Two-electron one-photon x-ray transition energy in the Kr isoelectronic series

S. C. Vinayagam and K. D. Sen
School of Chemistry, University of Hyderabad, Hyderabad 500 134, India
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Two-electron one-photon x-ray transition energies are calculated, using the Slater transition-state concept within the approximate local density-functional theory given by the $X\alpha$ model, for the krypton atom and isoelectronic Rb, Yt, and Zr, respectively. The new theoretical results suggest that the transition energy is a linear function of the atomic number within the isoelectronic series.

Since the original studies of cooperative x-ray processes in atoms involving multielectron one-photon transitions,[1,2] the experimental accuracy of such measurements have increased significantly as is shown in the most recent work on the krypton atom.[3] Such data is expected to accelerate developments leading to the most general theory of electronic transitions in matter. In this respect the density functional theory[4] offers an attractive testing ground. In an earlier work[5] we have shown that the local-density-functional (LDF) approximation within the $X\alpha$ theory[6] gives reliable estimates of multielectron one-photon x-ray transition energies in light atoms. This has been recently corroborated within other variants of $X\alpha$ theory by Nágy and Gaspar.[7] In this paper we report the results of our calculations of the two-electron one-photon x-ray transition energy involving s electrons in atomic krypton based on the concept of the Slater transition state.[8] We also report new theoretical results on the similar transitions in the isoelectronic atoms of Rb, Yt, and Zr. The latter calculations provide useful data on the isoelectronic variation of the x-ray transitions particularly in terms of the variation in atomic number Z within the series.

The method of calculation adopted in this work is the same as discussed earlier.[5] For each transition energy a single self-consistent-field calculation is carried out up to the stage of getting the one-electron eigenvalues, ε_i, corresponding to a well-defined transition-state configuration. The latter is defined as the configuration situated half way between the initial- and final-state electronic configuration, respectively. For example, if the initial- and final-state occupations in the various orbitals is given by $(n_i, n_j, \ldots)$ and $(n_i', n_j', \ldots)$, respectively, the transition-state configuration is defined as $[(n_i+n_i')/2, (n_j+n_j')/2 \ldots]$. The energy of the x-ray transition ΔE is given by

$$\Delta E = \sum_i (n_i' - n_i)\varepsilon_i^{\mathrm{tr}} , \tag{1}$$

where $\varepsilon_i^{\mathrm{tr}}$ denotes orbital eigenvalues in the transition state. We have used the $[1s]$ hole state as the initial reference state and have performed calculations on the final states corresponding to $[1s4s]5s5p$, $[1s3s]5s5p$, and $[1s2s]5s4p$, respectively. The choice of the exchange parameter α satisfies the virial theorem in the ground-state configuration of the neutral atom.[9]

Our results are given in Table I along with the experimental results on Kr taken from Ref. 3. The two sets of results are in excellent agreement except for the transition defined by $[1s3s]5s5p$. We note here in all other cases such as the $[1s4p]5s5p$, $[1s3d]5s5p$, the calculated values of 11.4 and 112.4 eV are also found to be in excellent agreement with the experimental estimates of 11 ± 2 and 113.4 ± 0.8 eV, respectively. The isoelectronic variation of these transitions have been excluded from the present study as the relativistic effects would be more important in such cases. In light of the overall good agreement between the theoretical and experimental results, we should like to trace the difference in the two results for $[1s3s]4s4p$ to the important correlation effects in the $3spd$ shell.

The transition energies within the series is found to decrease with an increase in atomic number Z. The varia-

TABLE I. Calculations of two-electron one-photon x-ray transition energies involving inner s electrons in Kr. All energies are given with reference to the $[1s]$ state in eV. Experimental values are given in parentheses.

Atom	$[1s2s]5s5p$	$[1s3s]5s5p$	$[1s4s]5s5p$
Kr	1940.1	287.8	28.5
	(1956.0)	(318.0)	(31.5)
Rb	2077.1	317.2	31.9
Sr*	2218.2	347.8	33.0
Yt	2363.7	377.3	35.6
Zr	2513.7	414.7	36.3

*Extrapolated using linear variation with Z.

tion is found to be linear. In the case of Sr, we have encountered problems with convergence, and the values given in Table I refer to the estimates based on the linear variation of transition energy with Z, the atomic number.

In conclusion we note that the approximate local density functional of $X\alpha$ theory gives a satisfactory account of multielectron one-photon x-ray transition in atoms. The results could in principle be improved via the several available methods of incorporating the electron correlation effects.[10] More extensive studies of this nature must be carried out as the proposed model is much simpler to apply than all the other existing methods to calculating energies of electronic transitions in general.

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