Energy shifts of $K\alpha$ x-ray satellites in low-Z atoms

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A study of the energy shift of x-ray $K\alpha$ satellites relative to the $K\alpha$ diagram lines for atoms having $10 \leq Z \leq 32$ is presented. Nonrelativistic Hartree-Fock (HF) total energies are employed, as well as the hydrogenic analytic model of Burch *et al.* [Phys. Rev. A **9**, 1007 (1974)] using both HF-derived and Slater-rule screening constants. The results are compared with an extensive body of experimentally derived ion-, electron-, and photon-excited shifts. The HF results are found to increasingly underestimate the measured shifts for $Z \geq 17$, while the analytic model using HF screening constants overestimates them uniformly by about 2.5 eV for almost all Z. Excellent agreement is found for the very recent self-consistent-field extension of Burch's model by Bhattacharya *et al.* [Phys. Rev. A **37**, 3162 (1988)]. A way of improving agreement between HF calculations and experiment is suggested.

X-ray satellites originate in electronic transitions involving more than a single electron and a single inner-shell hole in the same atom.[1] As such they can potentially provide information on intra-atomic electron correlations, excitation dynamics, relaxation, and other effects influencing the x-ray emission process.[2] Hence the ever increasing research activity in this field. In particular, the $K\alpha$ satellites, which originate in a $1s^{-1} \rightarrow 2p^{-1}$ transition in the presence of one additional $2s$ or $2p$ vacancy, have been investigated experimentally by ion,[3-20] electron, and photon excitations,[21-31] as well as through a variety of theoretical and computational approaches.[32-36] We present here the results of a study of the energy shift of the $K\alpha$ satellites relative to the $K\alpha$ diagram lines, for atoms with $10 \leq Z \leq 32$. Both *ab initio* nonrelativistic Hartree-Fock (HF) calculations and the analytic electrostatic shift model of Burch *et al.*[34] were employed. The calculated shifts are compared with other theoretical results as well as a large body of previously measured shifts including some recent ones from our laboratory.[31]

The nonrelativistic HF calculations were done in the intermediate coupling scheme using the MCHF78 program of Froese Fischer[37] and employing only single configurations. As the $2s$-spectator-hole contribution to the satellite spectrum was experimentally determined to be negligible for the present Z range,[31,34] only $2p$-spectator-hole configurations were considered. The satellite energy shift was calculated from

$$\Delta E_1 = [E(1s^{-1}2p^{-1}) - E(2p^{-2})] - [E(1s^{-1}) - E(2p^{-1})] , \quad (1)$$

where $E(nl)$ and $E(nln'l')$ were taken as the total energy of the nl and $nln'l'$ configurations, respectively, as obtained from the program. An alternative approach is to calculate the energies of each of the 14 possible lines in the fully split spectrum, then average over these energies with weights equal to the intensity of each line. This, however, could not be done as intermediate-coupling intensities for the lines are not available and the use of the known LS-coupling ones was not deemed to be justified even for the lower end of our Z range.[33,38]

The energy shifts were also calculated using the simple analytic model of Burch *et al.*[34] In this model, the effective charge of the long-lived $2p$ spectator vacancy is uniformly smeared over the $2p$ shell. This charged shell is the source of a perturbing electrostatic potential which shifts the inner levels of the atom nonuniformly, therefore causing a shift of the x-ray $K\alpha$ line relative to the spectatorless case. This model is simple enough to be tractable analytically, and gives a solid physical picture of the effects, magnitudes, and directions involved both in the x-ray and Auger-electron emissions.[34-36] For hydrogenic wave functions, this model yields for the shift,

$$\Delta E_2 = 1.66 Z_e \quad (2)$$

in eV units. Z_e is the effective charge of a $2p$ spectator hole, given by[39]

$$Z_e = Z - \sigma , \quad (3)$$

where Z is the atomic number and σ is the screening constant for the shell. Burch *et al.*[34] used the Slater screening rule,[40] which gives $\sigma = 4.15$ for all Z. As shown below, we obtained better agreement with experiment by using Z-dependent σ values obtained from our HF calculation. This simple model was successfully extended to include relativistic effects and arbitrary defect configurations.[35] While the present work was in progress, a further important extension of the model was published by the same group.[36] In that work analytic self-consistent-field (SCF) wave functions were employed rather than the screened hydrogenic ones used in the original model[34] and its other extensions.[35] As we show below, these results of Bhattacharya *et al.* are in excellent agreement with experiment for all Z considered here except the high-Z end of the range.

The results obtained from the HF calculations through Eq. (1) and from Burch's model, Eq. (2), using HF and

Slater screening, are listed in Table I for $10 \leq Z \leq 32$. The table also lists the recent theoretical SCF results of Bhattacharya *et al.*[36] as well as numerous experimentally determined shifts. Several detailed studies[10,13,19,41] clearly show that in addition to the $(2p)^{-n}$-spectator-vacancies ($n = 1,2,\ldots,$) ion excitation invariably creates vacancies at higher shells also, the number and distribution of which depend strongly on the mass, and possibly also the energy of the projectile. These additional vacancies, and, in particular, the $3p$ and $3s$ ones,[10,19] shift the x-ray satellites further away from $K\alpha$ lines by a variable amount dependent on the exciting projectile. Such effects are negligibly small for electron and photon excitations where only $3d,4s$ or higher shell additional shakeoff va-

TABLE I. Experimental and theoretical shifts, in eV, of $K\alpha$ satellites from the center of mass of the $K\alpha$ diagram lines. The excitation mode for the experimental data is given in the column headings and the chemical composition of the target is indicated where available. HF indicates results obtained from Eq. (1) using nonrelativistic Hartree-Fock calculated total energies. *B*-HF is the method of Burch *et al.* (Ref. 34), Eq. (2), with HF-calculated screening constants and *B-S* is the same for Slater rule screening constants. Bh indicates the analytic SCF results of Bhattacharya *et al.* (Ref. 36).

	Experimental		Theoretical			
Atom	Electrons and photons	Ions	HF[a]	*B*-HF[b]	*B-S*[c]	Bh[d]
^{10}Ne	6.4[e]	6.3±0.4[f] 6.05[g] 6.5[h] 7±2[i]	5.2	8.6	9.7	5.6
^{11}Na	7.73±0.07[j] 7.48±0.07[l] 7.46[m] 7.6±0.5[n]	7.0±0.3[k]	6.7	10.4	11.4	7.3
^{12}Mg	8.9[o] 8.6[q]	7.9±0.6[p]	8.2	12.1	13.0	9.0
^{13}Al	9.86[r]	10±0.7[s] 10.3±0.1[t]	9.5	13.8	14.7	10.7
^{14}Si	11.5[u] 12.5[w]	11.4±0.5[v] 11±0.7[x] 12.2±0.8[y] 14.7±1.2[z]	10.8	15.5	16.4	12.5
^{15}P	12.4±1[aa]	12.6±0.4[bb]	12.1	17.2	18.0	14.2
^{16}S	14.7±1.4[aa] 15.1[dd]	15.1±0.6[cc] 15.5±0.6[ee] 15.6±0.9[ff] 17.1±1.1[gg]	13.4	18.8	19.7	15.9
^{17}Cl	17.2±1.3[hh]	18.3±1.4[ii] 19±0.7[jj] 18.5±0.6[kk] 17.8±0.6[ll] 19.2±1.1[mm] 20.9±1.7[hh]	14.6	20.5	21.3	17.6
^{18}Ar		20±1[oo] 18.8±1.4[pp]	15.8	22.1	23.0	19.4
^{19}K	21±1.4[aa] 20.9[dd]	23±3[qq] 21.0±1.3[rr]	17.3	23.8	24.7	21.1
^{20}Ca	22±2[aa] 23.0[dd]	26[ss] 24[tt]	18.3	25.4	26.3	22.8
^{21}Sc	24.9[dd]	24[uu] 25[vv]	20.4	27.0	28.0	24.5
^{22}Ti	28.7[dd] 24.4[xx]	26[ww] 29[yy] 25.3±2[zz] 25±0.5[zz] 24.8±0.4[zz] 25±0.4[zz] 26.5±0.5[zz]	22.0	28.7	29.6	26.3
^{23}V	28.3[dd]		23.5	30.3	31.3	28.0
^{24}Cr	29.6[dd]		25.1	31.9	33.0	29.7
^{25}Mn	31.4[dd]		26.4	33.5	34.6	31.4

Table I (*Continued.*)

Atom	Experimental Electrons and photons	Ions	Theoretical HF[a]	*B*-HF[b]	*B*-*S*[c]	Bh[d]
^{26}Fe	33.4[dd]	38[aaa]	27.9	35.2	36.3	33.2
^{27}Co	35.2[dd]		29.3	36.8	37.9	34.9
^{28}Ni	38.1[dd]		30.8	38.4	39.6	36.6
^{29}Cu	40.6[dd]		32.4	40.0	41.3	38.3
	38.5±1.0[bbb]					
	38.6±1.0[ccc]					
^{30}Zn	43.5[dd]		33.7	41.6	42.9	40.1
^{31}Ga	46.2[dd]		34.9	43.2	44.6	41.8
^{32}Ge	48.8[dd]		36.2	44.8	46.2	43.5

[a]Nonrelativistic Hartree-Fock.
[b]Burch *et al.*, Ref. 34, using effective charges obtained from nonrelativistic Hartree-Fock calculations.
[c]Same as footnote b, but with Slater-rule screening.
[d]Bhattacharya *et al.*, Ref. 36.
[e]Reference 21.
[f]Reference 3.
[g]Reference 4.
[h]Reference 5.
[i]Reference 6.
[j]NaCl, Ref. 22.
[k]Sodium salts, Ref. 7.
[l]Metal, Ref. 22.
[m]Metal, Ref. 23.
[n]NaCl, Ref. 24.
[o]Oxide, Ref. 25.
[p]Metal, Ref. 8.
[q]Metal, Ref. 25.
[r]Metal, Ref. 26.
[s]Reference 9.
[t]Metal, Ref. 10.
[u]Elemental, Ref. 27.
[v]Elemental, Ref. 11.
[w]SiO_2, Ref. 27.
[x]Elemental, Ref. 12.
[y]SiF_4, Ref. 11.
[z]SiH_4, Ref. 11.
[aa]Unspecified salt, Ref. 28.
[bb]P_4, Ref. 11
[cc]S_8, Ref. 11.
[dd]Reference 29.
[ee]SF_6, Ref. 11.
[ff]SO_2, Ref. 11.
[gg]H_2S, Ref. 11.
[hh]KCl, Ref. 30.
[ii] NaCl, Ref. 10.
[jj]KCl, Ref. 11.
[kk]NaCl, Ref. 11.
[ll]CCl_4, Ref. 11.
[mm]Cl_2, Ref. 11.
[nn]HCl, Ref. 11.
[oo]Reference 13.
[pp]Reference 11.
[qq]KCl, Ref. 10.
[rr]KCl, Ref. 11.
[ss]Metal, Ref. 14.
[tt]Metal, Ref. 15.
[uu]Metal, Ref. 16.
[vv]Metal, Ref. 16.
[ww]Metal, Ref. 17.
[xx]Metal, Ref. 19.
[yy]Metal, Ref. 18.
[zz]Metal, increasing projectile mass, Ref. 19.
[aaa]Metal, Ref. 29.
[bbb]Metal, Gaussian resolution, Ref. 31.
[ccc]Metal, Lorentzian resolution, Ref. 31.

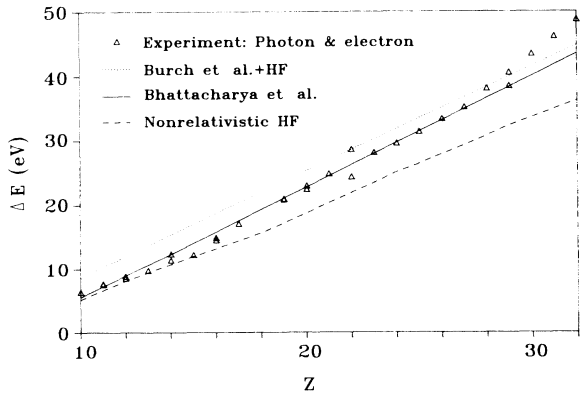

FIG. 1. Measured and calculated energy shifts of photon and electron excited x-ray $K\alpha$ satellites relative to the $K\alpha$ diagram lines. Note the excellent agreement with the analytic SCF calculations of Bhattacharya *et al.* (Ref. 36).

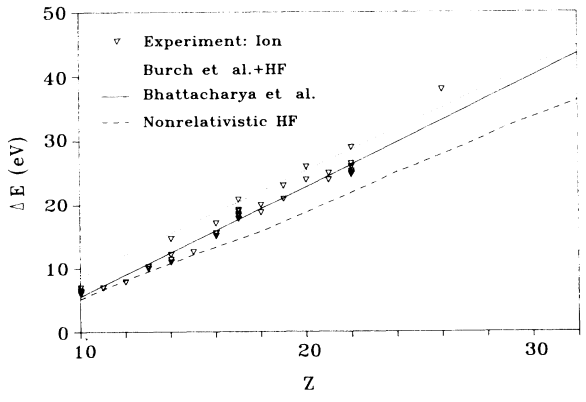

FIG. 2. Same as Fig. 1 but for ion-excited spectra.

cancies are likely to be created.[19] We have therefore listed the ion-excited satellite shifts separately from the electron and photon excited ones in Table I. The major part of the electron excited shifts are taken from the pioneering work of Parratt,[29] in which the satellite spectrum was resolved into four individual lines. We calculated the shift for each atom as an average of the energies of the resolved lines weighted by their relative intensities. The shifts so obtained are expected to be accurate to ± 2 eV. The same weighted averaging was used to calculate the nominal satellite or diagram line positions whenever a split spectrum was provided. The overall agreement between the various shifts measured for the same atom in the table is good. The contributions of the additional shifts in the ion-excited satellites seem to be small for all atoms with the possible exception of the highest-Z atom for which both photon and ion data are available: Fe. The variations of the shift with the chemical state of the emitting atom[11,12] are also small for our z range. Note that for Ti, the 28.7 eV shift measured by Parratt[29] deviates significantly not only from the 24.4 eV one measured by Hill *et al.*,[19] but also from the value of 26.2 eV interpolated by us from the shifts measured by Parratt for neighboring atoms.

A comparison between the measured and calculated shifts is given in Figs. 1 and 2. The agreement between the SCF analytic calculations of Bhattacharya *et al.* and the photon data in Fig. 1 is excellent, except for $Z \geq 28$, where systematic deviations occur. Even there the discrepancy should not be considered serious in view of the above-mentioned ± 2-eV uncertainty in the measured shifts, and the possible systematic ~ 1-eV calibration error in Parratt's work recently suggested in our work on the Cu satellites.[31] Even the simple hydrogenic approximation of Burch *et al.*[34] yields a not unreasonable agreement with experiment when HF-derived σ values are used. The Slater-rule-derived σ increases the deviations between theory and experiment uniformly by ~ 1.2 eV, as can be seen in Table I. Finally, the HF calculations agree with experiment only up to $Z = 16$. For larger Z they increasingly underestimate the measured shifts. These large deviations, amounting to ~ 13 eV for Ge, are not surprising, considering the fact that the shifts are calculated as differences between *total* energies. Using the weighted average scheme discussed above with published fully split spectra calculated in the intermediate-coupling scheme, and the known LS-coupling line intensities,[33] we obtain shifts of 36.8 eV for copper[31] and 7.3 eV for sodium,[38] in better agreement with experiment than the total energy HF values. With the availability of reliable intermediate-coupling line intensities, the weighted averaging scheme is expected to yield a much better agreement with experiment.

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