$L\alpha$ Satellite Lines for Elements Mo(42) to Ba(56)

CHARLES A. RANDALL AND LYMAN G. PARRATT
Cornell University, Ithaca, New York

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The x-ray satellite lines accompanying the $L\alpha_{1,2}$ emission for elements Mo(42) to Ba(56) have been systematically studied with a two-crystal vacuum spectrometer. Integrated relative intensities of the satellite group agree qualitatively but differ by a factor of about six with previous photographic measurements. The abrupt intensity change at $Z=50$ (the element at which the Coster-Kronig "cross-over" occurs) further confirms qualitatively the Coster-Kronig interpretation of Auger production of the initial state in satellite emission. The observed satellite contour for each element has been resolved arbitrarily into constituent component lines and wave-lengths and relative intensities measured. A few hitherto unreported satellite components are found: Theory predicts fifteen $L\alpha$ satellite components for Au(79), about twice as many as are included in the present analyses for the intermediate atomic numbers. The components farthest removed from the $L\alpha_1$ line seem not to exhibit the abrupt intensity change at $Z=50$ and, therefore, may not be from the $L_{\text{III}}M_{\text{IV,V}}$ initial state. These components may be Wentzel-Druyvesteyn satellites from another initial state or they may be Richtmyer satellites.

INTRODUCTION

THE Wentzel-Druyvesteyn theory seems to explain satisfactorily the origin of most and perhaps all of the numerous satellite lines in x-ray spectra.[1] Accordingly, satellites arise in radiative transitions between atomic states of double- or multiple-ionization of inner electron shells. A crucial test of the theory is the comparison of the predicted and observed intensities of each of the various groups of satellites. Prior to 1935 the strongest objection to the theory was its apparent failure to account for the curious intensity anomolies for certain ranges of atomic numbers: in particular, for the intensities of the $L\alpha$ and $L\beta_2$ satellites for atomic numbers near $Z=50$ and $Z=75$. In 1935 Coster and Kronig[2] suggested that radiationless transitions share with direct electron (or photon) impact the responsibility for the production of the initial satellite state. The probability of occurrence of the radiationless transitions that produce the doubly-ionized $L_{\text{III}}M_{\text{IV,V}}$ state was shown to agree sensibly with the observed[3–5] $L\alpha$ and $L\beta_2$ satellite intensities.

As yet, however, only qualitative agreement between the theoretical and experimental satellite intensities has been demonstrated. The assumptions and computations have not yet been refined in quantitative theoretical evaluations; and experimental information of L series satellites has been limited with few exceptions[1, 6, 7] to data obtained with the photographic method and with spectrographs of relatively low resolving power. Illustrative of the uncertainty in measurements of intensity are the following data for Ag(47): Hirsh[4] finds the intensity of the $L\alpha$ satellites to be 15.5 percent of the intensity of the $L\alpha_1$ line; Hirsh and Richtmyer[3] report 33 percent; Parratt,[8] from 6 to 16 percent depending on the choice of background.

The present paper reports systematic measurements of the $L\alpha$ satellites for a range of elements Mo(42) to Ba(56) that includes the Coster-Kronig "cross-over" at $Z=50$. These measurements were obtained from ionization curves recorded with a two-crystal spectrometer of high resolving power. The integrated relative intensities of the satellite group for the various elements agree qualitatively but differ by a factor of about six with the photographic measurements of Hirsh.[4] Also, in the present study, the observed satellite contour for each element has been resolved into constituent component lines and the component wave-lengths and relative intensities measured. Some component lines are found whose relative intensities do not

[1] F. K. Richtmyer, Rev. Mod. Phys. **9**, 391 (1937) and references.
[2] D. Coster and R. de L. Kronig, Physica **2**, 13 (1935).
[3] F. R. Hirsh and F. K. Richtmyer, Phys. Rev. **44**, 955 (1933).
[4] F. R. Hirsh, Phys. Rev. **48**, 722 (1935).
[5] Mrs. A. W. Pearsall, Phys. Rev. **46**, 695 (1934).
[6] L. G. Parratt, Phys. Rev. **54**, 99 (1938).
[7] F. K. Richtmyer and R. Shrader, Science **89**, 398 (1939); Phys. Rev. **55**, 605A (1939).
[8] L. G. Parratt, Phys. Rev. **50**, 598 (1936).

seem to exhibit the Coster-Kronig enhancement as the atomic number is decreased below 50. These components must be members of a different satellite group.

Experimental

The two-crystal vacuum spectrometer used in the present work has been described elsewhere.[6]

The calcite crystals, crystals A_4B_4 as noted in previous studies,[6,9] have again deteriorated, spectrometrically speaking, in the eighteen months since they were last etched. This decrease in degree of crystal perfection, as indicated by the crystal reflectivities, is shown in Table I. The importance of the spectrometric perfection of the crystals lies in the fact that it is our only measure of, or index to, the resolving power of the spectrometer,[9] the vertical divergence of the x-ray beam having been limited to relative unimportance. For purposes of standardization, the data of Table I are given for Mo $K\alpha_1$ radiation, $\lambda = 0.71$A. The decrease in the effective resolving power due to the crystal imperfections indicated in Table I is probably less[9] for the wave-lengths of the present study, 2.8 to 5.4A, than for 0.71A. When we consider, first, that the present $L\alpha$ lines are rather wide (the smallest width, 2.5 x. u., being more than nine times the $d\lambda$ interval of the crystals for the wave-length in question) and, second, that the uncertainty in the satellite background is many times greater than the uncertainties due to finite resolving power, we conclude that the resolving power used in the present satellite study is effectively infinite.

The x-ray tube targets of the various elements were prepared as follows: An 8-mil Mo(42) sheet was spot-welded to a 0.6-mil Ni sheet which was then soft-soldered to the water-cooled copper target carriage. Bits of pure Ru(44) were pressed with a hydraulic press into a roughened Cu sheet which was soft-soldered to the target carriage. Rh(45), Pd(46) and Ag(47) in sheet form, 4 to 10 mils thick, were each soft-soldered directly to the carriage. Cd(48), In(49) and Sn(50) were melted and flowed with rosin flux directly on to the carriage. Sb(51) was electroplated from a hot solution on to a Ni-coated Cu sheet which was soft-soldered to the carriage. Te(52) powder was pressed into a 15-mil sheet of Ag and heated to form a silver telluride. Pure Ba(56) powder, moistened with benzene, was pressed into a 5-mil sheet of Ag and the barium then oxidized by heating in air. The target of I(53) was produced by holding the previously warmed copper carriage in sublimated vapor from gently heated pure iodine crystals. The iodine and barium targets were operated with a power dissipation of 500 watts; the other targets, 600 watts. The focal-spot, fairly uniform in emission, was about 3×7 mm in size.

It has been shown[10] that an x-ray tube voltage of 2 to $2\frac{1}{2}$ times the excitation voltage gives a constant maximum satellite intensity relative to the intensity of the parent $L\alpha_{1,2}$ lines. For each of the elements of the present study the maximum satellite intensity was assured with a tube voltage of 10 kv above the L_{III} excitation voltage. The applied voltage was rectified and filtered, the ripple being about 1 percent.

In the ionization chamber argon gas was used at such pressures that 98 percent of the x-ray beam was absorbed. Since the wave-length of the K-absorption edge of argon, 3.866A, is within the wave-length range of the $L\alpha$ lines of the present study, the argon pressure in the chamber was varied between the limits of 128 cm of Hg (for Cd(48)) and 13 cm of Hg (for In(49)).

Reproduced in Fig. 1 are ionization curves for the $L\alpha$ spectral regions for Rh(45) and for I(53). These two curves are typical of the satellite regions for elements $41 < Z < 51$ and for elements $50 < Z < 57$, respectively.

Throughout the recording of an ionization

Table I. *Reflectivities of etched calcite crystals for* Mo $K\alpha$ *radiation.* $\lambda = 0.71A$.

	1935 Cleavage Surfaces Etched	1937 18 mo. Later Before After Re-etching		1938 18 mo. Later in Present Work
(1, −1) full width	5.2″	8.0″	5.0″	—
(1, +1) full width	21.0″	27.0″	21.0″	25.1″
(2, −2) full width	1.1″			2.1″
Percent reflection, first order	66.		67.	54.
Percent reflection, second order	49.			29.

[9] L. G. Parratt, Rev. Sci. Inst. **6**, 387 (1935).

[10] D. Coster, H. H. Kuipers and W. J. Huizinga, Physica **2**, 870 (1935).

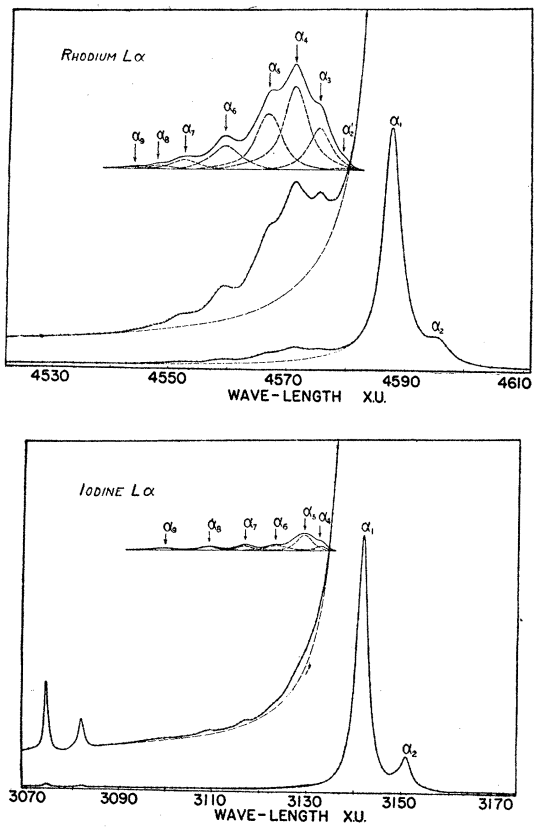

FIG. 1. Ionization curves of the $L\alpha$ regions for Rh(45) and for I(53). The satellite groups are recorded on an intensity scale 8.44 and 28.4 times the scale of the respective $L\alpha_{1,2}$ lines. (In the curve for I(53) the two spurious lines at the left are the Cu$K\alpha_{1,2}$ doublet in second-order reflection.)

curve the tube voltage and current were maintained constant within 1.5 percent by manual control. Before and after each curve was recorded, a time interval of about 4 hours, the maximum ordinate of the $L\alpha_1$ line was measured to detect any uncontrolled intensity change.* The greatest intensity change was for Mo(42), *viz.*, 1.8 percent; for the other elements the intensity change was less than 1 percent.

MEASUREMENTS AND RESULTS

Before we can make any satellite measurements we must resolve the satellites from the parent lines. The overlapping which is illustrated in Fig. 1 is an inherent characteristic of the spectral region and would not have been appreciably less had the resolving power of the spectrometer been infinite. The difficulty of drawing the satellite background has been discussed elsewhere.[8] In the present analyses, the background for each element is the "most reasonable" of many "reasonable" arbitrary curves. The arbitrariness of this choice introduces the greatest uncertainty in the present intensity measurements. The satellite contours, after the background subtractions, are reproduced in Fig. 2. The wave-length scale in x. u. is measured for each contour from the peak of the $L\alpha_1$ line; the intensity scale is arbitrary in each case.

The satellite contours in Fig. 2 are resolved into component lines in the more or less arbitrary manner discussed in a previous paper.[8] The criterion for the existence of a component is that a specific irregularity be observed in the contour and/or that all components be "reasonably" symmetrical. In designating the component satellites we have followed the usual system of

* E.g., any tungsten from the filament condensed on the target results in seriously decreased intensity because of absorption; and, in some cases, a target may melt or pit or its powder gradually disappear.

TABLE II. *Wave-lengths in x. u. of the Lα satellites. The wave-lengths of the $L\alpha_1$ line are taken from the measurements of Hjalmar, Zeits. f. Physik* **7**, *341 (1921).*

ELEMENT	Z	$L\alpha_1$	α'_2	α_3	α_4	α_5	α'_5	α_6	α_7	α_8	α_9	α'_9
Mo	42	5395.0	5388.8	5383.3	5380.0	5374.8	——	5371.1	5362.9	——	——	——
Ru	44	4835.7	4827.2	4822.8	4817.8	4813.3	——	4804.7	4797.9	——	——	——
Rh	45	4587.8	4579.4	4575.4	4571.1	4566.6	——	4559.1	4552.1	4547.5	4543.4	——
Pd	46	4358.5	4349.7	4347.0	4342.7	4338.1	4334.9	4331.4	4324.0	4319.8	4313.0	——
Ag	47	4145.6	4136.6	4134.7	4131.0	4126.5	4123.6	4119.6	4112.3	4107.8	——	——
Cd	48	3947.8	3939.7	3937.2	3933.8	3929.6	3926.5	3922.9	3917.8	3914.5	3910.0	——
In	49	3763.7	——	3573.7	3750.6	3744.6	3743.9	3739.4	3732.1	3725.1	3720.6	——
Sn	50	3592.2	——	3584.5	3579.7	3575.8	3571.3	3566.2	3561.8	3557.7	——	——
Sb	51	3431.8	——	——	3419.6	3416.2	3413.1	3409.2	3402.2	3397.4	3393.3	3387.2
Te	52	3282.0	——	——	3270.9	3267.7	——	3260.7	3252.6	3248.6	3242.7	3234.7
I	53	3141.7	——	——	3132.4	3129.0	——	3123.5	3116.6	3108.8	3099.3	——
Ba	56	2769.6	——	——	——	2758.0	——	2755.1	2743.2	2736.3	2728.3	2719.8

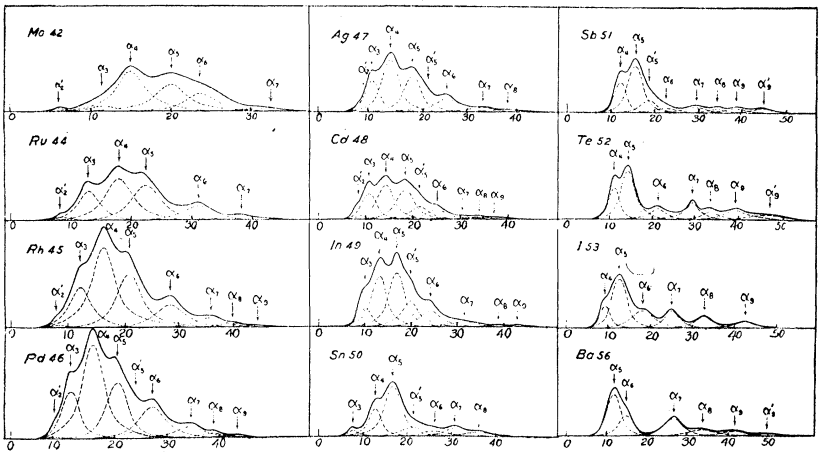

FIG. 2. Contours of the $L\alpha$ satellite groups with backgrounds subtracted. The abscissa scale is in x. u. measured from the $L\alpha_1$ peak; the ordinate scale of each contour is arbitrary.

numeral subscripts and primes. Semi-Moseley graphs are of help in tracing a given component from element to element. These graphs, $(\Delta\nu/R)^{\frac{1}{2}}$ *vs.* Z, where $\Delta\nu$ is measured from the peak of the $L\alpha_1$ line, are shown in Fig. 3. The wave-length positions of the components are listed in Table II.

The integrated intensity of the satellite group relative to the intensity of the $L\alpha_{1,2}$ lines is the ratio of the area contained under the satellite contour divided by the area under the $L\alpha_{1,2}$ lines. Listed in Table III are these integrated relative intensities together with the uncertainties due to the "reasonable" limits in choice of background. These data are shown graphically in Fig. 4. Corrections for differential absorption, reflection coefficients of the crystals, etc., are much less than the above-mentioned uncertainties and so have not been made in these data. Qualitatively the shape of the curve in Fig. 4 agrees well with the curve obtained by Hirsh[4] but the magnitudes of the relative intensities reported by Hirsh are about six times larger for $Z>50$ than those found in the present study.

According to the Wentzel-Druyvesteyn theory, the initial state for $L\alpha$ satellite emission is $L_{\mathrm{III}}M_{\mathrm{IV,V}}$. This state may be produced by any

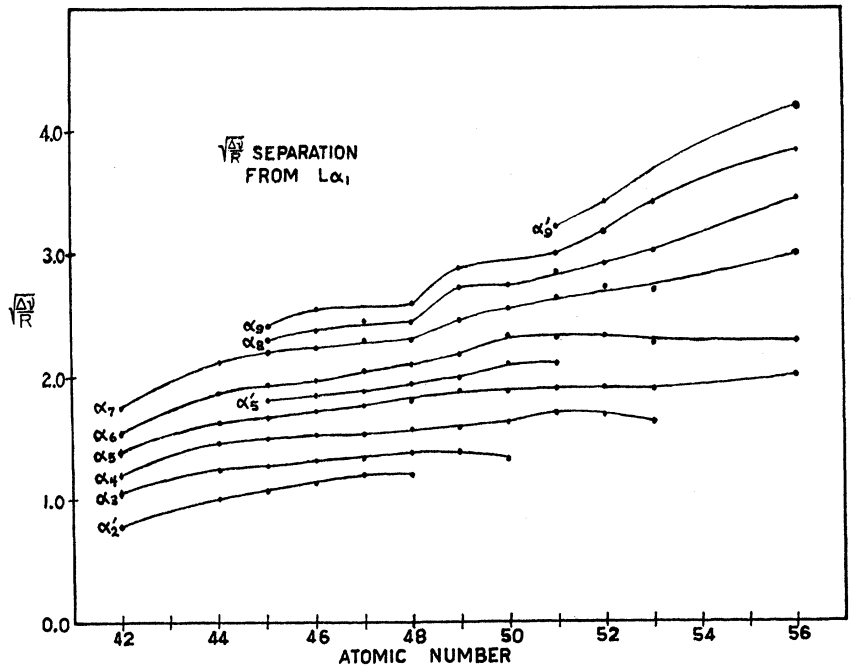

FIG. 3. Semi-Moseley graphs for the component satellites.

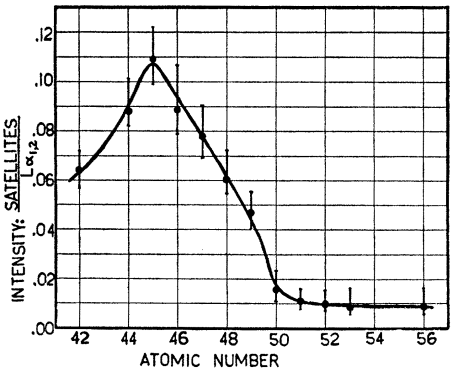

FIG. 4. Integrated intensity of the $L\alpha$ group of satellites relative to the intensity of the $L\alpha_{1,2}$ lines.

one of various methods. For elements $Z<50$ the probability of occurrence of the Auger or radiationless transition $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}M_{\mathrm{IV,V}}$ is relatively large[11] and is responsible apparently for almost all of the satellite intensity, at least to $Z=42$. The maximum in the curve in Fig. 4 is correlated with the maximum in the Auger probability. For elements $Z>50$ the Auger probability is extremely small and single electron impact is the likely ionizing process.

Figure 5 shows the ratio of the intensity of the various individual satellite components to the intensity of the $L\alpha_{1,2}$ lines. From Figs. 3 and 5 it is evident that α_8, α_9 and α_9', the components farthest removed from the $L\alpha_1$ line, and α_2', the component nearest the $L\alpha_1$ line, seem *not* to exhibit the abrupt intensity change at $Z=50$. These components, therefore, may not arise from the $L_{\mathrm{III}}M_{\mathrm{IV,V}}$ initial state; they may be Wentzel-Druyvesteyn type of satellites from another initial state, or they may be satellites arising from a "double-jump" transition according to

[11] See the Coster-Kronig diagram, Fig. 14 of reference 1.

TABLE III. *Integrated intensity of the $L\alpha$ satellite group relative to the $L\alpha_{1,2}$ lines. The column headed "Uncertainty" contains the respective maximum deviations due to the "reasonable" limits of background choice.*

Element	Atom. No.	Relative Intensity of Satellite Group	Uncertainty	
Mo	42	0.064	+0.015	−0.010
Ru	44	0.080	+0.020	−0.070
Rh	45	0.109	0.020	0.070
Pd	46	0.089	0.020	0.070
Ag	47	0.078	0.015	0.010
Cd	48	0.060	0.013	0.009
In	49	0.047	0.010	0.007
Sn	50	0.015	0.008	0.006
Sb	51	0.011	0.008	0.004
Te	52	0.010	0.006	0.004
I	53	0.0079	0.006	0.004
Ba	56	0.0091	0.006	0.004

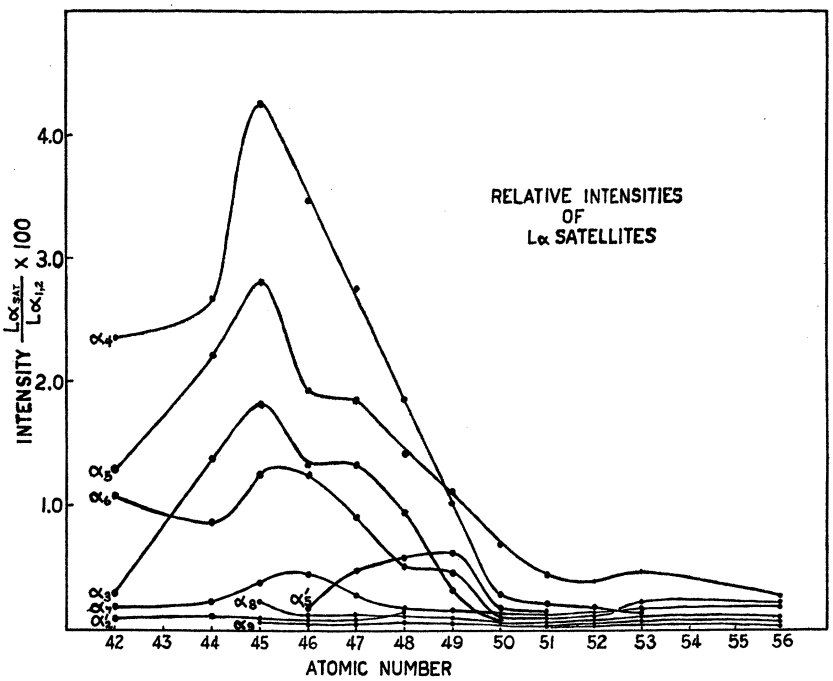

FIG. 5. Intensity of each satellite component relative to the intensity of the $L\alpha_{1,2}$ lines. Components α'_2, α_8, α_9 and α'_9 do not show the Coster-Kronig enhancement of intensity at $Z=50$.

the hypothesis of Richtmyer.[12] The accuracy of the measurements of these weak components is seriously impaired by the uncertainty of the backgrounds and corroborative results would be welcome.

It would be an idle gesture to claim uniqueness for the component resolutions in the present analyses. It is obvious that slightly different resolutions would eliminate most of the deviations from smooth curves in Figs. 3 and 5. Such juggling of the data has not been done because, first, we do not know which values to change, and second, the deviations may have real physical significance because of different atomic forces, e.g., due to chemical binding or crystal structure, in the actual targets of the elements.

[12] F. K. Richtmyer, J. Frank. Inst. **208**, 325 (1929).

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Binding Energy of Li^7 *

K. G. CARROLL†
Sloane Physics Laboratory, Yale University, New Haven, Connecticut
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A first-order Hartree calculation based upon a reasonable set of nuclear constants yields only one-third the known binding energy of Li^7. It is of interest to know whether this discrepancy is a real failure of assumed nuclear forces or merely a result of an inadequate method of calculation. The present note reports the effect of including higher orders in the perturbation treatment. In the final result about half the discrepancy remains and may be attributed to the exchange forces here assumed.

A. INTRODUCTION

IN spite of recent difficulties which the theory of nuclear forces has encountered, initial success has been obtained in explaining the mass defect curve for light nuclei. For nuclei of the two, three, and four-body types, mass defects based upon theory are in rather good agreement with experiment. However, the necessarily large number of arbitrary parameters contained in the nuclear Hamiltonian require for their determination most of the known properties of these nuclei. Application of the theory based on these lightest nuclei to other problems may be hoped to lead to a more satisfactory picture of nuclear forces, capable, among other things, of yielding quantitative information on the energy levels of light nuclei. The present work deals with the binding energy of Li^7. The Hartree method is improved by the use of Schrödinger perturbation theory, as in former work.[1,2] The information sought is whether the symmetric nuclear Hamiltonian, composed of exchange potentials of the Gauss type, is capable of yielding the correct binding energy for this problem when a more adequate method of calculation than the simple Hartree method is employed. Notation used here will be similar to that in a previous paper on Li^6.[2]

B. FIRST-ORDER HARTREE CALCULATION

The interaction between a pair of nuclear particles is taken as

$$V_{ij}=-A\exp[-r_{ij}^2/a^2]\times(w+mP_{ij}+bQ_{ij}+hP_{ij}Q_{ij}). \quad (1)$$

For Li^7 the ground state ($^2P_{3/2}$) in the Hartree approximation is a linear combination of the six harmonic oscillator functions belonging to the configuration $(1s)^4(2p)^3$. The ^2P state for two neutrons and one proton is a combination of

* Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

† Now at North Carolina State College, Raleigh, North Carolina.

[1] D. R. Inglis, Phys. Rev. **51**, 531 (1937).

[2] H. Margenau and K. G. Carroll, Phys. Rev. **54**, 705 (1938).