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VALENCE FORCES IN LITHIUM AND BERYLLIUM

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Abstract

With the nodeless wave functions of Guillemin and Zener, the method of Heitler and London is applied to determine how two normal lithium atoms, and also two normal beryllium atoms, influence each other (as a function of the distance). For the diatomic lithium molecule in the ground state, the equilibrium distance is calculated to be 2.4A, and the heat of dissociation to be 1.09 volts. The experimental values are 2.67A (Harvey and Jenkins) and 1.14 volts (Loomis and Nusbaum), respectively. Two normal beryllium atoms repel each other.

An accurate determination of the heat of dissociation and of the equilibrium separation of the nuclei in a diatomic molecule demands, if one uses the method of Heitler and London,[1] that the eigenfunctions of the individual atoms be known to a high degree of precision. Guillemin and Zener,[2] and later Zener[3] have succeeded in finding eigenfunctions for the atoms in the second row of the periodic table (starting with lithium), which are simple in form and give a quite accurate value for the ionization potential. This indicates that the valence electron is represented quite well, and that one should expect these eigenfunctions to be suitable for use in calculating the molecular constants.

In the present paper, we have made use of such functions. The first part is devoted to a revision of a calculation made by Delbrück,[4] who used atomic functions which gave a value of 3.9 volts for the ionization potential of lithium, as against the experimental value of 5.37 volts. In the second part, we investigate the interaction of two beryllium atoms, each in the normal state at infinite separation.

I. Molecular Constants of Li_2

Since Delbrück[4] has shown that the K-shells make only a very small contribution, we shall neglect them entirely. Accordingly, the lithium problem reduces to one which is analogous to that treated by Heitler and London,[1] the only difference being in the form of the atomic wave functions. We shall calculate (a) strictly along the lines of Heitler and London, using "nonpolar" wave functions, i.e., those which allow only one electron on each atom at infinite separation, and (b) according to the modification made by Slater,[5] which admits wave functions with two electrons on one atom and none on the other (corresponding to Li^- and Li^+, respectively).

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[1] W. Heitler u. F. London, Zeits. f. Physik **44**, 455 (1927).

[2] V. Guillemin u. C. Zener, Zeits. f. Physik **61**, 199 (1930).

[3] C. Zener, Phys. Rev. **36**, 51 (1930).

[4] M. Delbrück, Ann. d. Physik **5**, 36 (1930).

[5] J. C. Slater, Phys. Rev. **35**, 509 (1930).

Unless otherwise stated, the notation used throughout this paper will be the same as that used by one of the writers previously.[6] For s electrons, a (1) will denote the wave function describing electron 1 on nucleus a.

We shall use the nodeless functions, namely

$$a(1) = ca_1 e^{-\kappa a_1/2}, \text{ etc.}$$

(a) Calculation with nonpolar wave functions only

The zeroth approximation functions are:

$$^1\Sigma(S^N):\psi = a(1)b(2) + a(2)b(1)$$

$$^3\Sigma(A^N):\psi = a(1)b(2) - a(2)b(1).$$

The energies are:

$$^1\Sigma(S^N):E = \frac{J+K}{1+S}$$

$$^3\Sigma(A^N):E = \frac{J-K}{1-S}$$

where

$$J = \int H'[a(1)]^2[b(2)]^2 dv_1 dv_2$$

$$K = \int H'a(1)b(1)a(2)b(2)dv_1 dv_2$$

$$S^{1/2} = \int a(1)b(1)dv_1$$

$$H' = \frac{2}{R} + \frac{2}{r} - \frac{2}{a_2} - \frac{2}{b_1}\cdot$$

These energies are relative to the energy at infinite separation.

Writing

$$j = \int \frac{2}{r}\,[a(1)]^2[b(2)]^2 dv$$

$$k = \int \frac{2}{r}\,a(1)b(1)a(2)b(2)dv$$

$$I = \int \frac{2}{b_1}\,[a(1)]^2 dv_1$$

$$I' = \int \frac{2}{b_1}\,a(1)b(1)dv_1$$

[6] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).

we have

$$J = \frac{2}{R} - 2I + j$$

$$K = \frac{2}{R}S - 2S^{1/2}I' + k.$$

For the normalization, $2\pi c^2/\kappa^5 = 1/48$. From the previous paper,[6]

$$j = (4/9)(i_1 + i_3) + i_9/9.$$

Making the transformation

$$a = (R/2)(\lambda + \mu),\ \ b = (R/2)(\lambda - \mu),$$

and using Neumann's expansion,

$$\begin{aligned} k &= \int \frac{2}{r}\, c^4 a_1 a_2 b_1 b_2 e^{-(\kappa/2)(a_1+b_1+a_2+b_2)} dv_1 dv_2 \\ &= \frac{4}{R}\cdot 2\pi \int \sum_{\tau=0}^{\infty} D_{\tau 0} P_\tau\binom{\lambda_1}{\lambda_2} Q_\tau\binom{\lambda_2}{\lambda_1} P_\tau(\mu_1) P_\tau(\mu_2)\cdot c^4 (R/2)^{10} (\lambda_1^2-\mu_1^2)^2(\lambda_2^2-\mu_2^2)^2 \cdot \\ &\qquad e^{-\alpha(\lambda_1+\lambda_2)/2} d\lambda_1 d\lambda_2 d\mu_1 d\mu_2. \end{aligned}$$

The possible values of τ are 0, 2, and 4.

$$\begin{aligned} k^{(0)} &= (\alpha/2)^9(\kappa/288) \int Q_0\binom{\lambda_2}{\lambda_1} (\lambda_1^4 - 2\lambda_1^2/3 + \tfrac{1}{5})(\lambda_2^4 - 2\lambda_2^2/3 + \tfrac{1}{5}) e^{-\alpha(\lambda_1+\lambda_2)/2} d\lambda_1\, d\lambda_2 \\ &= (\alpha/2)^9(\kappa/144)\{s_0(44) - (\tfrac{2}{3})[s_0(24) + s_0(42)] + (\tfrac{1}{5})[s_0(04) + s_0(40)] \\ &\quad - (2/15)[s_0(02) + s_0(20)] + (4/9)s_0(22) + (1/25)s_0(00)\} \end{aligned}$$

where[6]

$$s_\tau(m, n) = \int_1^\infty Q_\tau(\lambda_1) e^{-\alpha\lambda_1/2} \lambda_1^m d\lambda_1 \cdot \int_1^{\lambda_1} e^{-\alpha\lambda_2/2} \lambda_2^n d\lambda_2$$

and

$$\alpha = \kappa R.$$

Now let

$$v_\tau(m, n) = \int_1^\infty d\lambda_1 \int_1^\infty d\lambda_2 Q_\tau\binom{\lambda_2}{\lambda_1} P_\tau\binom{\lambda_1}{\lambda_2} \lambda_1^m \lambda_2^n e^{-\alpha(\lambda_1+\lambda_2)/2}.$$

In particular,

$$\begin{aligned} v_2(m, n) &= (3/2)[s_2(m, n+2) + s_2(n, m+2)] \\ &\quad - (\tfrac{1}{2})[s_2(m, n) + s_2(n, m)]. \end{aligned}$$

Then

$$k^{(2)} = (\alpha/2)^9(\kappa/90)\{(1/9)v_2(22) - (2/21)v_2(20) + (1/49)v_2(00)\}.$$

For $\alpha=5$, one finds $k^{(0)}=0.1876\kappa$ and $k^{(2)}=0.0012\kappa$, so that the latter contribution is almost negligible.

We shall omit the further details of the calculation, which is quite easy, and give the results.

TABLE I. *Integrals and energies.*

α	$\alpha=3$	4	5	6	7	8	9	10
s	0.7916	0.6642	0.5316	0.4061	0.2968	0.2081	0.1405	0.0914
I/κ	.4468	.4022	.3564	.3138	.2772	.2463	.2206	.1995
I'/κ	.4324	.3835	.3289	.2738	.2221	.1761	.1368	.1045
j/κ	.3367	.3177	.2969	.2746	.2527	.2316	.2121	.1948
k/κ	.2856	.2379	.1888	.1432	.1022	.0714	.0477	.0302
${}^1\Sigma/\kappa$	.0858	−.0251	−.0614	−.0641	−.0548	−.0400	−.0267	−.0173
${}^3\Sigma/\kappa$	.316	.203	.133	.0854	.0555	.0332	.0194	.0116

With a value[2] of $\kappa=1.26$, the equilibrium distance is found to be 2.4A and the heat of dissociation is 1.09 volts. This is to be compared with the experimental values of 2.67A and 1.14 volts, respectively.[7,8] Delbrück obtained values of 4.6A and 1.4 volts, which indicates that the atomic wave functions did not describe the behavior of the valence electron over a sufficient range. This is traceable to the fact that he used a wave function with a large radial node, while we have used a nodeless function.

(b) Calculation with polar wave functions included

When we allow the possibility of two electrons being on one atom, then we have four possible resulting states. The wave functions are

$$^1\Sigma, S^N \quad \psi_1 = \begin{vmatrix} a_\alpha(1)+b_\alpha(1) & a_\beta(1)+b_\beta(1) \\ a_\alpha(2)+b_\alpha(2) & a_\beta(2)+b_\beta(2) \end{vmatrix}$$

$$A^N \quad \psi_4 = \begin{vmatrix} a_\alpha(1)+b_\alpha(1) & a_\beta(1)-b_\beta(1) \\ a_\alpha(2)+b_\alpha(2) & a_\beta(2)-b_\beta(2) \end{vmatrix}$$

$$A^N \quad \psi_3 = \begin{vmatrix} a_\alpha(1)-b_\alpha(1) & a_\beta(1)+b_\beta(1) \\ a_\alpha(2)-b_\alpha(2) & a_\beta(2)+b_\beta(2) \end{vmatrix}$$

$$^1\Sigma, S^N \quad \psi_2 = \begin{vmatrix} a_\alpha(1)-b_\alpha(1) & a_\beta(1)-b_\beta(1) \\ a_\alpha(2)-b_\alpha(2) & a_\beta(2)-b_\beta(2) \end{vmatrix}$$

where α and β specify the two possible spin orientations.

The function ψ_1 will give an approximation to the normal state, but the state represented by ψ_2 can exert a perturbing effect, so that the correct zeroth approximation to the wave function of the normal state is a certain linear combination of ψ_1 and ψ_2.

The secular equation is

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{22}-E \end{vmatrix} = 0$$

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

[8] F. W. Loomis and R. E. Nusbaum, Phys. Rev. **37**, 1712 (1931).

where

$$H_{11} = \frac{\int \psi_1{}^* H \psi_1 dv}{\int |\psi_1|^2 dv}, \quad H_{22} = \frac{\int \psi_2{}^* H \psi_2 dv}{\int |\psi_2|^2 dv}$$

and

$$H_{12} = \frac{\int \psi_1{}^* H \psi_2 dv}{\left[\int |\psi_1|^2 dv \cdot \int |\psi_2|^2 dv \right]^{1/2}} \cdot$$

there being no off-diagonal term containing E as a factor, because the wave function $a+b$ is orthogonal to $a-b$.

Let us now abbreviate as follows:

$$i = \int [a(1)]^2 [a(2)]^2 (2/r) dv$$

$$j'' = \int [a(1)]^2 a(2) b(2) (2/r) dv$$

$$H'c(1)d(2) = \left(\frac{2}{R} + \frac{2}{r_{12}} - \frac{2}{a_1} - \frac{2}{a_2} - \frac{2}{b_1} - \frac{2}{b_2} + \frac{2}{c_1} + \frac{2}{d_2} \right) c(1)d(2)$$

$$L = \int H' [a(1)]^2 [a(2)]^2 dv = \frac{2}{R} - 2I + i$$

$$J'' = \int a(1) a(2) H' a(1) b(2) dv = \frac{2}{R} S^{1/2} - S^{1/2} I - I' + j''$$

$$H_{11} = 2E_0 + \frac{2L + 2J + 4K + 8J''}{(2 + 2S^{1/2})^2}$$

$$H_{22} = 2E_0 + \frac{2L + 2J + 4K - 8J''}{(2 - 2S^{1/2})^2}$$

$$H_{12} = \frac{i - j}{2(1 - S)} \cdot$$

It is to be noticed that in addition to the "coulomb" and "exchange" integrals we have a new integral typified by J''. This keeps appearing in the subsequent calculations, and is in general of the same order of magnitude as the other integrals.

$$i = \int [a(1)]^2 [a(2)]^2 (2/r) dv = \lim_{R \to 0} \int [a(1)]^2 [b(2)]^2 (2/r) dv$$

$$
\begin{aligned}
&= c^4\left\{\frac{8\pi}{\kappa^4}\int a^2e^{-\kappa a}[\gamma_5(\kappa a)/\kappa a + \Gamma_4(\kappa a)]dv\right\}\\
&= (\kappa/288)\{24\Gamma_4 - 24\Gamma_4/2^4 - 18\Gamma_5/2^5 - 6\Gamma_6/2^6 - \Gamma_7/2^7\}\\
&= .3633\kappa.
\end{aligned}
$$

If $\kappa = 1.26,\qquad i = 6.2$ volts.

This value of i is larger than the ionization potential of lithium, which would indicate a negative electron affinity. No accurate calculations of the electron affinity of lithium have been made.

Calculation of j''

We may calculate j'' in two different ways, and thus obtain a check. The first way is direct, and the second requires the Neumann expansion. Here we give only the first method.

$$
\begin{aligned}
j'' &= \int (2/r)a(1)b(1)[a(2)]^2dv\\
&= (8\pi c^4/\kappa^4)\int abe^{-\kappa(a+b)/2}\{\gamma_5(\kappa a)/\kappa a + \Gamma_4(\kappa a)\}\cdot(2\pi/R)adabdb.
\end{aligned}
$$

Setting $y=\kappa a$,

$$
\int_{|R-a|}^{R+a} b^2dbe^{-\kappa b/2} = (2/\kappa)^3\left\{\Gamma_3\left|\frac{\alpha-y}{2}\right| - \Gamma_3\left(\frac{\alpha+y}{2}\right)\right\}
$$

$$
\begin{aligned}
j'' &= (128\pi^2c^4/\alpha\kappa^9)\int_0^\infty y^2dye^{-y/2}\{\gamma_5(y)/y + \Gamma_4(y)\}\left\{\Gamma_3\left|\frac{\alpha-y}{2}\right| - \Gamma_3\left(\frac{\alpha+y}{2}\right)\right\}\\
&= (128\pi^2c^4/\alpha\kappa^9)\Bigg[\int_0^\alpha ydy\{\gamma_5(y) + y\Gamma_4(y)\}e^{-\alpha/2}\cdot\{a_0 - a_1y + a_2y^2\}\\
&\qquad + \int_\alpha^\infty ydye^{-y}\{\gamma_5(y) + y\Gamma_4(y)\}e^{\alpha/2}\cdot\{b_0 + b_1y + b_2y^2\}\\
&\qquad - \int_0^\infty ydye^{-y}\{\gamma_5(y) + y\Gamma_4(y)\}e^{-\alpha/2}\{a_0 + a_1y + a_2y^2\}\Bigg]
\end{aligned}
$$

where

$$
\begin{aligned}
&a_0 = 2 + \alpha + \alpha^2/4 \quad a_1 = 1 + \alpha/2 \quad a_2 = b_2 = \tfrac{1}{4}\\
&b_0 = 2 - \alpha + \alpha^2/4 \quad b_1 = 1 - \alpha/2.
\end{aligned}
$$

The calculation gives:

$$
\begin{aligned}
j'' - I' = &- (\kappa/72\alpha)\{2e^{-\alpha/2}(134.01 - 56.531\alpha + 13.3125\alpha^2)\\
&- 32e^{-\alpha/2}[(\alpha/2)^7(A_6 - 2A_5 + A_4) + (\alpha/2)^6(A_5 - 4A_4 + 3A_3)\\
&+ (\alpha/2)^5(A_4/2 - 3A_3 + 9A_2/2) + (\alpha/2)^4(3A_3 + 3A_1)\\
&+ (\alpha/2)^3(3A_2 + 6A_1) + (\alpha/2)^2\cdot 6A_1]_\alpha\\
&+ 32e^{\alpha/2}[(\alpha/2)^7(A_6 - 2A_5 + A_4) + (\alpha/2)^6(5A_5 - 8A_4 + 3A_3)\\
&+ (\alpha/2)^5(12.5A_4 - 15A_3 + 4.5A_2) + (\alpha/2)^4(18A_3 - 15A_2 + 3A_1)\\
&+ (\alpha/2)^3(15A_2 - 6A_1) + (\alpha/2)^2\cdot 6A_1]_{2\alpha}\}
\end{aligned}
$$

where the subscript α after the bracket indicates that the A's inside have α as an argument.

TABLE II.

α	$\alpha=3$	4	5	6	7	8	9	10
j''/κ	0.3155	0.2834	0.2482	0.2124	0.1762	0.1426	0.1132	0.0876
L/κ	.1364	.0589	.0505	.0690	.0946	.1207	.1443	.1643
J''/κ	.0787	−.0204	−.0489	−.0490	−.0413	−.0318	−.0230	−.0167
J/κ	.1098	.0133	−.0159	−.0197	−.0160	−.0110	−.0069	−.0042
K/κ	.0439	−.0550	−.0782	−.0704	−.0550	−.0373	−.0236	−.0147
$(H_{11}-2E_0)/\kappa$	.0908	−.0181	−.0531	−.0536	−.0412	−.0217	−.0004	+.0188
$(H_{22}-2E_0)/\kappa$	.7888	.6392	.5028	.3972	.3229	.2745	.2331	.2029
H_{12}/κ	.0639	.0679	.0708	.0747	.0786	.0832	.0880	.0928
${}^1\Sigma/\kappa$	.0850	−.0250	−.0620	−.0657	−.0574	−.0435	−.0298	−.0194

The ${}^1\Sigma$ state referred to in Table II is the nonpolar one. It is seen that the two methods (a) and (b) of calculating the molecular constants lead to practically the same results. In what follows, we shall calculate by method (a).

II. INTERACTION OF TWO NORMAL BERYLLIUM ATOMS

There is but one possible state for the molecule when the two atoms are each in a ${}^1S$ state, and that is the ${}^1\Sigma$ state. We assume the wave function to be

$$\psi = \sum_P (-)^{\sigma_p} P a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4)$$

where P refers to a permutation of 1, 2, 3, 4 and σ_p is the order of P. The energy is

$$E = \frac{\int \psi^* H \psi dv}{\int \psi^* \psi dv}$$

where

$$H = \sum_{i=1}^{4} \Delta_i + \frac{8}{R} - \sum_{i=1}^{4} \left(\frac{4}{a_i} + \frac{4}{b_i}\right) + \sum_{i<j} \frac{2}{r_{ij}} \cdot$$

Then

$$E = \frac{\int \Big[\sum_{P'} (-)^{\sigma_{p'}} P' a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \Big] H \Big[\sum_{P''} (-)^{\sigma_{p''}} P'' a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \Big] dv}{\int \Big[\sum_{P'} (-)^{\sigma_{p'}} P' a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \Big] \cdot \Big[\sum_{P''} (-)^{\sigma_{p''}} P'' a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \Big] dv} \cdot$$

Summing over P'', and setting $P = P'P''^{-1}$:

$$E = \frac{\int \Big[\sum_P (-)^{\sigma_p} P a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \Big] H \left[a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \right] dv}{\int \Big[\sum_P (-)^{\sigma_p} P a_\alpha^*(1) a_\beta^*(2) b_\alpha^*(3) b_\beta^*(4) \Big] \cdot \left[a_\alpha(1) a_\beta(2) b_\alpha(3) b_\beta(4) \right] dv} \cdot$$

Splitting off the unperturbed energy,

$$E-E_0=\frac{\displaystyle\int\Big[\sum_P(-)^{\sigma_P}Pa_\alpha{}^*(1)a_\beta{}^*(2)b_\alpha{}^*(3)b_\beta{}^*(4)\Big]\cdot H'[a_\alpha(1)a_\beta(2)b_\alpha(3)b_\beta(4)]dv}{\displaystyle\int\Big[\sum_P(-)^{\sigma_P}Pa_\alpha{}^*(1)a_\beta{}^*(2)b_\alpha{}^*(3)b_\beta{}^*(4)\Big]\cdot[a_\alpha(1)a_\beta(2)b_\alpha(3)b_\beta(4)]dv}$$

where

$$\begin{aligned}H' &= \frac{8}{R}-\frac{4}{b_1}-\frac{4}{b_2}-\frac{4}{a_3}-\frac{4}{a_4}+\frac{2}{r_{13}}+\frac{2}{r_{14}}+\frac{2}{r_{23}}+\frac{2}{r_{24}}\\ &= H'(13)+H'(14)+H'(23)+H'(24)\\ H'(ij) &= \frac{2}{R}-\frac{2}{b_i}-\frac{2}{a_j}+\frac{2}{r_{ij}}\cdot\end{aligned}$$

The condition of spin orthogonality gives nonvanishing contributions from $P=1$, (13), (24), (13)(24) only. The contributions to numerator and denominator of the expression for $E-E_0$ are:

P	Numerator	Denominator
1	$4J$	1
(13) = (24)	$-K-2S^{1/2}J''-SJ$	$-S$
(13)(24)	$4SK$	S^2.

Then

$$E-E_0=\frac{4(J+SK)-2(K+SJ)-4S^{1/2}J''}{(1-S)^2}\cdot$$

α	$\alpha=3$	4	5	6	7	8	9	10
${}^1\Sigma/\kappa$	0.840	0.584	0.392	0.251	0.162	0.099	0.058	0.028

The ${}^1\Sigma$ state is seen to be a repulsive one.

DISCUSSION

The calculations for lithium show that good results may be obtained with simple wave functions. The success here justifies, we believe, the use of similar functions in the more complicated problems.

One would expect that two normal beryllium atoms would behave toward each other as do two normal helium atoms. This expectation is given support by our calculations, which show that the resulting molecular state is repulsive.

However, it is not at all obvious that two beryllium atoms, one of which is in the normal state, and the other of which is in the first excited state, should repel each other. The character of the states resulting from this configuration will be determined in the concluding installment of this paper, which is to follow shortly.