Table 4.2.2.2. *Directly measured L-series reference wavelengths in Å*

Numbers in parentheses are standard uncertainties in the least-significant figures.

Z	Symbol	$L\alpha_2$	$L\alpha_1$	$L\beta_1$	References
36	Kr	7.82032(13)	7.82032(13)	7.574441(98)	(*a*)
40	Zr	6.07710(48)	6.070250(79)	5.836214(76)	(*a*)
54	Xe	3.025940(22)	3.016582(15)	2.806553(19)	(*b*)
60	Nd	2.38079(52)	2.370526(16)	2.167008(19)	(*a*)
62	Sm	2.210430(24)	2.199873(13)	1.998432(30)	(*a*)
67	Ho	1.856472(15)	1.845092(17)	1.647484(32)	(*a*)
68	Er	1.795701(45)	1.784481(20)	1.587466(86)	(*a*)
69	Tm	1.738003(19)	1.7267720(70)	1.5302410(70)	(*a*)

References: (*a*) Mooney (1996); (*b*) Mooney *et al.* (1992).

1980; Nyholm & Mårtensson, 1980; Lebugle, Axelsson, Nyholm & Mårtensson, 1981; Powell, 1995). The number of values available offers the possibility of consistency checking, since the K and L shells are connected by emission lines to several final hole states, each of which has (possibly) been evaluated by photoelectron spectroscopy. For each of the elements for which well qualified reference spectra are available, we evaluated edge location estimates using several alternative transition cycles and used the distribution of results to provide a measure of the uncertainty. Comparison of edge estimates obtained by this procedure with experimental data provides a quantitative test of the utility of the chosen approach to edge location estimation. In Table 4.2.2.3, the numerical results in the column labelled 'Emission + binding energies' were obtained by combining emission energies and electron binding energies using all possible redundancies. The estimated uncertainties indicated were obtained from the distribution of the redundant routes. As can be seen, the results are in general agreement with the available directly measured values. Accordingly, we have used this protocol to obtain the edge locations listed in the summary tables below.

4.2.2.8. *Outline of the theoretical procedures*

Only recently has it become possible to understand the relativistic many-body problem in atoms with sufficient detail to permit meaningful calculation of transition energies between hole states (Indelicato & Lindroth, 1992; Mooney, Lindroth, Indelicato, Kessler & Deslattes, 1992; Lindroth & Indelicato, 1993, 1994; Indelicato & Lindroth, 1996). To deal with those hole states for atomic numbers ranging from 10 to 100, one needs to consider five kinds of contributions, all of which must be calculated in a relativistic framework, and the relative influence of which can change strongly as a function of the atomic number:

(i) nuclear size;

(ii) relativistic effects (corrections to Coulomb energy, magnetic and retardation energy);

(iii) Coulomb and Breit correlation;

(iv) radiative (QED) corrections (one- and two-electron Lamb shift *etc.*);

(v) Auger shift.

Such an undertaking, although much more advanced than any other done in the past, still suffers from severe limitations that need to be understood fully to make the best use of the table. The main limitation is probably that most lines are emitted by atoms in an elemental solid or a compound, while the calculation at present deals only with atoms isolated in vacuum. (A purely experimental database would have a similar limitation.) The second limitation is that it is not possible at present to include the coupling between the hole and open outer shells. Coupling between a $j = \frac{1}{2}$, $j = \frac{3}{2}$ or $j = \frac{5}{2}$ hole and an external $3d$ or $4f$ shell can generate hundreds of levels, with splitting that can reach an eV. One then should calculate all radiative and Auger transition probabilities between hundreds of initial and final states. (The Auger final state would have one extra vacancy, leading eventually to thousands of final states.) Such an approach would give not only the mean line energy but also its shape and would thus be very desirable, but is impossible to do with present day theoretical tools and computers. We have thus limited ourselves to an approach in which one computes the weighted average energy for each hole state, and ignores possible distortion of the line profile due to the coupling between inner vacancies and outer shells.

Since we want to have good predictions for both light and heavy atoms, we have to include relativity non-perturbatively. To get a result approaching 1×10^{-6} for uranium $K\alpha$ by applying perturbation theory to the Schrödinger equation, for example, one would need to go to order 22 in powers of $Z\alpha = v/c$. The natural framework in this case is thus to do a calculation exact to all orders in $Z\alpha$ by using the Dirac equation. We thus have used many-body methods, based on the Dirac equation, in which the main contributions to the transition energy are evaluated using the Dirac–Fock method. We use the Breit operator for the electron–electron interaction, to include magnetic (spin–spin, spin–other orbit and orbit–orbit interactions in the lower orders in $Z\alpha$ and $(v/c)^2$ retardation effects. Higher-order retardation effects are also included.