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.

Table 4.2.2.3. *Directly measured and emission + binding energies (see text) K-absorption edges in Å*

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

Z	Symbol	Directly measured	Emission + binding energies	References
23	V	2.269211(21)	2.26893(11)	(*a*)
24	Cr	2.070193(14)	2.07014(17)	(*a*)
25	Mn	1.8964592(58)	1.896457(42)	(*a*)
26	Fe	1.7436170(49)	1.743589(98)	(*a*)
27	Co	1.6083510(42)	1.60836(17)	(*a*)
28	Ni	1.4881401(36)	1.48823(25)	(*a*)
29	Cu	1.3805971(31)	1.38060(16)	(*a*)
30	Zn	1.2833798(40)	1.28338(15)	(*a*)
39	Y	0.7277514(21)	0.727750(23)	(*a*)
40	Zr	0.6889591(31)	0.688946(30)	(*a*)
41	Nb	0.6531341(14)	0.653112(29)	(*a*)
42	Mo	0.61991006(62)	0.619906(64)	(*a*)
45	Rh	0.5339086(69)	0.533951(10)	(*a*)
46	Pd	0.5091212(42)	0.509156(11)	(*a*)
47	Ag	0.4859155(57)	0.4859168(91)	(*a*)
48	Cd	0.4641293(35)	0.464135(12)	(*a*)
49	In	0.4437454(48)	0.443740(11)	(*a*)
50	Sn	0.4245978(29)	0.424590(13)	(*a*)
51	Sb	0.4066324(27)	0.406612(12)	(*a*)
68	Er	0.2156801(75)	0.2156762(50)	(*b*)
82	Pb	0.1408821(74)	0.1408836(11)	(*c*)

References: (*a*) Kraft *et al*. (1996); (*b*) Lum *et al*. (1981); (*c*) Bearden (1960).

Many-body effects are calculated by using relativistic many-body perturbation theory (RMBPT). Since inner vacancy levels are auto-ionizing, one must include shifts in their energy due to the coupling between the discrete levels and Auger decay continuua.

In the following subsections, we describe in more detail the calculation of the different contributions.

4.2.2.9. *Evaluation of the uncorrelated energy with the Dirac–Fock method*

The first step in the calculation, following Indelicato and collaborators (Indelicato & Desclaux, 1990; Indelicato & Lindroth, 1992; Mooney *et al.*, 1992; Lindroth & Indelicato, 1993; Indelicato & Lindroth, 1996) consists in evaluating the best possible energy with relativistic corrections, within the independent electron approximation, for each hole state (here $1s_{\frac{1}{2}}$, $2p_{\frac{1}{2}}$, $2p_{\frac{3}{2}}$, $3p_{\frac{1}{2}}$, $3p_{\frac{3}{2}}$ for K, $L_{\rm II}$, $L_{\rm III}$, $M_{\rm II}$, $M_{\rm III}$, respectively). Such a calculation must provide a suitable starting point for adding all many-body and QED contributions. We have thus chosen the Dirac–Fock method in the implementation of Desclaux (1975, 1993). This method, based on the Dirac equation, allows treatment of arbitrary atoms with arbitrary structure and has been widely used for this kind of calculation. We have used it with full exchange and relaxation (to account for inactive orbital rearrangment due to the hole presence). The electron–electron interaction used in this program contains all magnetic and retardation effects, which is very important to have good results at large Z. The magnetic interaction is treated on an equal footing with the Coulomb interaction, to account for higher-order effects in the wavefunction (which are also useful for evaluating radiative corrections to the electron–electron interaction). All these calculations must be done with proper nuclear charge models to account for finite-nuclear-size corrections to all contributions. For heavy nuclei, nuclear deformations must be accounted for (Blundell, Johnson & Sapirstein, 1990; Indelicato, 1990). For all elements for which experiments have been performed, we used experimental nuclear charge radii. For the others we used a formula from Johnson & Soff (1985), corrected for nuclear deformations for $Z > 90$. Contribution of deformation to the r.m.s. radius (the only parameter of importance to the atomic calculation) is roughly constant (0.11 fm) for $Z > 90$. There is an unknown region, between Bi and Th ($83 < Z < 90$), where deformation effects start to be important, but for which they are not known. When experiments are done for a particular isotope, we calculated separately the energies for each isotope.

As mentioned in the introduction, there are special difficulties involved when dealing with atoms with open outer shells (obviously this is the most common case). Computing all energies E_J for total angular momentum J would be both impossible and useless. The Dirac–Fock method circumvents this difficulty. One can evaluate directly an average energy that corresponds to the barycentre of all E_J with weight $(2J + 1)$. There are still a few cases for which the average calculation cannot converge (when the open shells have identical symmetry). In that case, the outer electrons have been rearranged in an identical fashion for all hole states of the atom, to minimize possible shifts due to this procedure.

4.2.2.10. *Correlation and Auger shifts*

Once the Dirac–Fock energy is obtained, many-body effects beyond Dirac–Fock relaxation must be taken into account. These include relaxation beyond the spherical average, correlation (due to both Coulomb and magnetic interaction), and corrections due to the autoionizing nature of hole states (Auger shift). Since the many-body generalization of the Dirac–Fock method, the so-called MCDF (multiconfiguration Dirac–Fock), is very inefficient for hole states, we turned to RMBPT to evaluate those quantities. These many-body effects contribute very significantly to the final value. Coulomb correlation is mostly constant along the Periodic Table (at the level of a few eV). Magnetic correlations are very strong at high Z. Auger shift is very important for p states. The interested reader will find more details of these complicated calculations in the original references (Indelicato & Lindroth, 1992; Mooney *et al.*, 1992; Lindroth & Indelicato, 1993; Indelicato & Lindroth, 1996). As these calculations are very time consuming, they are performed only for selected Z and interpolated. Since the Auger shifts do not always have a smooth Z dependence, care has been taken to evaluate them at as many different Z's as practical to ensure a good reproduction of irregularities.

4.2.2.11. *QED corrections*

The QED corrections originate in the quantum nature of both the electromagnetic and electron fields. They can be divided in two categories, radiative and non-radiative. The first one includes self-energy and vacuum polarization, which are the main contributions to the Lamb shift in one-electron atoms. These corrections scale as Z^4/n^3 (n being the principal quantum number) and are thus very important for inner shells and high Z. The second category is composed of corrections to the electron–electron interaction that cannot be accounted for by RMBPT or MCDF. These corrections start at the two-photon interaction and include three-body effects. The two-photon, non-radiative QED contribution has been calculated recently only for the ground