Energy and screening in the $K\alpha$ x-ray satellite spectra

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Nonrelativistic intermediate-coupling Hartree-Fock calculations of fully split x-ray $K\alpha$ satellite spectra of atoms with $10 \leq Z \leq 32$ were carried out. The average energy shift of the satellite with respect to the $K\alpha$ line was calculated from a weighted average of the individual lines using known *LS*-coupling relative intensities. The results are found to be in excellent agreement with an extensive set of measured energy shifts and with recent self-consistent-field calculations based on an electrostatically induced level-shift model for the $2p$ spectator vacancy. The measured data are also used to calculate the effective screening parameter of the $2p$ spectator vacancy. A value of ~ 0.6 is found for our Z range, in close agreement with the published value for the $1s$ spectator vacancy. The weak linear decrease in this value with increasing Z is attributed to the presence of additional high-level vacancies as well as preemission electronic level rearrangement.

Multielectronic transitions in the same atom provide important information on intra-atomic electron correlations and excitation dynamics.[1] The most conveniently accessible manifestation of such processes are the x-ray satellites and hypersatellites which attracted an ever increasing research interest over the last two decades. In particular, several studies of the Z dependence of the energy shifts of the $K\alpha$ satellite lines relative to the $K\alpha$ diagram ones were recently published.[2–7] Several of the recent theoretical predictions were compared in our previous work with a large body of experimental energy shifts measured for low-Z atoms using photon, electron, and ion excitations. Bhattacharya's[3] self-consistent-field wave-function calculations were found to yield an excellent agreement with the data up to $Z \approx 29$, above which small, but systematically increasing, deviations occur. This agreement is, however, somewhat spurious, as Bhattacharya *et al.* do not take into consideration the different relative intensities of the individual spectral lines, but rather use a equally-weighted average. Their calculation is based on a model by Burch *et al.*[6] which treats the additional $2p$ vacancy existing throughout the emission process as a source of perturbing electrostatic potential. This caused a nonuniform shift of the inner levels, and thus also of the energy of the emitted photon. The original hydrogenic wave function predictions of Burch *et al.*[6] overestimate the measured shifts significantly. Moreover, our Hartree-Fock (HF) total-energy calculations[7] underestimate the measured shifts for $Z > 17$. These HF calculations have now been extended to averages over the fully split spectrum for each atom in the range $10 \leq Z \leq 32$ and the results are presented here. An excellent agreement is found with the experimental data for $Z \leq 29$. The experimental data is also used to derive an effective screening parameter $\Delta Z_{2p^{-2}}$ for the additional $2p$ spectator hole following the method of Bergstrom and Hill.[8] The dominant influence of additional spectator holes at higher levels on $\Delta Z_{2p^{-2}}$ is also discussed.

The satellite lines originate in the transitions $(1s2s)^{-1} \rightarrow (2s2p)^{-1}$ and $(1s2p)^{-1} \rightarrow (2p)^{-2}$. However, the contribution of the former was determined to be negligible[4,9] for our Z range, and thus only the latter will be considered here. This transition involves (sp) and (pp) configurations, which in the intermediate-coupling scheme, and taking into account spin-orbit and electrostatic splitting, has the following sublevels:[4,10,11] for the (sp) configuration

$$\begin{aligned} &E_0+G_1/6+\zeta/4\pm[(G_1/3-\zeta/4)^2+\zeta^2/2]^{1/2} \quad \text{for } {}^1P_1 \text{ and } {}^3P_1\,, \\ &E_0-G_1/6+\zeta \quad \text{for } {}^3P_0\,, \\ &E_0-G_1/6-\zeta/2 \quad \text{for } {}^3P_2\,, \end{aligned} \tag{1}$$

and for the (pp) configuration,

$$\begin{aligned} &E_0'+\zeta'/2+9F_2/50\pm[(3F_2/10-\zeta'/2)^2+2\zeta'^2]^{1/2} \quad \text{for } {}^1S_0 \text{ and } {}^2P_0\,, \\ &E_0'-3F_2/25+\zeta'/2 \quad \text{for } {}^3P_1\,, \\ &E_0'-\zeta'/4\pm[(3F_2/25+\zeta'/4)^2+\zeta'^2/2]^{1/2} \quad \text{for } {}^1D_2 \text{ and } {}^3P_2\,, \end{aligned} \tag{2}$$

where E_0 and E_0' are the total energies of the two configurations, G_1 and F_2 the usual Slater integrals,[11] and ζ and ζ' are the spin-orbit parameters for the two configurations. Among these levels there are 14 transitions which are dipole-allowed in the intermediate coupling scheme.[10] A relative-intensity-weighted average should yield the average satellite shift to be compared with the measured value. However, as intermediate-coupling intensities are not available and in view of the low-Z range under consideration, we have chosen to approximate them by the known[4] *LS*-coupling intensities listed in Table I. Averaging over these intensities and the intermediate couplings energies, Eqs. (1) and (2), we ob-

TABLE I. Electric-dipole-allowed $(1s2p)^{-1}\rightarrow(2p)^{-2}$ transitions and their intensities in the LS-coupling scheme, normalized to a total intensity of 1.

Transition	$^1P_2\rightarrow{}^1D_2$	$^3P_2\rightarrow{}^3P_2$	$^3P_1\rightarrow{}^3P_2$	$^3P_2\rightarrow{}^3P_1$	$^1P_1\rightarrow{}^1S_0$	$^3P_0\rightarrow{}^3P_1$	$^3P_1\rightarrow{}^3P_0$	$^3P_1\rightarrow{}^3P_1$
Intensity	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{1}{15}$	$\frac{1}{15}$	$\frac{1}{15}$	$\frac{1}{20}$

tain for the satellite shift

$$\Delta E_s = E_0 + G_1/30 + \zeta/20 + [(G_1/3-\zeta/4)^2+\zeta^2/2]^{1/2}/5 - E_0' - \varepsilon_0 \ , \tag{3}$$

where ε_0 denotes the *calculated* diagram line energy,

$$\varepsilon_0 = E(1s^{-1}) - E(2p^{-1}) \ . \tag{4}$$

The use of the calculated, rather than the measured ε_0 eliminates the large deviation from experimental values known[3] to plague calculated HF levels involving $1s$ vacancies. Numerical values for E_0, G_1, ζ, E_0', and ε_0 in Eq. (3) were calculated using the nonrelativistic HF code of Froese Fischer,[12] employing single configurations only. The spin-orbit parameters ζ calculated by the HF code are known to be unrealistically large. The value calculated for $2p^{-2}$ was therefore scaled by the ratio between the calculated $2p^{-1}$ parameter ζ^c and the measured one ζ^m according to the procedure given by Kuhn and Scott:[4]

$$\zeta(2p^{-2}) = \zeta^c(2p^{-2})[\zeta^m(2p^{-1})/\zeta^c(2p^{-1})] \ ,$$

where the subscripts m and c indicate "measured" and "calculated", respectively, and

$$\zeta^m(2p^{-1}) = 2[E(K\alpha_1) - E(K\alpha_2)]/3 \ .$$

$E(K\alpha_1)$ and $E(K\alpha_2)$ are the measured diagram line energies of Bearden and Burr.[13]

The results obtained from Eq. (3) are shown in Fig. 1

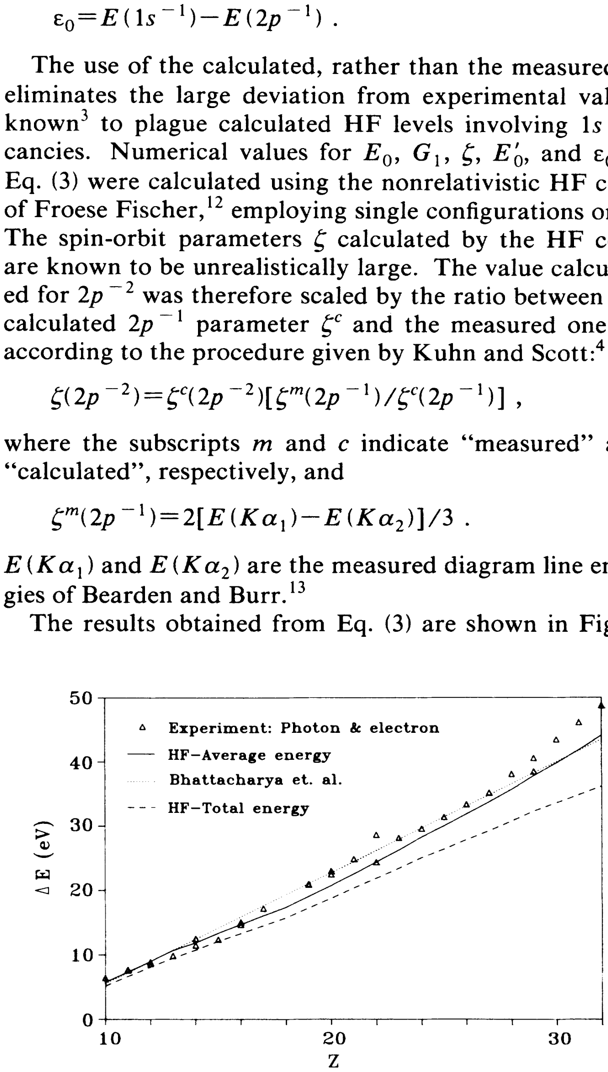

FIG. 1. Energy shifts of $K\alpha$ satellite lines relative to the diagram $K\alpha_1$ line. The measured values of photon- or electron-excited spectra are taken from Ref. 7 as are the Hartree-Fock total-energy calculations. HF average energy denotes the present LS coupling intensity weighted average of intermediate-coupling Hartree-Fock energies. Note that the HF average energies not only fit the measured values well but also follow its upward trend for $Z>32$.

along with experimental measured shifts and our earlier HF total-energy results from Ref. 7, and the self-consistent-field calculation of Bhattacharya *et al.*[3] Ion excitation was shown[14] to produce invariably additional vacancies at levels higher than $2p$ which, in turn, cause an increase in the measured energy shift of the satellite line. We chose, therefore, to compare the theoretical results in Fig. 1 to photon- or electron-excited shifts which are expected to be considerably less plagued by this effect. As can be seen the agreement between the present calculation and experiment is very good, as is the agreement with Bhattacharya's results. The discrepancy at the upper end of the z range should not be considered too serious in view of the ±2-eV error estimate in the measured shifts and a possible 1-eV calibration error in the measured values.[7] Also, with increasing Z the approximation of intermediate-coupling intensities by LS coupling intensities becomes gradually worse. Relativistic effects and an increasing ease of creating additional vacancies at higher levels as Z is increased may also contribute to the deviation of theory from experiment at high Z. Extrapolation of the high-Z end of both the experimental and the various theoretical curves beyond $Z=32$ seems to indicate that while Bhattacharya's model will increasingly underestimate the measured shifts, the HF average-energy calculation will follow the upward trend of the experimental shifts.

A phenomenological description of the Z dependence of x-ray satellite and, in particular, Auger line energies, was given by the generalized $Z+1$ approximation of Bergstrom and Hill[8] and Briand *et al.*[15] For our case where $(1s2p)^{-1}\rightarrow(2p)^{-2}$ it states that the effective screening parameter of the $2p$ spectator vacancy $\Delta Z_{2p^{-2}}$ defined by

$$\Delta Z_{2p^{-2}} = \frac{B_Z(2p^{-2}) - B_Z(2p^{-1})}{B_{Z+1}(2p^{-1}) - B_Z(2p^{-1})} \tag{5}$$

is a constant independent of Z. Here $B_Z(2p^{-1})$ and $B_{Z+1}(2p^{-1})$ denote the binding energy of a $2p^{-1}$ electron for atoms Z and $Z+1$ and $B_Z(2p^{-2})$ is the energy required to remove one $2p$ electron in an atom Z having already one $2p$ vacancy. Similar expressions can be written for $\Delta Z_{(1s)^{-2}}$ and $\Delta Z_{(1s2p)^{-1}}$ as shown by Briand *et al.*[15] Using Eq. (5) to calculate the energy of the $2p^{-2}$ ionized atom,

$$E_Z(2p^{-2}) = B_Z(2p^{-2}) + B_Z(2p^{-1}) \ ,$$

and a similar expression for $E_Z((1s2p)^{-1})$, we obtain for the satellite line energy

$$\begin{aligned}E_s&=E_Z((1s2p)^{-1})-E_Z(2p^{-2})\\&=B_Z(1s^{-1})-B_Z(2p^{-1})\\&\quad+\Delta Z_{(1s2p)^{-1}}[B_{Z+1}(2p^{-1})-B_Z(2p^{-1})]\\&\quad-\Delta Z_{2p^{-2}}(B_{Z+1}(2p^{-1}))\ .\end{aligned}\tag{6}$$

It has been shown[16] that $\Delta Z_{(1s2p)^{-1}}=1$ to about 1% in our Z range. Also note that the first two terms of the last equation give the energy of the $K\alpha$ line. Thus the energy shift of the satellite line from the diagram $K\alpha$ one is given by

$$\begin{aligned}\Delta E_s&=E_s-E(K\alpha)\\&=[1-\Delta Z_{2p^{-2}}][B_{Z+1}(2p^{-1})-B_Z(2p^{-1})]\ .\end{aligned}\tag{7}$$

We used this expression to calculate $\Delta Z_{2p^{-2}}$ from the measured[7] satellite shifts ΔE_s and electron binding energies.[17] The results are given in Fig. 2 separately for ion and electron or photon excited data. Although the scatter in the results is considerable, both sets of data yield $\Delta Z_{2p^{-2}}\approx 0.6$. The only exception is Ne which yields a surprisingly low $\Delta Z_{2p^{-2}}\approx 0.35$. This can be accounted for by relaxing the frozen orbital assumption and allowing an exceptionally high degree of atomic level rearrangement to occur for this atom before the photon is emitted. As shown by Briand *et al.*[15] such a rearrangement would influence $2p$ levels much more strongly than the $1s$ level, which accounts for the fact that a corresponding decrease in $\Delta Z_{1s^{-2}}$ for Ne was not observed.[15] No reason, however, can be given at present why such an increased rearrangement rate should apply to Ne, and to it only.

The value obtained here for $\Delta Z_{2p^{-2}}$, 0.6, is in close agreement with the value of $\Delta Z_{1s^{-2}}=0.625$ expected from first-order perturbation theory of the total energy of helium-like ions[1,18] and the values obtained from measured hypersatellite shifts by Briand *et al.*[15] Note also that both $\Delta Z_{1s^{-2}}$ and $\Delta Z_{2p^{-2}}$ are consistent with a linear dependence on Z, as can be seen in Fig. 5 of Ref. 15 and the linear fits in our Fig. 2. The reasons, however, for these are different. As discussed by Briand *et al.*[15] for the doubly ionized $1s$ levels, the dominant correction is the spin-spin interaction. Its increase with Z will cause a corresponding increase in $\Delta Z_{1s^{-2}}$. In our case, a decrease in $\Delta Z_{2p^{-2}}$ is observed. This can be accounted for by considering the influence of additional vacancies at levels higher than $2p$. It has been shown[14] that such vacancies will increase the energy shift of the satellites and hence decrease the calculated $\Delta Z_{2p^{-2}}$. The creation of

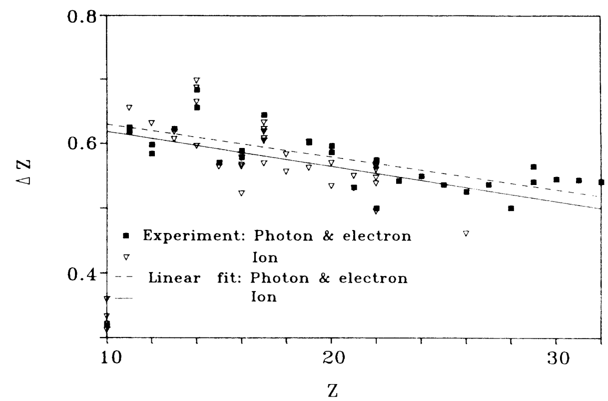

FIG. 2. Effective screening parameter $Z_{2p^{-2}}$ as calculated using Eq. (7), from the ion and electron- or photon-excited measurements listed in Ref. 7. Linear fits were done separately for each of the two excitation modes. The downsloping trend and lower values for ion-excited data are discussed in the text.

additional vacancies becomes increasingly easier with increased Z and exciting projectile mass.[14] This, in turn, implies that ion excited data should yield lower $\Delta Z_{2p^{-2}}$ values than the photon or electron excited ones and also that $\Delta Z_{2p^{-2}}$ will decrease with increasing Z for both sets of data due to the increasing probability of additional high level vacancy creation. Both predictions are in fact borne out by the fits to the data presented in Fig. 2. By contrast, the hypersatellites involve high energy $1s^{-2}$ and $(1s2p)^{-1}$ levels only, the influence on which of additional high-level vacancies is negligible. Consequently, hypersatellite-derived $\Delta Z_{1s^{-2}}$ data will not exhibit this effect. A gradual increase with Z of the post-ionization rearrangement rate may also contribute to the decrease observed in $\Delta Z_{2p^{-2}}$ with increasing Z.

The results presented here and in our previous study[7] indicate that the overall features of the satellite energy shifts for the present Z range are rather well understood. However, with the availability of sophisticated atomic structure computational methods and codes[12,19] a much more detailed understanding could be achieved provided that a systematic body of high-accuracy experimental data is also available. At present the majority of the photon- and electron-excited data and the only one available for $Z\geq 22$ is the 50-year-old pioneering work of Parratt.[20] Clearly a systematic body of high-accuracy experimental data on the Z dependence of the satellite on hypersatellite spectra is called for.

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