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K X-Ray Isotope Shifts[*]

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Numerical data are presented for the analysis of *K* x-ray isotope shift experiments for $30 \leq Z \leq 103$. The isotope shift is expressed in terms of the change in the even moments of the nuclear charge. Additional contributions to the isotope shift are briefly discussed.

THE study of *K* x-ray isotope shifts gives one an absolute method of determining changes in the nuclear charge moments between isotopes. We shall, in this paper, be mainly concerned with the analysis of that part of the isotope shift which is due to the change of the nuclear size. Other contributions to the isotope shift are mentioned and problems deserving further study indicated. A summary of the results of an experimental program at Caltech are presented in the following paper.

Coulomb shift. The largest contribution in heavy atoms to the energy shift observed on going from one isotope to another comes from the modification of the nuclear charge distribution. This shift, which we will call the Coulomb shift, is in lowest order equal to

$$\delta E_{\text{Coulomb}} = -\alpha \int \delta\rho_N \left(r_N^{-1} \int_0^{r_N} \rho_e dV_e + \int_{r_N}^{\infty} \frac{\rho_e}{r_e} dV_e \right) dV_N, \tag{1}$$

ρ_n and ρ_e being the nuclear and electron charge distributions. Since the total charge is unchanged between two isotopes, we may rewrite Eq. (1)

$$\delta E_{\text{Coulomb}} = -\alpha \int \delta\rho_N \left(r_N^{-1} \int_0^{r_N} \rho_e dV_e - \int_0^{r_N} \frac{\rho_e}{r_e} dV_e \right) dV_N. \tag{2}$$

For any reasonable nuclear charge distribution, the electronic factor in parentheses may be adequately represented by an even power series in r_n, starting with r^{2j+1}. Therefore, the isotope shift for $s_{1/2}$ and $p_{1/2}$ levels is expressed in terms of a sum of the change in the r^2, r^4, r^6,... moments of the nuclear charge distribution; the $p_{3/2}$ and $d_{3/2}$ levels being sensitive to the r^4, r^6,... moments. The usefulness of expressing the energy shift by Eq. (2) is that the electronic and nuclear parts factor. Since the electronic part can be readily calculated, the energy shift may be expressed directly in terms of nuclear moments. We will discuss the accuracy of Eq. (2) in a later section.

The electron-wave functions were obtained from self-consistent field calculations starting with the Dirac equation and using the Slater free-electron exchange approximation. Vacuum-polarization effects were included. A Fermi charge distribution was used to calculate the nuclear Coulomb potential. For $j=\frac{1}{2}$ electrons, Eq. (2) is rewritten

$$\delta E_{\text{Coulomb}} = C_1 \delta\langle r^2 \rangle + C_2 \delta\langle r^4 \rangle + C_3 \delta\langle r^6 \rangle + \cdots, \tag{3}$$

where

$$\delta\langle r^{2N} \rangle = \int \delta\rho_N r^{2N} dV_N / \int \rho_N dV_N. \tag{4}$$

The C_i are tabulated in Table I for the 1*s* level. Table II gives the size of C_1 for the 2*s*, 3*s*, and $2p_{1/2}$ levels relative to that for the 1*s* level. Although a model charge distribution is used to calculate the electron-wave functions and therefore the C_i, we have shown by direct calculation that for changes in the nuclear size, which are larger than expected in actual cases, C_1 changes by only a few parts per thousand.

Atomic isotope shifts are measured in both optical and x-ray spectra. Since the Coulomb potential at the nucleus is so much larger than the binding energy, the *s*-wave wave function is largely independent of the principal quantum number. For instance, the change in C_2/C_1 in going from 1*s* to 2*s* amounts to only a few tenths of percent. Beyond the 2*s* level, there is very little further change. C_2/C_1 for a $p_{1/2}$ level is within a few percent of C_2/C_1 for a $s_{1/2}$ level (4% for $Z=80$). This means that both atomic optical and x-ray isotope shifts measure the same nuclear parameter,

$$\lambda = \delta\langle r^2 \rangle + C_2/C_1 \delta\langle r^4 \rangle + C_3/C_1 \delta\langle r^6 \rangle. \tag{5}$$

The self-consistent field calculations that were performed to get the results in Table I could also be performed for optical transitions if we understood the configurations involved. We have already studied, in this way, the effect of changes in *d*-electron shielding on the inner *s*-wave groups. These results are useful in interpreting the isomer shifts seen in Mössbauer experiments. Of course, the isomer shift determines the same parameter λ [Eq. (5)] between isomeric levels rather than between the ground states of different isotopes.

Perturbation theory was used in the original work on isotope shifts by Racah[1] and Rosenthal and Breit.[2] The last-named authors pointed out that lowest-order perturbation theory starting from the Dirac-Coulomb wave function gave an overestimate. The singularity of the $1/r$ potential leads in the case of the Dirac equation to a singularity in the wave function, which gives an unreasonably large electron density at the nucleus. An exact method due to Broch[3] and Smorodinski[4] leads to an expression for the energy shift between a nuclear point charge and a finite nuclear charge dis-

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[1] G. Racah, Nature **129**, 723 (1932).

[2] J. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932).

[3] E. K. Broch, Arch, Math. Naturvidenskab. **48**, 25 (1945).

[4] Ia. A. Smorodinskii, Zh. Eksperim, i Teor, Fiz. **17**, 1034 (1957).

TABLE I. Units are such that the energy shifts defined by Eq. (3) are given in milli-electron-volts if the charge moments are given in fermis (10^{-13} cm).

Z	C_1	C_2	C_3	Z	C_1	C_2	C_3
30	0.683×10	-0.232×10^{-2}	0.950×10^{-5}	67	0.468×10^{3}	-0.412	0.114×10^{-2}
31	0.795×10	-0.277×10^{-2}	0.109×10^{-4}	68	0.515×10^{3}	-0.463	0.128×10^{-2}
32	0.918×10	-0.331×10^{-2}	0.128×10^{-4}	69	0.565×10^{3}	-0.518	0.143×10^{-2}
33	0.106×10^{2}	-0.398×10^{-2}	0.152×10^{-4}	70	0.623×10^{3}	-0.579	0.158×10^{-2}
34	0.122×10^{2}	-0.471×10^{-2}	0.174×10^{-4}	71	0.683×10^{3}	-0.648	0.177×10^{-2}
35	0.140×10^{2}	-0.565×10^{-2}	0.208×10^{-4}	72	0.750×10^{3}	-0.722	0.196×10^{-2}
36	0.161×10^{2}	-0.662×10^{-2}	0.237×10^{-4}	73	0.825×10^{3}	-0.807	0.219×10^{-2}
37	0.183×10^{2}	-0.788×10^{-2}	0.282×10^{-4}	74	0.904×10^{3}	-0.899	0.242×10^{-2}
38	0.208×01^{2}	-0.926×10^{-2}	0.325×10^{-1}	75	0.991×10^{3}	-0.100×10	0.271×10^{-2}
39	0.237×01^{2}	-0.110×10^{-1}	0.385×10^{-4}	76	0.109×10^{4}	-0.111×10	0.299×10^{-2}
40	0.267×10^{2}	-0.128×10^{-1}	0.445×10^{-4}	77	0.119×10^{4}	-0.124×10	0.333×10^{-2}
41	0.303×10^{2}	-0.150×10^{-1}	0.517×10^{-4}	78	0.131×10^{4}	-0.139×10	0.370×10^{-2}
42	0.341×10^{2}	-0.173×10^{-1}	0.588×10^{-4}	79	0.144×10^{4}	-0.155×10	0.414×10^{-2}
43	0.384×10^{2}	-0.203×10^{-1}	0.687×10^{-4}	80	0.157×10^{4}	-0.171×10	0.455×10^{-2}
44	0.432×10^{2}	-0.233×10^{-1}	0.770×10^{-4}	81	0.172×10^{4}	-0.191×10	0.505×10^{-2}
45	0.485×10^{2}	-0.269×10^{-1}	0.885×10^{-4}	82	0.188×10^{4}	-0.211×10	0.559×10^{-2}
46	0.543×10^{2}	-0.309×10^{-1}	0.100×10^{-3}	83	0.207×10^{4}	-0.236×10	0.625×10^{-2}
47	0.609×10^{2}	-0.356×10^{-1}	0.115×10^{-3}	84	0.228×10^{4}	-0.266×10	0.709×10^{-2}
48	0.680×10^{2}	-0.405×10^{-1}	0.128×10^{-3}	85	0.249×10^{4}	-0.297×10	0.795×01^{-2}
49	0.758×10^{2}	-0.462×10^{-1}	0.144×10^{-3}	86	0.272×10^{4}	-0.320×10	0.831×10^{-2}
50	0.845×10^{2}	-0.523×10^{-1}	0.161×10^{-3}	87	0.297×10^{4}	-0.356×10	0.931×10^{-2}
51	0.939×10^{2}	-0.594×10^{-1}	0.181×10^{-3}	88	0.326×10^{4}	-0.396×10	0.103×10^{-1}
52	0.104×10^{3}	-0.662×10^{-1}	0.196×10^{-3}	89	0.357×10^{4}	-0.443×10	0.116×10^{-1}
53	0.117×10^{3}	-0.775×10^{-3}	0.232×10^{-3}	90	0.392×10^{4}	-0.489×10	0.127×10^{-1}
54	0.129×10^{3}	-0.872×10^{-1}	0.258×10^{-3}	91	0.429×10^{4}	-0.549×10	0.144×10^{-1}
55	0.144×10^{3}	-0.995×10^{-1}	0.293×10^{-3}	92	0.470×10^{4}	-0.601×10	0.156×10^{-1}
56	0.158×10^{3}	-0.111	0.322×10^{-3}	93	0.516×10^{4}	-0.676×10	0.178×10^{-1}
57	0.177×10^{3}	-0.127	0.368×10^{-3}	94	0.563×10^{4}	-0.740×10	0.192×10^{-1}
58	0.195×10^{3}	-0.144	0.419×10^{-3}	95	0.618×10^{4}	-0.830×10	0.218×10^{-1}
59	0.214×10^{3}	-0.163	0.474×10^{-3}	96	0.676×10^{4}	-0.918×10	0.240×10^{-1}
60	0.238×10^{3}	-0.185	0.534×10^{-3}	97	0.744×10^{4}	-0.103×10^{2}	0.271×10^{-1}
61	0.263×10^{3}	-0.210	0.607×10^{-3}	98	0.814×10^{4}	-0.114×10^{2}	0.299×10^{-1}
62	0.291×10^{3}	-0.234	0.667×10^{-3}	99	0.892×10^{4}	-0.126×10^{2}	0.331×10^{-1}
63	0.320×10^{3}	-0.264	0.750×10^{-3}	100	0.980×10^{4}	-0.142×10^{2}	0.376×10^{-1}
64	0.351×10^{3}	-0.292	0.817×10^{-3}	101	0.107×10^{5}	-0.157×10^{2}	0.417×10^{-1}
65	0.388×10^{3}	-0.330	0.921×10^{-3}	102	0.118×10^{5}	-0.178×10^{2}	0.479×10^{-1}
66	0.427×10^{3}	-0.368	0.102×10^{-2}	103	0.130×10^{5}	-0.197×10^{2}	0.530×10^{-1}

tribution. Unfortunately, it requires the knowledge of the wave function for the finite charge distribution. Bodmer[5] has derived a factor starting from the Broch expression which corrects the original perturbation formula. The only previous work on x-ray shifts, by Babuskin,[6] also uses the Broch method. Babuskin finds the correct wave function by matching the internal solution to an external Coulomb wave function. Actually, this gives his result for the energy shift without going on to use the Broch formula. Due to certain unnecessary approximations, his results are in error by several percent for heavy nuclei. Bodmer's approach is to write an integral equation for the exact wave function that must be found before using the Broch formula. This integral equation is solved by iteration. An important conclusion is that the solutions depends only the r^2 moment of the charge distribution. One must remember that the Broch method as used gives the energy shift between a point and a finite-size charge. This shift may be determined largely by $\langle r^2\rangle$,but the isotope shift, which is a difference of two such shifts, contrary to Bodmer, is sensitive to the higher moments.

In order to check the accuracy of lowest-order perturbation theory [Eq. (2)], we simply solved the differential equation for various charge distributions with high precision. The difference of the eigenvalues is the Coulomb shift. The perturbation method, Eqs. (2) or (3), agreed with the exact results to within a few parts per thousand. For heavy nuclei ($Z=90$) the r^4

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[5] A. R. Bodmer, Proc. Soc. (London) **A66**, 1041 (1953).

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TABLE II. Ratios of $C_1(2s_{1/2})$, $C_1(3s_{1/2})$, and $C_1(2p_{1/2})$ to $C_1(1s_{1/2})$.

Z	$2s_{1/2}$	$3s_{1/2}$	$2p_{1/2}$
30	0.00985	0.0146	0.000742
40	0.0108	0.0188	0.00157
50	0.117	0.0228	0.00284
60	0.127	0.0266	0.00465
70	0.138	0.0304	0.00735
80	0.152	0.0348	0.0113
90	0.167	0.0396	0.0173
100	0.186	0.0451	0.0264

moment made a 10% contribution. Therefore, the lowest-order perturbation expression used together with reasonable electron wave functions is both accurate and transparent.

Electron shielding enters in two related ways into the calculation of the C_i of Eq. (3). The usual shielding effect that reduces the effective charge of the nucleus is taken into account by the self-consistent field calculations. The corrections to the C_i for the $1s$ level range from $+2.3\%$ ($Z=50$), -0.7% ($Z=70$), and -0.5% ($Z=80$), to $+0.5\%$ ($Z=90$) of the unscreened values. At the highest Z value, vacuum polarization effects are becoming dominant. The change in the density of spectator electrons at the nucleus should also be taken into account.[7] For instance, $d\rightarrow f$ optical transitions in the rare earths have appreciable isotope shifts due to the modification of the inner s-electron distribution. This effect may be readily attacked by self-consistent field calculations. Much more uncertain, however, is the case of K x-ray transitions. The K hole is a bound state in the continuum which is very broad, 30–100 eV. It is doubtful that there can be very much relaxation on the part of the spectator electrons when an L electron fills the K hole. To see how large the effect might be in any case, we performed self-consistent field calculations for atoms with K and L holes. The corrections to the C_i would be about 3% for $Z=50$ and 1% for $Z=70$. Since it was felt that relaxation does not occur for the K x ray, no corrections were made for this effect in Table I.

Mass shifts. The removal of the c.m. coordinate leads to the appearance of a two-body kinetic energy term

$$(2M)^{-1}\sum_{i,j}\mathbf{P}_i\cdot\mathbf{P}_j.$$

When separated into one-body and two-body terms,

$$(2M)^{-1}\sum_{i,j}\mathbf{P}_i\cdot\mathbf{P}_j=(2M)^{-1}\sum_{i}\mathbf{P}_i^2+(2M)^{-1}\sum_{i\neq j}\mathbf{P}_i\cdot\mathbf{P}_j, \tag{6}$$

the first term leads to the normal mass shift and the second to the specific mass shift or the Hughes-Eckart effect.[8] Introducing the single-particle Hamiltonian $\sum\mathbf{P}_i^2=2m(H-V)$, and using the Virial theorem $\langle V\rangle=2E$, the first term is shown to lead to a compression of the energy-level spectrum by the amount m/M, where m and M are the electron and nuclear masses, respectively. This is just the usual reduced-mass effect. The second term, the specific mass term must be evaluated numerically. In the case of the K x-ray transition, the electron levels that are important for the calculation are well defined and so the evaluation of the specific mass shift is straightforward. Chesler[9] has shown the specific mass shift to be approximately $-\frac{1}{3}$ of the normal mass shift for $40>Z>70$. Independent calculations by the author confirm this result. The total mass shift for K x-ray transitions is usually less than a few percent of the total isotope shift. The specific mass shift for optical transitions in heavy atoms is usually neglected. Unlike the x-ray case, the specific mass shift in optical transitions can be a large part of the total isotope shift. Instances of this are shown in the following paper. Relativistic corrections to the mass shift may be significant.[10,11]

Polarization shifts. Configurations involving excitations of one nucleon and one electron, as well as two electrons contribute to the atomic wave function. While such effects have not been observed in electronic spectra they are quite appreciable in muonic atom transitions. Extensive calculations have been made recently to estimate the size of these shifts.[12,13] The greatest uncertainty comes from the lack of knowledge of the excitation spectrum of the nuclear ground state, especially the monopole states. An attempt to estimate the electronic quadrupole polarization shifts has been made by Reiner and Wilets,[14] but this calculation is in doubt.[15] The polarization shifts in x-ray spectra must be treated somewhat differently than for optical spectra. As an example, the quadrupole polarization shift from the $1s$ electrons is reduced by approximately 40%, since we must take the difference between the shifts when one and two $1s$ electrons are present. The necessity of antisymmetrizing the electron wave function decreases the shift. A polarization effect of lower order is possible in odd A isotopes. The ground-state electromagnetic moments may distort the electron wave functions (Sternheimer shielding) without involving excited nuclear states. A preliminary investigation of this effect by Faessler and Walther[16] for the odd Nd isotopes shows that significant shifts may be expected.

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[8] D. J. Hughes and D. Eckart, Phys. Rev. **36**, 694 (1930).

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Radiative corrections. The radiative corrections to the Coulomb interaction are dependent to a small extent on the nuclear charge radius. Breit and Clendenin[17] have examined some of the terms that give rise to the anomalous magnetic moment of the electron. They use a long-wavelength approximation which is not appropriate and so their result is in doubt. The author has examined the energy shift due to the effect of a change in nuclear charge radius on the vacuum polarization potential. Since the vacuum polarization potential extends over an electron Compton wavelength, the 1*s* electron wave function overlaps any change in this potential to a much greater extent than for the nuclear Coulomb potential. For a reasonable ΔR, a shift of 0.5% of the Coulomb shift was found for $Z=74$. All the radiative corrections together might amount to a few percent of the Coulomb shift and should be investigated further.

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Nuclear Charge Radii from Atomic *K* X Rays*

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Isotope shifts of *K* x-ray transitions have been measured in several isotopes of Gd, Dy, Er, and Hf. The results of these observations, together with results of previously communicated measurements on Sn, Nd, Sm, W, Hg, Pb, and U, have been analyzed in terms of even nuclear charge moments. The dominant moment $\delta\langle r^2\rangle$ is listed for 26 isotope pairs. A comparison of the x-ray shifts with the optical isotope shifts furnishes in several cases the optical specific mass shifts. The difficulties of comparison with muonic x-ray isotope shifts are discussed.

INTRODUCTION

It is well known that the energies of atomic transition, particularly those associated with *s* states, differ slightly from one isotope to the next. This isotope shift arises predominantly from two causes, namely, from the difference of the nuclear masses of the two isotopes and from the difference of the nuclear Coulomb field experienced by the atomic electron undergoing a transition. Effects of nuclear polarization associated with the interaction between atomic and nuclear states also give rise to isotope shifts; their contributions, however, are expected to be small for atomic transitions.

In the case of x-ray transitions between the 2*p* and 1*s* states, the mass shift amounts to only a small contribution of the total shift for medium-heavy and heavy nuclei. As we shall see below, the mass shift can be calculated with good accuracy. Except for the small higher-order correction mentioned above, we are thus left with the Coulomb contribution, historically also referred to as "volume effect."

To evaluate the Coulomb contribution, we need to know the electronic wave function of the states undergoing a transition as well as the nuclear charge distribution. The energy of the 1*s* electron, for example, by virtue of its penetration into the nucleus, depends on the particular form of the charge distribution. The isotope shift thus measures the change in charge distribution between two isotopes. The energy shift can be factorized into an atomic part amenable to a self-consistent atomic calculation and a nuclear part. The latter represents the main objective of the present investigations.

For atomic x rays, it is appropriate to express the nuclear part in terms of even-charge moment variations $\delta\langle r^{2n}\rangle$ as described in the preceeding paper by Seltzer.[1] In the particular case of transitions associated with the $1s_{1/2}$ state, the dominant term in the isotope shift is given by the variation of the second moment $\delta\langle r^2\rangle$. To lowest approximation, a measurement of the isotope shift δE of the $2p_{3/2}$-$1s_{1/2}$ x ray determines the variation of the second charge moment. To the extent that higher moments are included in the analysis, additional measurements on atomic states responding to different combinations of moments are required. The $2p_{3/2}$ state, for example, involves charge moment ratios different from the $1s_{1/2}$ states. The *L* x rays leading to this state are the $\alpha_1(3d_{5/2})$, $\alpha_2(3d_{3/2})$, $\beta_2(4f_{5/2})$, and $\beta_5(5d_{3/2})$ transitions. A measurement of the $K\alpha_1$, as well as the $L\alpha_1$ x ray, would permit us to find $\delta\langle r^2\rangle$ and $\delta\langle r^4\rangle$. Obviously, there are practical difficulties owing to the smallness

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[1] E. Seltzer, preceeding paper, Phys. Rev. **188**, 1916 (1969).