Effect of Exchange on M/L Electron Capture Ratios*

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Theoretical expressions that include the effect of electron exchange are given for M/L electron-capture ratios; the results are presented in a form that makes clear the physical origin of the exchange corrections. Accurate values for M/L ratios both with and without exchange corrections are tabulated for Z between 13 and 37; these numerical results were calculated using the analytic Hartree-Fock wave functions of Watson and Freeman. The exchange correction for Z greater than or equal to 38 has been estimated by a least squares extrapolation of the correction for lower Z values. The effect of electron exchange on electron capture to positron-emission ratios is also discussed. The exchange-corrected theoretical M/L ratio for $_{32}Ge^{71}$ is 0.173, in disagreement with the recent measurement of Manduchi and Zannoni. It is suggested that some additional precision measurements of M/L ratios be performed in order to clarify this discrepancy between theory and experiment.

I. INTRODUCTION

THE observed ratio of L to K electron-capture probabilities exceeds[1-4] the standard[5] theoretical prediction by 5 to 25% for all nine of the precisely measured allowed electron captures with atomic number between 18 and 36. We have recently shown[4,6] that this systematic discrepancy between theory and experiment can be removed by using a more general theoretical treatment that includes atomic states in the description of the radioactive system. In this paper we present the generalized theoretical expression for M/L ratios in a form that makes clear the physical origin of the exchange correction. We also discuss the effect of electron exchange on electron-capture to positron-emission ratios.

In order to facilitate comparison with experiment, we list, for Z between 13 and 37, accurate values for the theoretical M/L ratio both with and without exchange correction. These numerical values were calculated using the analytic Hartree-Fock wave functions of Watson[7] and Watson and Freeman[8] and are probably accurate, within the Hartree-Fock formalism, to 0.5%. Most of the presently available experimental information concerning M/L ratios pertains to fairly heavy isotopes.

Hence, we have estimated the exchange correction for Z greater than or equal to 38 by least-squares extrapolation of the correction for lower Z values; we believe that this least-squares extrapolation results in an uncertainty due to electron exchange of less than 2% in capture ratios for large Z.[9]

Manduchi and Zannoni[10] have performed the only precision measurement to date of an M/L capture ratio for a fairly light isotope; they measured an M/L ratio of 0.141 ± 0.010 for $_{32}Ge^{71}$. Our exchange-corrected theoretical result for Ge^{71} is 0.173, in disagreement with the measurement of Manduchi and Zannoni.

II. THEORETICAL EXPRESSIONS

A. M/L Capture Ratios

In I and II, we followed the suggestions of Benoist-Gueutal[11] and Odiot and Daudel[12] and generalized the usual theory of allowed electron capture to include atomic variables in the initial and final states of the radioactive system. One can show, by arguments similar to the arguments given in I and II for L/K ratios, that the M_I to L_I capture ratio is given by

$$\frac{\lambda_{M_I}}{\lambda_{L_I}} = \left| \frac{q(3s')f(3s')}{q(2s')f(2s')} \right|^2 , \tag{1}$$

where $q(3s')$ and $q(2s')$ are the neutrino energies[13] for M_I and L_I capture, respectively, and $f(3s')$ and $f(2s')$ are the amplitudes for the production of a hole in the final

[1] B. L. Robinson and R. W. Fink, Rev. Mod. Phys. **32**, 117 (1960).

[2] R. Bouchez and P. Depommier, Rept. Progr. Phys. **23**, 395 (1960).

[3] R. R. Moler and R. W. Fink, Phys. Rev. **131**, 821 (1963).

[4] J. N. Bahcall, Phys. Rev. Letters **9**, 500 (1962), hereafter called I. This reference contains a list of the most recent experimental results on L to K capture ratios of light nuclei.

[5] H. Brysk and M. E. Rose, Rev. Mod. Phys. **30**, 1169 (1958).

[6] J. N. Bahcall, Phys. Rev. **129**, 2683 (1963), hereafter called II. This work contains a discussion of the effect of exchange on electron-emission probabilities as well as an evaluation of the effect of imperfect atomic overlap on allowed electron and positron-emission probabilities and on total electron-capture rates.

[7] R. E. Watson, Technical Report Number 12, 1959, Solid-State and Molecular Theory Group, MIT, Cambridge, Massachusetts (unpublished); Phys. Rev. **118**, 1036 (1960).

[8] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); **124**, 1117 (1961). The Cl $2s$ wave function given by these authors has a minus-sign error in the sixth row of the C_{ij} table.

[9] Capture ratios without exchange are currently being computed for large Z by J. M. Pearson and B. L. Robinson.

[10] C. Manduchi and G. Zannoni, Nucl. Phys. **36**, 353 (1962); Nuovo Cimento **24**, 181 (1962).

[11] P. Benoist-Gueutal, Compt. Rend. **230**, 624 (1950); Ann. Phys. (N.Y.) **8**, 593 (1953).

[12] S. Odiot and R. Daudel, J. Phys. Radium **17**, 60 (1956).

[13] It is shown in Ref. 5 that the binding energy of the $3s'$ electron ($2s'$ electron) in the *final* atom should be used in calculating $q(3s')$ [$q(2s')$]. The difference between electron binding energies in the initial and final atoms is usually small compared to the total energy available to the emitted neutrino and hence this point is usually unimportant.

$3s'$ or $2s'$ shell. The amplitudes are

$$f(3s') = \langle 1s' | 1s \rangle \langle 2s' | 2s \rangle \psi_{3s}(0) - \langle 1s' | 3s \rangle \langle 2s' | 2s \rangle \psi_{1s}(0)$$
$$- \langle 2s' | 3s \rangle \langle 1s' | 1s \rangle \psi_{2s}(0); \quad (2a)$$

$$f(2s') = \langle 1s' | 1s \rangle \langle 3s' | 3s \rangle \psi_{2s}(0) - \langle 1s' | 2s \rangle \langle 3s' | 3s \rangle \psi_{1s}(0)$$
$$- \langle 3s' | 2s \rangle \langle 1s' | 1s \rangle \psi_{3s}(0). \quad (2b)$$

In Eqs. (2), we have omitted constants that are the same for both amplitudes. The atomic matrix elements $\langle ns' | ms \rangle$ represent the overlap of the ms wave function of an electron in the initial atom with the ns' wave function of an electron in the final atom. The $\psi_{ns}(0)$ are one-electron wave functions, evaluated at the nucleus, of electrons in the initial atom.

An M_{I} capture can occur in three important ways which are experimentally indistinguishable: (a) annihilation of a $3s$ electron with the $1s$ and $2s$ electrons appearing in the final $1s'$ and $2s'$ states, (b) annihilation of a $1s$ electron with a $3s$ electron jumping into the final $1s'$ shell, (c) annihilation of a $2s$ electron with a $3s$ electron jumping into the final $2s'$ shell. The three processes (a)–(c) correspond to the three terms in the M_{I} capture amplitude, $f(3s')$; the usual theory[5] only considers process (a). The minus signs in the amplitude $f(3s')$ occur because (b) and (c) differ from (a) only in the exchange of a single electron.

The amplitude for L_{I} capture, $f(2s')$, can be interpreted in a similar way.

In deriving Eqs. (1) and (2), we summed over all final electron states different from the $1s'$, $2s'$, $3s'$ states. We assumed that these core s electrons are inert if not captured, i.e., the overlap integral $\langle ns' | ns \rangle$ was assumed to be approximately 1 for n equal to 1, 2, or 3; this assumption is well satisfied for Z in the range we are considering.[14] We have also neglected small exchange effects between the core s electrons and other s electrons present in the initial atom.

Equations (1) and (2) can be written in the form:

$$\frac{\lambda_{M_{\mathrm{I}}}}{\lambda_{L_{\mathrm{I}}}} = \left(\frac{\lambda_{M_{\mathrm{I}}}}{\lambda_{L_{\mathrm{I}}}} \right)^0 X^{M/L}, \quad (3a)$$

where

$$\left(\frac{\lambda_{M_{\mathrm{I}}}}{\lambda_{L_{\mathrm{I}}}} \right)^0 = \left| \frac{q(3s') \psi_{3s}(0)}{q(2s') \psi_{2s}(0)} \right|^2 \quad (3b)$$

is the usual[5,13] M_{I} to L_{I} capture ratio and

$$X^{M/L} = \left| \frac{\langle 2s' | 2s \rangle}{\langle 3s' | 3s \rangle} \right|^2 \left| \frac{1 - \dfrac{\langle 1s' | 3s \rangle}{\langle 1s' | 1s \rangle} \dfrac{\psi_{1s}(0)}{\psi_{3s}(0)} - \dfrac{\langle 2s' | 3s \rangle}{\langle 2s' | 2s \rangle} \dfrac{\psi_{2s}(0)}{\psi_{3s}(0)}}{1 - \dfrac{\langle 1s' | 2s \rangle}{\langle 1s' | 1s \rangle} \dfrac{\psi_{1s}(0)}{\psi_{2s}(0)} - \dfrac{\langle 3s' | 2s \rangle}{\langle 3s' | 3s \rangle} \dfrac{\psi_{3s}(0)}{\psi_{2s}(0)}} \right|^2 \quad (3c)$$

is the exchange correction to the usual M_{I} to L_{I} capture ratio.

In order to compare Eqs. (3) with experimentally observed M/L capture ratios, the small probability for decay by the capture of a $p_{1/2}$ electron should be taken into account. Thus, we write for the total M/L capture ratio:

$$\frac{\lambda_M}{\lambda_L} = \left(\frac{\lambda_{M_{\mathrm{I}}}}{\lambda_{L_{\mathrm{I}}}} \right)^0 \left[X^{M/L} + \frac{M_{\mathrm{II}}}{M_{\mathrm{I}}} - \frac{L_{\mathrm{II}}}{L_{\mathrm{I}}} \right]. \quad (4)$$

However, the ratio

$$\left| \frac{\psi_{np_{1/2}}(0)}{\psi_{ns_{1/2}}(0)} \right|^2 \cong \tfrac{3}{16} (\alpha Z)^2, \quad (5)$$

and depends only on nuclear charge for a point nucleus; hence, $M_{\mathrm{II}}/M_{\mathrm{I}}$ and $L_{\mathrm{II}}/L_{\mathrm{I}}$ almost exactly cancel in Eq. (4). Therefore,

$$\frac{\lambda_M}{\lambda_L} \cong \frac{\lambda_{M_{\mathrm{I}}}}{\lambda_{L_{\mathrm{I}}}}. \quad (6)$$

B. Electron-Capture to Positron-Emission Ratios

The arguments presented in II can also be used to predict the effect of exchange on electron-capture to positron-emission ratios. We find, with the same assumptions as in the preceding subsection,

$$\frac{\lambda_{L_{\mathrm{I}}}}{\lambda_{\beta^+}} = \left(\frac{\lambda_{L_{\mathrm{I}}}}{\lambda_{\beta^+}} \right)^0 B_{L_{\mathrm{I}}}, \quad (7a)$$

where $(\lambda_{L_{\mathrm{I}}}/\lambda_{\beta^+})^0$ is the usual[5] L_{I} capture to positron-emission ratio,

$$\left(\frac{\lambda_{L_{\mathrm{I}}}}{\lambda_{\beta^+}} \right)^0 = \frac{2\pi^2 [q(2s')]^2 | \psi_{2s}(0) |^2}{f(W_0, -Z)}, \quad (7b)$$

and

$$B_{L_{\mathrm{I}}} = \left| \frac{f(2s')}{\psi_{2s}(0)} \right|^2 \quad (7c)$$

is the appropriate exchange correction. The total L capture to positron-emission ratio is, therefore,

$$\frac{\lambda_L}{\lambda_{\beta^+}} = \left(\frac{\lambda_{L_{\mathrm{I}}}}{\lambda_{\beta^+}} \right)^0 \left[B_{L_{\mathrm{I}}} + \frac{L_{\mathrm{II}}}{L_{\mathrm{I}}} \right]. \quad (8)$$

Similar expressions obtain for K (and M) to β^+-emission ratios. Tables of the overlap and exchange integrals necessary to compute B_K, $B_{L_{\mathrm{I}}}$, and $B_{M_{\mathrm{I}}}$ will be included in a forthcoming paper on L to K electron-capture ratios.[14]

The complete electron-capture amplitudes $f(2s')$ and $f(3s')$ should also be used in calculating fluorescent yields from observed ratios of x-ray rates to total disintegration rates.[14,15]

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[14] J. N. Bahcall (to be published). The smallest overlap integral that occurred in our calculations, the $\langle 3s | 3s' \rangle$ integral for Z' equal to 13, has a value of 0.98.

[15] I am grateful to Dr. J. G. V. Taylor for bringing this interesting problem to my attention.

III. NUMERICAL RESULTS

In Table I, we list numerical values for

$$\left(\frac{M}{L}\right)^0 \equiv \left|\frac{\psi_{3s}(0)}{\psi_{2s}(0)}\right|^2 \tag{9}$$

and $X^{M/L}$, the theoretical M/L exchange correction defined by Eq. (3c). Note that Table I does not include the correction for atomic binding energies [see Eq. (3b)]. The values of $(M/L)^0$ for potassium and calcium were calculated from the numerical Hartree-Fock wave functions of Hartree and Hartree[16] and are marked with a superscript a in Table I; all other values of $(M/L)^0$ were calculated with the analytic Hartree-Fock wave functions of Watson[7] and Watson and Freeman.[8] The analytic Hartree-Fock wave functions[7,8] were also used to calculate all non-superscripted values of $X^{M/L}$ listed in column 4 of Table I.

Analytic Hartree-Fock functions were used to calculate the exchange corrections since the integrals occurring in this quantity are sensitive to small departures from orthonormality[4] of the basis wave functions. The analytic wave functions that were used satisfy the orthonormality conditions,

$$\langle ns | ms \rangle = \delta_{m,n} \tag{10}$$

to better than one part in 10^{+6}. Most of the older numerical Hartree-Fock wave functions that are given in the literature do not satisfy Eq. (10) to better than one part in 10^3 or 10^4 and, hence, cannot be used to calculate accurate values of the exchange correction. However, where comparisons are possible, the Hartree-

Hartree[17] wave functions do yield values of $(M/L)^0$ that agree to better than a percent with values obtained from the analytic Hartree-Fock wave functions. Hence, we believe that the values of $(M/L)^0$ that are listed in Table I for potassium and calcium are, within the restricted Hartree-Fock formalism, accurate to 1%.

The iron series (Sc to Ni) wave functions of Watson[7] were calculated for $3d^n$ configurations, where the number of electrons outside an argon-like core is denoted by n. However, the ground states of the iron series atoms actually have configurations of the form $3d^{n-1}4s$ or $3d^{n-2}4s^2$. In order to test whether $(M/L)^0$ and $X^{M/L}$ are sensitive to the shape of the charge distribution of the outermost electrons, we calculated $(M/L)^0$ and $X^{M/L}$ for a large number of singly ionized atoms, again using wave functions obtained by Watson[7] and Watson and Freeman.[8] The differences between the values listed in Table I and the values computed for singly ionized atoms with configurations $3d^{n-1}$ were almost always less than $\frac{1}{10}$%. Hence, we conclude that the iron series values listed in Table I would be essentially unchanged if the Hartree-Fock wave functions used in our calculations had been obtained for the true ground-state configurations instead of for the configurations $3d^n$.

The values of $(M/L)^0$ given in Table I for copper rubidium were calculated with wave functions describing a singly ionized atom since no neutral atom wave functions were available for these elements.

The values of $X^{M/L}$ in Table I with a superscript b were calculated from the following formula:

$$X^{M/L} = 1 + 5.593Z^{-1} - 59.5Z^{-2} + 1111Z^{-3}. \tag{11}$$

Formula (11) was obtained by a least-squares fit of the non-superscripted values of $X^{M/L}$ in Table I to a polynomial in inverse powers of Z. This least-squares formula reproduces all the non-superscripted values to better than $\frac{1}{2}$% with an accuracy that increases as Z increases. Since the difference between $X^{M/L}$ and unity is small for large Z, we believe that formula (11) can be used to calculate M/L values that, with a conservative estimate of the uncertainties, are accurate to 2%.

All of the wave functions that have been used in our calculations were obtained by solving a nonrelativistic Schrödinger equation with a nuclear Coulomb potential corresponding to a point-charge. We can estimate relativistic effects on M/L capture ratios by examining M/L ratios calculated with point-charge, unscreened Dirac wave functions. We find to order $(\alpha Z)^2$:

$$\left(\frac{M}{L}\right)^0 = \left(\frac{M}{L}\right)^0_{\text{N-R}} \left[1 + (\alpha Z)^2 \left(-\frac{17}{48} + \ln\frac{3}{2}\right)\right],$$

$$\cong \left(\frac{M}{L}\right)^0_{\text{N-R}} [1 + 0.05(\alpha Z)^2], \tag{12}$$

TABLE I. M/L capture ratios and exchange corrections.

Element	Z	$(M/L)^0$	$X^{M/L}$
Al	13	0.0534	1.584
Si	14	0.0655	1.505
P	15	0.0754	1.433
S	16	0.0842	1.387
Cl	17	0.0914	1.347
Ar	18	0.0976	1.316
K	19	0.109[a]	1.291[b]
Ca	20	0.118[a]	1.270[b]
Sc	21	0.1210	1.251[b]
Ti	22	0.1248	1.241
V	23	0.1282	1.225
Cr	24	0.1315	1.212
Mn	25	0.1342	1.201
Fe	26	0.1365	1.190
Co	27	0.1386	1.181
Ni	28	0.1400	1.172
Cu	29	0.1420	1.164
Zn	30	0.1435	1.161[b]
Ga	31	0.1462	1.156
Ge	32	0.1492	1.151
As	33	0.1523	1.146
Se	34	0.1555	1.141
Br	35	0.1585	1.137
Kr	36	0.1615	1.133
Rb	37	0.1645	1.129

a Calculated from Hartree-Hartree functions.
b Values interpolated by formula (11).

[16] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) 164, 167 (1938); 166, 450 (1938).
[17] W. Hartree, D. R. Hartree, and M. F. Manning, Phys. Rev, 59, 299 (1941); 59, 306 (1941).

where $(M/L)_{\text{N-R}}{}^0$ is the nonrelativistic Coulomb value for the M/L ratio. All terms that depend on the logarithm of the nuclear radius cancel out in the capture ratio. Equation (12) suggests that relativistic effects on $(M/L)^0$ are small for the values of Z listed in Table I. Using arguments of the kind given by Layzer and Bahcall,[18] one can see that relativistic corrections for $X^{M/L}$ are also of order $(\alpha Z)^2$ and, hence, small. The calculations of Band et al.[19] show that nuclear size effects on M/L ratios amount to less than 0.3% for Z less than 50. Hence, nuclear size effects can safely be neglected for Z less than 50.

IV. EXPERIMENTAL TEST. Ge^{71}

We have calculated the exchange-corrected M/L value for Ge^{71} using Eqs. (3) and Table I; we find[20]:

$$(M/L)_{\text{Th}} = 0.173, \tag{13}$$

[18] D. Layzer and J. Bahcall, Ann. Phys. (N. Y.) **17**, 177 (1962).
[19] I. M. Band, L. N. Zyrianóva, and Tsin Chen-Zhui, Izv. Akad. Nauk SSSR Ser. Fiz. **20**, 1389 (1956).
[20] The self-consistent field value of the M/L ratio without exchange is 0.151 and is not in disagreement with the results of Manduchi and Zannoni, although there are contrary statements in their papers (Ref. 10). The Hartree-Hartree wave functions

which is in good agreement with a similar calculation that we have performed using the somewhat less accurate wave functions of Hartree and Hartree.[17] Our theoretical prediction disagrees with the experimental result of Manduchi and Zannoni who obtained[10]:

$$(M/L)_{\text{Ex}} = 0.141 \pm 0.010. \tag{14}$$

It would be useful to perform other precision measurements of M/L ratios (e.g., for Zn^{65}, Ge^{71}, or Kr^{79}) in order to clarify this discrepancy between theory and experiment.

ACKNOWLEDGMENTS

(Ref. 17) and the Watson-Freeman wave functions (Ref. 8) both give $(M/L)^0 = 0.149$ for Ge^{71}.

Nuclear Reaction Energies with an Absolute Ion Velocity Gauge

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A time-of-flight technique was used to find the $Li^7(p,n)Be^7$ threshold energy and an $Al^{27}(p,\gamma)Si^{28}$ resonant energy. Results place the $Li^7(p,n)$ threshold at 1879.8 ± 0.3 keV and the $Al^{27}(p,\gamma)$ resonance at 991.6 ± 0.2 keV. The lithium threshold was determined by use of a (yield)$^{2/3}$ extrapolation. The aluminum resonant energy is taken as the half-height energy of a thick-target yield. Except for the earliest electrostatic analyzer results, there was good agreement with previous determinations of these energies. The proton beam was modulated at approximately 50 Mc/sec by use of an Einzel lens driven by a crystal controlled oscillator-amplifier at the ion source of an electrostatic accelerator. The time-of-flight equipment consisted of a drift tube of adjustable length, a "phase meter" employing a variable delay line, and two pickups consisting of tuned cylindrical tubes through which the proton beam passed. Frequency was measured by zero beating a variable-frequency crystal oscillator against the signal picked off the beam and counting the crystal frequency with a frequency counter standardized to WWV. The lithium and aluminum targets were protected from organic vapors by a concentric liquid nitrogen trap.

INTRODUCTION

THE present work was stimulated by an apparent systematic difference between absolute magnetic-deflection and absolute electric-deflection methods of measuring nuclear energies. Some of these earlier results are shown in Table I.

Very recent results (NRL,[1] 991.9 ± 0.3, and Zurich,[2]

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[1] R. O. Bondelid and J. W. Butler (private communication).
[2] A. Rytz, H. H. Staub, and W. Zych, Helv. Phys. Acta **35**, 341 (1962).

991.8 ± 0.1) apparently remove the worst discrepancies. An absolute velocity device[3] used by Shoupp, Jennings, and Jones[4] at Westinghouse resulted in a threshold energy for the $Li(p,n)$ threshold which, perhaps unfortunately, overlapped the early electrostatic and magnetic-deflection results, thus giving no indication

[3] W. Altar and M. Garbuny, Phys. Rev. **76**, 496 (1949). A 1.25-m coaxial resonant cavity was excited at both ends by a 70-Mc/sec modulated proton beam. The center conductor was a field-free drift tube. The beam energy was varied to obtain minimum rf excitation when the transit time was an odd-multiple of half-cycles.
[4] W. E. Shoupp, B. Jennings, and W. Jones, Phys. Rev. **76**, 502 (1949).