Valence electron momentum distributions in cadmium

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Abstract. The valence 5s and 4d electron momentum distributions in cadmium have been measured using non-coplanar symmetric (e, 2e) electron coincidence spectroscopy at a total energy of 1200 eV. They are in close agreement with Hartree-Fock momentum distributions both in shape and relative magnitudes. Some satellite lines of very low intensity have been detected. A CI calculation of the Cd ground state and several Cd⁺ ion states has been carried out to predict cross reactions for the ground state and various satellite transitions. The predictions are in agreement with the data.

1. Introduction

It is of some interest to determine the extent to which single particle Hartree-Fock wavefunctions describe the valence orbitals of group II atoms such as cadmium, which have valence configurations \((n-1)d^nns^2\). Such atoms can exhibit strong initial-state configuration interaction in the ground state and for the higher atomic numbers may also deviate from the simple Hartree-Fock description due to relativistic effects. High-energy symmetric (e, 2e) spectroscopy allows a direct measurement to be made of the square of the momentum space overlap function between the many-body ground state and final ionic state (McCarthy and Weigold 1976). To a good approximation this is in many cases (such as transitions with large pole strengths) just the momentum distribution of an electron in its independent particle orbital. The reaction has been used to measure momentum distributions and electron correlation effects in closed-shell targets such as argon (Weigold and McCarthy 1978, Weigold et al 1973), krypton (Fuss et al 1981), in the ‘hydrogenic’ atoms sodium and potassium (Frost and Weigold 1982) as well as in hydrogen (Lohmann and Weigold 1981) and other inert-gas atoms (Weigold and McCarthy 1978).

The valence separation energy spectrum of cadmium has been studied by photoelectron spectroscopy (PES) using primarily He I radiation (Harrison 1970, Walker et al 1973, Süber and Shirley 1974, Süber et al 1976, 1977, Hush and Süber 1977, Shannon and Codling 1978). In addition to the 5s ground-state transition at 8.99 eV and the 4d_{5/2,3/2} transitions at 17.58 and 18.27 eV, some satellite lines were observed. These satellite lines were attributed to initial-state configuration interaction effects and to interchannel coupling (Süber and Shirley 1974, Süber et al 1976, Shannon and Codling 1978). Relativistic effects have also been noted by Shannon and Codling in state branching ratios.

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In principle, (e, 2e) spectroscopy should permit the measurement of both the spectroscopic factors and momentum distributions for the main transition and for all satellite lines, from which the extent of correlation and relativistic effects could be determined and each state could be assigned to the dominant single-particle configuration. In this paper we report the momentum distributions of the two main transitions leading to the \( 4d^{10}5s^2(5S_{1/2}) \) and \( 4d^{9}5s^2(5D_{5/2}, 5D_{3/2}) \) ion states. We also report the results of a configuration interaction (CI) calculation which predicts the relative cross sections for the dominant 5s and 4d transitions and the cross section for exciting the \( 4d^{10}6s \) and \( 4d^{10}5p \) ion states. It was not possible with the present apparatus to measure accurately the cross sections due to these satellite transitions due to their small intensities.

2. Methods and equipment

The equipment and methods used have been described in a previous publication (Frost and Weigold 1982). Briefly, a resistively heated oven was used to vapourise 99.99% pure cadmium samples. Two cylindrical mirror electron energy analysers, mounted coaxially on two horizontal concentric turntables at a polar angle \( \theta \) of 45° to the central axis, were used to select the energy and angle of emission of the two outgoing electrons. The out-of-plane angle of the analysers was set by the PDP-11 computer, as was the incident energy. The outgoing energies of the two electrons were kept fixed at 600 eV. Coincidence count rates measured as a function of the incident energy gave the separation energy spectra, whereas the angular correlation measurements gave the momentum profiles (McCarthy and Weigold 1976). The momentum of the bound electron is related to the out-of-plane azimuthal angle \( \phi \) in the plane wave limit by

\[
q = |p_A + p_B - p_0| = \left[ (2p_A \cos \theta - p_0)^2 + 4p_A^2 \sin^2 \theta \sin^2 \frac{1}{2} \phi \right]^{1/2}
\]

where \( p_0, p_A \) and \( p_B \) are the momenta of the incident and outgoing electrons respectively, and \( p_A = p_B, \theta_A = \theta_B = \theta \) in the non-coplanar symmetric geometry and \( \phi = \phi_A - \phi_B - \pi \) is the out-of-plane azimuthal angle. In the present experiment \( \theta \) was kept fixed at 45°.

Two features of the cadmium separation energy spectrum were studied in detail: the \( 4d^{10}5s \) peak at 9 eV resulting from the knockout of an outer 5s electron and the \( 4d^{9}5s^2 \) peak at 18 eV resulting from the knockout of a 4d electron.

The \( ^2D_{3/2} \) and \( ^2D_{3/2} \) multiplets at 17.58 and 18.27 eV respectively were not resolved in the experiment which was run with an energy resolution of 2.4 eV FWHM. In each case the peaks were first located by varying the incident electron energy from 1200 to 1219 eV to measure the coincidence count rate as a function of the separation energy, the out-of-plane azimuthal angle \( \phi \) of the analysers being set near the maxima in the corresponding calculated cross sections (0° for the 5s\(^{−1}\) transition and 16° for the 4d\(^{−1}\) transition). An angular correlation measurement was then made for each state by fixing the incident energy at the corresponding maximum in the separation energy spectrum and varying the out-of-plane azimuthal angle from −25 to +25° repeatedly. The maximum coincidence count rate at the peak of the 5s angular correlation (\( \phi = 0^\circ, q = 0.04a_0^{-1} \)) was 0.1 Hz, so that a considerable time was required to accumulate data with adequate statistics.

The angular resolution of the apparatus, obtained using the techniques described by Frost and Weigold (1982), was \( \Delta \phi = \pm 1^\circ \) and \( \Delta \theta = \pm 0.5^\circ \). In order to allow direct
comparison of the results with theoretical calculations the measured angular correlation for the outer 5s orbital was deconvoluted to allow for finite angular resolution, using the method described by Frost and Weigold (1982). The deconvolution has the effect of narrowing the angular correlation by almost 10 per cent. The 4d angular correlation was not deconvoluted, since deconvolution had a negligible effect on that data.

3. Results and discussion

In the plane wave impulse approximation (PWIA), the non-coplanar symmetric (e, 2e) cross section to final ion state $|\Psi_f\rangle$ is given by (McCarthy and Weigold 1976)

$$\sigma_f = \frac{4p^2}{p_o K^4} \frac{2\pi\eta}{\exp(2\pi\eta) - 1} |\langle q | \Psi_f | \Psi_0 \rangle|^2$$

where $K = |p_0 - p_A| = |p_0 - p_B|$ is the magnitude of the momentum transfer, and $\eta = \frac{1}{4||p_A - p_B||^{-1}}$. The momentum space overlap between the initial target state $|\Psi_0\rangle$ and final ion state $|\Psi_f\rangle$ for C1 wavefunctions can be conveniently written in second quantised form as

$$\langle q | \Psi_f | \Psi_0 \rangle = G_f(q) = \left( \sum_i \phi_i(q) \right)^\dagger \Psi_f$$

where $\phi_i(q)$ is the momentum space representation of the orbital from which the electron has been ejected, and $a_i$ acts as a single particle destruction operation on the ket $|\Psi_0\rangle$.

The spectroscopic sum rule for ejecting electrons of a particular l value is obtained by forming the complete sum over all accessible ion states

$$W_l(q) = \sum_f |G_f(q)|^2 = \sum_f \left| \left( \sum_i \phi_i(q) \right)^\dagger \Psi_f \right|^2.$$  

Using closure and completeness relations this simplifies to

$$W_l(q) = \left( \Psi_0 \right) \left( \sum_i \sum_j a_+^{\ast} \phi_{i,l}(q) a_\phi \phi_{j,l}(q) \right) \left( \Psi_0 \right)$$

This expectation value can be used to evaluate systematically the importance of electron correlations in the target wavefunction. The spectroscopic factor can then be defined as the quotient

$$S_{fl}(q) = \left| G_{fl}(q) \right|^2 / W_l(q)$$

where by definition

$$\sum_f S_{fl}(q) = 1.$$  

In the target Hartree–Fock approximation (THFA) the wavefunction of the target atom is assumed to be well described by a Hartree–Fock (HF) wavefunction, and the overlap function reduces to

$$G_{fl}(q) = \left( \Psi_f | a_\phi \phi_c(q) | \Psi_{HF} \right)$$

where $\phi_c(q)$ is the momentum space wavefunction of the HF orbital from which the
electron has been ejected. In this approximation the spectroscopic factor is independent of $q$ and simplifies to

$$S_n = |\langle \psi_f | a_e | \psi_{HF} \rangle|^2$$

which is just the square of the amplitude of the single hole configuration $(a_e | \psi_{HF} \rangle)$ in the CI expansion of the ion state $| \psi_f \rangle$, and consequently the cross section is proportional to

$$|G_n(q)|^2 = S_n |\phi_e(q)|^2 .$$

(10)

Since the $(np^2; \, ^1S_0)$ configuration is 'quasi-degenerate' with the $(ns^2; \, ^1S_0)$ configuration in group II atoms such as cadmium (Kim and Bagus 1973) considerable configuration interaction could be present in the outer valence shell. We therefore have carried out a CI calculation for Cd and Cd$^+$ using the Hartree–Fock wavefunctions of Clementi and Roetti (1974) as a starting point, considering only correlations between the two valence electrons in the $5s$ subshell. The CI wavefunction for the Cd ground state can be written as:

$$|\psi_0; ^1S_0 \rangle = \sum_{ij} c_{ij} |n_i l_i n_{ij}; ^1S_0 \rangle$$

(11)

where reference to the (frozen) core electrons $(1s^2 – 4d^{10})$ has been suppressed. The virtual orbitals were defined by a two-step procedure. Firstly, for each partial wave from $l = 0$ to $l = 3$ separate CI calculations including only the $|5s^2 \rangle$ configuration and configurations of the type $|n l' n' l' \rangle$ were used to determine the principal 'natural orbitals' by diagonalising the resulting single-particle density matrices for each value of $l$. These natural orbitals $(6s, 5p, 5d, 4f)$ were then incorporated in the single-particle basis set.

Frozen-core Hartree–Fock calculations for the ion states $|5s; ^2S_{1/2} \rangle$, $|6s; ^2S_{1/2} \rangle$, $|5p; ^2P_{1/2}; ^2P_{3/2} \rangle$ and $|5d; ^2D_{3/2}; ^2D_{5/2} \rangle$ (using the core orbitals from the frozen-core ground state), were then used to generate the appropriate valence orbitals characterising these states (6s', 6p', 5p', 6p', and 5d'). After orthogonalisation, with respect to the natural orbitals, these were then also included into the single-particle basis set to ensure that this basis was flexible enough to give a good description of both atom and ion states.

With this basis set for the Cd ground state, at least 98% of the correlation energy was recovered for the $5s^2$ electron pair, the calculated correlation energy being 0.0312 au. The CI wavefunction obtained for the ground state is

$$|\psi_0 \rangle = 0.9680|5s^2 \rangle - 0.0229|5s6s \rangle - 0.0118|5s5s \rangle - 0.0302|6s^2 \rangle + 0.2457|5p^2 \rangle$$

$$- 0.0181|5d^2 \rangle + 0.0126|4f^2 \rangle + 0.0182|5s6s \rangle \ldots \ldots$$

(12)

As expected the dominant contribution comes from the $5p$ natural orbitals.

Using the same single particle basis for the CI wavefunction of the ion states gives the simple expansions

$$|\psi_f \rangle = \sum_i c_i |n_i l_i \rangle$$

(13)

for the final ion states. The overlap of the ion and ground state could then be calculated.

The energies and overlap functions for the ion states are presented in table 1, where only the outer two electrons in the ground state have been taken into account (i.e. only states with $n \geq 5$ have been included).
Table 1. Separation energies (in au) and overlap functions for the \((e, 2e)\) reaction on cadmium. The overlap functions arising from the various orbitals \((n > 5)\) are in the labelled column.

<table>
<thead>
<tr>
<th>Ion state</th>
<th>(4d^{10}5s)</th>
<th>(4d^{10}6s)</th>
<th>(4d^{10}5p)</th>
<th>(4d^{10}5d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation energy (theory) (au)</td>
<td>0.287</td>
<td>0.611</td>
<td>0.459</td>
<td>0.633</td>
</tr>
<tr>
<td>Separation energy (expt) (au)</td>
<td>0.329</td>
<td>0.706</td>
<td>0.536</td>
<td>0.739</td>
</tr>
<tr>
<td>Overlap function</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5s</td>
<td>1.355</td>
<td>5s</td>
<td>0.180</td>
<td>5p</td>
</tr>
<tr>
<td>6s</td>
<td>-0.015</td>
<td>6s</td>
<td>-0.042</td>
<td>5p'</td>
</tr>
<tr>
<td>5s'</td>
<td>-0.013</td>
<td>5s'</td>
<td>0.005</td>
<td>6p'</td>
</tr>
<tr>
<td>6s'</td>
<td>-0.004</td>
<td>6s'</td>
<td>0.0163</td>
<td></td>
</tr>
</tbody>
</table>

Thus the \((e, 2e)\) transitions from the cadmium ground state to the ground state of the ion \((4d^{10}5s)\) should be dominated by the momentum distribution of the 5s Hartree–Fock orbital of the ground state, although small contributions from the 6s natural orbital and 5s' ion orbital should also contribute. If the overlap between the two ground states were to be exactly equal to the HF 5s ground-state orbital, which would be the case in the frozen-core HF approximation for target and ion states \((S_f = 1\) in equation (10)), then the reduced overlap function would be \(\sqrt{2}\) 5s for the ion ground state. When the full CI calculation for the overlap function is carried out we find that the CI calculation predicts a loss of intensity of the order of 20% for the ground-state transition over that predicted by the frozen-core independent particle model.

This loss of intensity is due to several effects. Firstly the ion and atom 5s orbitals are not the same (i.e. \(\langle 5s_{atom}\rangle \langle 5s_{ion}\rangle < 1\) ). This is commonly referred to as a ‘relaxation’ effect. Secondly the amplitude for the 5s\(^2\) configuration in the expansion for the target wavefunction is less than unity (equation (12)). These two effects are responsible for approximately half the reduction in intensity. Finally there are other terms besides \(\phi_{5s}(q)\) which contribute to \(|G_f(q)|^2\) as shown in table 1. These terms interfere destructively with \(\phi_{5s}(q)\).

The measured angular correlation for the ground-state transition at 1200 eV, deconvoluted for the effects of finite angular resolution, is shown in figure 1 as a function of the momentum \(q\). The full curve is the 1200 eV plane-wave impulse approximation cross section obtained using the calculated CI overlap function between the atom and ion ground states. Since absolute cross sections were not measured in the present experiment, the data have been arbitrarily normalised to this cross section. Agreement between the measured and calculated momentum profiles is excellent.

The broken curve is the 1200 eV PWIA cross section using the the 5s Hartree–Fock wavefunction of Clementi and Roetti (1974) as the overlap function. This is equivalent to the frozen-core independent-particle approximation for the target and ion. If correlations are important only in the final state \((THFA)\), the broken curve would still give the shape of the cross section but its absolute value would be reduced by the spectroscopic factor \(S_f\), which would then be less than unity (equations (9) and (10)).

The simple HF 5s cross section should be larger than that given by the CI overlap function, since as discussed earlier the latter leads to a loss of intensity due to correlation and relaxation effects. In order to allow for a direct comparison of the shapes of the calculated cross sections with each other and the data, the 5s HF cross section has
Figure 1. The non-coplanar symmetric (e, 2e) differential cross section at 1200 eV for the ground-state transition in Cd plotted as a function of the momentum $q$. The full curve is the PWIA cross section obtained using the calculated CI overlap function, and the broken curve is the cross section obtained using the Hartree-Fock 5s wavefunction of Clementi and Roetti (1974) multiplied by 0.82. The data have been normalised to the PWIA CI cross section in the low momentum region.

Therefore been multiplied by a factor of 0.82 in figure 1 to bring the low momentum cross sections into agreement. The agreement with the data is good, showing that the non-relativistic Hartree-Fock wavefunction provides a very good description of the behaviour of the outer two valence electrons in Cd. The small, but nevertheless significant differences between the shapes of the curves arise from the extra components in the CI overlap function (column 1 in table 1). Given the present experimental uncertainties it is difficult to decide between the two calculated cross section shapes.

The momentum distribution measured at a separation energy of 18 eV is shown in figure 2. This momentum distribution should be dominated by the 4d$^{-1}$ transition.

Figure 2. The non-coplanar symmetric (e, 2e) cross section at 1200 eV for Cd leading to the 4d$^5$5s$^2$(2D$_{3/2}$, 2D$_{5/2}$) ion states plotted as a function of the momentum $q$. The full curve is the PWIA calculation using the 4d Hartree-Fock momentum distribution corrected for relaxation effects as described in the text. The hatched area shows the estimated uncertainty in adding the calculated contributions to the 18 eV transition from excitation of the neighbouring 4d$^1$6s and 4d$^1$6p ion states (figure 3). The experimental data are normalised relative to the ground-state cross section (figure 1).
which leads to the $4d^95s^2(2D_{5/2}, 2D_{3/2})$ ion states at 17.58 and 18.28 eV. This spin–orbit splitting cannot be resolved with the present energy resolution. Since both the ground state $4d^{10}5s$ and the 18 eV transitions were measured concurrently, no separate normalisation was required for the 18 eV transitions, and the data in figure 2 is therefore normalised relative to the ground-state cross section (figure 1), the peak in the 18 eV cross section being approximately 1% of the peak ground-state cross section.

In the present calculation it has been assumed that the 4d electrons are part of a fixed core. Therefore the shape of the calculated cross section for $4d^95s^2$ ion states at around 18 eV should be determined by the 4d HF momentum distribution. However, removal of a 4d electron will cause the outer 5s electron to 'relax' and consequently reduce the cross section. Since a CI calculation of the $4d^95s^2$ state was not practical, an estimation of this effect was carried out at the HF level. In this approximation the overlap function is

$$G_f(q) = \phi_{4d}(q)(5s_{atom}|5s_{ion}).$$

From the frozen-core HF calculation of the $|4d^95s^2; 2D\rangle$ ion state, the value of the overlap integral was found to be 0.952. This implies that the spectroscopic factor for 4d knockout is 0.906. The last column in table 1 shows that the d-wave components of the CI function for the 5s pair are negligible.

The calculated PWIA cross section, obtained using the 4d orbital wavefunction of Clementi and Roetti (1974) and the spectroscopic factor of 0.906 arising from relaxation effects, is shown by the full curve in figure 2. Excellent agreement in both shape and magnitude is obtained between data and theory in the momentum region above approximately 0.6 \(a_0^{-1}\). In the low momentum region, however, considerable intensity is seen where the 4d wavefunction predicts essentially zero momentum density.

This extra intensity at low momentum could arise from the excitation of neighbouring satellites whose transition cross sections are dominated by low-momentum components, such as the excitation of the $4d^{10}6s(2S_{1/2})$ ion state at the separation energy of 19.28 eV, and the $4d^{10}5p(2P_{1/2}, 2P_{3/2})$ doublet at 14.46 eV and 14.79 eV. These states, although separated from the $4d^95s^2$ doublet by approximately 1.3 and 3.3 eV, could contribute to the 18 eV cross section due to the broad experimental energy resolution of 2.4 eV (FWHM), which was chosen to increase the counting rate. A careful study of the shape of the coincidence energy peak shows that the 19.28 eV 6s ion state would contribute 38 ± 7% to the 18 eV cross section, whereas the 14.46 and 14.79 eV transitions would contribute 7 ± 4% of their strengths.

As can be seen from table 1 the overlap functions for the $4d^{10}6s$ and $4d^{10}5p$ ion states with the Cd ground state are not negligible, although they are small compared with the $4d^{10}5s$ overlap function. The $4d^{10}6s$ ion state can be excited because the Hartree–Fock 5s ground state is not orthogonal to the ion state as a result of the different self-consistent fields of the atom and ion (relaxation effects). The $4d^{10}5p$ ion state on the other hand can only be excited if ground-state correlations are important, which indeed they are (see equation (13) and table 1).

The PWIA cross sections obtained for these transitions using the calculated overlap functions (table 1) are shown in figure 3. Although the cross sections for exciting the $4d^{10}6s$ and $4d^{10}5p$ ion states are predicted to be quite small compared with the 5s ground-state transition, their peak values are comparable with the maximum in the 4d cross section (figure 2). Of course the calculated cross sections for these satellite transitions integrated over all momentum space are again very much smaller than the
Figure 3. The calculated non-coplanar symmetric \((e, 2e)\) cross sections at 1200 eV for the transitions to the \(4d^{10}6s\) (broken curve) and \(4d^{10}5p\) (full curve) ion states of Cd plotted as a function of the momentum \(q\). The curves are obtained using the PWIA and the ion-atom overlap functions derived from the present CI calculation.

integrated 4d cross section, since this latter cross section is much more extended in momentum space.

Süzer and Shirley (1974) in their He I photoelectron spectra observed some excitation of the 14.46 and 14.47 (4d\(^{10}\)5p) ion eigenstates, but they saw no excitation of the 4d\(^{10}\)6s ion eigenstate. They attributed approximately one fifth of their 4d\(^{10}\)5p intensity to interchannel coupling, and the rest to ground-state correlation effects. The momentum component probed by the photoelectron reaction is approximately that of the free electron, i.e. of the order of 0.5 \(a_0^{-1}\) with the He I radiation. The He I PES cross section is therefore very insensitive to the s orbitals and more sensitive to p orbitals (see figure 3) and it is not surprising that no evidence was found for the excitation of the 4d\(^{10}\)6s ion eigenstate.

In the present experiment separation energy spectra were taken at \(\phi = 0^\circ (q \approx 0.04 \ a_0^{-1})\) over the range from 14 to 19 eV. These indicated the presence of a satellite near 14.5 eV of approximately 0.5\% of the ground-state peak intensity with limited statistical accuracy, and at 19 eV a state with intensity of 1 ± 0.4\% of the ground-state peak intensity. The CI calculation predicts that at \(q \sim 0.04 \ a_0^{-1}\) the 19 eV 4d\(^{10}\)6s state should be excited with an intensity of 1.3\% of the ground-state peak intensity.

As discussed earlier, with the present energy resolution approximately 38\% of the strength of the 4d\(^{10}\)6s transition and 7\% of the strength of the 4d\(^{10}\)5p transition should contribute to the 18 eV momentum distribution. We have therefore included these contributions in figure 2, using the calculated 6s and 5p cross sections for this purpose (figure 3). These contributions give the total calculated cross section indicated by the cross hatched area leading into the full curve. The cross hatched area indicates the uncertainty in estimating the 4d\(^{10}\)6s and 4d\(^{10}\)5p contributions from the calculated cross sections due to possible drifts in energies. Inclusion of these satellite components considerably improves the agreement with the measured momentum profile.
In summary the momentum densities obtained using the calculated overlap functions are in excellent agreement with the measured 5s and 4d momentum distributions, both in shape and relative magnitudes. The shapes of the cross sections are essentially given by the Hartree–Fock 5s and 4d wavefunctions of Clementi and Roetti (1974). The good agreement in magnitude between the measured and calculated 4d cross sections shows that the strength of the 4d orbital cannot be significantly split. The low momentum data for the 4d transitions are in good agreement with the present CI calculations which predict significant excitation of the 4d^{10}5p and 4d^{10}6s ion eigenstates. It would be most interesting to make detailed measurements of the momentum distributions for these satellite transitions, in particular the 4d^{10}5p transition, since this provides a sensitive measure of correlations in the target ground-state wavefunction. In order to carry out such measurements it will be necessary to improve significantly the data-taking rate as well as to improve the energy resolution. Equipment which will enable us to do this is currently under development.

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