

# Resolving the Mysteries of a Hollow Atom

S. Huotari<sup>1</sup>, K. Hämäläinen<sup>1</sup>, C.-C. Kao<sup>2</sup>, R. Diamant<sup>3</sup>, R. Sharon<sup>3</sup>, and M. Deutsch<sup>3</sup>

<sup>1</sup>Division of X-ray Physics, Department of Physical Sciences, University of Helsinki, Finland

<sup>2</sup>National Synchrotron Light Source, Brookhaven National Laboratory

<sup>3</sup>Physics Department, Bar-Ilan University, Israel

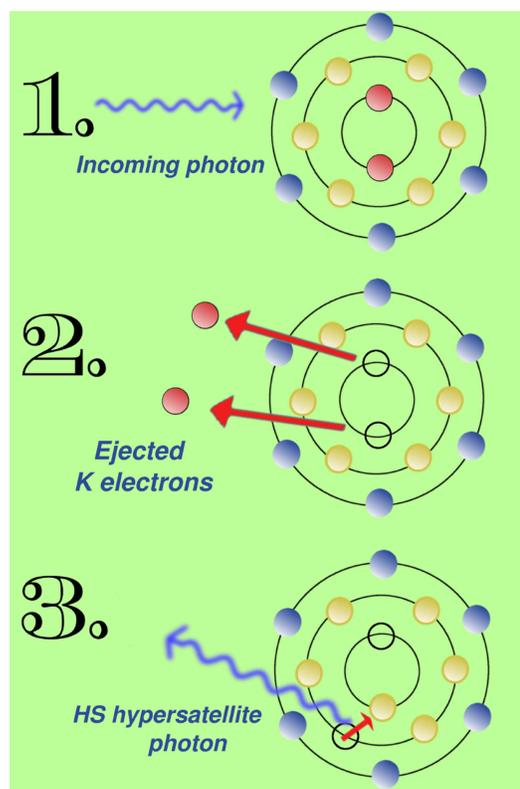
The concept of standard fluorescence spectroscopy is well known. A particle (usually a photon or an electron) is used as a projectile impinging on an atom, which absorbs the energy of the particle. In this process an electron from an occupied shell gets excited to a higher electronic state, for example into the continuum. When the newborn hole is filled by an electron from another shell, a fluorescence photon is emitted. If the incident particle has enough energy, it can induce a multielectronic excitation. If this happens so that the atom is left with a completely empty  $K$  shell, while the outer shells remain intact, we have a so-called *hollow atom*. When one of the  $K$  holes is filled in the presence of the second  $K$  hole, the emitted fluorescence lines are called hypersatellite (HS) lines [1,2]. These lines constitute the "diagram" spectrum of the hollow atom, exactly in the same way as the emission lines resulting from the filling of a single  $K$  hole in the presence of the second  $K$  electron constitute the "diagram" spectrum of a conventional atom.

The creation of a hollow atom and the consecutive emission of the HS photon are schematically presented in Figure 1. In the top panel a photon with energy greater than twice the  $K$  electron binding energy is absorbed by the atom. The atom has  $K$ ,  $L$  and  $M$  electrons colored in red, yellow and blue, respectively. When the photon ionizes directly one  $K$  electron, there is a finite, though small, probability of the second  $K$  electron being carried away as well due to intra-shell correlation. The consequent hollow atom excited state in the middle panel relaxes then through a one-electron transition, in this example, from the  $L$  shell. In this case a  $K^{\alpha}$  HS photon is emitted. When the filling electron comes from the  $M$  shell, a  $K^{\beta}$  HS photon is emitted.

Well-resolved studies of the photoexcited hypersatellite lines have been extremely rare due to the low cross-section for their creation process. For medium- $Z$  elements, the intensity of the HS lines is  $\sim 10^{-4}$  of that of the conventional "diagram"  $K\alpha_{1,2}$  lines [3]. Nevertheless, studies of the formation mechanism and electronic structure of hollow atoms are very important, since they relate closely to such concepts of basic atomic physics as correlation, relativity, Breit interaction, and quantum electrodynamical (QED) effects. Firstly, the process in which one photon excites two electrons is only possible if the two electrons interact,

i.e. it cannot be described in an independent-electron picture. The process is a direct consequence of, and hence allows studying intra-shell correlation. Relativistic effects also play a crucial role here. For medium- $Z$  and heavier atoms, the  $K$  shell is significantly relativistic and thus such effects on atomic correlation can be studied using the HS spectra.

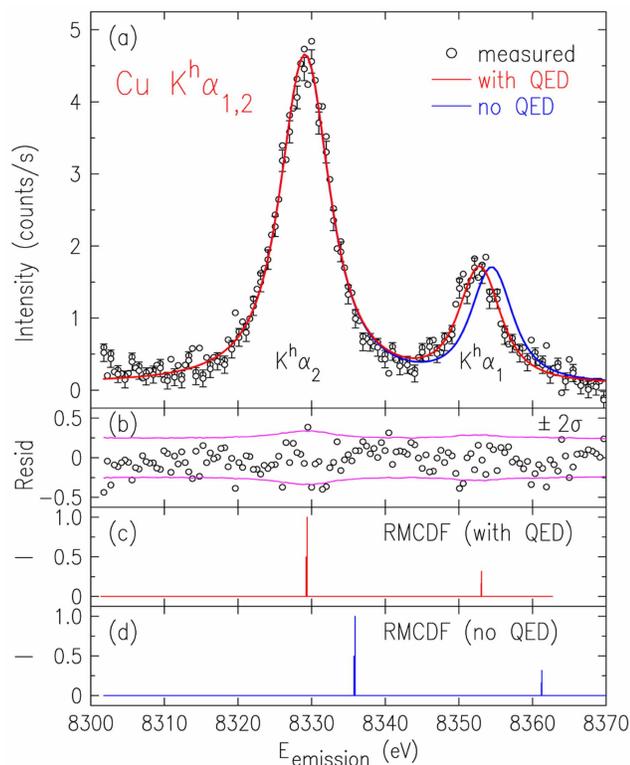
One of the least studied atomic interactions is the Breit interaction, which in a certain approximation, involves such effects as the spin-spin, spin-orbit and spin-other-orbit-interactions. Almost all atomic transitions are dominated by the Coulomb interaction, and the contri-



**Figure 1.** The formation mechanism of a hollow atom and the creation of a hypersatellite (HS) fluorescence photon. For clarity, the electrons in different shells are color-labeled;  $K$  electrons are red,  $L$  electrons are yellow and  $M$  electrons are blue. In this figure the formation of a  $K^{\alpha}$  fluorescence photon is depicted. In this case, an electron from the  $L$  shell fills the core hole. The corresponding  $K^{\beta}$  line is created when an electron from the  $M$  shell fills the core hole.

bution of the Breit interaction amounts in these transition probabilities to less than 1%. However, for the HS transitions the contribution of the Breit interaction is calculated to reach as high as 20% in heavy atoms [4]. Thus, the HS spectra allow also the study of these interactions.

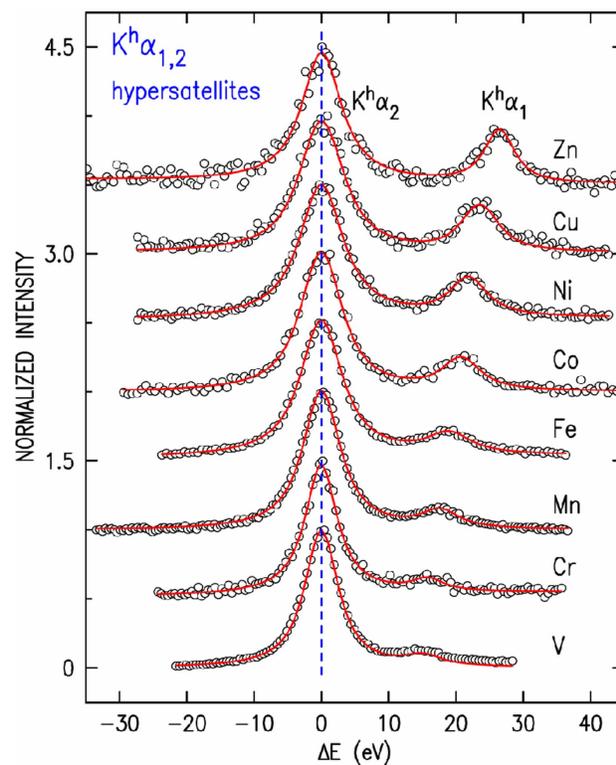
One of the most outstanding features of the  $K^h\alpha_{1,2}$  HS spectra is the weak  $K^h\alpha_1$  line. This line originates in the  $^1S_0 \rightarrow ^3P_1$  spin-flip transition, which is dipole-forbidden in the pure  $LS$  coupling scheme and fully allowed only in the  $jj$  coupling. The intensity ratio  $R=I(K^h\alpha_1)/I(K^h\alpha_2)$  depends, therefore, strongly on the intermediacy of the coupling. This makes the HS spectrum the most sensitive - and practically the only - method for quantitatively studying the coupling variation with  $Z$  from the



**Figure 2.** (a) The  $K^h\alpha_{1,2}$  fluorescence hypersatellite lines of Cu. As is the case in regular fluorescence lines, the  $K^h\alpha_2$  line is the one with lower energy. However, the intensity ratio is now reversed, the  $K^h\alpha_1$  line being lower in intensity than the  $K^h\alpha_2$  line. The solid lines represent the theoretical prediction by the program GRASP for the lines, the red line with and the blue line without QED corrections included. (b) The difference between the theoretical (red line, including QED) calculation and the experimental data points. All residuals lie between the  $\pm 2\sigma$  confidence limit, indicating a good fit. (c,d) The stick diagrams for the calculated lines and their relative strength. While not including the QED gives wrong energies for the HS lines, the blue line in (a) is shifted so that the  $K^h\alpha_2$  line falls to the correct energy. As can be seen, even then the splitting of the two lines is comes out incorrect, proving the importance of the QED effects here.

$LS$  coupling scheme at low  $Z$ , where the ratio  $R=0$  to the  $jj$  coupling limit at high  $Z$  where  $R=2$ , the canonical value observed in the corresponding diagram lines.

We have measured the  $K^h\alpha_{1,2}$  spectra of transition metals ranging from V to Zn. The experiments were done at the NLSL wiggler beamline X25 using monochromatized synchrotron radiation with incident energies of 10-25 keV. The radiation was focused by a toroidal mirror and monochromatized by a two-bounce Si(111) monochromator. The resulting energy bandwidth was  $\sim 6$  eV, and the photon flux  $\sim 10^{12}$  photons/sec in a spot size of  $\sim 0.5$  mm<sup>2</sup>. The sample-emitted radiation was measured using a Johann-type scanning spectrometer on a Rowland circle of  $\sim 1$  m radius. The Bragg angles were kept as high as possible ( $\theta \geq 70^\circ$ ) to obtain



**Figure 3.** The HS spectra of transition metal elements ranging from V ( $Z=23$ ) to Zn ( $Z=30$ ). All spectra have been shifted on the energy scale by the energy of the  $K^h\alpha_2$  line.

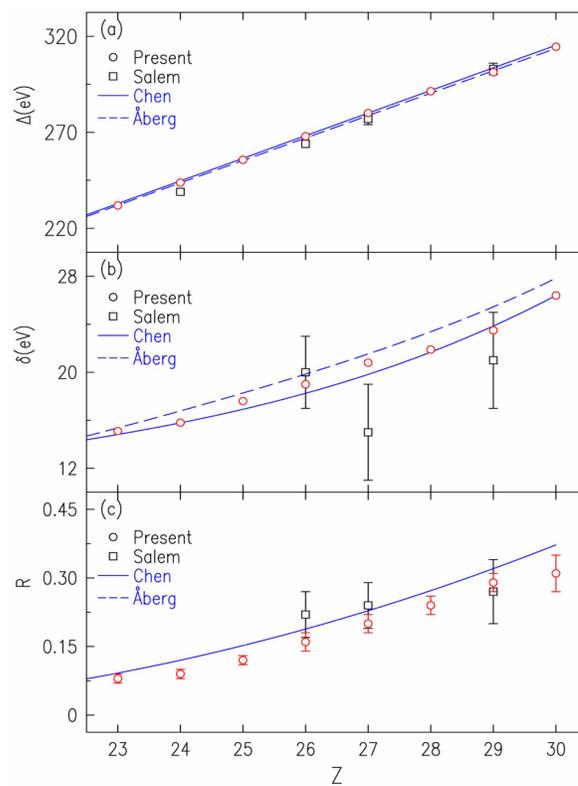
high energy resolution of about 1-4 eV. All analyzer crystals were spherically bent Si or Ge wafers. An angle of  $90^\circ$  was employed between the incident and emitted x-ray beams at the sample to minimize elastic and Compton background scattering. The analyzer-focused photons were recorded by an ultrapure Ge detector. The experimental results were compared with ab-initio calculations done using the relativistic multi-configurational Dirac-Fock (RMCDF) package GRASP, with some supplementary code written in house [2,5].

An example of HS lines of Cu is presented in Figure 2. In (a) the experimental spectrum is shown with a fit to our RMCDF calculations, shown in (c). The low fit residuals, shown in (b), almost all within  $\pm 2\sigma$  where  $\sigma$  is the standard deviation in the points, indicate a very good fit. The inverted  $R$  discussed above immediately stands out: instead of the  $K\alpha_{1,2}$  diagram lines' standard intensity ratio of  $R \approx 2$ , we obtain here  $R \approx 0.3$  for HS, due to the spin-flip forbidden  $K^n\alpha_1$  line. The incorrect doublet splitting obtained when QED corrections are neglected (a,d) demonstrates the exceptionally large Breit contribution in HS. As the coupling scheme evolves from  $LS$  coupling at low- $Z$  toward  $jj$  coupling at higher  $Z$ , the intensity of the  $K^n\alpha_1$  line, and hence  $R$ , also grows. This is seen clearly in Figure 3, where we plot the  $K^n\alpha_{1,2}$  HS spectra we measured for the  $3d$  transition metals, shifted to a common energy origin. The evolution of the (a) intensity of the  $K^n\alpha_1$  peak and the (b)  $K^n\alpha_1$ - $K^n\alpha_2$  spin doublet splitting with  $Z$  is very clear. The variation with  $Z$  of the shift,  $\Delta$ , of the HS from the diagram lines, the HS doublet splitting,  $\delta$ , and  $R$  are plotted in Figure 4, along with two theoretical calculations by Åberg and Suvanén [6] and by Chen *et al.* [7], and previous measurements [8]. While the shifts are reproduced well by both theories, the splittings are overestimated by the former, where correlations are neglected. For  $R$ , the best theoretical values [7] systematically overestimate the experimentally observed ratio. This suggests that the intermediacy of the coupling is not properly accounted for. Non-relativistic calculations, or those excluding the Breit interaction, yield even larger, 20%-30% overestimations.

An extremely important feature of the photoexcitation method is the ability to tune the energy of the exciting photons. This allows one to study the evolution of the excited emission spectrum from the energy threshold for creating the initial state (adiabatic regime), to the high excitation energy limit (isothermal regime), where the intensity and shape of the emission spectrum saturate. The electronic excitation and de-excitation processes of an atom high above the excitation threshold, in the isothermal regime, are separate and consecutive. They have been successfully studied and accounted for within the standard independent-electron/frozen core/sudden approximations. Near threshold, however, the time required for the ejected electrons to leave the atom is comparable to the lifetime of the excited state. Thus, the excitation and the de-excitation processes occur on comparable time scales, merging into a single complex process. Studies of the adiabatic regime for any emission line has been very scarce since they require tunable x-ray sources of a high intensity, which became available only recently with the advent of insertion device beamlines at synchrotrons. All measurements carried out to date

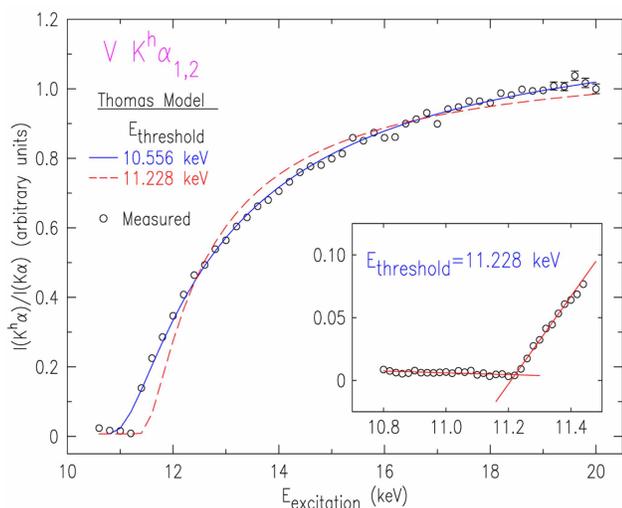
for diagram [9], satellite [10] and hypersatellite [1,2] spectra have shown that the *shape* of the emission spectra saturates very fast (less than 50 eV from the threshold) but that the *intensity* may require a surprisingly long energy range to saturate. An example of the evolution of the V  $K^n\alpha$  lines' intensity (normalized to that of the V  $K\alpha$  diagram spectrum) with incident photon energy is shown in Figure 5.

The experimental data is compared to the Thomas model [11], which employs time-dependent perturbation theory to describe the excitation (shake) process near threshold. Two different fits to the model are plotted. The best overall fit (solid blue line) results in a clearly erroneous value for the energy threshold. Fixing the threshold energy at the measured value (dashed red



**Figure 4.** (a) The shift of the HS lines from the diagram lines  $\Delta$ , (b) the mutual energy difference (splitting) of the HS lines  $\delta$ , and (c) the intensity ratio  $R = I(K^n\alpha_1)/I(K^n\alpha_2)$ , as a function of the atomic number  $Z$ . The circles refer to the present experimental results, squares to results by Salem *et al.* [8], and dashed and solid lines to theoretical results by Åberg *et al.* [6] and Chen *et al.* [7], respectively.

line) gives, in turn, a poor overall behavior. This suggests that the Thomas model, found successful for outer-shell shake processes, requires modification when the correlation-excited electron comes from an inner shell.



**Figure 5.** The relative intensity evolution of the  $V K^h \alpha$  lines. Circles represent the experimental data, while two different fits to the Thomas model [11] are represented by solid blue and dashed red lines (see text).

It has been shown [12] that there is a different threshold behavior for electron shake-off and shake-up processes. The cross section for shake-up jumps discontinuously at threshold to a significant fraction of its high-energy value. By contrast, for shake-off processes, the intensity of the resultant emission lines rises smoothly from zero at threshold. Thus the continuous rise from zero at threshold observed for the HS line intensity in the inset to Figure 5 implies an exclusive shake-off character for the second  $K$  hole, as indeed predicted by shake theory [12].

As can be seen, the onset of the excitation (i.e. the threshold energy) is roughly 11.2 keV, while the line intensity saturates only close to  $\sim 18$  keV. The anomalously long saturation range,  $\sim 7$  keV or  $\sim 60\%$  of the threshold energy, is by far the largest observed for any line to date. The lines' intensity behavior is also similar for all other elements we have measured. The explanation must be sought in the adiabatic (slow) nature of the excitation and de-excitation processes. Theoretical calculations for these processes in the adiabatic regime, not available at present, are sought for to shed light on the trends observed in these experiments.

## Acknowledgments

Expert help, advice and discussions with Zhijian Yin and Lonny Berman are gratefully acknowledged. This work has been supported by The Israel Science Foundation, Jerusalem (M.D.) and the Academy of Finland (grants no. 7379/40732) (K.H. and S.H). Research was carried out in whole at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-98CH10886.

## References

- [1] R. Diamant, S. Huotari, K. Hämäläinen, C.-C. Kao, and M. Deutsch, "Evolution from Threshold of a Hollow Atom's X-Ray Emission Spectrum: The  $Cu K^h \alpha_{1,2}$  Hypersatellites", *Physical Review Letters* **84**, 3278, 2000.
- [2] R. Diamant, S. Huotari, K. Hämäläinen, C.-C. Kao, and M. Deutsch, " $Cu K^h \alpha_{1,2}$  hypersatellites: Suprathreshold evolution of a hollow-atom x-ray spectrum", *Physical Review A* **62**, 052519, 2000.
- [3] E.P. Kanter, R.W. Dunford, B. Krässig, and S.H. Southworth, "Double  $K$ -Vacancy Production in Molybdenum by X-Ray Photoionization", *Physical Review Letters* **83**, 508, 1999.
- [4] J.P. Desclaux, B. Briancon, J.P. Thibault, and R.J. Walker, "Breit Interaction and Double  $K$  Vacancies in Nuclear Transitions", *Physical Review Letters* **32**, 447, 1974.
- [5] M. Deutsch, G. Holzer, J. Hartwig, J. Wolf, M. Fritsch, and E. Forster, " $K\alpha$  and  $K\beta$  x-ray emission spectra of copper", *Physical Review A* **51**, 283, 1995.
- [6] T. Åberg and M. Suvanen, "Relativistic theory of x-ray satellites", in *Advances in X-ray Spectroscopy*, edited by C. Bonnelle and C. Mande (Pergamon, New York), 1980.
- [7] M.H. Chen, B. Crasemann, and H. Mark, "Effect of the Breit interaction on  $K$ x-ray hypersatellite spectra", *Physical Review A* **25**, 391, 1982.
- [8] S.I. Salem, A. Kumar, B.L. Scott, and R.D. Ayers, "Splitting of the Two-Electron, One-Photon Transitions in Fe and Co", *Physical Review Letters* **49**, 1240, 1982; S.I. Salem, A. Kumar, and B.L. Scott, "Two-electron, one-photon transitions in Cr, Fe, Co, and Cu", *Physical Review A* **29**, 2634, 1984.
- [9] M. Deutsch et al., to be published.
- [10] M. Deutsch, O. Gang, K. Hämäläinen, C.-C. Kao, "Onset and Near Threshold Evolution of the  $Cu K\alpha$  X-Ray Satellites", *Physical Review Letters* **76**, 2424, 1996.
- [11] T.D. Thomas, "Transition from Adiabatic to Sudden Excitation of Core Electrons", *Physical Review Letters* **52**, 417, 1984.
- [12] T. Åberg, "Theory of multiple ionization processes", in *Proceedings of the International Conference on Inner-shell Ionization Phenomena and Future Applications*, edited by R.W. Fink, S.T. Manson, J.M. Palms, and P.V. Rao, U.S. AEC Report No. CONF-720404 (NTIS, U.S. Dept. of Commerce, Springfield, VA), 1509, 1972.