)	6·4 (−2)
	76	0·39	6·8 (−2)	6·1 (−2)
Cl^{17+} + Kr	100	0·33	1·55	0·60[d]
	120	0·36	1·40	1·15
	140	0·39	1·62	1·90
	160	0·42	2·50	2·8

[a] Woods *et al* (1976).
[b] Winters *et al* (1973).
[c] Hopkins *et al* (1976a).
[d] Hopkins *et al* (1976b).
† Projectile velocity with respect to the orbital velocity of the K-shell electron defined by $V_K = \sqrt{2I_K}$, where I_K is the K-shell ionisation energy of the target.
‡ Typical experimental uncertainty is of the order of 20%.

too large, while the Jackson–Schiff method for these systems are usually a few hundred times too large (Halpern and Law 1975, Band 1976). Although the approach introduced by Lapicki and Losonsky (1977) is also capable of obtaining cross sections in reasonable agreement with experimental data, it involves semi-empirical corrections. It is to be emphasised that the capture probabilities for the systems considered in table 1 are quite large and the validity of applying the above-mentioned first-order theories is doubtful.

It is important to discuss the expected region of validity of the present approach. The first approximation lies in the adoption of a single-electron approximation to

a multi-electron problem. In equation (1), the effect of the passive electrons is completely neglected except for the use of screened charge. This approximation is consistent with the simplest MO model in which the promoted electron is assumed to be in the field of two bare nuclei. Improvement within the single-particle model by using the Thomas–Fermi potential or more sophisticated ones is underway but requires further numerical development. The second approximation is the truncated solution of equation (1) using only the two-state atomic expansion method. It is well known that an expansion using a molecular basis set is appropriate for low-energy collisions. However, it is less clear what is the region of validity of the two-state atomic expansion method. We point out here that the two-state atomic expansion method for electron capture is suitable when $V_p \simeq V_{el}$. According to the Massey criterion, this is the region where the capture cross section peaks for asymmetric systems. In this energy region the capture occurs primarily at an impact parameter near the characteristic orbital radius of the electron or greater. It is quite clear that the distortion of the electron at such internuclear separations R can be reasonably represented by the two-state atomic expansion. This can be easily seen by comparing the molecular potential curves calculated by the two-state LCAO and other accurate methods. By choosing a travelling atomic basic set, on the other hand, the translational factors are easily included. From this discussion it is evident that the present model is not sufficient for scattering occurring at small impact parameters. Thus, if the capture occurs primarily at small impact parameters, the calculated total capture cross sections by the present method will not be adequate. Thus, our model is not expected to be valid for $V_p \gg V_{el}$ since capture by fast projectiles occur near the target nucleus. For $V_p \ll V_{el}$, the probability $P(\rho)$ usually oscillates violently with ρ (Winter and Lane 1978) and the calculation is very sensitive to the accurate representation of the distortion at small R. There are clear indications in table 1 that the computed capture cross sections depart from experimental data for small V_p/V_{el}.

In conclusion, we show that electron capture cross sections for ion–atom collisions at intermediate energies ($V_p \sim V_{el}$) can be obtained by the simple two-state atomic expansion method with reasonable accuracy. The validity region of the model is also discussed.

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