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

references