PHYSICAL REVIEW A VOLUME 37, NUMBER 12 JUNE 15, 1988

Simple derivation of x-ray hypersatellite and two-electron–one-photon transition energies for low-Z atoms

Tapan Kumar Mukherjee and Kamal Kumar Ghosh
Department of Physics, Jadavpur University, Calcutta 700 032, India

(Received 5 August 1987)

Transition energies for x-ray hypersatellite lines ($K^h_{\alpha_2}$) and two-electron–one-photon lines ($K\alpha$-$K\alpha$) have been calculated for low-Z atoms using a simple variational method with a two-electron correlated wave function. The method gives real insight into the structure of energies of the initial and final states. The results are very encouraging.

I. INTRODUCTION

The study of x-ray satellite and hypersatellite lines and also two-electron–one-photon transition lines has recently gained new impetus both theoretically and experimentally.[1] Work relevant for the present calculations can be found in Knudson *et al.*,[2] Stoller *et al.*,[3] Vinti,[4] and Baptista.[5] In this paper we have calculated the transition energies for the $K\alpha_2^h$ and $K\alpha$-$K\alpha$ lines from a simple point of view. We have calculated the energy of the $1s^{-2}({}^1S)$-$1s^{-1}2p^{-1}({}^1P)$ and $1s^{-2}({}^1S)$-$2s^{-1}2p^{-1}({}^1P)$ transition for low-Z atoms using a simple variational calculation with a two-electron correlated wave function. In a doubly ionized atom the two vacancies would function spectroscopically in much the same way as two valence electrons. The appropriate energies for the relevant two-particle system are calculated following Breit's calculation[6] on the $1s2p({}^1P)$ and $1s^2({}^1S_0)$ states of helium by Datta Majumder and Chowdhury.[7] The appropriate screening constants are computed following Burns's[8] procedure. Work along similar lines was initiated by Stoller *et al.*[3] In their works energies for the $1s^{-2}$-$2s^{-1}2p^{-1}$ transition in heliumlike ions were calculated using Vinti's[4] method. Though relativistic corrections to the binding energy were taken into account, the correlated part of the wave function was not taken into account, and the results showed a large discrepancy with experimental values as shown in Table I. This is due to neglect of correlations which for low-Z atoms may be more important than the relativistic effects. The present procedure accommodates the correlation effect and the results show a substantial improvement. Another point to be noted is that though treated on the same footing as the two-electron system, the screening effect of other electrons is important and should be taken into consideration in writing the wave function of the system. Error will be committed if one treats the screening factor as a variation parameter. The present authors are of the opinion that screening should be preassigned after taking into consideration all of the other electrons.

II. THEORY FOR HYPERSATELLITE ($K\alpha_2^h$) LINES

The origin of $K\alpha_2^h$ and $K\alpha_1^h$ are, respectively,

$$K^{-2}({}^1S_0)\rightarrow K^{-1}L_2^{-1}({}^1P_1)\ ,$$

$$K^{-2}({}^1S_0)\rightarrow K^{-1}L_3^{-1}({}^3P_1)\ .$$

The difference between $K\alpha$ satellite and $K\alpha^h$ hypersatellite lines is given in Ref. 1. For x-ray diagram lines ($K\alpha$) it has historically been developed that there is a similarity between the energy-level schemes of the hydrogenlike ions and the K-ionized multielectron atoms. The calculations, however, dramatically fail to display the experimental values for elements heavier than atomic number 50 owing to the growing importance of the relativistic effects. The hypersatellite lines can be compared in a similar way to the heliumlike ions. The screening effect should also be introduced here as in the case of the calculation of the energy of x-ray diagram lines. The value of screening constants have been computed by Burns's[8] procedure. We have taken for the K shell the following function:

$$\psi=\exp[-a(r_1+r_2)](1+br_{12})\ . \tag{1}$$

a is the screening constant and b is the variation parameter, which is obtained by minimizing the energy expression with respect to it. The use of the wave function (1) leads to the following expression for the energy of the atom:

$$E=\int \psi H\psi\, dv \Big/ \int \psi^2 dv=\frac{M+L}{N}\ , \tag{2}$$

where $dv=d\tau_1 d\tau_2 d\tau_3=dx_1/dy_1 \cdots dz_2$ and L, M, and N stand for the integrals

$$L=\int \left[\frac{1}{r_{12}}-\frac{Z}{r_1}-\frac{Z}{r_2}\right]\psi^2 dv\ ,$$

where Z is the atomic number,

$$\begin{aligned} M=\int \Bigg[& \frac{1}{2}\left[\frac{\delta\psi}{\delta r_1}\right]^2+\frac{1}{2}\left[\frac{\delta\psi}{\delta r_2}\right]^2+\left[\frac{\delta\psi}{\delta r_{12}}\right]^2 \\ & +\frac{r_1^2-r_2^2+r_{12}^2}{2r_1r_{12}}\frac{\delta\psi}{\delta r_1}\frac{\delta\psi}{\delta r_{12}} \\ & +\frac{r_2^2-r_1^2+r_{12}^2}{2r_2r_{12}}\frac{\delta\psi}{\delta r_2}\frac{\delta\psi}{\delta r_{12}}\Bigg]dv\ , \\ N=\int & \psi^2 dv\ . \end{aligned} \tag{3}$$

TABLE I. Comparison of two-electron–one-photon transition energies as obtained by different workers.

Element	Configuration *KL*	Stoller[a]	Present	Betz[a]	Nussbaumer[a]	Hodge[b]	Experimental energies (eV)[a,b]
		Calculated energies (eV)					
Mg	026 215		2652.8				2655
Al	026 215	3270	3188.4				3119, 3180±20
Cl	026 215		5489				5418
Ar	026 215		6177.9				6128, 6158
Ca	026 215	7950	7678.2				7637±10, 7660±30, 7552±20
Ti	026 215		9369.1				9273
Fe	026 215	13 580	13 158.6	13 032	13 080	12 985	13 075±35, 13 050±30, 13 090±20, 13 025
Fe	025 214			13 098		13 055	
Ni	026 215	15 820	15 311.8	15 205	15 290	15 146	15 230±10, 15 200±40, 15 250±50, 15 220±20
Ni	025 214			15 275		15 223	

[a] Reference 3.
[b] Reference 2.

For the calculation of the energy of the heliumlike ions in the $1s2p\,(^1P)$ state, we have taken the wave function following the method of Breit,[6]

$$\phi = F_1\cos\theta_1 - F_2\cos\theta_2 \ . \tag{4}$$

With the use of the preceding wave function the expression for the energy of the atom becomes

$$E = \frac{\int \phi H \phi \, d\tau}{\int \phi^2 d\tau} = \frac{L_1 + M_1}{N_1} \ , \tag{5}$$

where

$$d\tau = r_1^2 r_2^2 \sin\theta \, dr_1 \, dr_2 \, d\theta \sin\theta' \, d\theta' \, d\phi \, d\phi'$$

and θ is the angle between r_1 and r_2. The notations are the same used by Breit.[6] L_1, M_1, and N_1 stand for the integrals

$$\begin{aligned}
L_1 &= \frac{(4\pi)^2}{6} \int \left[\frac{1}{r_{12}} - \frac{Z}{r_1} - \frac{Z}{r_2} \right] (F^2 + \tilde{F}^{\,2} + 2F\tilde{F}\cos\theta) \, dV_{r_1, r_2, \theta} \ , \\
M_1 &= \frac{(4\pi)^2}{6} \int \left\{ \sum_{i=1}^{2} \frac{1}{2} \left[\frac{\delta F}{\delta r_i} \right]^2 + \frac{1}{2} \left[\frac{\delta \tilde{F}}{dr_i} \right]^2 + \cos\theta \frac{\delta F}{\delta r_i} \frac{\delta \tilde{F}}{\delta r_i} + \frac{r_i^{-2}}{2} \left[\left[\frac{\delta \tilde{F}}{\delta\theta} \right]^2 + \left[\frac{\delta F}{\delta\theta} \right]^2 + 2\cos\theta \frac{\delta F}{\delta\theta} \frac{\delta \tilde{F}}{\delta\theta} \right] \right. \\
&\qquad \left. + r_1^{-2} F^2 + r_2^{-2} F^2 - r_1^{-2} \tilde{F} \sin \frac{\delta \tilde{F}}{\delta\theta} - r_2^{-2} F \sin\theta \frac{\delta F}{\delta\theta} \right\} dV_{r_1, r_2, \theta} \ , \qquad (6) \\
N_1 &= \frac{(4\pi)^2}{6} \int (F^2 + \tilde{F}^{\,2} + 2F\tilde{F}\cos\theta) \, dV_{r_1, r_2, \theta} \ ,
\end{aligned}$$

where

$$dV_{r_1,r_2,\theta}=r_1^2r_2^2\sin\theta\, dr_1dr_2d\theta \ ,$$

$$F_1=F(r_1,r_2;\theta),\quad F_2=-\tilde{F}(r_1,r_2;\theta) \ ,$$

$$\tilde{F}(r_1,r_2;\theta)=F(r_2,r_1;\theta) \ ,$$

$$F=r_1(1+C\cos\theta)\exp(-ar_{1/2}-br_{1/2}) \ .$$

Here a and b are screening constants and C is the variation parameter, which is also obtained by minimizing energy expression with respect to it. This procedure differs from that of Stoller *et al.*,[3] where they have treated the screening as a variation parameter. When calculating the energy of the atom in the $1s2p\,(^1P)$ state, if one considers a and b as variation parameters then one will obtain the energy of the member of the helium isoelectronic sequence. However, we want to find the energy required to remove the electrons from the $1s$ state and $2p$ state, i.e., the binding energy of $1s2p\,(^1P)$ state of the neutral atom. For example, in a magnesium atom, if one considers a and b as variation parameters, then one will obtain the energy of Mg^{10+} in the $1s2p\,(^1P)$ state, which is the binding energy of the $1s2p\,(^1P)$ state of Mg^{10+}. However, we want to find the binding energy of the $1s2p\,(^1P)$ state of a neutral magnesium atom. Hence we should consider the effect of the other ten electrons which we have considered through screening constant a and b. Similar consideration has been taken into account for calculating the energy of the atom in the $1s^2(^1S_0)$ state. It is clear that there is a similarity between the energy-level schemes of the heliumlike ions and the doubly ionized multielectron atoms analogous to that of hydrogenlike ions and K-ionized multielectron atoms. However, to calculate the energy of doubly ionized multielectron atoms screening constants should be chosen properly. The relevant integrals are derived according to the method given by Datta Majumdar and Chowdhury[7] and Breit.[6] The results of calculations are given in Table II. It appears that our present method is quite satisfactory and yields values comparable to sophisticated Dirac-Hartree-Fock calculations.

III. THEORY FOR TWO-ELECTRON– ONE-PHOTON ($K\alpha$-$K\alpha$) LINES

The origin of $K\alpha$-$K\alpha$ line is

$$1s^{-2}(^1S_0)\rightarrow 2s^{-1}2p^{-1}(^1P) \ .$$

We now want to extend our calculations of the $1s2p\,(^1P)$ state to the case of the $2s2p\,(^1P)$ state with some modifications. The difference between these two states is that a K electron which is present in the $1s2p$ state is missing in the $2s2p$ state. When a K electron is missing the inner screening is smaller by unity than in the case of atom in the $1s2p$ state, so that the binding energy of the $2s2p$ electron is approximately that for the corresponding element with the next higher atomic number. The same idea can be found in the previous calculation of the x-ray satellite line (KL-LM). Calculated on the basis of the single-particle model the difference in frequency between the satellite $(KL\text{-}LM)_Z$ and the parent line $(K\text{-}M)_Z$ becomes

$$\Delta\nu=\nu_{(KL_Z-LM_Z)}-\nu_{(K_Z-M_Z)}=\nu_{(L_{Z+1}-L_Z)}-\nu_{(M_{Z+1}-M_Z)} \ .$$

We have extended this idea in the present procedure. It therefore follows that

$$\Delta\nu_{(K\alpha\text{-}K\alpha)_Z}=\nu_{(1s^{-2})_Z}-\nu_{(2s^{-1}2p^{-1})_{Z+1}} \ .$$

The radial wave function for the $2s2p$ state is

$$F=r_1(1+C\cos\theta)\left[1-\frac{br_2}{2}\right]\exp\left[\frac{-ar_1}{2}-\frac{br_2}{2}\right] ,$$

where a and b are screening constants and C is the variation parameter. The energy of $2s2p$ state is

$$E=\frac{L_1+M_1}{N_1} \ ,$$

where

$$L_1=L_{10}+L_{11}C+L_{12}C^2 \ ,$$

$$M_1=M_{10}+M_{11}C+M_{12}C^2 \ ,$$

$$N_1=N_{10}+N_{11}C+N_{12}C^2 \ .$$

TABLE II. The values of a, b, and E for the $1s^2(^1S)$ state; a, b, C, and E for the $1s2p\,(^1P)$ state; and calculated $E^h_{K\alpha_2}$ (eV). The values in parentheses denote experimental uncertainty.

		$1s^2(^1S)$				$1s2p\,(^1P)$			$E^h_{K\alpha_2}$ (eV)	
Element	a	b	E (a.u.)	a	b	c	E (a.u.)	Present method	Other method[b]	Experimental[b]
Mg	11.65	0.1508	−136.6180	7.95	23.3	0.000 45	−85.8573	1381.3	1368.8	1367.7(6)
V	22.65	0.1497	−514.7432	18.65[a]	45.3	0.000 92	−323.3934	5206.5	5176.9	5178(2)
Cr	23.65	0.1496	−561.1182	19.65	47.3	0.000 91	−352.5092	5676.6	5649.2	5649(2)
Mn	24.65	0.1496	−609.4932	20.65	49.3	0.000 899	−382.8745	6166.7	6143.0	6142(3)
Fe	25.65	0.1495	−659.8682	21.65	51.3	0.000 898	−414.4898	6677.1	6658.2	6658(2)

[a] The screening constant (a) of a $2p$ electron of $V(Z=23)$ is given in the following: $V(1s,2p)(1s^12s^22p^53s^23p^63d^34s^2)=1+2(0.5)+5(1.35)+2(0.15)+6(0.05)=4.35$; $a=23-4.35=18.65$.

[b] Reference 1.

TABLE III. The values of a, b, C, and E for the $2s2p\,(^1P)$ state.

	$1s^2(^1S)$			$2s2p\,(^1P)$			
Element	a	b	E (a.u.)	a	b	C	E (a.u.)
Mg	11.65	0.1508	−136.6180	10.4	11.65	−0.0854	−39.1296
Al	12.65	0.1506	−160.9930	11.35	12.65	−0.0795	−45.6601
Cl	16.65	0.1502	−278.4931	15.15	16.65	−0.0628	−76.7758
Ar	17.65	0.1500	−312.8681	16.15	17.65	−0.0595	−85.8346
Ca	19.65	0.1499	−387.6181	18.15	19.65	−0.0537	−105.4520
Ti	21.65	0.1497	−470.3681	19.15	20.65	−0.0696	−126.0632
Fe	25.65	0.1495	−659.8682	24.15	25.65	−0.0416	−176.3039
Ni	27.65	0.1494	−766.6182	26.15	27.65	−0.0387	−203.9211

When calculating the energy of the $(2s2p)_{Z+1}$ state, the dependence on the initial configuration, i.e., $1s^{-2}$, of the decaying atom is considered through the screening constants used to write the single-electron wave function. For example, for aluminum ($Z=13$) the screening constant of a $2p$ electron in the $(2s2p)_{Z+1}$ state is, according to the configuration $1s^0 2s^1 2p^5 3s^2 3p^2$, $(0.5)+5(0.35)+2(0.15)+2(0.05)=2.65$. Hence $a=14-2.65=11.35$.

The dependence of the screening constant on the initial configuration was also suggested by Baptista.[5] The results are given in Table III. A comparison of the present calculation with those of different authors is given in Table I.

IV. DISCUSSION

The screening constant a of a $2p$ electron is $(Z-3.35)$, for $Z>18$, which indicates that screening is independent of $3d$ or $3s$ electrons. Hence the energy value of the $2s2p$ state of the atom does not change appreciably if $3d$ and $4s$ electrons are removed from the atom. For example, the energy value of the $2s2p$ state of iron is approximately the same as that of Fe^{8+}. According to Nussbaumer[9] the transitions are mostly from the $2s^2 2p^6(^1S_0)$ to the $1s^2 2s 2p^5(^1P_1)$ state in Fe^{18+} and Ni^{20+}. This means that there is vacancy in the L shell initially. This contradicts the data obtained by Jundt and Nagel.[10] This indicates that on the average about three L-shell vacancies accompany the production of a K-shell vacancy. According to Knudson *et al.*,[2] Hartree-Fock energy calculations assuming an $E1$ transition with two L-shell vacancies in the initial state agree with their experimental values for $Z=12$ to 22. However, these values cannot be included in Table I because of nonavailability. The agreement between the experimental and their theoretical values can be ascertained from the graph of Fig. 2 of Ref. 2. The L vacancy in the initial state will give two-electron satellite lines. According to Stoller[3] the two-electron satellite lines could not be resolved. Hence a precise state assignment is not possible. A comparison with calculations of different authors is given in Table I. Such a comparison reveals that there is a good deal of discrepancy in the calculations of Betz *et al.* and Hodge though both authors used relativistic Hartree-Fock computer codes. The present calculation assumes closed L shell and results are in qualitative agreement.

ACKNOWLEDGMENTS

The authors express gratitude to Dr. Sankar Sengupta for stimulating discussions. One of the authors (T.K.M.) is indebted to the Council for Scientific and Industrial Research (C.S.I.R.), India, for granting partial support.

---

[1] T. K. Mukherjee and S. Sengupta, Can. J. Phys. **65**, 54 (1987).

[2] A. R. Knudson, K. W. Hill, P. G. Burkhalter, and D. J. Nagel, Phys. Rev. Lett. **37**, 679 (1976).

[3] Ch. Stoller, W. Wolfli, G. Bonani, M. Stockli, and M. Suter, Phys. Rev. A **15**, 990 (1977).

[4] J. P. Vinti, Phys. Rev. **42**, 632 (1932).

[5] G. B. Baptista, J. Phys. B **17**, 2177 (1984).

[6] G. Breit, Phys. Rev. **36**, 383 (1930).

[7] S. Datta Majumdar and D. C. Chowdhury, Z. Phys. **128**, 455 (1950).

[8] G. Burns, J. Chem. Phys. **41**, 1521 (1964).

[9] H. Nussbaumer, J. Phys. B **9**, 1757 (1976).

[10] F. Jundt and D. J. Nagel, Phys. Lett. **50A**, 179 (1974).