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Quantum Mechanics of Lithium Hydride

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Quantum mechanical calculations have been carried through for the normal state of the lithium hydride molecule. Two cases were considered. First, the radial eigenfunction of the valence electron of lithium was taken as nodeless as given by Slater. Second, the function derived by Guillemin and Zener with a node at $0.18a_0$ was used. In both cases the K electrons of lithium were neglected. The results are as follows:

Type of Eigenfunction	Equilibrium distance (angstroms)	Heat of dissociation (electron volts per molecule)	Fundamental frequency (cm^{-1})
Slater	1.44	2.30	1.4×10^3
Guillemin and Zener	1.45	2.21	1.4×10^3
Experimental values	1.6	2.56	1.38×10^3

INTRODUCTION

MOST of the quantum mechanical investigations[1–5] of the interaction of two neutral atoms have treated only those atoms which form symmetrical molecules. The present paper deals with the interaction of lithium and hydrogen. These elements were chosen for two reasons: first, they are the pair of dissimilar atoms of simplest structure; and second, they permit an explicit test of the quantitative effect of nodes in the eigenfunctions of electrons that are not in 1*s* states. Thus, calculations were carried through both on the assumption that the lithium eigenfunction possesses a node as derived by Guillemin and Zener[6] and on the assumption that the lithium eigenfunction is nodeless but is adjusted according to the rules of Slater.[7]

THEORY

While the present calculations were in progress Rosen[5] published general expressions for the interaction energies of two atoms, each with one valence electron. Hence, the final equations used in the numerical computations need only be quoted. Formally the combined energy of the two atoms is

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[1] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).
[2] E. C. Kemble and C. Zener, Phys. Rev. **33**, 512 (1929).
[3] J. H. Bartlett, Jr., Phys. Rev. **37**, 507 (1931).
[4] J. H. Bartlett and W. H. Furry, Phys. Rev. **37**, 1712 (1931).
[5] N. Rosen, Phys. Rev. **38**, 255 (1931).
[6] V. Guillemin, Jr. and C. Zener, Zeits. f. Physik **61**, 199 (1930).
[7] J. C. Slater, Phys. Rev. **36**, 59 (1930).

$$W = E_H + E_{Li} + E_{11} \pm \frac{E_{12} - SE_{11}}{1 \pm S}$$

Here the upper sign yields the stable molecular state (singlet) associated with the symmetrical eigenfunction and the lower sign gives the repulsive state (triplet) associated with the antisymmetrical eigenfunction. E_{H} and E_{Li} are the atomic energies of hydrogen and lithium respectively. E_{11} represents the Coulomb interaction of the two atoms and the last terms give the exchange energy (the meaning of E_{12} and S will be clear from the equations given below).

The hydrogen eigenfunction was taken in the form:

$$\psi = c_2 e^{-\gamma r}$$

where r represents the distance from the hydrogen nucleus, γ is a constant that was later set equal to $1/a_0$ where a_0 is the radius of the first Bohr orbit, and c_2 is a normalization constant.

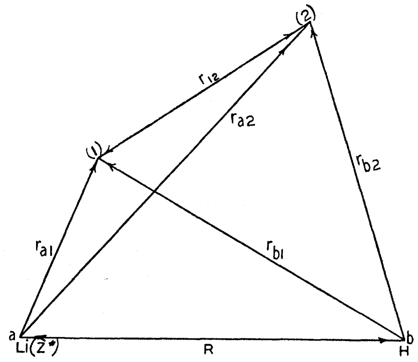

Fig. 1. Illustration of the notation used.

The lithium eigenfunctions were those given by Guillemin and Zener and had the form

$$\phi = c_1(r - \alpha R)e^{-\delta r}$$

where, here, r is the distance from the lithium nucleus, R is the separation between the nuclei, α is the constant determining the position of the node and is taken, for the numerical computations, as given by: $\alpha R = 0.18\ a_0$; δ, too is a constant, and is later assumed to have the value $0.63/a_0$. Finally c_1 is a normalization constant. When α is set equal to zero the above ϕ reduced to the Slater eigenfunctions.

Denoting by ψ_1, ψ_2, ϕ_1, ϕ_2 the hydrogen and lithium eigenfunctions for electrons 1 and 2 respectively the following expressions were obtained (the notation used is indicated in Fig. 1):

$$\frac{E_{11}}{e^2} = \int \phi_1^2(r_{a1})\psi_2^2(r_{b2})\left\{\frac{1}{r_{12}} + \frac{Z^*}{R} - \frac{1}{r_{b1}} - \frac{Z^*}{r_{a2}}\right\} d\tau_1 d\tau_2$$

$$
\begin{aligned}
&= Z^*\gamma e^{(\beta-\epsilon)}\left(1+\frac{2}{\epsilon-\beta}\right)-\frac{\pi^2c_1{}^2c_2{}^2R^5}{4\gamma^2}\Bigg[-\frac{B_4(\beta)A_0(\epsilon)}{4}\\
&+B_3(\beta)\left\{-\frac{A_1(\epsilon)}{2}+\left(\alpha+\frac{1}{2\gamma R}\right)A_0(\epsilon)\right\}-B_2(\beta)\left\{\left(\alpha^2+\frac{2\alpha}{\gamma R}\right)A_0(\epsilon)\right.\\
&\left.-\left(\alpha+\frac{3}{2\gamma R}\right)A_1(\epsilon)\right\}+B_1(\beta)\left\{\frac{A_3(\epsilon)}{2}+\left(\frac{3}{2\gamma R}-\alpha\right)A_2(\epsilon)\right.\\
&\left.-\frac{4\alpha}{\gamma R}A_1(\epsilon)+\frac{2\alpha^2A_0(\epsilon)}{\gamma R}\right\}+B_0(\beta)\left\{\frac{A_4(\epsilon)}{4}+\left(\frac{1}{2\gamma R}-\alpha\right)A_3(\epsilon)\right.\\
&\left.+\left(\alpha^2-\frac{2\alpha}{\gamma R}\right)A_2(\epsilon)+\frac{2\alpha^2}{\gamma R}A_1(\epsilon)\right\}\Bigg].
\end{aligned}
$$

$$
\begin{aligned}
\frac{E_{12}}{e^2} &= \int \phi_1(r_{a1})\psi_1(r_{b1})\phi_2(r_{a2})\psi_2(r_{b2})\left\{\frac{1}{r_{12}}+\frac{Z^*}{R}-\frac{1}{r_{b1}}-\frac{Z^*}{r_{a2}}\right\}d\tau_1 d\tau_2\\
&= \frac{Z^*S}{R}-\frac{\pi c_1c_2R^3S^{1/2}}{4}\Big[Z^*\{-B_2(\beta/2)A_0(\epsilon/2)+2\alpha B_1(\beta/2)A_0(\epsilon/2)\\
&\quad+B_0(\beta/2)(A_2(\epsilon/2)-2\alpha A_1(\epsilon/2))\}+B_2(\beta/2)A_0(\epsilon/2)\\
&\quad+B_1(\beta/2)\{2A_1(\epsilon/2)-2\alpha A_0(\epsilon/2)\}+B_0(\beta/2)\{A_2(\epsilon/2)-2\alpha A_1(\epsilon/2)\}\Big]+I_2.
\end{aligned}
$$

$$
\begin{aligned}
S &= \int \phi_1(r_{a1})\psi_1(r_{b1})\phi_2(r_{a2})\psi_2(r_{b2})\,d\tau_1 d\tau_2\\
&= \Big[\frac{\pi c_1c_2R^4}{4}\{\tfrac{1}{2}(A_3(\epsilon/2)B_0(\beta/2)-A_0(\epsilon/2)B_3(\beta/2))\\
&\quad-\alpha(A_2(\epsilon/2)B_0(\beta/2)-A_0(\epsilon/2)B_2(\beta/2))\\
&\quad-\tfrac{1}{2}(A_1(\epsilon/2)B_2(\beta/2)-A_2(\epsilon/2)B_1(\beta/2))\}\Big]^2
\end{aligned}
$$

$$
\begin{aligned}
I_2 &= \int [\phi_1(r_{a1})\psi_1(r_{b1})\phi_2(r_{a2})\psi_2(r_{b2})]/r_{12}\,d\tau_1 d\tau_2\\
&= (c_1{}^2c_2{}^2\pi^2R^7/16)\sum_0^\infty(2\tau+1)C_\tau
\end{aligned}
$$

$$
\begin{aligned}
C_\tau = &\int_1^\infty d\lambda_1\int_1^\infty d\lambda_2\int_{-1}^{+1}d\mu_1\int_{-1}^{+1}d\mu_2 e^{-[\epsilon(\lambda_1+\lambda_2)+\beta(\mu_1+\mu_2)]/2}(\lambda_1{}^2-\mu_1{}^2)(\lambda_2{}^2-\mu_2{}^2)\\
&\left(\frac{\lambda_1+\mu_1}{2}-\alpha\right)\left(\frac{\lambda_2+\mu_2}{2}-\alpha\right)P_\tau\begin{pmatrix}\lambda_1\\ \lambda_2\end{pmatrix}Q_\tau\begin{pmatrix}\lambda_2\\ \lambda_1\end{pmatrix}P_\tau(\mu_1)P_\tau(\mu_2).
\end{aligned}
$$

$$\epsilon = R(\gamma+\delta);\quad \beta = R(\delta-\gamma);\quad \gamma = 1/a_0;\quad \delta = 0.63/a_0$$

$$A_n(\epsilon) = \int_1^\infty e^{-\epsilon x}x^n dx;\quad B_n(\beta) = \int_{-1}^{+1}e^{-\beta x}x^n dx.$$

C_τ may be reduced to a sum of terms $s_\tau(m, n, \epsilon)$ with coefficients that are functions of $B_n\ (\beta/2)$ where:

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

COMPUTATIONS AND RESULTS

The evaluation of the integrals involved in the above expressions was extremely tedious. The procedure was to choose first values of the nuclear separation R such that ϵ was integral. The integrals $A(\epsilon)$ and $A(\epsilon/2)$ were then taken from the published tables of Bartlett and of Rosen. The values of $s_\tau\ (m, n, \epsilon)$ were taken from the published tables of Bartlett[3] and of W. H.

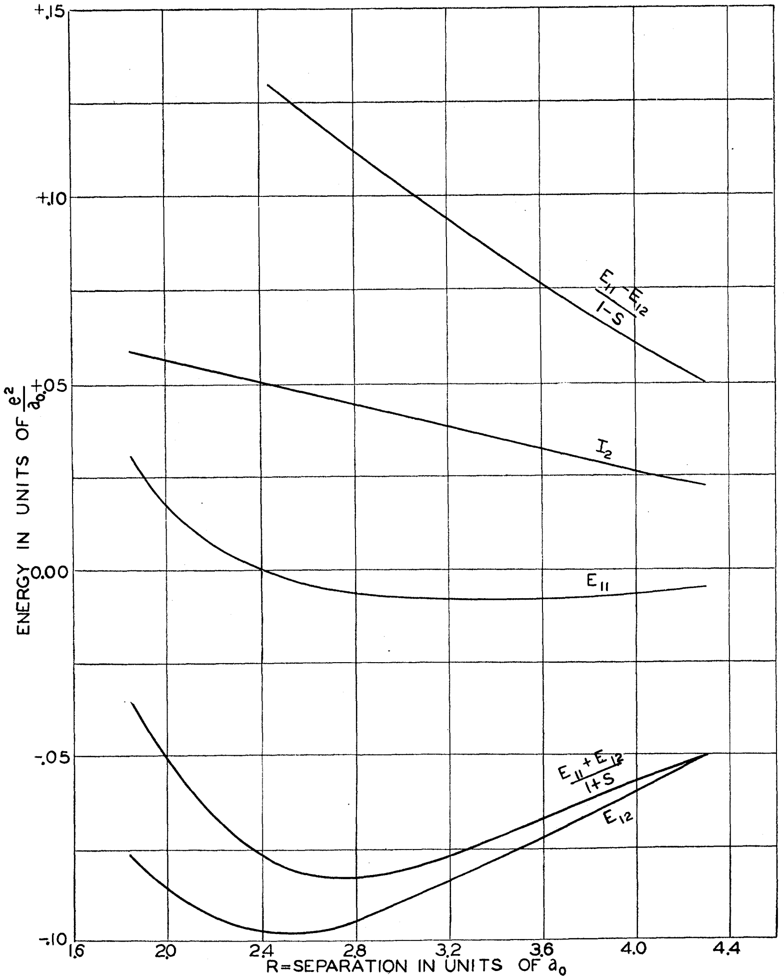

Fig. 2. Curves showing the variation of the various energy terms with the separation of the atoms.

Furry and J. H. Bartlett.[8] The $B_n(\beta)$ were computed from B_0 and the recurrence relation:

$$\beta B_{n+1}(\beta) = (n+1)B_n(\beta) - \left\{e^{-\beta} + (-1)^n e^{\beta}\right\}.$$

The series for I_2 was broken off with C_1 since it was found that 3 C_1 was of the order of 1/15 of C_0.

The results of these computations led, as usual, to a monotonic increase in the energy of the triplet state with decreasing R and a pronounced negative minimum in the variation of the singlet energy with R. The detailed variation of the functions E_{11}, E_{12}, I_2 and the final interaction energies $(E_{11} \pm E_{12})/(1 \pm S)$ are shown in Fig. 2, plotted as a function of R. As already mentioned the above computations were carried out first with the lithium functions having a node at $\alpha = 0.18\, a_0/R$ and the curves of Fig. 2 are the results of these calculations. Besides these, however, the same computations were carried through with the Slater nodeless eigenfunctions obtained by simply setting $\alpha = 0$ in all the above expressions. The resulting modifications in the curves of Fig. (2) are small and hence are not drawn. The final constants of the equilibrium state, however, are given for both cases in Table I. The experimental values as given by G. Nakamura[9] are also included.

TABLE I.

Type of eigenfunction	Equilibrium distance (angstroms)	Heat of dissociation (electron volts per molecule)	Fundamental frequency (cm^{-1})
Slater	1.44	2.30	1.4×10^3
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Experimental Values	1.6	2.56	1.38×10^3

As indicated in the table the difference between the results obtained by the use of the Guillemin and Zener functions and the nodeless Slater functions is inappreciable compared with their deviations from the experimental values. This fact may be considered as a justification for the use of the simpler Slater functions in other first order perturbation calculations of this type. The values obtained from either calculation show as good agreement with experiment as those obtained for other problems treated by the Heitler and London method.

It is of interest to note that the Sugiura exchange integral I_2 which is especially tedious to calculate is of the same order of magnitude as the other integrals occurring in this calculation. For this reason such calculations as those made by Starodubrowsky[10] in which the Sugiura integral was neglected, cannot lead to correct results.

The writers wish to express their appreciation to Drs. Bartlett and Furry for the use of their tables of $s_\tau\ (m, n, \epsilon)$ before publication.

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[8] W. H. Furry and J. H. Bartlett, Jr., Phys. Rev. **39,** 210 (1932).

[9] G. Nakamura, Zeits. f. Physik **59,** 218 (1930).

[10] P. Starodubrowsky, Zeits. f. Physik **70,** 812 (1931).