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LETTER TO THE EDITOR

Coupled-subshell approximation for L-shell ionisation

P A Amundsen†§ and D H Jakubaßa-Amundsen‡§

† Physik Department T30, Technische Universität München, D-8046 Garching, West Germany

‡ Sektion Physik, Universität München, Am Coulombwall 1, D-8046 Garching, West Germany

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Abstract. The ionisation probability for target L subshells by light ion impact is calculated in the semiclassical approximation, including the couplings between the subshells during the collision. The inclusion of these couplings is found to modify the subshell occupation numbers only slightly for proton and alpha particle impact on heavy target atoms, but a marked effect is found for heavier projectiles. Numerical results for the systems He+Pt, Ne+Pt and Ne+Yb are presented.

There is in general quite satisfactory agreement between perturbation theory and experiments for inner-shell ionisation in very asymmetric ion-atom collisions (see e.g. the contributions in Paul 1982). However, when one considers L-subshell ionisation, some significant discrepancies have persisted since the first cross section measurements were reported, in particular at very low collision energies (Datz *et al* 1974, Chang *et al* 1975). Introducing a relativistic electron description, using united-atom (UA) binding energies and wavefunctions and corrections for projectile Coulomb deflection only marginally improves the situation (Amundsen 1977, Aashamar and Amundsen 1982). It was unclear, however, for a long time to what extent these discrepancies are spurious, in the sense that they arise from errors in the values of the fluorescence yields and Coster-Kronig ratios used to convert measured x-ray intensities into subshell ionisation cross sections. Recent accurate measurements of the radiative and radiationless yields for Au (Jitschin *et al* 1985) have indeed given results significantly different from those recommended by Krause (1979), but, as these authors note, it does not explain all the differences between theory and experiment for ionisation. Such discrepancies also appear in some of the recent measurements of impact-parameter-dependent ionisation probabilities, $P(b)$ (Dexheimer *et al* 1986, Zehender *et al* 1986).

A widely accepted explanation for the disagreements between theory and experiment is that perturbation theory is inadequate even in rather asymmetric collisions. This effect was first studied quantitatively by Sarkadi and Mukoyama (1981) for systems like C+Au in a simple two-step model, treating ionisation and subshell couplings as independent processes. This two-step model has subsequently been refined (Fink *et al* 1983, Sarkadi and Mukoyama 1984, Sarkadi 1986a). Full coupled-channel calculations, including the continuum, have been reported by Martir *et al* (1982), using pseudostates for the continuum, and Mehler *et al* (1987), using wavepackets. However, for very asymmetric collisions, where the total L-shell ionisation probabilities are well

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reproduced by perturbation theory, it is hard to see how couplings in the continuum can be crucial for predicting the subshell vacancy production. Indeed, Mehler *et al* (1987) report that these couplings may change the calculated $P(b)$ by about 20% for such systems. It should thus be fairly accurate to treat the couplings *between* the subshells in a close-coupling approach, while calculating the coupling to the continuum in perturbation theory, thus avoiding the numerical intricacies of the continuum–continuum couplings. Such an approximation is of course only tenable for collision systems asymmetric enough so that no quasimolecular orbital correlating to the projectile interacts with those correlating to the target L shell.

The first calculations based on this idea, which we shall refer to as 'the coupled subshell approximation' (CSA), were reported by Spies *et al* (1984) for the L-shell alignment parameter A_{20} at fixed δ-electron momentum. Kocbach (1984), reporting on a model calculation with three bound and one continuum states, has suggested the name 'generalised distortion approximation' for this kind of approach. Subsequently, Sarkadi (1986b) (see also Sarkadi and Mukoyama 1987) has performed calculations of the L-vacancy production probability with non-relativistic wavefunctions, but with the bound–continuum matrix elements approximated by their $E_f = 0$ values, E_f being the δ-electron kinetic energy, restricted to multipole components with $l = 0$ and 1 in the final state. Berinde *et al* (1985) have reported a close-coupling calculation of A_{20} using a UA basis; however, the ionisation was assumed to take place suddenly at the turning point of the classical trajectory, providing the starting amplitudes for the coupled-channel calculations.

In this letter we report improvements of these approximations by using target (separated-atom) hydrogenic Dirac wavefunctions, including multipole transitions up to $l = 2$ with arbitrary electron final states. Since we consider an initially full shell, it is most convenient to regard vacancies instead of electrons as the active particles in the collision. Thus ionisation is described as capture of a vacancy from the continuum, and we denote by $a_n(t)$ the amplitude for the presence of a single vacancy in the target eigenstate $|n\rangle$, where n comprises the angular quantum numbers $\{j_n, l_n, m_n\}$ of the L shell. In the independent-particle approximation used, the energy of the state $|n\rangle$, E_n, is minus the energy of the corresponding electron state, up to a total energy which is irrelevant for our purpose. The scattering wavefunction is expanded in the subspace $\{n, f\}$, where $\{|f\rangle\}$ are the (energy normalised) continuum states, as follows (atomic units are used unless otherwise indicated):

$$\psi(t) = \sum_{n=1}^{8} a_n(t)|n\rangle + \sum_f a_f(t)|f\rangle. \tag{1}$$

Inserting this into the Dirac equation and neglecting the vector potential leads to the usual coupled equations for the amplitudes. If the couplings to the continuum are treated in first order, which means that the continuum–continuum couplings and the back-coupling from the continuum to the L shell are neglected, the equations for the amplitude a_n in the presence of an initial 'vacancy' in the continuum state $|f\rangle$ reduce to:

$$\begin{aligned} &\dot{a}_n = -\mathrm{i}a_n E_n - i\sum_k a_k M_{nk} - \mathrm{i}M_{nf}\exp(-\mathrm{i}E_f t) \qquad a_n(t\to-\infty)\to 0 \\ &M_{nk} = \langle n|(V_\mathrm{P} + V_\mathrm{R})|k\rangle \\ &V_\mathrm{P} = -\frac{Z_\mathrm{P}}{|\boldsymbol{r}-\boldsymbol{R}|} \qquad V_\mathrm{R} = -\frac{\mu}{M_\mathrm{T}}(1-\delta m)\boldsymbol{r}\cdot\ddot{\boldsymbol{R}} \end{aligned} \tag{2}$$

$$\mu^{-1} = M_P^{-1} + M_T^{-1}$$

where $\boldsymbol{R}$ is the internuclear distance, Z_P and Z_T (M_P and M_T) are the projectile and target charges (masses), respectively, and V_R is the recoil potential arising because the target centred coordinate system used is not inertial, δm being a relativistic mass correction (Amundsen 1978). It is seen that the couplings to the continuum give rise to a source term in the conventional close-coupling equations. Keeping in mind that for fermions the matrix elements of an operator between vacancy states are minus the complex conjugate of the matrix element between the corresponding particle states (again up to an irrelevant total energy), one sees that a_n is just the complex conjugate of the amplitude for ionisation of a single electron in the electron state $|n\rangle$. Thus, in particular, if M_{nk} is set to zero, equation (2) just reproduces the SCA amplitude. The neglect of the back-couplings from the continuum is physically motivated by the fact that once an electron has been ionised, it is unlikely to recombine again with the original atom.

Making a multipole expansion of the potential:

$$V(\boldsymbol{r}, \boldsymbol{R}) = \sum_{l,m} V_l(r, R)\, Y_{lm}(\hat{\boldsymbol{r}})\, Y^*_{lm}(\hat{\boldsymbol{R}}) \tag{3}$$

and taking the internuclear motion to be in the xz plane (so that $Y_{lm}(\hat{\boldsymbol{R}})$ is real), with the z axis as the quantisation axis along the incoming beam direction, the matrix elements are:

$$M_{nk} = \sum_{l,m} Y^*_{lm}(\hat{\boldsymbol{R}}) \langle j_n l_n m_n | Y_{lm} | j_k l_k m_k \rangle \langle V_l \rangle_{nk} \tag{4}$$

where $\langle V_l \rangle_{nk}$ denotes the radial matrix element. For hydrogenic Dirac wavefunctions, the latter can be expressed explicitly in terms of incomplete gamma functions for the bound-bound transitions, while for the bound-continuum matrix elements we have:

$$\begin{aligned} \langle V_l \rangle_{nf} = -\frac{4\pi Z_P}{2l+1} \Bigg[\left(1 + \delta_{l1} \frac{Z_T}{M_T}(1-\delta m)\right) \frac{1}{R^{l+1}} \int_0^\infty \mathrm{d}r\, r^{l+2} G_{nf}(r) \\ + \int_R^\infty r^2 \mathrm{d}r \left(\frac{R^l}{r^{l+1}} - \frac{r^l}{R^{l+1}} \right) G_{nf}(r) \Bigg] \\ G_{nf}(r) = g^*_n(r) g_f(r) + f^*_n(r) f_f(r) \end{aligned} \tag{5}$$

where g_n and f_n are the large and small components of the Dirac wavefunction. The term with δ_{l1} comes from the recoil. The first of these integrals can again be done analytically, while the second one is evaluated numerically.

The matrix elements obey a symmetry relation with respect to the magnetic quantum number m_n:

$$M_{nk}(-m_n, -m_k) = (-1)^{j_n + l_n + m_n} (-1)^{j_k + l_k + m_k} M_{nk}(m_n, m_k). \tag{6}$$

Recalling that the amplitudes a_n depend on $|f\rangle$ through the source term, one finds that this expression also holds for $a_n(-m_n, -m_f)$, with the subscript k replaced by f. Introducing the linear combinations

$$\alpha_n^{(=)} = a_n \pm i(-1)^{j_n + l_n - m_n} a_{\tilde{n}} \qquad \tilde{n} = \{j_n, l_n, -m_n\} \tag{7}$$

and exploiting equation (6), the original 8×8 (complex) system (2) decouples in two 4×4 systems for $\alpha_n^{(+)}$ and $\alpha_n^{(-)}$, respectively. The probability of a vacancy in the state $|n\rangle$ at time t is then

$$P_n(b) = \tfrac{1}{2} \int_0^\infty \mathrm{d}E_f \sum_{j_f, l_f} \sum_{m_f > 0} \left(|\alpha_n^{(+)}|^2 + |\alpha_n^{(-)}|^2 \right) \tag{8}$$

where the sums over the angular momentum quantum numbers are restricted by the selection rules. The internuclear path is taken to be a Rutherford trajectory of impact parameter b. In the calculations we have included all transitions with $l \leq 2$, which means that for each of the altogether 11–15 values of E_f, 16 final states are included.

We have made calculations for some very asymmetric systems, including p + Au, α + Pt and α + Dy. In figure 1 we show $P_{L_i}(b)$ for the L subshells for 0.9 MeV amu^{-1} α + Pt, comparing it with the experimental results of Dexheimer *et al* (1986). Also shown are perturbative results, using UA wavefunctions and binding energies, as is customary at these low collision energies. It is seen that in general the CSA and the SCA results agree quite closely in shape. An interesting feature of this figure is the enhanced CSA probability for L_2-shell ionisation at small b, and it is also evident that outside the L-shell radius (1350 fm), the CSA results for the L_3 shell agree significantly better with the experiments—as might be expected, since the UA approximation is certainly not valid at large impact parameters. As for the discrepancies between theory and experiment for the L_1 shell at large b, we note that $P_{L_1}(b)$ is very small compared with $P_{L_3}(b)$, so that the experimental analysis is extremely difficult.

For total subshell cross sections, σ_{L_i}, we find the difference in $\sigma_{L_1}/\sigma_{L_3}$ between the CSA and the SCA to be very small at all collision energies for these systems. The same is true for $\sigma_{L_2}/\sigma_{L_3}$ for collision velocities $v/Z_T > 0.08$ (about 1 MeV amu^{-1} for a gold target). However, in slower collisions the CSA results become noticeably larger than those of the SCA, improving the agreement with the trend of the experimental results,

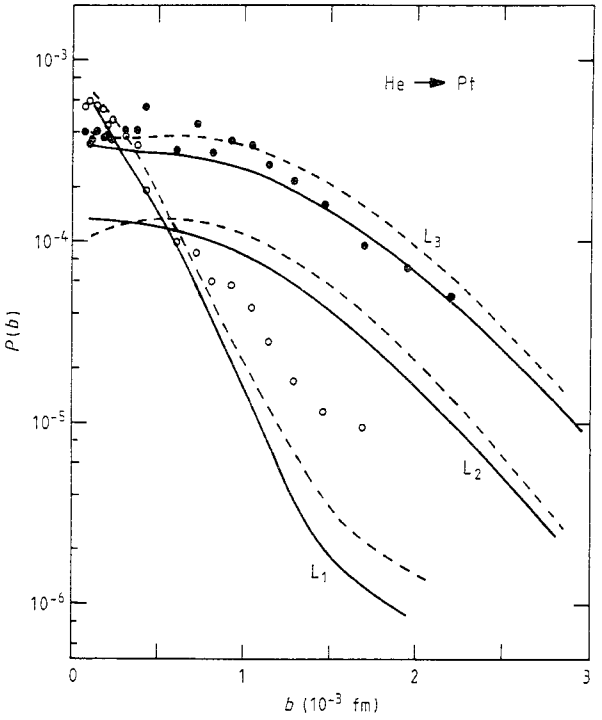

Figure 1. L-subshell ionisation probabilities as functions of impact parameter for 0.9 MeV amu^{-1} α + Pt. Full curves: CSA results. Broken curves: UA SCA results. Experimental points for the L_1 shell (open circles) and L_3 shell (full circles) from Dexheimer *et al* (1986).

as compiled by Jitschin *et al* (1982, 1985). Thus, for sufficiently slow collisions, there is even in the most asymmetric systems a non-negligible transfer of vacancies to the L_2 shell, predominantly from the L_3 shell. That this coupling, which is purely quadrupole, is important only in very slow collisions is a simple consequence of the fact that the subshell energy differences for heavy atoms are typically some 10% of the corresponding binding energies. According to the Massey criterion, a coupling is most efficient at velocities $v_m = \Delta E / v_e$, v_e being the velocity of the active electron, so that for the present systems the maximum intrashell transition probabilities peak at a velocity of about 10% of v_m for the ionisation process itself.

For more symmetric collision systems, $Z_P \geqslant 10$, UA perturbation theory fails completely for the L subshells (Jitschin *et al* 1983, Berinde *et al* 1985, Dexheimer *et al* 1986). Thus, for the system 0.9 MeV amu^{-1} Ne+Pt, $P_{L_1}(b)$ and $P_{L_3}(b)$ do not experimentally cross at small b, as they do for the analogous system α+Pt (Dexheimer *et al* 1986), while the SCA predictions for the two systems are essentially the same, up to a total normalisation factor. In figure 2 we compare the CSA results with the SCA and the experiments. We see that the CSA reproduces the relative shapes of the impact parameter distributions better than the SCA, both at small b (no crossing of the curves) and at large b (the slopes are much better reproduced). This results in an improved

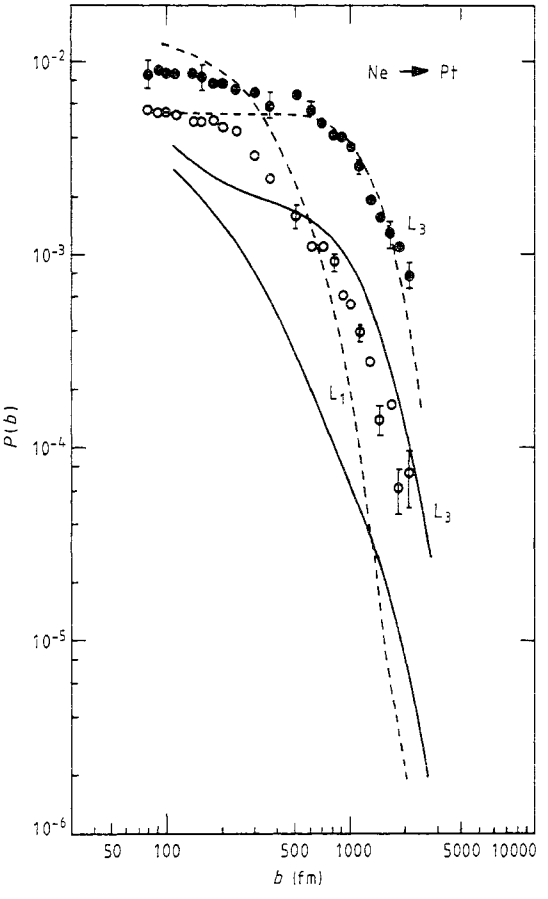

Figure 2. Same as in figure 1, but for 0.9 MeV amu^{-1} Ne+Pt.

ratio $\sigma_{L_1}/\sigma_{L_3}$ as compared with the SCA (figure 3(*a*)). The same is true for the even more symmetric system Ne+Yb (figure 3(*b*)). However, as far as the absolute magnitude of the measured ionisation cross sections is concerned, the CSA seriously underestimates the experimental results, in contrast to the SCA (see figure 2). Interestingly enough, this is not only true for the CSA but also for the more sophisticated continuum coupled-channel calculations of Mehler *et al* (Soff 1987). On the other hand, our results significantly improve upon the simplified CSA calculations recently reported by Sarkadi and Mukoyama (1987).

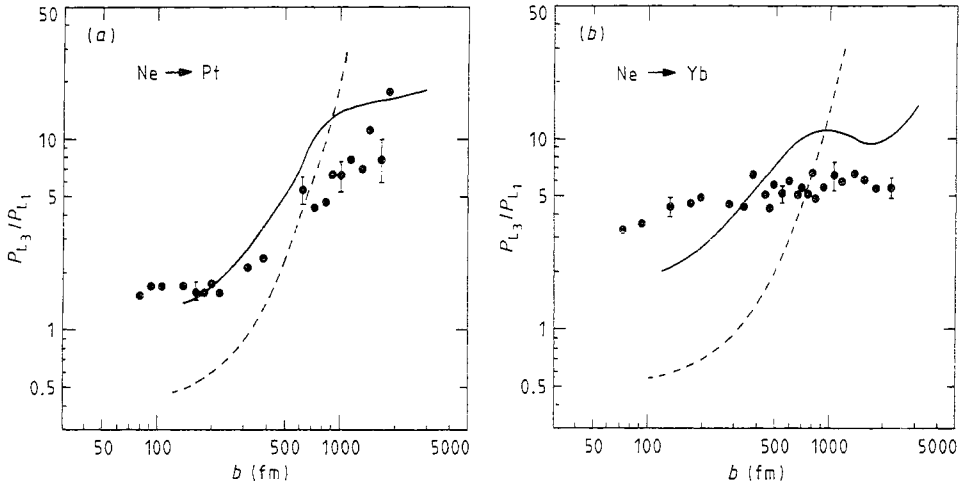

Figure 3. Impact parameter dependence of the ionisation probability ratio $P_{L_1}(b)/P_{L_3}(b)$ for an energy of 0.9 MeV amu^{-1} for (*a*) Ne+Pt and (*b*) Ne+Yb. Full curve, CSA; broken curve, SCA. Experimental results from Dexheimer *et al* (1986).

In conclusion, the simple CSA scheme reproduces results of more complex continuum coupled-channel calculations quite well, and improves significantly upon the SCA for predicting relative L-subshell cross sections. However, the large discrepancies in absolute magnitude between the experimental and all theoretical results for the ionisation probabilities in the less asymmetric collision systems remain a challenge.

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