# THE EFFECT OF THE MOTION OF THE NUCLEUS ON THE SPECTRA OF Li I AND Li II

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### Abstract

The wave equation for a system of $N$ electrons (mass $m$) and one nucleus (mass $M$) is set up and solved approximately. If $W(m)$ are the energy levels for $M = \infty$, the energy levels for finite $M$ are $(\mu W(m)/m) + \Delta W$, where $\mu = mM/(m+M)$ and $\Delta W$ is calculable.

In case $N = 2$ or $3$, $\Delta W$ is zero except for $P$ levels. For these it is given by Eq. (13), which is derived on the assumption that the wave function is a polynomial of hydrogen functions, each with its own effective nuclear charge. The values of the latter previously determined by one of the authors are used in comparing the calculation with Schüler's experimental data on Li II, $\lambda 5485$ and Li I, $\lambda 6708$. The agreement is satisfactory and eliminates one objection to Schüler's interpretation of $\lambda 5485$.

I T IS well known that the effect of the motion[1] of the nucleus on the spectra of hydrogen and ionized helium may be accounted for by replacing $m$, the mass of the electron, by $\mu = mM/(m+M)$, $M$ being the mass of the nucleus. This simple procedure does not suffice for elements of more than one electron, and as an effect observed in the spectrum of lithium has been ascribed to this cause, a theoretical discussion of the expected effect seems in order. Some of the results obtained are applicable to the general case of $N$ electrons, others only to Li I and Li II.

## 1. General

The kinetic energy operator for a system of $N$ electrons and one nucleus is

$$T = -\frac{h^2}{4\pi^2}\left\{\frac{1}{2\mu}\sum_{1 \to N}\nabla_k{}^2 + \frac{1}{M}\sum_{(k,j)}\nabla_k\cdot\nabla_j + \frac{1}{2(M+Nm)}\nabla^2\right\} \tag{1}$$

in which

$$\nabla_k = i\frac{\partial}{\partial x_k} + j\frac{\partial}{\partial y_k} + k\frac{\partial}{\partial z_k}$$

$$\nabla = i\frac{\partial}{\partial X} + j\frac{\partial}{\partial Y} + k\frac{\partial}{\partial Z}$$

where $x_k$, $y_k$, $z_k$ are the rectangular coordinates of the $k^{th}$ electron in a system whose origin is located at the moving nucleus, and $(X, Y, Z)$ are the coordinates of the center of mass of the atom in another system of arbitrary fixed origin. The quantities $m$, $M$, and $\mu$ have the significance already defined.

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[1] This term will be used to describe the translatory motion of the nucleus about the center of mass of the atom, as distinguished from the nuclear "spin".

The wave equation is thus

$$\{T + V(x) - W\}\psi = 0 \tag{2}$$

where $V$ is the potential energy of the atom and is independent of the coordinates of the center of the mass. For simplicity, it may be assumed that the latter is at rest, so that $\psi$ will also be independent of $(X, Y, Z)$.

If it be assumed that the characteristic values $W(m)$ and solutions $\psi(m)$ of Eq. (2) are known for $M = \infty$ (stationary nucleus), the effect of the finiteness of $M$ may be approximately resolved into two parts:

a. $M$ is replaced by $\mu$ in $W(m)$ and $\psi(m)$.

b. The energy level is displaced by an additional amount $\Delta W$ given by

$$\psi(m)\Delta W = H'\psi(m) = -\frac{h^2}{4\pi^2 M} \sum_{(k,j)} \nabla_k \cdot \nabla_j \psi. \tag{3}$$

The perturbed energy value is thus $W(\mu) + \Delta W$. The statement (b) assumes that there is no degeneracy other than that conditioned by the rotational symmetry of the problem (degeneracy in the magnetic quantum number).

These two effects may be treated independently; for the first,[2] it is necessary to investigate the dependence on $\mu$ of the characteristic values of the equation

$$-\frac{h^2}{8\pi^2\mu} \sum_{1-N} \nabla_k^2\psi + [V(x) - W(\mu)]\psi = 0. \tag{4}$$

Since $V = \Sigma(Ze^2/r_k) - \Sigma(e^2/r_{jk})$ is a homogeneous function of degree $-1$ in the $3N$ variables[3] the calculation may be made rigorously without knowing $\psi$: on introducing new variables $x_k' = \alpha x_k$, $y_k' = \alpha y_k$, $z_k' = \alpha z_k$, where $\alpha = \mu/m$, and noting that $V(x) = \alpha V(x')$, Eq. (4) becomes

$$-\frac{h^2}{8\pi^2 m} \sum_{1-N} \Delta_k'^2\psi + [V(x') - W(\mu)/\alpha]\psi = 0.$$

Hence

$$W(\mu) = \alpha W(m). \tag{5}$$

Since $\alpha$ is less than 1, this causes a general contraction of the spectrum relative to that of an atom whose nucleus has infinite mass. This may be called the normal effect, since it is the only effect in the case of the simplest spectra.

The specific effect $\Delta W$ cannot be evaluated without some assumption regarding $\psi(m)$. It is simplest to assume it as a polynominal of hydrogen functions, each with a different nuclear charge determined by the variational method of calculating characteristic values.[4] The coefficients of the poly-

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[2] The calculation is merely an extension of that usually given for hydrogen.

[3] This is true only if the electron spin energy is not included in V.

[4] C. Eckart, Phys. Rev. **36**, 149 (1930). It is not known whether such a polynomial is really a good approximation to $\psi(m)$ or not, but it may be shown to yield approximately correct values for the energy. There is also some justification for its use in a perturbation calculation, but the magnitude of the error introduced is uncertain. Experience would seem to show that it is smaller than if the true nuclear charge was used in each hydrogen function; cf. W. Heisenberg, Zeits. f. Physik **39**, 511 (1926). Whatever may be the theoretical status of effective nuclear charges, it should be remarked that the values of $Z_1$ and $Z_2$ used in these calculations have not been determined *ad hoc* but are the results of independent calculations made without reference to the present problem.

nominal are determined so that $\psi(m)$ has the proper permutational symmetry. Calculations based on this assumption follow for the cases of two and three electron systems.

## 2. Two Electron Systems

The wave function may be approximated by

$$\psi = [u(1)v(2) \pm v(1)u(2)]/2^{1/2} \qquad (6)$$

in which $u$ is the characteristic function of the $1s$ state, $v$ of the excited state $(n, l)$, and the numerals designate the variables of the two electrons. The effective nuclear charge for the function $u$ is to be taken approximately equal to $Z$, the true nuclear charge. If $v$ represents a $2p$ state, its effective nuclear charge is approximately $Z_2 = Z - 1.0$. The precise theoretical[4] values for Li II, $2^3P$ are $Z_1 = 2.98$, $Z_2 = 2.16$. The upper sign in Eq. (6) is for the singlet level, the lower for the triplet. The perturbation operator in this case is simply

$$H' = - h^2 \nabla_1 \cdot \nabla_2 / 4\pi^2 M$$

and

$$\Delta W = \int \int \psi^* H' \psi d\tau_1 d\tau_2.$$

On integrating by parts with respect to the variables 2,

$$\Delta W = (h^2/4\pi^2 M) \int \int (\nabla_1 \psi)(\nabla_2 \psi^*) d\tau_1 d\tau_2;$$

noting that

$$\int (\nabla u) u^* d\tau = \tfrac{1}{2} \int \nabla \mid u \mid^2 d\tau = 0,$$

and making use of Eq. (6), this reduces to

$$\Delta W = \pm (h^2/4\pi^2 M) \left| \int u^* \nabla v d\tau \right|^2. \qquad (7)$$

This integral will be evaluated at the end of the next section.

## 3. Three Electron Systems

In this case, it may be well to take account of the permutation degeneracy directly: there are three independent characteristic solutions

$$\psi_1 = v(1)u(2)u(3), \quad \psi_2 = v(2)u(3)u(1), \quad \psi_3 = v(3)u(1)u(2) \qquad (8)$$

and

$$H' = - (h^2/4\pi^2 M)(\nabla_1 \cdot \nabla_2 + \nabla_2 \cdot \nabla_3 + \nabla_3 \cdot \nabla_1). \qquad (9)$$

The function $u$ again represents the $1s$ state, this time with $Z_1$ approximately equal to $Z - 0.3$, while $v$, in the case of the configuration $(1s)^2 (2p)$, has the approximate nuclear charge $Z_2 = Z - 2.0$. In the case of Li I, $2^2P$, the theo-

retical values are[4] $Z_1 = 2.69$, $Z_2 = 1.02$. The Eq. (3) is to be replaced by the three equations

$$a\Delta W = aA + bB + cB$$
$$b\Delta W = aB + bA + cB \qquad (10)$$
$$c\Delta W = aB + bB + cA$$

in which

$$A = \int\int\int \psi_i^* H' \psi_i d\tau_1 d\tau_2 d\tau_3$$
$$B = \int\int\int \psi_i^* H' \psi_j d\tau_1 d\tau_2 d\tau_3. \qquad (11)$$

The quantities $A$ and $B$ are real and independent of $i$ and $j$ since the operator $H'$ is symmetric in the three sets of coordinates. The determinent of Eqs. (10) has one single root $\Delta W = A + 2B$ and one double root $\Delta W = A - B$. The former belongs to a state which is excluded by the Pauli principle, the latter to the actual doublet state.

On substituting Eqs. (8) and (9) into (11), it is found that

$$A = 0, \quad B = -(h^2/4\pi^2 M)\left|\int u^*(\nabla v)d\tau\right|^2,$$

so that $\Delta W$ has the same functional form as in the case of a two electron system.

This integral is readily evaluated: as a generallization of a well-known equation, it is readily shown that

$$-(h^2/4\pi^2 m)\int u^*(\partial v/\partial x)d\tau = (W_u - W_v)\int xu^*vd\tau$$
$$-e^2(Z_1 - Z_2)\int (xu^*v/r)d\tau, \qquad (12)$$

$W_u$ and $W_v$ being the Balmer term-values associated to $u$, $Z_1$ and $v$, $Z_2$, respectively. By a slight generallization of the methods used to derive the selection principles for spectral lines[5] it may be shown that both integrals on the right vanish unless the values of the azimuthal quantum numbers of $u$ and $v$ differ by exactly one unit. As $u$ represents the $1s$ state, $\Delta W$ will therefore vanish unless $v$ represents a $p$ state, and the specific effect is shown only by $P$ levels (in this approximation at least). The displacement of these is found to be

$$\Delta W = \pm\frac{128}{3}\frac{m}{M}R_\infty Z_1^5 Z_2^5 n^3(n^2 - 1)\frac{(Z_1 n - Z_2)^{2n-4}}{(Z_1 n + Z_2)^{2n+4}}$$

[5] A. Sommerfeld, Wellenmechanischer Ergänzungsband, p. 92. (Vieweg, Braunschweig, 1929).

in which $R_\infty$ is the Rydberg constant, $2\pi^2 me^4/h^2$, and $n$ is the true principal quantum number. The increment of energy will be negative for the three electron system and the triplets of the two electron system, positive for the singlets.

## 4. Comparison with Observed Effects

H. Schüler[6] has proposed an interpretation of the hyperfine structure of the Li II line $2^3P - 1^3S$, $\lambda5485$, according to which the nucleus of Li (6) has no angular momentum while that of Li (7) has 1/2 unit. On the basis of his analysis it is possible to calculate the displacement of the Li (6) lines from the position which the Li (7) lines would occupy if there were no nuclear spin. These displacements are given in the last column of Table I. The three values should be identical to at least two significant figures, so that the differences are to be ascribed to errors, either in measurement or interpretation, or in both.

Table I.

|  | Li (6) | Li (7) | $\Delta\lambda$ |
|---|---|---|---|
| $^3P_0 - ^3S$ | 5484.10 | 5483.81 | 0.29A |
| $^3P_2 - ^3S$ | 5485.02 | 5484.69 | 0.32 |
| $^3P_1 - ^3S$ | 5485.65 | 5485.31 | 0.34 |

Using the values of $Z_1 = 2.98$, $Z_2 = 2.16$ Eq. (13) yields 0.256 A for the displacement produced by the specific effect, while Eq. (5) yields 0.071 A for the normal effect. The resultant is 0.327 A, the Li (6) line being to the long wave-length side of Li (7). This value is in excellent agreement with those of Table I. This calculation therefore supports part of Schüler's interpretation of this line though the present considerations would not defend it against attacks from other directions.[7]

Schüler and Wurm[8] have also found that the lines $2^2P - 1^2S$ of Li I, $\lambda6708$, are doubled, with a separation of 0.15A. This has been confirmed by one of us (H), the observed separation being between 0.155 and 0.160A. Assuming the nuclear spin to be 1/2 for Li (7), the structure due to this cause should be only 0.03–0.04A wide. The effect has therefore been interpreted as being primarily due to the motion of the nucleus.

The calculated values, using $Z_1 = 2.69$ and $Z_2 = 1.02$ (cf. Section 4) are 0.087A for the normal effect and 0.036A for the specific, a total of 0.123A. The agreement is as good as might be expected, since the difference between observed and calculated is of the order of the unresolved spin structure.

We would like to conclude from these results that Schüler's interpretation of $\lambda5485$ is correct, but, in view of the results Harvey and Jenkins[7] have obtained from the band spectra of lithium, the question had best be left open.

[6] H. Schüler, Zeits. f. Physik **58**, 741 (1929); and H. Brück, ibid **42**, 489 (1927).

[7] A. Harvey and F. A. Jenkins, Phys. Rev. **35**, 789 (1930).

[8] H. Schüler and E. Wurm, Naturwiss. **15**, 971 (1927).