LETTER

On the Binding Energy of LiH

By Iwao YASUMORI

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As an typical application of quantum mechanics to chemical problems, the energy' of the ground state of lithium hydride was first calculated by Hutchisson and Muskat(1) by a similar method to Heitler and London's procedure on the hydrogen molecule. Their result was reported to be in good agreement with the observed value and quoted often in many text-books.

Recently, when calculating the adsorption energy of a hydrogen atom on the lithium surface,(2) the author was forced to recalculate the energy of the lithium hydride molecule by the same method as H.-M.'s. The wave function used is just the same as theirs, i. e.,

$$\Psi=\phi(1)\psi(2)+\phi(2)\psi(1), \qquad (1)$$

where $\phi=\sqrt{\delta^5/3\pi}re^{-\delta r}$ with $\delta=0.63$ is the 2s function of lithium, and $\psi=\sqrt{1/\pi}e^{-r}$ is the 1s function of hydrogen. For the effective charge of lithium ion core $z=1.26$ was adopted. All numerical values for the elementary integrals appearing in the expression of the energy were taken from Kotani, Amemiya and Shimose's tables.(3) The results obtained by the present author are very different from H.-M.'s (Table 1.) For reference the computed fundamental frequencies are also compared in the table.

Table 1

	Equilibrium distance (A.)	Heat of dissociation (e.v.)	Fundamental frequency (cm.$^{-1}$)
Hutchisson and Muskat	1.44	2.30	1.40×10^3
Yasumori	1.53	1.30	1.37×10^3
Observed value	1.60	2.56	1.40×10^3

This large discrepancy was found to originate in the fact that, when expanding the Sugiura integral $I_2=\int[\phi(1)\psi(2)\phi(2)\psi(1)]/r_{12}d\tau_1d\tau_2$ by Neumann series, H.-M. had mistaken a coefficient (1/16) just half of the correct value (1/8). The correct formula is as follows:(4)

$$I_2=c_1^2c_2^2\pi^2R^7/8\sum_{\tau=0}^{\infty}(2\tau+1)C_\tau \qquad (2)$$

In consequence of the reduction by mistake of I_2 which is a positive term, the energy calculated by them was incidentally close to the observed one. From another point of view also, it seems unacceptable that the coulombic fraction ρ in the region near the equilibrium distance is 0.06~0.07 as deduced from their figure; according to my calculation ρ is 0.14~0.71, which is reasonable in comparison with the values $\rho_{H_2}=0.12$ and $\rho_{Li_2}=0.22$ computed by Rosen et al.(5)

Thus it becomes clear that the simple wave function (1) of covalent form does not give the right value of the dissociation energy of lithium hydride as in the case of hydrogen molecule. In order to obtain closer agreement with the observed value, it is necessary, as pointed out by Fischer,(6) to include a term for the ionic structure Li^+H^- in (1). Detailed discussions will be published later elsewhere.

Laboratory of Physical Chemistry,
Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo, Japan.

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(1) E. Hutchisson and M. Muskat, *Phys. Rev.*, **40**, 340 (1932).

(2) I. Yasumori, Speech at the 5th annual meeting of the Chemical Society of Japan.

(3) M. Kotani, A. Amemiya and T. Shimose, *Proc. Phys.-Math. Soc. Japan*, **20**, Extra 1 (1938); **22**, Extra 1 (1940).

(4) Ref., 1) p. 342.

(5) N. Rosen and S. Ikehara, *Phys. Rev.*, **43**, 5 (1933); S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes" (1941). p. 84.

(6) I. Fischer, *Nature*, **168**, 1002 (1951).