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The Binding Energy of Li^6

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The mass defect of Li^6 has been calculated with the use of a symmetric Hamiltonian. Perturbation theory was employed in the main part of the work, and an upper limit for the contribution of all functions to the first and second order perturbation energies was obtained. This upper limit is 10 percent smaller than the experimental binding energy. It was then shown on the basis of variational calculations that perturbation theory, carried to this stage, overshoots the mark, and the upper limit to the binding energy is reduced to 26 Mev, which is 6 Mev short of the experimental value. These figures are based on a set of nuclear constants which favor large mass defects. The perturbational effect of all doubly excited configurations upon the ^3D state of Li^6 was investigated and compared with the effect of similar functions upon the ^3S state. The result is that the first order $^3D-{}^3S$ splitting, which is about 2 Mev, is enlarged to 6 Mev, both levels being depressed.

THERE is now considerable evidence suggesting that a nuclear Hamiltonian function which is symmetrical in neutrons and protons, and in which the coordinate part of the interaction between two particles is of simple exponential type, will not be capable of correlating all experimental data. First Rarita and Present,[1] using an elaborate variational method to calculate the mass defect of H^3, showed that with the same set of constants the mass defect of He^4 comes out too great. Their most accurate variational calculation was made with potentials of the form $e^{-r/a}$, while somewhat more qualitative considerations involving the use of "equivalent two-body methods" and leading to the same results, were presented in connection with other forms of potential. Following up these interesting indications two further searching variational calculations were made[2, 3] in which potentials of the type $\exp(-r^2/a^2)$ were used and in which a single method was applied to both the H^3 and the He^4 problems, the results being further corroborated by employing two different sets of functions (functions of individual particle coordinates and of relative coordinates). While in these papers interest was concentrated chiefly on the mathematical aspects of the question of convergence, a discrepancy similar to that of Rarita and Present came to light (obscured, perhaps, in the first paper by an underestimate of the rate of convergence). The discrepancy was less strong because Margenau and Warren had chosen a smaller value of g, the ratio of Heisenberg to Majorana forces. Indeed it was shown afterward[3] that the discrepancy in the binding energies of H^3 and He^4 can be made very small by choosing $g=0.175$. This, however, leads to a bound ^1S state for the deuteron, which, at present at least, is incompatible with known facts.

Another difficulty exists in connection with the excited states of the alpha-particle which, according to the interpretation by Crane of his and his co-workers' experiments,[4] should be stable. According to theory[5] they are unstable for all acceptable values of nuclear constants. A similar situation holds with regard to the excited states of He^3: Bonner[6] finds a stable state experimentally; theory[7] denies its existence.

As soon as we depart from consideration of the lightest nuclei, definite theoretical predictions become difficult. Inglis[8] has calculated the binding energy of Li^6 and has concluded the

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[1] W. Rarita and R. D. Present, Phys. Rev. **51**, 788 (1937).

[2] H. Margenau and D. T. Warren, Phys. Rev. **52**, 790 (1937); D. T. Warren and H. Margenau, Phys. Rev. **52**, 1027 (1937).

[3] H. Margenau and W. A. Tyrrell, Jr., Phys. Rev. **54**, 422 (1938).

[4] Crane, Delsasso, Fowler and Lauritsen, Phys. Rev. **48**, 125 (1935).

[5] H. Margenau, Phys. Rev. **53**, 198 (1938); S. S. Share, Phys. Rev. **53**, 875 (1938).

[6] T. W. Bonner, Phys. Rev. **53**, 711 (1938); Baldinger, Huber and Shaub, Helv. Phys. Acta **XI**, 245 (1938).

[7] L. I. Schiff, Phys. Rev. **54**, 92 (1938).

[8] D. R. Inglis, Phys. Rev. **51**, 531 (1937). To compare the results of Inglis with ours, note should be taken of errata listed by Inglis, Phys. Rev. **53**, 880 (1938). The algebraic expressions for $E_D^{(2)}$ given by Inglis are somewhat in error.

existence of another discrepancy: With a reasonable choice of the force constants, the calculated mass defect is too small. There is, however, some question as to the convergence of the contributions of the higher excited states. The interest of this example in view of the increasing doubt as to the validity of the symmetric Hamiltonian has led us to reinvestigate this problem by a different and more painstaking procedure. The present work, though its results differ in some details from those of Inglis, rather strengthens the conclusion that the theoretical mass defect is too small. It goes beyond the scope of the latter in the following respects: (1) A variational method is used in an attempt to correct the perturbational procedure; (2) An upper limit for the second order perturbational contribution to the binding energy is derived; (3) the second order effect on the ${}^3D$ state as well as the ground state is calculated. Besides, the whole calculation has been conducted with a different (but equivalent) set of functions so that an independent check on previous results is provided.

ASSUMPTIONS AND METHOD

Only the symmetric Hamiltonian is used in the present paper, the interactions being written in the following form:

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

For A and a we use throughout the values 35.60 Mev and 2.25×10^{-13} cm, which seem in best agreement with scattering data. The other numerical parameters in (1) are varied, attention being concentrated chiefly upon the following two sets:

$$w=-2/15;\ m=14/15;\ b=7/15;\ h=-4/15 \quad \text{(a)}$$

$$=-1/12 \quad =10/12 \quad =5/12 \quad =-2/12. \quad (b)$$

They will henceforth be designated as choices (a) and (b). Both satisfy the usual requirements; the first corresponds to $g(=b+h)=0.20$, the second to $g=0.25$, two rather extreme cases. Furthermore, they are so adjusted as to give as large as possible a mass defect for Li^6 and yet satisfy the requirements.[9] The functions used are functions of individual particle coordinates; therefore the kinetic energy operator contains, besides the terms in ∇^2, terms in $\nabla_i\cdot\nabla_j$ which correct for the motion of the center of mass.[2, 8] In the greater part of the paper the Schrödinger perturbation theory up to second order terms is employed; later a variational procedure is discussed. The former involves formally the calculation of nondiagonal energy elements H_{0i}', H' being the perturbing operator, the latter involves H_{ij}. Since the unperturbed energy does not possess nondiagonal elements, H_{0i}' may be replaced by H_{0i}. This keeps the relation between the two procedures more in evidence.

TABLE I. *Individual particle functions.*
$\rho=(q/\pi)^{\frac{3}{4}}\exp(-qr^2/2)$.

$$(1s)=\rho$$
$$(2s)=(2/3)^{\frac{1}{2}}(qr^2-3/2)\rho$$
$$(3s)=(2/15)^{\frac{1}{2}}(q^2r^4-5qr^2+15/4)\rho$$

$$(2p_{\pm1})=q^{\frac{1}{2}}(x\pm iy)\rho$$
$$(2p_0)\ =(2q)^{\frac{1}{2}}z\rho$$

$$(3p_{\pm1})=(2/5q)^{\frac{1}{2}}(qr^2-5/2)(x\pm iy)\rho$$
$$(3p_0)\ =(4/5q)^{\frac{1}{2}}(qr^2-5/2)z\rho$$

$$(4p_{\pm1})=(2/35q)^{\frac{1}{2}}(q^2r^4-7qr^2+35/4)(x\pm iy)\rho$$
$$(4p_0)\ =(4/35q)^{\frac{1}{2}}(q^2r^4-7qr^2+35/4)z\rho$$

$$(3d_{\pm2})=(1/2)^{\frac{1}{2}}q(x\pm iy)^2\rho$$
$$(3d_{\pm1})=(2)^{\frac{1}{2}}q(x\pm iy)z\rho$$
$$(3d_0)\ =(1/3)^{\frac{1}{2}}q(3z^2-r^2)\rho$$

$$(4d_{\pm2})=(1/7)^{\frac{1}{2}}q(qr^2-7/2)(x\pm iy)^2\rho$$
$$(4d_{\pm1})=(4/7)^{\frac{1}{2}}q(qr^2-7/2)(x\pm iy)z\rho$$
$$(4d_0)\ =(2/21)^{\frac{1}{2}}q(qr^2-7/2)(r^2-3z^2)\rho$$

$$(4f_{\pm3})=(1/6)^{\frac{1}{2}}q^{\frac{3}{2}}(x\pm iy)^3\rho$$
$$(4f_{\pm2})=\qquad q^{\frac{3}{2}}(x\pm iy)z\rho$$
$$(4f_{\pm1})=(1/10)^{\frac{1}{2}}q^{\frac{3}{2}}(5z^2-r^2)(x\pm iy)\rho$$
$$(4f_0)\ =\ (6/5)^{\frac{1}{2}}q^{\frac{3}{2}}(5/3z^2-r^2)z\rho$$

Numerical calculations of the type here presented involve many details which cannot all be mentioned. Our aim is to clarify the method and to present examples of critical points in the procedure. If matters essential to an understanding of the work seem omitted, the reader will probably find them discussed in various references.[2, 3, 8] The next sections deal with an application of perturbation theory to the problem. Their aim is, after selection of a suitable set of functions for the ground state (ψ_0) and for the higher unperturbed states (ψ_i), the evaluation of

$$E=H_{00}+\sum_i{}'\frac{|H_{0i}|^2}{E_0-E_i}. \tag{2}$$

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[9] G. Breit and E. Feenberg, Phys. Rev. **50**, 850 (1936); N. Kemmer, Nature **140**, 192 (1937).

ψ_0 must be so chosen as to possess the correct symmetry of the ground state; the other ψ's need not have this property.

FUNCTIONS

All unperturbed functions are linear combinations of products of six single-particle functions. We first discuss these single-particle functions. To be manageable in the integrations, they must be Gauss exponentials multiplied by polynomials. For convenience, these polynomials should make the functions orthogonal. This leads immediately to the selection of either Hermite polynomials or Legendre polynomials, as the simplest sets. Calculations including "doubly excited states" (see below) have been made with the use of both, the results being, of course, identical. This not only checked the correctness of the calculation, but also showed Legendre polynomials to be superior in practice, giving rise to fewer functions associated with a given degree of excitation. Inglis used Hermite functions throughout.

Legendre functions have the further advantage of being eigenfunctions of the angular momenta of individual particles, so that they can be designated easily in the customary spectroscopic way. The functions contain the common parameter q which will later be adjusted for minimum energy. Table I is a list of normalized functions required here.

The unperturbed energies E_i appearing in (2) are simply the sums of the six single-particle energies ϵ belonging to the functions in Table I. The ϵ's are best expressed in terms of the "oscillator quantum number" n associated with each of these functions, thus:

$$\epsilon=(n+\tfrac{3}{2})h\nu=(n+\tfrac{3}{2})(\hbar^2/M)q. \qquad (3)$$

The correspondence between the functions and n is given in Table II.

TABLE II. *Correspondence between the normalized functions and n.*

FUNCTION	n	FUNCTION	n	FUNCTION	n
1s	0	2p	1	3d	2
2s	2	3p	3	4d	4
3s	4	4p	5	5d	6 etc.

To construct the ψ_i it is most convenient to introduce the isotopic spin quantum number τ_ζ,[10] and to define four generalized spin functions:

$$\eta_1=\delta(s_z,\ -\tfrac{1}{2})\delta(\tau_\zeta,\ -\tfrac{1}{2}),$$

$$\eta_2=\delta(s_z,\ \tfrac{1}{2})\delta(\tau_\zeta,\ -\tfrac{1}{2}),$$

$$\eta_3=\delta(s_z,\ -\tfrac{1}{2})\delta(\tau_\zeta,\ \tfrac{1}{2}),$$

$$\eta_4=\delta(s_z,\ \tfrac{1}{2})\delta(\tau_\zeta,\ \tfrac{1}{2}).$$

The ground state function for the Li^6 nucleus must satisfy the following conditions:[11]

$$\left.\begin{aligned} S_z&\equiv\sum_k s_{z,\,k}=1,\\ T_\zeta&\equiv\sum_k \tau_{\zeta,\,k}=0,\\ Y_\zeta&\equiv\sum_k s_{z,\,k}\tau_{\zeta,\,k}=0,\end{aligned}\right\} \qquad (4)$$

where the summation is extended over the six particles. The last of these is not exact if the Hamiltonian contains spin dependent forces. Its imposition amounts to an omission of constituents representing spin distributions different from the normal one (+ − + for the neutrons, as for the protons) in the ground state function. The effect of these upon the masses of H^3 and He^4 is known to be small,[1, 2] so that the approximation made here in maintaining the last condition is probably sufficient. The three conditions limit the set of η's to

$$\eta_1(1)\eta_2(2)\eta_3(3)\eta_4(4)\eta_2(5)\eta_4(6)$$

and permutations of arguments among these η's. It is here understood that 5 and 6 are the two particles which, because of the Pauli principle, are in excited states. The advantage in introducing the η-functions is that they enable us to write the complete ψ-functions as single determinants instead of a product of two determinants, one for the neutrons and one for the protons. If now the single-particle functions are designated by u with an appropriate subscript, every ψ_i has the form

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[10] B. Cassen and E. U. Condon, Phys. Rev. **50**, 846 (1936).

[11] Cf. E. Wigner, Phys. Rev. **51**, 106 (1937).

$$\left(\frac{1}{n!}\right)^{\frac{1}{2}}\begin{vmatrix} u_{l1}(1)\cdot\eta_{r1}(1) & u_{l2}(1)\cdot\eta_{r2}(1) & \cdots & u_{ln}(1)\cdot\eta_{rn}(1) \\ u_{l1}(2)\cdot\eta_{r1}(2) & u_{l2}(2)\cdot\eta_{r2}(2) & \cdots & u_{ln}(2)\cdot\eta_{rn}(2) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ u_{l1}(n)\cdot\eta_{r1}(n) & u_{l2}(n)\eta_{r2}(n)\cdot & \cdots & u_{ln}(n)\cdot\eta_{rn}(n) \end{vmatrix}, \tag{5}$$

where in our case $n=6$, and the η's are those listed above in some permutation. Henceforth this determinant will be abbreviated into $|u_{l1}\eta_{r1}\cdots u_{ln}\eta_{rn}|$.

Functions like (5), while obeying conditions (4), do not represent the correct total angular momentum, nor in general the correct total spins. The lowest state for Li^6 is presumably that for which $L=0$, $S=1$, $T=0$. In order to satisfy these conditions, linear combinations of functions like (5) must be taken. The procedure for this is well known from the theory of atomic spectra. The function which satisfies all these conditions, and which will be taken as our ψ_0, is

$$\psi_0=\left(\frac{1}{6!}\frac{1}{3}\right)^{\frac{1}{2}}\{|s\eta_1\cdot s\eta_2\cdot s\eta_3\cdot s\eta_4\cdot p_1\eta_2\cdot p_{-1}\eta_4| + |s\eta_1\cdots s\eta_4\cdot p_{-1}\eta_2\cdot p_1\eta_4| + |s\eta_1\cdots s\eta_4 p_0\eta_2 p_0\eta_4|\}. \tag{6}$$

It corresponds to the configuration $(1s)^4(2p)^2$.

Combination (6) is orthogonal to all other functions arising from this configuration. Hence there are no vanishing denominators in the summation of (2), and this relieves us of the necessity of selecting proper linear combinations for all the other ψ_i. These may then be taken in the crude form (5).

TABLE III. *List of doubly and quadruply excited configurations.*

CONFIGURATIONS	NO. OF FUNCTIONS	CONFIGURATIONS	NO. OF FUNCTIONS
Doubly excited		Quadruply excited	
$(1s)^4 2p3p$	6	$(1s)^4 2p4p$	6
$(1s)^4(2s)^2$	1	$(1s)^4(3p)^2$	3
$(1s)^4(3d)^2$	5	$(1s)^3 2s2p3p$	42
$(1s)^3(2p)^2 2s$	26	$(1s)^3 3d2p3p$	126
$(1s)^3(2p)^2 3d$	78	$(1s)^3 3d2p4f$	210
$(1s)^2(2p)^4$	36	$(1s)^3 3s(2p)^2$	26
		$(1s)^3 4d(2p)^2$	76
		$(1s)^2(2s)^2(2p)^2$	18
		$(1s)^2(3d)^2(2p)^2$	54
		$(1s)^2(2p)^3 3p$	96

SELECTION OF EXCITED-STATE FUNCTIONS AND DETERMINATION OF THEIR NUMBER

Excited-state functions are best classified according to their degree of excitation, i.e., the value of $\sum n_k$ minus this sum for the ground state, the latter being obviously 2. The functions belonging to a given degree of excitation may again be subdivided into groups belonging to different configurations, and these groups can be constructed almost mechanically by writing down the permutations of a given set of symbols. This procedure will be illustrated by reference to the first of the configurations listed in Table III, which is an exhaustive tabulation of the doubly and quadruply excited configurations.[12]

Suppose we wish to construct the functions belonging to $(1s)^4(2p)3p$. We note first all combinations of orbitals which satisfy $\sum m_z=0$ (S-state). They are (omitting the four s-orbitals): $2p_{-1}3p_1$, $2p_1 3p_{-1}$, and $2p_0 3p_0$. A function is obtained by assigning six orbitals to a fixed arrangement of η's in such a way that no two equal orbitals have the same η, since otherwise the determinant (5) would vanish. Thus in our case a pair of distributions arise from each set of orbitals and we get the possible distributions listed in Table IV. Thus we have obtained six functions, the first of them being $(1/6!)^{\frac{1}{2}}|s\eta_1\cdots s\eta_4\cdot 2p_{-1}\eta_2\cdot 3p_1\eta_4|$, etc. After one has constructed all functions belonging to a given configuration, it is easy to single out by inspection

TABLE IV. *Possible distributions.*

η_1	η_2	η_3	η_4	η_2	η_4
s	s	s	s	$2p_{-1}$	$3p_1$
s	s	s	s	$3p_1$	$2p_{-1}$
s	s	s	s	$2p_1$	$3p_{-1}$
s	s	s	s	$3p_{-1}$	$2p_1$
s	s	s	s	$2p_0$	$3p_0$
s	s	s	s	$3p_0$	$2p_0$

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[12] Configurations which do not combine with the ground state have been omitted.

those which will not combine with the ground state. The numbers appearing in Table III do not include these functions. It is essential in calculations of this sort to have a complete and nonredundant list of all excited functions, and the present method is one which will yield it almost automatically. Functions belonging to the same configuration do not have the same matrix elements with the ground state, but divide into a small number of groups having equal elements.

CALCULATION OF MATRIX ELEMENTS

H_{0i} consists of three parts:[13] first the terms $-(5/6)(\hbar^2/2M)\sum_k \nabla_k^2$; second the cross terms $(1/6)(\hbar^2/2M)\sum_{k>l}\nabla_k\cdot\nabla_l$; third the potential energy, a sum over (1). The first may be transformed by the relation

$$-\frac{\hbar^2}{2M}\sum_k \nabla_k^2\psi = E\psi - \frac{\hbar^2}{2M}q^2(\sum_k r_k^2)\psi. \tag{7}$$

We introduce the abbreviations

$$T\equiv\hbar^2/Ma^2 = 8.10 \text{ Mev};\quad \sigma\equiv qa^2. \tag{8}$$

The nondiagonal elements of the first part of H therefore reduce, in view of (7), to the integrals

$$-\frac{5}{6}\int\psi_0^*\left(\frac{\hbar^2}{2M}\sum_k\nabla_k^2\right)\psi_i d\tau = -\frac{T\sigma}{2}\int\psi_0^*(\sum_k qr_k^2)\psi_i d\tau,$$

and these latter reduce to simple elements of the form $(u_1|qr^2|u_2)$, where the u's are single-particle functions. Of these, only the following are different from zero:

$$(1s|qr^2|2s) = (3/2)^{\frac{1}{2}},$$

$$(2p_{\pm 1}|qr^2|3p_{\pm 1}) = (2p_0|qr^2|3p_0) = (5/2)^{\frac{1}{2}}.$$

Here again the simplicity in the use of Legendre functions is apparent.

Next we consider the second part of H. By a well-known theorem connecting momentum and coordinate matrices we have

$$\int u_\lambda^*\nabla u_\mu d\tau = \frac{M}{\hbar^2}(\epsilon_\mu - \epsilon_\lambda)\mathbf{r}_{\lambda\mu},$$

and since $\epsilon_\lambda = T\sigma(n_\lambda + 3/2)$ because of (3) and (8), we find

$$\int u_\lambda^*\nabla u_\mu d\tau = q^{\frac{1}{2}}(n_\mu - n_\lambda)(q^{\frac{1}{2}}\mathbf{r})_{\lambda\mu}.$$

The expression $(1/6)(\hbar^2/2M)\sum_{k>l}\nabla_k\cdot\nabla_l$ is therefore equivalent to $(1/6)T\sigma\sum_{k>l}\Delta n_k\Delta n_l q\mathbf{r}_k\cdot\mathbf{r}_l$. Here we have written Δn for the difference of the oscillator quantum numbers of the two single-particle functions between which the matrix element is to be computed. $\Delta n = \pm 1$. Thus it is seen that the second part of H_{0i} breaks down into products of two elements, each of the form $\Delta n(u_1|q^{\frac{1}{2}}\mathbf{r}|u_2)$. A list of the nonvanishing elements of this kind which are needed in the present work follows. The three values in brackets are the vector components of the elements, and r' is written for $q^{\frac{1}{2}}r$.

$$\Delta n(s|r'|2p_{\pm 1}) = \tfrac{1}{2}[1, \pm i, 0],$$

$$\Delta n(2s|r'|2p_{\pm 1}) = (\tfrac{1}{6})^{\frac{1}{2}}[-1, \mp i, 0],$$

$$\Delta n(s|r'|2p_0) = (\tfrac{1}{2})^{\frac{1}{2}}[0, 0, 1],$$

$$\Delta n(2s|r'|2p_0) = (\tfrac{1}{3})^{\frac{1}{2}}[0, 0, -1],$$

$$\Delta n(2p_{\pm 1}|r'|3d_0) = \tfrac{1}{2}(\tfrac{1}{3})^{\frac{1}{2}}[-1, \mp i, 0],$$

$$\Delta n(2p_{-1}|r'|3d_{-2}) = (\tfrac{1}{2})^{\frac{1}{2}}[1, i, 0],$$

$$\Delta n(2p_1|r'|3d_2) = (\tfrac{1}{2})^{\frac{1}{2}}[1, -i, 0],$$

$$\Delta n(2p_{-1}|r'|3d_{-1}) = \Delta n(2p_1|r'|3d_1) = (\tfrac{1}{2})^{\frac{1}{2}}[0, 0, 1],$$

$$\Delta n(2p_0|r'|3d_{\mp 1}) = \tfrac{1}{2}[1, \pm i, 0],$$

$$\Delta n(2p_0|r'|3d_0) = (\tfrac{2}{3})^{\frac{1}{2}}[0, 0, 1].$$

We now turn to the evaluation of the matrix elements of the potential energy, which is a little more tedious. The fundamental formulae are easily developed. Denote two general functions like (5) by ψ_A and ψ_B:

$$\psi_A = (1/n!)^{\frac{1}{2}}|u_{l1}\eta_{r1}\cdots u_{ln}\eta_{rn}|,$$

$$\psi_B = (1/n!)^{\frac{1}{2}}|u_{\lambda 1}\eta_{\rho 1}\cdots u_{\lambda n}\eta_{\rho n}|.$$

Then, if H is symmetrical with respect to an interchange of any two particles,

$$H_{AB} = \int(u_{l1}\eta_{r1}\cdots u_{ln}\eta_{rn}) \times H|u_{\lambda 1}\eta_{\rho 1}\cdots u_{\lambda n}\eta_{\rho n}|d\tau. \tag{9}$$

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[13] See, for instance, reference 2, Eq. (11).

The first factor of the integrand here is no longer a determinant but a product of n single-particle functions. If H is a sum of terms each involving the coordinates of but one particle, as was the case with the ∇^2-part of the energy, (9) reduces immediately to the single integrations discussed before. If H is a sum of terms involving the coordinates of two particles, as with the $\nabla_i \cdot \nabla_j$-part and the potential energy, further reduction proceeds as follows.

Introduce the symbol θ_{ij} which is defined to be 1 if every $u_{ls}\eta_{rs} = u_{\lambda s}\eta_{\rho s}$ for $s \neq i, j$; i.e., θ_{ij} is zero whenever the functions of more than two particles are different; it is 1 if the two non-matching functions refer to particles i and j. Then, if we let $H = V = \sum_{i>j} V_{ij}$, (9) becomes

$$\begin{aligned} V_{AB} = \sum_{i>j} \Big\{ \int & u_{li}(i)\eta_{ri}(i) \cdot u_{lj}(j)\eta_{rj}(j)\, V_{ij} \\ & \times u_{\lambda i}(i)\eta_{\rho i}(i) u_{\lambda j}(j)\eta_{\rho j}(j) d\tau \\ - \int & u_{li}(i)\eta_{ri}(i) \cdot u_{lj}(j)\eta_{rj}(j)\, V_{ij} \\ & \times u_{\lambda j}(i)\eta_{\rho j}(i) u_{\lambda i}(j)\eta_{\rho i}(j) d\tau \Big\} \theta_{ij}. \end{aligned}$$

Here as well as in Eq. (9) the integration is understood to include a summation over spins.

Now $V_{ij} = V_{ij}' + V_{ij}'' Q_{ij}$, where V' and V'' act on the particle coordinates alone. This leads to the further decomposition

$$V_{AB} = V_{AB}' + V_{AB}''. \tag{10}$$

In V_{AB}', the summation over spins may be performed with the use of the relation

$$\sum_{\sigma\tau} \eta_a(1)\eta_b(2)\eta_c(1)\eta_d(2) = \delta(a, c)\delta(b, \delta), \tag{11}$$

so that

$$\begin{aligned} V_{AB}' = \sum_{i>j} \Big\{ \int & u_{li}(1)u_{lj}(2)\, V'(12) u_{\lambda i}(1) \\ & \times u_{\lambda j}(2) d\tau\, \delta(r_i, \rho_i)\delta(r_j, \rho_j) \\ - \int & u_{li}(1)u_{lj}(2)\, V'(12) u_{\lambda j}(1) \\ & \times u_{\lambda i}(2) d\tau\, \delta(r_i, \rho_j)\delta(r_j, \rho_i) \Big\} \theta_{ij}. \end{aligned} \tag{12}$$

This is the formula used in evaluating the Wigner and Majorana parts of the matrix elements.

In V_{AB}'', the spin summation involves a Q-operator in the manner

$$\sum_{\sigma\tau} \eta_a(1)\eta_b(2) Q_{12} \eta_c(1)\eta_d(2) \equiv Q(a, b; c, d). \tag{13}$$

This summation also reduces to δ-functions in a simple way because

$$Q\eta_1\eta_2 = \eta_2\eta_1; \quad Q\eta_1\eta_3 = \eta_1\eta_3; \quad Q\eta_1\eta_4 = \eta_2\eta_3;$$

$$Q\eta_2\eta_3 = \eta_1\eta_4; \quad Q\eta_2\eta_4 = \eta_2\eta_4; \quad Q\eta_3\eta_4 = \eta_4\eta_3;$$

and $$Q^{-1} = Q.$$

When these relations are inserted in (13) and (11) is used, the $Q(a, b; c, d)$ are found. We then obtain

$$\begin{aligned} V_{AB}'' = \sum_{i>j} \Big\{ \int & u_{li}(1)u_{lj}(2)\, V''(12) u_{\lambda i}(1) \\ & \times u_{\lambda j}(2) d\tau \cdot Q(r_i, r_j; \rho_i, \rho_j) \\ - \int & u_{li}(1)u_{lj}(2)\, V''(12) u_{\lambda j}(1) \\ & \times u_{\lambda i}(2) d\tau \cdot Q(r_i, r_j; \rho_j, \rho_i) \Big\} \theta_{ij}. \end{aligned} \tag{14}$$

Thus far we have traced the decomposition of the general matrix element into simpler integrals

$$\int u_a(1)u_b(2) \exp(-r_{12}^2/a^2) u_c(1)u_d(2) d\tau_1 d\tau_2. \tag{15}$$

Their calculation may also be systematized. The integrations over the x, y, and z coordinates are independent, so that (15) is a product of three factors, each of the form

$$\begin{aligned} g_{lm} = \frac{1}{\pi} \int\int & \xi_1^l \xi_2^m \\ & \times \exp\left[-\left(1 + \frac{1}{\sigma}\right)(\xi_1^2 + \xi_2^2) + \frac{2}{\sigma}\xi_1\xi_2 \right] d\xi_1 d\xi_2. \end{aligned}$$

Only relatively few of the g's occur; they are listed in Table V where we have written $u \equiv 1/(\sigma+2)$. All formulae necessary in the calculation of H_{0i} have now been developed; the remainder of the work is numerical.

RESULTS FOR THE GROUND STATE

The first order energy H_{00} is identical with that of Inglis (cf. his errata), since the lowest Hermite and Legendre functions agree.

$$H_{00}=(19/4)T\sigma-\{5+10w-8h+[8-2(w+h)-18(w+b)](\sigma+2)^{-1}+5(\sigma+2)^{-2}\}(\sigma/\sigma+2)^{\frac{3}{2}}B+1.43\sigma^{\frac{1}{2}}.$$

The last term is the Coulomb energy, which has been neglected in the higher approximations. The contributions of this and the doubly excited states in accordance with formula (2) are listed in Table VI for three values of σ near the energy minimum. One of these values was checked independently by using Inglis' method of oscillator functions. It is seen that the sum falls quite short of the experimental binding energy, 32 Mev. The second order contributions are smaller by about 4 Mev than those listed by Inglis; the difference is explained in his errata. Choice (*b*) gives less binding energy than Choice (*a*), as is also true for the alpha-particle.

A calculation of the contribution of all quadruply excited states is very laborious if all terms of the Hamiltonian are included. Since this contribution is smaller[8] we have computed it retaining only Majorana forces, and for the single value $\sigma=1$. The value chosen for mA is -28.7 Mev. (This gives the correct energy of the alpha-particle.) For this case $H_{00}(=-5.6$ Mev) is far smaller than the values in Table VI, because the large value of the first order kinetic energy is not affected by this choice. But the second order contribution for Majorana forces only, -7.8 Mev, is quite comparable to the value obtained including all the interactions. We may thus have confidence that the contribution of the functions of higher excitation computed with Majorana forces alone is a good approximation. It turns out to be -4.1 Mev (Inglis, reference 8, calculated -3 Mev).

TABLE V. *List of g's* $[u=1/(\sigma+2)]$.

$g_{00}\equiv g=(\sigma u)^{\frac{1}{2}}$	$g_{60}=(15/8)g(1-u)^3$
	$g_{51}=(15/8)gu(1-u)^2$
$g_{11}=(1/2)gu$	$g_{42}=(3/8)g(1-3u+7u^2-5u^3)$
$g_{20}=(1/2)g(1-u)$	$g_{33}=(3/8)gu(3-6u+5u^2)$
$g_{40}=(3/4)g(1-u)^2$	$g_{80}=(105/16)g(1-u)^4$
$g_{31}=(3/4)gu(1-u)$	$g_{71}=(105/16)gu(1-u)^3$
$g_{22}=(1/4)g(1-2u+3u^2)$	$g_{62}=(15/16)g(1-4u+12u^2-16u^3+7u^4)$
	$g_{53}=(15/16)gu(3-9u+13u^2-7u^3)$
	$g_{44}=(3/16)g(3-12u+42u^2-60u^3+35u^4)$

TABLE VI. *Summary of numerical results. Doubly excited states.*

	CHOICE *a*			CHOICE *b*		
σ	1	1.2	1.4	1	1.2	1.4
H_{00}	−10.0	−10.8	−10.7	−7.3	−7.7	−7.1 Mev
$E_D^{(2)}$	−6.8	−7.2	−7.4	−6.0	−6.4	−6.7 Mev
Sum.	−16.8	−18.0	−18.1	−13.3	−14.1	−13.8 Mev

It is obvious that contributions due to successive stages of excitation do not decrease rapidly enough to permit an estimate of the convergence limit. There is, however, a way in which one may ascertain a lower limit of the second term in (2). We note that

$$E^{(2)}=\sum_i{}'\frac{|H_{0i}|^2}{E_0-E_i}=\frac{S_2}{E_0-E_2}+\frac{S_4}{E_0-E_4}+G,$$

where S_2 and S_4 are the sums of $|H_{0i}|^2$ taken over all doubly and quadruply excited states, respectively. They have already been calculated. G is the remainder of the sum, in which the smallest denominator is $E_0-E_6=-6T\sigma$. Hence

$$|G|<\frac{\sum_i{}'|H_{0i}|^2-S_2-S_4}{6T\sigma}.$$

But by matrix algebra, $\sum_i{}'|H_{0i}|^2=(H^2)_{00}-(H_{00})^2$. Thus

$$|G|<\frac{(H^2)_{00}-H_{00}{}^2-S_2-S_4}{6T\sigma}. \tag{16}$$

Of all quantities needed, only $(H^2)_{00}$ remains to be calculated. A simplification arises from the fact that the matrix elements appearing in G are free from kinetic energy terms (selection rules!), which means that we may leave out all kinetic energy terms in $(H^2)_{00}$, $H_{00}{}^2$, S_2 and S_4, for they would cancel. Thus we can restrict the calculation to $(V^2)_{00}$. Again, this was done for Majorana forces only, with $(mA)\equiv B=28.7$ Mev.

$$V^2=B^2\{\textstyle\sum_{i>j}J_{ij}{}^2+\sum_{i>jk}J_{ij}J_{ik}P_{ij}P_{ik}+\sum_{i>j}\sum_{k>l}J_{ij}P_{ij}J_{kl}P_{kl}\}.$$

The corresponding three terms in $(V^2)_{00}$ are given by

$$(V^2)_{00}=B^2\{0.98+1.36+1.01\}=3.35B^2.$$

Moreover, $(V_{00})^2=2.50B^2, S_2=0.29B^2, S_4=0.16B^2$, giving

$$|G|<6.6 \text{ Mev}.$$

This bound is almost certainly several Mev too great. Summarizing our results so far, we may say, even referring to the more advantageous choice of constants in Table VI, that the first and second order perturbational contributions to the binding energy of Li^6 are *in toto* smaller than $(18.1+4.1+6.6)$ Mev$=28.8$ Mev. In the next section we shall show that the perturbation method, carried up to the second order, yields too large a result for the binding energy in this problem.

VARIATIONAL THEORY[14]

The variational procedure here adopted is that outlined in reference 2. It was carried out before the present perturbational calculations were made, unfortunately with a slightly different set of constants, namely those used in reference 2. Since we are only interested in a general correlation between variational and perturbational results a repetition of the laborious variational work with another choice of constants did not seem worthwhile.

The major difficulty lies in the large number of functions which, for obvious practical reasons, must be reduced. It is because of this necessity that a complete variational treatment of the six-body problem is very unlikely to be achieved. But it is possible, by surveying the tendency of such a calculation and correlating it with a less perfect procedure which can be carried through, to correct the result of the latter.

The functions used are the oscillator functions employed by Inglis.[8] The "types" will here be numbered in the order in which they appear in his Table IV. Only some, not even all, of the doubly excited states have been used, but the eleven types here chosen give more than 80 percent of the total perturbational contribution.

TABLE VII. *Lowering of H_{00} by perturbation and variation methods (in Mev).*

NUMBER OF FUNCTIONS INCLUDED	SECOND ORDER PERT. CONTRIBUTION	VARIATIONAL $E-H_{00}$
6	-5.53	-4.19
8	-6.85	-4.85
10	-7.05	-5.12

In reducing the number of functions the known H_{0i} elements served as a guide. Types with small H_{0i} were rejected. The remaining functions were combined in such a way that all ψ_i having equal H_{0i} were given the same coefficient, and hence could be taken as a single variation function. This produces as many independent functions as there are types. The word "function" in Table VII refers to such rigid linear combinations. The effect of this initial fixation of some of the functions upon the variational result could be investigated; but we feel that it is inappreciable.

The work now involves the calculation of all elements H_{ij} for the functions selected, and a subsequent reduction of the determinant. The result is equivalent to an inclusion of all higher perturbations in the Schrödinger-Rayleigh scheme, provided that they converge. The direction and extent of its deviation from the second order perturbation result indicate the correction necessary.

To explain this we indulge in a digression on a relation between the method of linear variation functions and perturbation theory. If the functions employed are orthogonal, the former leads to the equation for the energy

$$|H_{ij}-\delta_{ij}E|=0,\ i,\ j=0,\ 1\cdots n \tag{17}$$

and E is the true solution in case the functions form a complete set. Now if in (17) all nondiagonal elements, except the H_{0i} and their conjugates, are neglected, the determinant may at once be expanded by adding rows with suitable factors, and (17) yields

$$\left(H_{00}-E+\sum_{i=1}^{n}\frac{|H_{0i}|^2}{E-H_{ii}}\right)\times(H_{11}-E)\cdots(H_{nn}-E)=0.$$

On replacing the denominator $E-H_{ii}$ by $E_0-(H_0)_{ii}$ this becomes identical with (2), after cancellation of factors producing the higher roots. The second order perturbation result is thus seen to differ from the truth in 2 respects: (1). It neglects all nondiagonal elements except those in the first row and column. (2). It neglects

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[14] The results of this section have already been presented at the Washington Meeting of the A. P. S., April 1938.

the difference between perturbed and unperturbed energies in the diagonal terms. Now one can easily see that inclusion of nondiagonal terms lowers the root E; as to (2) we note that replacing $E-H_{ii}$ by $E_0-(H_0)_{ii}$ lowers the root if, for the preponderant functions, $|E-H_{ii}| > |E_0-(H_0)_{ii}|$, raises it otherwise.

In the He^4 problem[3] the H_{ij}-terms neglected in the perturbation scheme were of considerable size; their effect overshadowed the inequalities of the diagonal energy differences. This is the reason why the variational method gave a greater binding energy than the other. For Li^6, we find the reverse to be the case: Nondiagonal elements are small (cancellation between a greater number of functions); the diagonal energy differences are predominantly larger than the zero order differences. The net effect is a greater perturbational than variational contribution. Table VII shows this clearly. The calculations were made for $\sigma=1$. The functions used are (1, 2, 3, 7, 8, 16)+(6, 18)+(4, 5) in Inglis' table of types.

CONCLUSIONS REGARDING THE GROUND STATE

The present investigation is made with the symmetric form of the Hamiltonian, the nuclear constants being specified in two definite ways. Our conclusions will be based upon choice (*a*) which is probably at the favorable limit of the permissible range of force parameters for producing as large as possible a binding energy of Li^6. With this choice, second order perturbation theory leads to a value certainly smaller than -28.8 Mev for the energy of Li^6. Of this -10.7 Mev are due to excited configurations.

Furthermore we have shown in the last section that perturbation theory magnifies the effect of the excited configurations. If the initial trend which is evident in Table VII persists, we may say that the true contribution of the excited states is not more than 75 percent of the perturbational one. This leads to the value $-(18.1+\frac{3}{4}\cdot 10.7)$ Mev $\doteq -26$ Mev as a lower bound for the computed energy of Li^6. The present analysis of the problem thus corroborates the conclusion of Inglis that a symmetric Hamiltonian is inadequate to produce agreement with the experimental value, -32 Mev.

TABLE VIII. *List of perturbing doubly excited configurations.*

CONFIGURATIONS	NO. OF FUNCTIONS	CONFIGURATIONS	NO. OF FUNCTIONS
$(1s)^4 2p3p$	2	$(1s)^3(2p)^2 2s$	8
$(1s)^4 2p4f$	4	$(1s)^3(2p)^2 3d$	22
$(1s)^4(3d)^2$	3	$(1s)^2(2p)^4$	12

EFFECT OF EXCITED CONFIGURATIONS ON ^3D-STATE

In the papers by Feenberg and Wigner[15] and by Feenberg and Phillips[16] the first order energies of the low lying levels of a large number of nuclei have been calculated. The question arises as to how much the first order arrangement of levels will be disturbed by second order effects. Li^6 offers an easy opportunity for testing this matter.

The result will be sufficiently significant if we work with Majorana forces only and make a 2nd order perturbation calculation including only the doubly excited states. For the ^3S state this procedure has already been carried through: it yields a lowering of 7.8 Mev for $B=-28.7$ Mev.

The first order function for the ^3D state is

$$\psi_0=\left(\frac{1}{6!}\right)^{\frac{1}{2}}|s\eta_1 s\eta_2 s\eta_3 s\eta_4 p_1\eta_2 p_1\eta_4|.$$

It has a first order energy

$$H_{00}=E(^3S)-3\sigma^{\frac{3}{2}}(\sigma+2)^{-7/2}B,$$

and therefore lies in this approximation (with $\sigma=1$) about 2 Mev above the ground state. It is perturbed by the doubly excited configurations given in Table VIII.

The lowering effect of these functions is 3.8 Mev for $\sigma=1$, 3.9 Mev for $\sigma=1.2$ and 1.4.

In this approximation, then, the first order $^3D-{}^3S$ energy difference is altered by 4 Mev. A correlation between computed first order levels and experimental data is therefore in general not to be expected. One should observe, however, that the order of the terms remains unchanged, which is in agreement with Feenberg and Wigner's expectation.

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[15] E. Feenberg and E. Wigner, Phys. Rev. **51**, 95 (1937).

[16] E. Feenberg and M. Phillips, Phys. Rev. **51**, 597 (1937).