On the First Singlet and Triplet Excited States of the Lithium Molecule

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The first singlet and triplet excited states of Li_2 are studied by the MO and VB methods. As basis, only 1*s* and 2*s* AO's are used. In the MO description, the antibonding MO is more diffuse than the bonding MO and the difference is bigger in $^1\Sigma_u{}^+$ than $^3\Sigma_u{}^+$. In the VB description, splitting of the 2*s* orbital in the purely ionic ($^1\Sigma_u{}^+$) and covalent ($^3\Sigma_u{}^+$) wave functions does not lead to any energy lowering. An interpretation of this result is suggested. The calculated singlet-triplet separation is compared with previous calculations.

The lithium molecule is the simplest diatomic molecule with inner shells. In this paper, the first singlet and triplet excited states are studied by the molecular orbital (MO) and valence bond (VB) methods.

In conventional MO and VB calculations, only those atomic orbitals (AO's) which are occupied in the ground state of free atoms are usually used as a basis and the same basis is used to describe different excited states as well as the ground state. These conventional MO and VB calculations failed badly in predicting the *V-T* separation in C_2H_4[1] and the $^3\Sigma_u{}^- - {}^3\Sigma_u{}^+$ separation in O_2[2]. In order to overcome this difficulty within the framework of the MO method, Huzinaga[3,4] advocated the use of different AO's for bonding and anti-bonding MO's and the view that these AO's could also be different in different states. He applied this idea to C_2H_4 and obtained a much better value for the *V-T* separation. His antibonding MO in the *V* state is very diffuse and the optimum orbital exponent of $2p\pi$ AO turns out to be as small as 0.2. This remarkable result was confirmed later by Goddard, Hunt, and Dunning,[5] who used a very flexible basis in their calculation. Ohno and Itoh[6,7], on the other hand, had attacked the same problem by the VB method. Their method is characterized by the use of different AO's for a neutral atom and for its positive and negative ions. Although their calculations were approximate, the *V-T* and $^3\Sigma_u{}^- - {}^3\Sigma_u{}^+$ separations they obtained were fairly good.

In this work, the first singlet and triplet excitation energies of Li_2 are calculated both by Huzinaga's MO method and by the spirit of Ohno and Itoh's VB method. The aim of the work is not to achieve a numerical accuracy for these excited states but to gain qualitative idea about charcteristics of these states. Thus, only 1*s* and 2*s* Slater-type orbitals are used as the basic AO's. The orbital exponent of 1*s* is fixed at 2.685, which is the potimum value for the neutral Li atom.[8] The internuclear distance is also fixed at the observed value of 5.051 a.u.[9]

Molecular Orbital Treatment

In the MO treatment with the limited basis explained above, the wave functions for the first singlet and triplet excited states are written as

$$\Psi^{\mathrm{MO}}(^1\Sigma_u{}^+) = 1/\sqrt{2}\,[\det|1\sigma_g\overline{1\sigma}_g1\sigma_u\overline{1\sigma}_u2\sigma_g\overline{2\sigma}_u| - \det|1\sigma_g\overline{1\sigma}_g1\sigma_u\overline{1\sigma}_u\overline{2\sigma}_g2\sigma_u|], \qquad (2.1)$$

and

$$\Psi^{\mathrm{MO}}(^3\Sigma_u{}^+) = 1/\sqrt{2}\,[\det|1\sigma_g\overline{1\sigma}_g1\sigma_u\overline{1\sigma}_u2\sigma_g\overline{2\sigma}_u| + \det|1\sigma_g\overline{1\sigma}_g1\sigma_u\overline{1\sigma}_u\overline{2\sigma}_g2\sigma_u|], \qquad (2.2)$$

where spins α and β are associated with the orbitals with out and with a bar, respectively.

Following Huzinaga's procedure, we take the orbital exponents of the 2*s* orbitals used in $2\sigma_g$ and $2\sigma_u$ as two independent variational parameters. They are denoted by δ_g for $2\sigma_g$ and δ_u for $2\sigma_u$. The orbitals $2\sigma_g$ and $2\sigma_u$ are orthogonalized to $1\sigma_g$ and $1\sigma_u$, respectively, by the Schmidt procedure. The latter are constructed from the $1s_a$ and $1s_b$ AO's.

The energy is thus a function of two parameters, *i.e.*, δ_g and δ_u for each state. The results are collected in Table 1. When we use the same AO's in constructing the two MO's $2\sigma_g$ and $2\sigma_u$ (MO2=VB2), the optimum orbital exponents for $^1\Sigma_u{}^+$ and $^3\Sigma_u{}^+$ turned out to be close to the optimum value of Li^- and Li, respectively. The latter values are 0.547 for Li^-[10] and 0.637 for Li.[8] This could be expected since when the restriction $\delta_u=\delta_g$ is imposed, the MO functions Eq. (2.1) and Eq. (2.2) are identical with the VB functions which are inoic for $^1\Sigma_u{}^+$ and covalent for $^3\Sigma_u{}^+$.

When we use different AO's in different MO's (MO3), the antibonding $2\sigma_u$ becomes more diffuse than the bonding $2\sigma_g$. The degree of splitting is bigger in $^1\Sigma_u{}^+$ than in $^3\Sigma_u{}^+$. This is in accord with the observations made by Huzinaga,[11] and

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[1] R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.* **16**, 526 (1948).

[2] W. Moffitt, *Proc. Roy. Soc*, **A210**, 224 (1951).

[3] S. Huzinaga, *J. Chem. Phys.*,**36**, 453 (1962).

[4] S. Huzinaga, *Theoret. Chim. Acta*, **15**, 12 (1969).

[5] T. H. Dunning, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969).

[6] K. Ohno and T. Itoh, *J. Chem. Phys.*, **23**, 1468 (1955).

[7] T. Itoh and K. Ohno, *ibid.*, **25**, 1098 (1956).

[8] J. Ransil, *Rovs. Mod. Phys.*, **32**, 245 (1960).

[9] G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, Toronto, p 546 (1950).

[10] S. Kohda (unpublished result).

[11] S. Huzinaga, Prog. *Theoret. Phys.*, **19**, 125 (1957) and **20**, 15 (1958).

TABLE 1. ELECTRONIC ENERGY OF Li_2 AS A FUNCTION OF $2s$ ORBITAL EXPONENTS δ_g AND δ_u

Computational method	2s-Orbital exponents $^1\Sigma_g{}^+$ δ_g	$^1\Sigma_g{}^+$ δ_u	$^3\Sigma_g{}^+$ δ_g	$^3\Sigma_g{}^+$ δ_u	Total energy (a.u.) $^1\Sigma_u{}^+$	Total energy (a.u.) $^3\Sigma_u{}^+$	$^1\Sigma_u{}^+ - {}^3\Sigma_u{}^+$ (eV)
MO 1=VB 1[a)]	0.637	0.637	0.637	0.637	−14.7130	−14.8079	2.58
MO 1′=VB 1′[b)]	0.65	0.65	0.65	0.65	−14.7072	−14.8040	2.63
MO 2=VB 2[a)]	0.582	0.582	0.647	0.647	−14.7173	−14.8079	2.46
MO 3[a,c)]	0.737	0.437	0.702	0.612	−14.7350	−14.8109	2.06
MO+CI (5)[b)]	0.65	0.65	0.65	0.65	−14.7912	−14.8145	0.63

a) Present work. $R=5.051$ a.u. $\delta_{1s}=2.6865$
b) Ref. 15. $R=5.00$ a.u. $\delta_{1s}=2.65$ $\delta_{2p}=0.65$
c) Variation with $\delta_u \neq \delta_g$.

Phillipson and Mulliken[12)] on H_2, by Huzinaga[3,4)] and Dunning *et al.*[5)] on C_2H_4, and by Taketa *et al.* on O_2[13)]. However, even the splitting between $2\sigma_g$ and $2\sigma_u$ in $^1\Sigma_u{}^+$ is smaller than that found in H_2, C_2H_4, and O_2. This is probably connected with the fact that the equilibrium internuclear distance is large in comparison with the radius of the valence orbital in the case of Li_2.

Valence Bond Treatment

In the VB treatment with the limited bais we employed, the wave functions for the first singlet and triplet excited states can be written as

$$\begin{aligned}\Psi^{\mathrm{VB}}({}^1\Sigma_u{}^+) = N[&\det|1s_a\overline{1s_a}1s_b\overline{1s_b}2s_a\overline{2s_a{}'}]\\ &-\det|1s_a\overline{1s_a}1s_b\overline{1s_b}\overline{2s_a}2s_a{}'|\\ &-\det|1s_a\overline{1s_a}1s_b\overline{1s_b}2s_b\overline{2s_b{}'}|\\ &+\det|1s_a\overline{1s_a}1s_b\overline{1s_b}\overline{2s_b}2s_b{}'|], \qquad (3.1)\end{aligned}$$

and

$$\begin{aligned}\Psi^{\mathrm{VB}}({}^3\Sigma_u{}^+) = N'[&\det|1s_a\overline{1s_a}1s_b\overline{1s_b}2s_a\overline{2s_b{}'}|\\ &-\det|1s_a\overline{1s_a}1s_b\overline{1s_b}\overline{2s_a}2s_b{}'|\\ &-\det|1s_a\overline{1s_a}1s_b\overline{1s_b}2s_b\overline{2s_a{}'}|\\ &-\det|1s_a\overline{1s_a}1s_b\overline{1s_b}\overline{2s_b}2s_a{}'|]. \qquad (3.2)\end{aligned}$$

These wave functions correspond to the structures Li^+-Li^- for $^1\Sigma_u{}^+$ and Li-Li for $^3\Sigma_u{}^+$ and contain two variational parameters δ_{2s} and $\delta_{2s}{}'$. All $2s$ orbitals $2s_a$, $2s_b$, $2s_a{}'$ and $2s_b{}'$ are orthogonalized to the $1s$ orbitals by the Schmidt procedure.

The energy again becomes a function of two parameters. Contrary to our expectation, the energy minima are found at $\delta_{2s}=\delta_{2s}{}'=0.582$ for $^1\Sigma_u{}^+$ and at $\delta_{2s}=\delta_{2s}{}'=0.647$ for $^3\Sigma_u{}^+$. When $\delta_{2s}=\delta_{2s}{}'$, the wave functions in Eqs. (3.1) and (3.2) are identical with those in Eqs. (2.1) and (2.2), respectively, under the restriction $\delta_u=\delta_g$. This means that no improvement over the simple VB function comes about by allowing the wave functions an extra freedom of $\delta_{2s}\neq\delta_{2s}{}'$. An exactly similar conclusion is reached in the VB treatment of the $^1\Sigma_u{}^+$ and $^3\Sigma_u{}^+$ states of H_2 with the two $1s$-type AO's.[14)]

In these cases, the wave function is symmetric with respect to the two parameters and the energy must have a extremum at $\delta_{2s}=\delta_{2s}{}'$ when δ_{2s} and $\delta_{2s}{}'$ change along a line perpendicular to the line $\delta_{2s}=\delta_{2s}{}'$. The results we have obtained mean that the point where $\delta_{2s}=\delta_{2s}{}'=0.582$ ($^1\Sigma_u{}^+$) or 0.647 ($^3\Sigma_u{}^+$) is a minimum and not a saddle point. This may seem less strange when the valence bond wave functions in Eqs. (3.1) and (3.2) are expressed in the following way:

$$\Psi^{\mathrm{VB}}({}^1\Sigma_u{}^+) \propto \Psi^{\mathrm{MO}}({}^1\Sigma_u{}^+) + \Psi'^{\mathrm{MO}}({}^1\Sigma_u{}^+)$$

$$\Psi^{\mathrm{VB}}({}^3\Sigma_u{}^+) \propto \Psi^{\mathrm{MO}}({}^3\Sigma_u{}^+) + \Psi'^{\mathrm{MO}}({}^3\Sigma_u{}^+)$$

where Ψ^{MO} ($^1\Sigma_u{}^+$) and Ψ^{MO}($^3\Sigma_u{}^+$) have been given in Eqs. (2.1) and (2.2), respectively, and Ψ'^{MO} has the same functional form as Eq. (2.1) or Eq. (2.2) but δ_{2s} and $\delta_{2s}{}'$ are interchanged in $2\sigma_g$ and $2\sigma_u$. We have seen that the energies of the wave functions Ψ^{MO} ($^1\Sigma_u{}^+$) and Ψ^{MO}($^3\Sigma_u{}^+$) are quite low. However, Ψ'^{MO}($^1\Sigma_u{}^+$) and Ψ'^{MO}($^3\Sigma_u{}^+$) are expected to have very high energies, since they correspond to an unlikely model in which the bonding MO is diffuse and the anti-bonding MO is tight. The wave functions in Eqs. (3.1) and (3.2) are forced to contain equal amount of Ψ^{MO} and Ψ'^{MO}. This might be the reason why the extra degree of freedom introduced in the VB calculation turns out to be superfluous.

Summary

The calculated singlet-triplet separation is compared with other calculations in Table 1. Unfortunately, the $^3\Sigma_u{}^+$ state has not been observed. If we take the value of 0.63 eV obtained by the best calculation among the listed as a standard, the separation we obtained is only slightly better than the conventional calculation. However, the modification introduced here makes it clear that the $2\sigma_u$ orbital in the $^1\Sigma_u{}^+$ state is more diffuse than the $2\sigma_g$ orbital and both of the $2\sigma_u$ and $2\sigma_g$ orbitals in the $^3\Sigma_u{}^+$ state. It should also be noted that the use of two $2s$-type AO's in the ionic ($^1\Sigma_u{}^+$) and covalent ($^3\Sigma_u{}^+$) functions does not lead to any improvement over the conventional treatment.

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[12)] P. E. Phillipson and R. S. Mulliken, *J. Chem. Phys.*, **28**, 1248 (1958).

[13)] H. Taketa, H. Tatewaki, O Nomura, and K. Ohno, *Theoret. Chim. Acta*, **11**, 369 (1968).

[14)] T. Noro, K. Tanaka, and K. Ohno (unpublished result).

[15)] E. Ishiguro, K. Kayama, M. Kotani, and Y. Mizuno, *J. Phys. Soc. Japan*, **12**, 1355 (1957).