X-ray shifts for additional atomic vacancies

S. K. Roy, D. K. Ghosh, and B. Talukdar
Department of Physics, Visva-Bharati University, Santiniketan 731235, West Bengal, India
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The simple analytical model of Burch *et al.* for the calculation of K x-ray and Auger energy shifts resulting from an additional vacancy in the $2p$ orbital is extended to arbitrary defect configurations. The energy shifts for K, L, and M x-ray series of ^{86}Rn are calculated for vacancies in $1s$, $2p$, $3d$, and $4f$ orbitals. The relative importance of inner- and outer-shell vacancies in producing the x-ray shifts is discussed.

X-ray spectra are related primarily to the inner atomic structure. The effect of concurrent changes that may occur elsewhere in the atom is generally regarded to be small since these changes are expected to have little influence upon the radiative and/or nonradiative processes resulting from inner vacancies. Despite that, certain finer features of the x-ray spectra may involve in their explanation a consideration of the outer part of the atom. For example, the effect of L-shell vacancies on the K transition has been traced and studied in some detail.[1] Missing electrons in atomic shells higher than the L have little influence on the K-shell transition energies. But M- and N- shell vacancies might play a significant role in changing the L and M transition energies. In the present note we propose to investigate how vacancies in different subshells manifest themselves in producing changes in the K, L, and M x-ray transition energies. To that end we make use of the basic philosophy of a simple analytical model proposed by Burch *et al.*[2] An interesting aspect of this model is that by invoking a few judicious approximations one can focus attention on the conceptual aspects of the problem and gain some physical weight without making substantial deviations with regard to numerical accuracy. Burch *et al.*[2] studied the effects of L-shell ionization on K-shell transition energies. In the following we extend their model to arbitrary defect configurations.

Vacancies in circular obits ($l=n-1$) produce a perturbing potential

$$V_{n,n-1}(r)=\frac{1}{r}-\frac{1}{r}\int_r^\infty \rho_{n,n-1}(s)(s^2-rs)\,ds \quad , \tag{1}$$

where the charge density

$$\rho_{n,n-1}(r)=\psi^2_{n,n-1}(r) \tag{2}$$

is given in terms of screened hydrogenic wave functions

$$\Psi_{n,l}(r)=-\left[\left(\frac{2Z^*}{n}\right)^3\frac{(n-l-1)!(n+l)!}{2n}\right]^{1/2}e^{-Z^*r/n}\left(\frac{2Z^*r}{n}\right)^l\sum_{k=0}(-1)^{k+2l+1}\frac{(2Z^*r/n)^k}{(n-l-1-k)!(2l+1+k)!k!} \quad . \tag{3}$$

Here Z^* is the effective nuclear charge. The potential in Eq. (1) causes increase in the binding energy of each of the atomic levels and in turn influences the x-ray and Auger energies. We shall use atomic units throughout. From Eqs. (1)–(3) we have

$$V_{n,n-1}(r)=\frac{1}{(2n)!}\frac{1}{r}\left[\Gamma\left(2n+1,\ \frac{2Z_v r}{n}\right)-\frac{2Z_v r}{n}\Gamma\left(2n,\ \frac{2Z_v r}{n}\right)\right] \quad , \tag{4}$$

where Z_v is the effective charge at the vacancy and $\Gamma(m,x)$, an incomplete γ function given by

$$\Gamma(m,x)=(m-1)!e^{-x}\sum_{s=0}^{m-1}\frac{x^s}{s!} \quad . \tag{5}$$

The energy shift of an $n_1 l_1$ electron due to this potential can be written as

$$\langle n_1 l_1|V_{n,n-1}|n_1 l_1\rangle=\int_0^\infty \Psi^2_{n_1 l_1}(r)\,V_{n,n-1}(r)r^2\,dr \quad . \tag{6}$$

From Eqs. (3) and (6) we have

$$\langle n_1 l_1 | V_{n,n-1} | n_1 l_1 \rangle = \left[\frac{2Z_s}{n_1}\right]^{2l_1+3} \frac{(n_1+l_1)!(n_1-l_1-1)!}{2n_1}$$
$$\times \sum_{k=1}^{n_1-l_1} \sum_{q=1}^{n_1-l_1} (-1)^{q+k+4l_1} \frac{(2Z_s/n_1)^{k+q-2}}{(n_1-l_1-k)!(k-1)!(2l_1+k)!(n_1-l_1-q)!} \frac{1}{(q-1)!(2l_1+q)!}$$
$$\times \frac{1}{M^{2l_1+k+q}} \left[\frac{1}{(2n)!} \left[\frac{2Z_v}{n}\right]^{2n} \frac{(2n+2l_1+k+q-1)!}{M^{2n}} + (2l_1+k+q-1)! \right.$$
$$+ \frac{2Z_v}{n} \frac{(2l_1+k+q)!}{M} + \sum_{i=2}^{2n-1} \frac{1}{i!} \left[\frac{2Z_v}{n}\right]^i \frac{(2l_1+k+q+i-1)!}{M^i}$$
$$- \frac{1}{2n} \left[\frac{2Z_v}{n}\right] \frac{(2l_1+k+q)!}{M} - \frac{1}{2n} \left[\frac{2Z_v}{n}\right]^2 \frac{(2l_1+k+q+1)!}{M^2}$$
$$\left. - \frac{1}{2n} \sum_{i=2}^{2n-1} \frac{1}{i} \left[\frac{2Z_v}{n}\right]^{i+1} \frac{(2l_1+k+q+i)!}{M^{i+1}} \right] , \quad (7)$$

where

$$M = 2Z_s/n_1 + 2Z_v/n \quad (8)$$

with Z_s, the effective nuclear charge of the $n_1 l_1$ atomic subshell.

Calculation of level shifts based on Eq. (7) is now in order provided we have a simple model for calculating the effective nuclear charges, Z_v and Z_s. Burch *et al.*[2] used the Slater's rule[3] to calculate the values of Z_v and Z_s. We shall use a different method for our purpose. This method consists in obtaining the effective nuclear charge Z_{eff} by the following procedure.

Consider an electron bound with a binding energy B in the field of a screened point nucleus of charge Z. With the viewpoint that screening may be accounted for by replacing Z by $Z_{\text{eff}} < Z$, our problem reduces to a consideration of an electron bound with binding energy B_{expt} in the field of an unscreened point nucleus of charge Z_{eff}, where B_{expt} is the experimentally determined binding energy. We thus fit Z_{eff} for a bound state to its binding energy using the relation[4]

$$\gamma' = -b + (1 - B_{\text{expt}})(\kappa' - Nb)^{1/2} , \quad (9)$$

where

$$\gamma' = (\kappa'^2 - \alpha^2 Z_{\text{eff}}^2)^{1/2} ,$$
$$b = N' B_{\text{expt}}(2 - B_{\text{expt}}) ,$$
$$N' = N - \kappa'$$

with N and κ' the principal and Dirac quantum numbers. Here α is the fine-structure constant. The values of κ' for different subshells have been given by Rose.[5] Clearly, Eq. (9) represents a straightforward relation between the effective nuclear charge of an atomic electron with its experimental binding energy. Computation of Z_{eff} based on Eq. (9) has thus the obvious virtue of directness and simplicity and at the same time it appears more realistic than an approach based on the Slater's rule.

Since our object here is to study the energy shift due to various atomic configurations, we have chosen to work with a rather high-Z atom, namely, ^{86}Rn. Admittedly, for this atom relativistic effects are expected to play a significant role in x-ray transitions. We point out that the effects of relativity may be made transparent even within the framework of this simple analytical model by working with screened hydrogenic functions which are solutions of the Bieden-

TABLE I. Effective nuclear charge from Eq. (9).

Subshell	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*
Effective nuclear charge	80.908	69.709	66.775	53.386	49.428	44.077	35.611	31.866	25.355	16.382

harn symmetric Dirac-Coulomb Hamiltonian.[6] The symmetric Hamiltonian is an approximation to the Dirac Hamiltonian for the Coulomb field and the radial parts of its solution are formally nonrelativistic to within a simple mapping so that many of the advantages of a nonrelativistic calculation can be carried over.[7] While we take up this consideration in a future publication, we turn our attention to the nonrelativistic model considered here.

In Table I we present the values of effective nuclear charges of $1s$ to $4f$ subshells calculated by the use of Eq. (9). The binding energies used are those of Hagström *et al.*[8] In general our values of Z_{eff} are smaller than the corresponding values based on Slater's rule. In Fig. 1 we portray the energy shifts obtained from Eq. (7) as a function of effective nuclear charges. Looking closely into this figure we see that for the $4f$ vacancy the energy shifts in different subshells (which we differentiate by effective nuclear charges) are about constant. For other vacancies the energy shifts tend to increase monotonically with increasing effective nuclear charges or decreasing n. However, within a given major shell the energy shifts in subshells exhibit variations which may be attributed to the overlap between the defect configuration and the atomic subshell for which the shift is calculated. For example, for the $1s$ vacancy the energy shift of the $2p$ electron ($Z_{\text{eff}} = Z_s = 66.775$) is larger than the energy shift of the $2s$ electron ($Z_{\text{eff}} = Z_s = 69.709$). Similar arguments hold good for each of the kinks of the curves shown in the figure.

In Table II we present results for the K, L, and M x-ray energy shift arising from different defect configuration. The results for $K\alpha$ and $K\beta$ shifts due to a missing $2p$ electron from the works of Burch *et al.*[2]

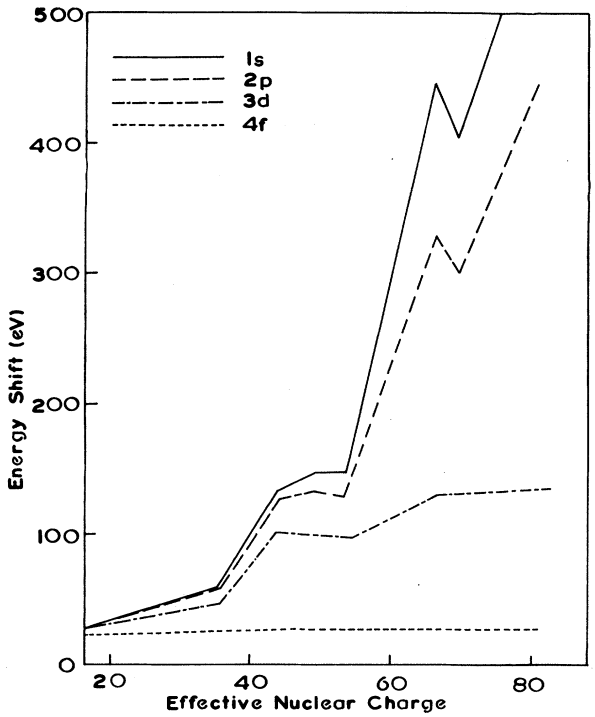

FIG. 1. Energy shifts of different subshells due to vacancies in $1s$, $2p$, $3d$, and $4f$ atomic orbitals as a function of effective nuclear charges.

are also included in this table. The difference between our numbers and those of Burch *et al.* may be attributed to different handling of the screening effects. Unfortunately, no Hartree-Fock-Slater results are available to facilitate comparison. However, the entire set of numbers presented by us exhibits

TABLE II. K, L, and M x-ray energy shifts in electronvolts due to missing $1s$, $2p$, $3d$, and $4f$ electrons, respectively. The numbers in the parentheses stand for powers of 10 by which the entries are to be multiplied.

Series	$4f$	$3d$	$2p$	$1s$
$K\alpha$	2.4000 (−5)	1.4989 (0)	1.1617 (2) 1.3587 (2)[a]	9.2935 (2)
$K\beta$	2.1672 (−2)	3.4541 (1)	3.1263 (2) 3.1103 (2)[a]	1.2269 (3)
$K\gamma$	1.9951 (0)	8.8045 (1)	3.9400 (2)	1.3213 (3)
$L\alpha$	1.8339 (−2)	2.8545 (1)	1.9821 (2)	3.1288 (2)
$L\beta$	2.1637 (−2)	3.2376 (1)	1.6881 (2)	2.5747 (2)
$L\gamma$	1.9950 (0)	8.5879 (1)	2.5017 (2)	3.5189 (2)
$M\alpha$	5.4507 (0)	7.5329 (1)	1.0396 (2)	1.0535 (2)
$M\beta$	5.4507 (0)	7.5329 (1)	1.0396 (2)	1.0535 (2)
$M\gamma$	2.9958 (0)	5.7890 (1)	9.0400 (1)	1.0542 (2)

[a] These shifts are taken from work of Burch *et al.* (Ref. 2).

the following.

In general, shifts due to inner-shell vacancies are larger than those resulting from outer vacancies. Focusing our attention to particular vacancies we see that the $4f$ vacancy produces appreciable energy shifts only in the M series. The energy shift of the $L\gamma$ radiation is also appreciable. For the $3d$ vacancy the shift in $K\alpha$ series appears to be negligible as compared to those in series onward the $K\beta$ line. Each of the K, L, and M series appears to be equally affected by the $1s$ and $2p$ vacancies. Thus we conclude by noting that the inner vacancies tend to affect the entire x-ray series. In contrast, the outer vacancies affect relatively softer x radiation.

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