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Abstract

Experimental and theoretical x-ray transition energies are precisely estimated and compared for 40<Z<100. All allowed and forbidden intervals for the n=1 to n=2, 3 levels are determined. The experimental values are derived from absolute wavelength measurements of Kα and Kβ transitions and from L series x-ray measurements. The theoretical values are obtained using a multiconfiguration Dirac-Fock code with some modifications in the Lamb shift calculations. Comparison between experiment and theory for Z<85 now provides a more coherent qualitative picture: (1) for the $1s^{-1}\rightarrow 2s^{-1}$, $1s^{-1}\rightarrow 3s^{-1}$, and $1s^{-1}\rightarrow 3p^{-1}$ transitions, experimental energies are 5-10 eV larger, consistent with the magnitude and sign of the level shifts resulting from pair correlation and configuration mixing with Coster-Kronig and Auger transitions which were not included in the theory and (2) for the $1s^{1}\rightarrow 2p^{-1}$ and $1s^{-1}\rightarrow 3d^{-1}$ transitions, experimental energies are ≈3 eV larger, of which ≈1.5 eV can be attributed to pair correlation leaving ≈1.5 eV to higher order effects not included in our theory.

Introduction

Several comparisons between experimental and theoretical allowed transition energies have been published over the past ten years [1, 2, 3]. The experimental and theoretical estimates have improved to the point that the differences are regarded as significant and qualitatively attributed to pair correlations and configuration mixing with autoionizing channels. In this report, we extend the experiment-theory comparisons to all transitions between K and L, M shells in order to further test the importance of these correlations. We begin by briefly describing the experimental and theoretical estimation procedures and then attempt to qualitatively explain the experiment-theory differences by the above mentioned corrections. Lastly, areas in which experiment and theory are deficient are identified.

Experimental Estimates

Experimental x-ray energies must be measured on a wavelength (energy) scale which is consistent with that used for theoretical calculations if meaningful comparisons are to be made. Since the Rydberg establishes the scale for theoretical calculations, the energy scales of all experimental measurements included in this report are connected in a rigorous way to the Rydberg constant.

Accurate estimates of x-ray energies for $K\alpha_1$, $K\alpha_2$, $K\beta_1$ and $K\beta_3$ transitions (allowed transitions) have been made over a wide range of Z. The input data include (1) measurements using calibrated crystals and absolute angle measuring spectrometers, (2) measurements of wavelength ratios, and (3) measurements of K series x-rays for $Z \geq 90$ which were referenced to Y transitions. All of these measurements are on a scale consistent with the theoretical calculations.

To estimate the forbidden transitions ($1s^{-1} \rightarrow 2s^{-1}$, $1s^{-1} \rightarrow 3s^{-1}$, and $1s^{-1} \rightarrow 3d^{-1}$) the allowed K transitions were combined with L series measurements. Two routes are available for 3 of the 4 forbidden transitions and they generally agree to within ±1 eV. The combinations which were used are:

$$E(1s^{-1} \rightarrow 2s^{-1}) = E(K\beta_1) - E(L\beta_3) = E(K\beta_3) - E(L\beta_4)$$

$$E(1s^{-1} - 3s^{-1}) = E(K\alpha_1) + E(L\ell) = E(K\alpha_2) + E(Ln)$$

$$E(1s^{-1} - 3d_{3/2}{}^{-1}) = E(K\alpha_1) + E(L\alpha_2) = E(K\alpha_2) + E(L\beta_1)$$

$$E(1s^{-1} - 3d_{5/2}{}^{-1}) = E(K\alpha_1) + E(L\alpha_1)$$

The L series x-ray measurements were taken from the compilation by J.A. Bearden [4]. Since this compilation is in xu and was based on an assigned wavelength of 208.5770 xu for the $WK\alpha_1$ line, the published values were converted to meters by using the ratio of the measured wavelength of the $WK\alpha_1$ line [5] to the above xu value. All conversions from wavelengths (meter) to energies (eV) used the value $1.23984244 \times 10^{-6}$ eV·m from the 1986 adjustment of the fundamental constants [6].

Theoretical Estimates

Existing versions of multiconfiguration Dirac-Fock programs are different mostly in estimating QED corrections. For instance, the program by Grant et al. [7] uses the hydrogenic self energy values calculated by Mohr [8] for the 1s, 2s, $2p_{1/2}$, and $2p_{3/2}$ electrons with a point nucleus. Actually, these values are modified to account for the screening of the nuclear charge by other electrons, according to the ratio of Dirac-Fock <r> to the hydrogenic <r> for those electrons. For the ns, $np_{1/2}$, and $np_{3/2}$ ($n \geq 3$) electrons, the self energy values of the 2s, $2p_{1/2}$, and $2p_{3/2}$ electrons are scaled by the n^3 ratio, i.e., self energy of 3s = self energy of 2s · $(2^3/3^3)$, etc. Vacuum polarization contributions are calculated using the Uehling potential for all electrons.

On the other hand, Desclaux's earlier program [9] included the same QED corrections only for the 1s, 2s, $2p_{1/2}$, and $2p_{3/2}$ electrons. The more recent version of this program includes self-energy corrections for all electrons, including those for $\ell \geq 2$, and vacuum-polarization correction for all electrons using the Uehling potential [order $\alpha(Z\alpha)$] and the first order correction to the Uehling potential [order $\alpha(Z\alpha)^3$] [10]. Self energy of the ns and np ($n \geq 3$) electrons are extrapolated from the corresponding 2s and 2p values by the n^3 scaling. Those for the 3d, 4d, 4f,... electrons are extrapolated from the corresponding values for the hydrogen atom [11] using the Z^4 scaling and assuming the $F(Z\alpha)$ function to be independent of Z. Screening of the self-energy correction for each electron is determined by the ratio of the Dirac-Fock (extended nucleus) charge density to the hydrogenic (point nucleus) density integrated from the origin to 0.3 Compton wavelength. A study of transition wavelengths of Na-like ions indicates that the screening by the ratio of charge density agrees slightly better with experiment than the screening by the ratio of <r>.

After these QED corrections, the next leading theoretical corrections are those due to correlation. There are two types of correlation corrections required [12]: (a) the usual pair correlation corrections, for which an approximate value (1-2 eV for inner-shell electrons) can be assigned for each electron, and (b) corrections due to configuration mixing of hole states with those that lead to

Coster-Kronig Auger transitions. For instance, a 2s hole state is energetically degenerate with the final state of a Coster-Kronig transition where a 2p electron fills the 2s hole and another 2p electron is ejected into the continuum. Hence, a 2s hole state must be described as a mixture of the hole state with another state with two 2p holes and an electron in the continuum with appropriate energy.

This correction due to the mixing with autoionizing states applies primarily to the 2s, 3s, and 3p hole states, since Auger transitions involving electrons with different principal quantum numbers are much less likely to happen than the Coster-Kronig transitions. According to Chen et al., [12] this correction grows slowly with Z to about 6-7 eV around Z=80, and rapidly decreases for higher Z. With this correction, the energy levels of the 2s, 3s, and 3p hole states become lower with respect to the 1s hole state and the corresponding x-ray energies are increased accordingly. In contrast, the effect of the pair correlation is minor. This correction should increase theoretical values by 1-2 eV.

Experiment-Theory comparison

Experiment and theory are compared in Figs. 1, 2, and 3 where the experiment-theory differences are plotted as a function of Z for the n=1 to n=2,3 transitions. The separation of the plotted points from the horizontal axis is a measure of how well the above described theory without correlation corrections predicts the experimental results.

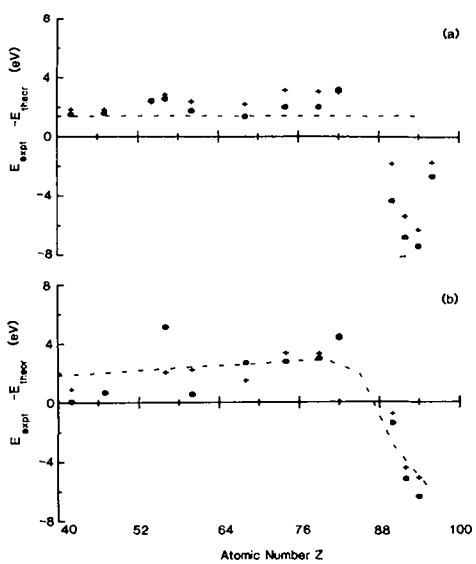

Fig. 1 Differences between experimental and theoretical energies for (a) $1s^{-1} \rightarrow 2p_{1/2}^{-1}$ (+) and $1s^{-1} \rightarrow 2p_{3/2}$ ( ) transitions and (b) $1s^{-1} \rightarrow 3d_{3/2}$ (+) and $1s^{-1} \rightarrow 3d_{5/2}^{-1}$ ( ) transitions vs. Z. The dashed lines are the corrections to theory for (a) pair correlation and (b) pair correlation + higher order terms (see text).

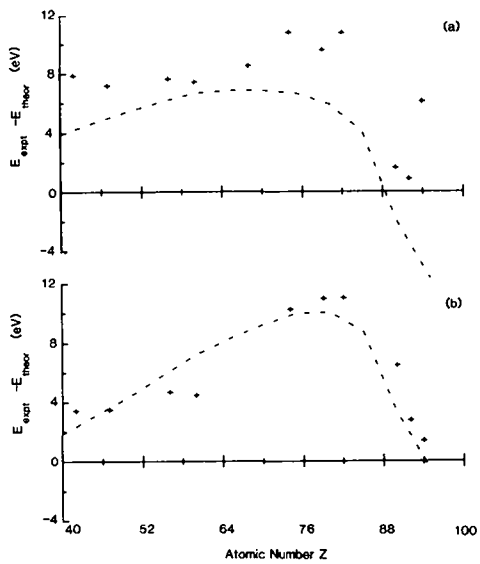

Fig. 2 Differences between experimental and theoretical energies for (a) the $1s^{-1} \rightarrow 2s^{-1}$ (+) transition and (b) the $1s^{-1} \rightarrow 3s^{-1}$ (+) transition vs. Z. The dashed lines are the correction to theory for correlations + higher order terms (see text).

Level shifts due to pair correlation and configuration mixing have been calculated for the n=1, 2, and 3 levels for a number of elements in the region 40<Z<95 [12]. The calculations have not been made for many of the elements shown in the figures. Since the configuration mixing corrections do not vary smoothly with Z, interpolation procedures to obtain uncalculated corrections are uncertain at the few eV level. Nevertheless, we have attempted to make qualitative estimates of these corrections for each transition as a function of Z by graphical interpolation of the values in Tables I and II of Ref. 12.

In Fig. 1a, the dashed line at 1.4 eV is the pair correlation correction to the theory for the $1s^{-1}\rightarrow 2p^{-1}$ transition and the difference between the points and the dashed line can be attributed to higher order effects not included in the theory. Since the $1s^{-1}\rightarrow 2p^{-1}$ transition is the most accurately measured interval, this is the preferred transition to estimate higher order effects. In Figs. 1b, 2, and 3 the dashed lines are the corrections to the theory resulting from pair correlation, configuration mixing and uncalculated higher order effects estimated from the $1s^{-1}\rightarrow 2p^{-1}$ transition. The separations between the points and the dashed lines are differences between experiment and theoretical estimates including estimates of correlation and higher order effects.

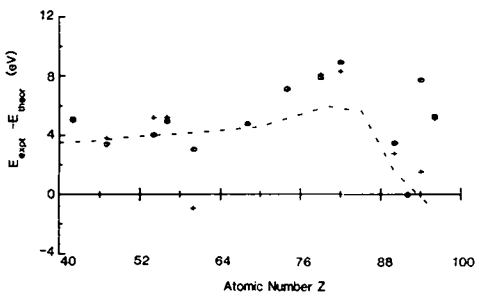

Figure 3 Differences between experimental and theoretical energies for the $1s^{-1}\rightarrow 3p_{1/2}{}^{-1}$ (+) and $1s^{-1}\rightarrow 3p_{3/2}{}^{-1}$ ( ) transitions vs. Z. The dashed line is the correction to theory for correlations + higher order terms.

From these systematic experiment-theory comparisons we conclude that: (1) multi-configuration Dirac-Fock theory with no correlation corrections underestimates the n=1 to n=2, 3 intervals, (2) inclusion of pair correlation and configuration mixing correlation corrections significantly reduces the discrepancy between experiment and theory, (3) uncalculated higher order effects having a magnitude of 1 to 2 eV for Z<85 are needed to reconcile experiment and theory even for the well-measured $1s^{-1}\rightarrow 2p^{-1}$ transitions, and (4) experiment-theory differences for all the n=1 to n=2, 3 transitions change rapidly for Z>85 and may change sign more than one time as Z increases from 85 to 95.

In addition to the two methods of estimating the screening of self energy described above, another method based on the Welton approximation [13] can be used. Although the Welton approximation yields screened self-energy values very close to those based on charge density ratios for Z < 90, all three methods lead to x-ray energies different by as much as 10 eV for transuranic elements.

Areas in which experiment and theory are deficient are identified by the above comparisons. The interpolation method used here for configuration mixing corrections is uncertain. A systematic theoretical study of this correction is needed because its magnitude for the 2s, 3s, and 3p electrons is comparable to or even larger than the screening of their self energies. Higher order effects which might contribute to the theory such as improved finite nuclear size values and nonperturbative treatment of the Breit interaction need to be investigated. Finally, more accurate experimental data in the Z=90 to 98 range are needed in order to critically test the theory in this very high Z region.

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