The effect of electron correlations on the polarization of atomic line radiation excited by electron impact

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The effect of long-range electron correlations on the polarisation of atomic line radiation, excited by electron impact

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Abstract. The polarisation of atomic spectral lines, excited by electron impact, shows in some cases an anomalous behaviour near threshold. It is suggested that this anomaly may be caused by the influence of electron correlation effects similar to those which give rise to specific threshold laws for electron impact ionisation. Both model calculations and experiments have been performed which tend to support the proposed model.

1. Introduction

The polarisation of atomic spectral lines, excited by electrons, shows in some cases an anomalous behaviour near threshold. This anomaly was first observed more than 50 years ago (Skinner and Appleyard 1927) and still has not yet been explained satisfactorily. In the case of helium, for instance, the polarisation of all spectral lines studied exhibits a large dip, which extends from threshold to about 5 eV above (see e.g. McFarland and Mittleman 1968). Theory provides clear predictions in two limiting cases: at high collision energies where the Born approximation is valid and at the threshold. In the latter case the polarisation can be calculated exactly using nothing but simple angular momentum considerations. At threshold the scattered electron has zero velocity and hence zero orbital angular momentum. Therefore, in the case of helium, only magnetic substates with $m = 0$ (quantisation axis along the incident beam) can be excited; and this determines the polarisation completely†. At high energies, where the Born approximation prevails, the polarisation is expected to decrease monotonically and to approach a constant value after a sign reversal at about ten times the threshold energy. This latter behaviour is reasonably well confirmed by the available experimental results. Interpolation between the theoretical results, valid in the two limits, would seem plausible, but leads to predictions which are in most cases in disagreement with experiment. The first experimental results on mercury (Skinner and Appleyard 1927) and helium (McFarland and Soltysik 1962) even seemed to indicate that the polarisation tends to zero when the incident electron energy is lowered to the threshold value. More refined experiments (McFarland 1964, Heddle and Keesing 1967, Heideman *et al*

† This is no longer true when spin-flip transitions can occur. However, in the case of helium such transitions are not expected to make any observable contribution to the polarisation (see McFarland and Mittleman 1968).

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1969) have shown that in fact after a gradual decrease the polarisation rises sharply again to a finite value at threshold; the rise being so fast that it escapes experimental detection when the resolution of the electron beam is worse than about 0·2 eV. For $^1D \rightarrow {}^1P$ transitions, for instance, the theoretical threshold polarisation amounts to 60%.

It is remarkable that the anomalous dip in the polarisation is not observed in the case of the alkali resonance lines (Hafner and Kleinpoppen 1967, Enemark and Gallagher 1972). For these lines the observed polarisation increases monotonically to the expected value when the incident electron energy is lowered from higher values to the excitation threshold. Figure 1 shows the results of Enemark and Gallagher (1972) for the polarisation of the $3p \rightarrow 3s$ resonance transition in sodium. A similar behaviour is observed for the resonance transitions in the two isotopes of lithium (Hafner and Kleinpoppen 1967). Also for the $(4s4p)^1P_1 \rightarrow (4s^2)^1S_0$ transition in the alkaline-earth atom calcium the measured polarisation rises very clearly to the theoretical value at threshold, although in this case a narrow structure is observed near 4·5 eV (Ehlers and Gallagher 1973). However, contrary to the broad dip in the case of helium and mercury, this structure is only a few tenths of an eV wide and does not extend beyond the ionisation threshold. It can be explained in a straightforward manner by resonance and cascade effects.

There have been several attempts to explain the observed threshold anomaly in the polarisation of helium and mercury lines. None of these is able to deal satisfactorily with the whole effect. There is of course no doubt that negative-ion resonances will contribute to the depression of the polarisation just above threshold. In the case of a resonance, higher partial waves with $l \geq 1$ (depending on the angular momentum of the intermediate state) may make large contributions to the excitation cross section even if the excess energy of the scattered electron is very small. As a result, excitation of

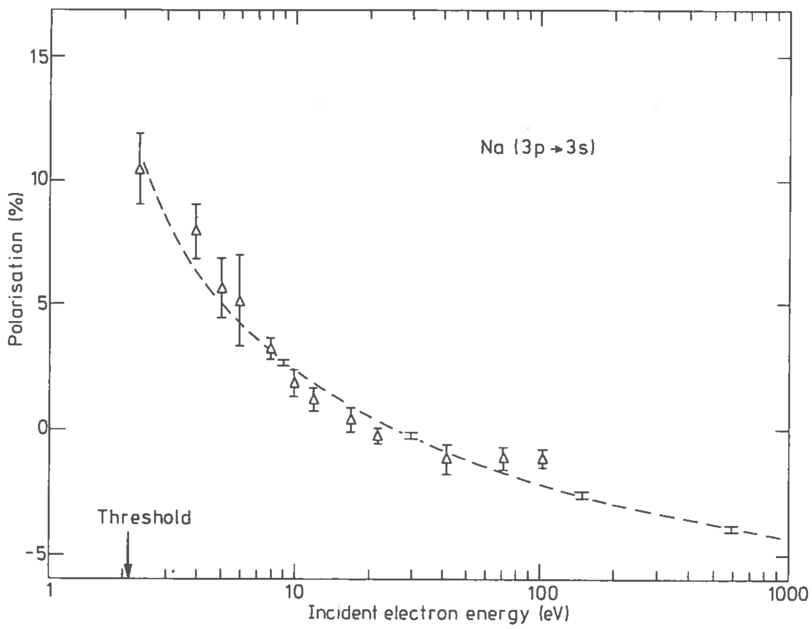

Figure 1. Measured polarisation of the $3p \rightarrow 3s$ transition in sodium as a function of the incident electron energy. $\overline{\Delta}$: Gould (1970); --I--: Enemark and Gallagher (1972).

magnetic substates with $m = \pm 1$ or ± 2 can be quite likely near threshold and the polarisation may deviate appreciably from the value at threshold, where only $m = 0$ excitation is possible. That resonances do play an important role has been confirmed by the observations of narrow structures near threshold in the polarisation curves of various transitions (Heideman *et al* 1969, Heddle *et al* 1974, Ottley and Kleinpoppen 1975). Also close-coupling calculations by Burke *et al* (1969) on the 2^1P excitation in helium have shown that the polarisation of impact radiation may vary rapidly in the vicinity of a resonance. However, it is unlikely that resonances are the only cause of the dip in the polarisation curves. They cannot account for that part of the dip which extends beyond the ionisation threshold, because in the case of helium no (discrete) negative-ion resonances are expected there.

Another process which tends to reduce the observed polarisation is the indirect excitation of the upper state concerned via cascade from higher lying levels, in particular from S levels. This effect is probably the main cause of the strong depolarisation of the $n\,^1\mathrm{P} \to m\,^1\mathrm{S}$ transitions in helium. For the 5016 Å line ($3^1\mathrm{P} \to 2^1\mathrm{S}$), for instance, the cascade fraction is estimated to amount to almost 50% in the threshold region (Moiseiwitsch and Smith 1968). However, one would not expect the cascade effect to cause a dip in the polarisation curve, which is only a few eV broad. The same applies to other indirect population mechanisms such as collisional transfer of excitation energy. Summarising one may conclude that neither negative-ion resonances nor secondary processes such as cascade or collisional transfer of excitation energy are able to account, even qualitatively, for the threshold dip observed in many polarisation curves of helium and mercury.

In the present paper we wish to consider an additional mechanism that may give rise to a decrease of the polarisation in a limited energy range around the ionisation threshold. This mechanism concerns the influence of electron correlation effects similar to those that give rise to specific threshold laws for electron impact ionisation of atoms (Wannier 1953, Rau 1971, Fano 1974).

2. Electron correlation effects near the ionisation threshold

It has been emphasised by Fano (1974) that in the case of electron–atom collisions near the ionisation threshold the motions of the incident and atomic electrons may become closely correlated. Actual ionisation near threshold can only occur if in the course of their escape both the distances and velocities of the two electrons with respect to the nucleus stay nearly equal up to large distances from the ionic core. If this 'radial' correlation is disturbed at some distance within a critical radius (Wannier radius) an exchange of energy sets in, the result of which is that the faster electron escapes and the slower is recaptured by the residual ion; so excitation has taken place instead of ionisation. Similarly, if the collision energy is slightly below the ionisation threshold, the excitation of states having energies near the available energy is only possible if the motion of the two electrons remains correlated in the same way as required for near-threshold ionisation. As argued by Fano (1974) the Coulomb repulsion between the two electrons causes a (stable) angular correlation, as a result of which the two electrons may acquire significant orbital angular momenta (with opposite sign), even if their velocities are very small. This is the important point! If the scattered electron despite of its low velocity can carry away an orbital angular momentum unequal to zero, the excited atom is not necessarily left in a $m = 0$ magnetic substate. The probability for excitation of $m \neq 0$ substates may become quite appreciable resulting in a decrease of the polarisation of the emitted radiation. One would expect that the effect becomes increasingly prominent for the excitation of states with larger principal quantum numbers (larger radii). Namely, the excitation of these states in the threshold region requires that the correlation persists up to larger distances, so that the angular momentum exchange can be more effective.

It is clear that the above described correlation mechanism is only of importance in a limited energy range around the ionisation threshold. For impact energies well above the threshold the final kinetic energy of the excited electron is appreciably different from that of the scattered electron, so that the possible correlated motion is either disturbed at a very early stage or is not established at all. The correlation mechanism may be viewed upon as an indirect excitation process with a relatively long interaction time. As such it may give rise to a typical threshold behaviour or to structures on the excitation curves of higher lying states. Experimental evidence for the existence of such structures has been reported by Heideman *et al* (1976). They show up as relatively broad oscillatory structures proceeding through the ionisation threshold.

3. Model calculations

We have performed some simple model calculations to show that the electron correlation effects described in the previous section indeed may give rise to a considerable decrease in the polarisation of the impact radiation. We make the assumption that as a result of their correlated motion the excited atomic electron and the scattered electron acquire orbital angular momenta, which are equal in magnitude. According to the physical picture sketched in the previous section this assumption should become increasingly better for the excitation of states with larger principal quantum numbers. Writing down the reaction equation, for instance for 5^1D excitation in helium, we have:

$$\begin{array}{cccc} e_0 & +\mathrm{He}(1^1\mathrm{S}) \rightarrow & \mathrm{He}^*(5^1\mathrm{D})+ & e_s \\ (l_0, m_0) & (0,0) & (l_e, m_e) & (l_s, m_s) \end{array}$$

with (l_0, m_0), (l_e, m_e) and (l_s, m_s) denoting the absolute values and z components of the orbital angular momenta of the incident, excited and scattered electrons, respectively. Since $m_0 = 0$ we must have $m_s = -m_e$. Our assumption that $l_s = l_e$ $(=2)$ together with the parity conservation law restricts the values of l_0 to 0, 2 or 4. By applying simple angular momentum algebra (see also van Ittersum 1976 and Heddle *et al* 1977) we can find the relative populations Q_0, Q_1 and Q_2 of the $m=0$, $m=\pm1$ and $m=\pm2$ sublevels of the excited 5^1D state. The result is:

$$\begin{array}{ll} Q_0:Q_1:Q_2 = 1:1:1 & \text{for } l_0 = 0 \text{ (trivial!)} \\ Q_0:Q_1:Q_2 = 4:1:4 & \text{for } l_0 = 2 \\ Q_0:Q_1:Q_2 = 36:16:1 & \text{for } l_0 = 4. \end{array}$$

The polarisation of the radiation emitted in the transition $5^1\mathrm{D} \rightarrow 2^1\mathrm{P}$ can now be calculated using the polarisation formula of Percival and Seaton (1958).

$$P = 300\frac{Q_0+Q_1-2Q_2}{5Q_0+9Q_1+6Q_2}.$$

We find $P=0$, -15 and $+45\%$ for $l_0=0$, 2 and 4, respectively. Although we do not know the ratios of the $l_0=0$, 2 and 4 contributions ($l_0=4$ is probably least important) we may conclude from this result that the correlation effect may cause a significant decrease in the polarisation. The threshold polarisation amounts to 60%, as is seen by substituting $Q_1=Q_2=0$ in the polarisation formula.

4. Experiments

We have also performed a set of experiments in order to test the proposed model. As mentioned in the second section one might expect that the electron correlation effects near the ionisation threshold become increasingly important for the excitation of states with larger principal quantum numbers. Therefore, we measured the polarisation curves (near threshold) of the $n\,^1\mathrm{D}\rightarrow 2\,^1\mathrm{P}$ transitions in helium for $n=4$, 5 and 6. The experimental set-up is basically the same as that used by Heideman *et al* (1969) and by van Ittersum *et al* (1976). An electron beam of about 10 μA is directed through an excitation chamber containing helium gas at a pressure of about 10^{-3} Torr. The light originating from a cross section of the beam and emitted at right angles to the beam passes successively through a polariser and a quarter-wave filter and is focused on the entrance slit of a grating monochromator. The light of the selected spectral line is detected with a photomultiplier. The output pulses of the multiplier are stored and accumulated in a multichannel analyser. The degree of polarisation is now measured by determining $P=100(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the intensities of the emitted light with electrical vector parallel and perpendicular to the electron beam, respectively. The system is fully automatic, so that long integration times can be used. The beam energy is varied in discrete steps synchronously with the address advance of the multichannel analyser. At each energy setting three successive measurements are performed: the two polarisation components $I_\parallel$ and $I_\perp$ (selected by a step-motor-driven polariser) and the dark current of the multiplier (by turning off the electron beam). The quarter-wave plate serves to change the linearly polarised light transmitted by the polariser into circularly polarised light. In this way the difference in sensitivity of the apparatus for the two polarisation components is eliminated.

The results of our polarisation measurements are shown in figure 2. The steep rise of the polarisation when the energy approaches the threshold is clearly brought out in all three curves. The theoretical threshold value of 60% is not reached due to the finite resolution of the electron beam. More important, however, is the observation that the anomalous dip in the polarisation seems to become deeper with increase of the principal quantum number of the upper state. Additional evidence for this trend is provided by the polarisation measurements on the $3\,^1\mathrm{D}\rightarrow 2\,^1\mathrm{P}$ transition by Heddle *et al* (1977). This result is in agreement with our expectation that the correlation effects should be more important for the excitation of states with larger radii. Conversely, the experimental results provide strong evidence that the polarisation dip indeed is caused (or at least partly) by the discussed electron correlation effects.

It is now easily understood why the anomalous dip is not observed in the polarisation curves of the alkali resonance lines. The excitation of the alkali resonance levels does not involve a change in principal quantum number; their radii are relatively small and comparable to those of the respective ground states. Therefore, no correlated motion of excited and scattered electron is needed. In the case of $6\,^1\mathrm{D}$ excitation in helium, however, the atomic electron has to 'travel' about 40 au in order to reach its excited

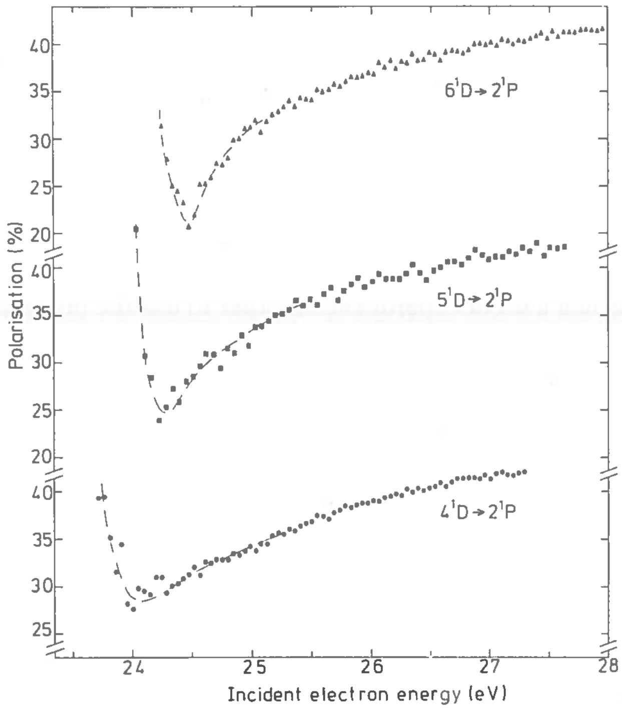

Figure 2. Measured polarisation near threshold of three $n\,^1D \rightarrow 2\,^1P$ transitions in helium as a function of the incident electron energy. The dip in the polarisation curve becomes deeper with increase of the principal quantum number n.

position. At low energies it will fail to get there, unless its motion remains strongly correlated with that of the scattered electron up to large distances.

The polarisation measurements of Hafner and Kleinpoppen (1976) provide an extra support for the proposed explanation. Apart from the alkali resonance lines these authors also studied the $3^2D \rightarrow 2^2P$ transition in lithium. The polarisation anomaly appears to be present there again, as expected.

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