

The theoretical determination of the $B^1\Pi_u$ potential energy curve for Li_2^*

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The Li_2 $B^1\Pi_u$ potential energy curve has been calculated with a multiconfiguration SCF (MCSCF) wavefunction. Several different types of wavefunctions and basis sets have been examined and their accuracy determined. The most accurate wavefunction used predicts a binding energy of 0.3015 eV (0.08 eV above the experimental value of 0.385 eV) and a potential barrier of 0.0724 eV with its maximum at 10.6 bohr. It is argued that the theoretical value of the barrier is an upper bound to the experimental value. The long range behavior of the potential energy is found to match smoothly onto the form predicted from dispersion forces.

I. INTRODUCTION

The $B^1\Pi_u$ electronic excited state of Li_2 has been closely connected with the spectroscopic determination of the dissociation energy of the $X^1\Sigma_g^+$ electronic ground state of Li_2 . In 1931 Loomis and Nusbaum,¹ from an extrapolation of the vibrational energy spacings of the $B^1\Pi_u$ state, determined the dissociation energy of the $B^1\Pi_u$ state to be $D_0 = 3738 \text{ cm}^{-1} = 0.46 \pm 0.03 \text{ eV}$.² From this datum they then deduced the dissociation energy of the $X^1\Sigma_g^+$ ground state as follows:

$$\begin{aligned} D_0(X^1\Sigma_g^+) &= \nu_{00} + D_0(B^1\Pi_u) - \nu(\text{Li } 2^2S - 2^2P) \\ &= 20\,398 \text{ cm}^{-1} + 3738 \text{ cm}^{-1} - 14\,904 \text{ cm}^{-1} \\ &= 9232 \text{ cm}^{-1} = 1.14 \pm 0.03 \text{ eV}. \end{aligned} \quad (1)$$

Here ν_{00} is the energy between the zeroth vibrational levels of the $X^1\Sigma_g^+$ and $B^1\Pi_u$ states, and $\nu(\text{Li } 2^2S - 2^2P)$ is the atomic excitation energy from the $\text{Li } 2^2S$ to the $\text{Li } 2^2P$ states. Thermochemical data by Lewis³ indicated a dissociation energy for the $X^1\Sigma_g^+$ state of $D_0 = 1.03 \pm 0.04 \text{ eV}$, and a thorough theoretical calculation by Das⁴ recently placed the dissociation energy at $D_0 = 0.99 \text{ eV}$ (probably a lower limit). Thus, a need arose to reexamine the spectroscopic data.

Inherent in the analysis by Loomis and Nusbaum, as summarized by Eq. (1), is the assumption that the $B^1\Pi_u$ potential energy curve does not have a barrier at large internuclear distances. However, for molecular states which arise from a 2^2S atom and a 2^2P atom, such as the Li_2 $B^1\Pi_u$ state, King and Van Vleck^{5,6} have shown that the corresponding $1^1\Pi_u$ potential curve is repulsive at large internuclear separations. Analogous results were also found by Mulliken,⁷ who reexamined the nature of these long-range interactions in great detail. Coupling this long distance behavior with the known stability of the

$B^1\Pi_u$ state one can then predict that this state has a potential barrier, and as a consequence the spectroscopic data by Loomis and Nusbaum lead only to an upper bound on the ground state dissociation energy of Li_2 .

Velasco, Ottinger, and Zare,⁸ redetermined the dissociation energy for the ground state of Li_2 by direct extrapolation of the ground state vibrational energies which they obtained from the fluorescence spectra $B^1\Pi_u - X^1\Sigma_g^+$ of Li_2 . Their value for the dissociation energy (which is independent of any assumptions about the nature of the $B^1\Pi_u$ potential curve) is $D_0 = 1.026 \pm 0.006 \text{ eV}$. This value is in agreement with the previous thermochemical data by Lewis, as well as consistent with the expected accuracy of the theoretical calculations by Das.⁴ Using this new value for the ground state dissociation energy together with the previous data by Loomis and Nusbaum, Velasco *et al.*⁸ predict that the potential energy curve for $B^1\Pi_u$ state of Li_2 has a barrier of magnitude $0.115 \pm 0.036 \text{ eV}$.

More recently, from an analysis of the $B-X$ system of Li_2 , Hessel and Vidal⁹ have determined the dissociation energy of the B state to be 0.450 eV including a potential barrier of 0.065 eV, leading to a binding energy of 0.385 eV. The measured value of 0.065 eV is consistent with the earlier theoretical work by Kahn¹⁰ that indicated the value determined by Velasco *et al.* was too large by approximately 0.04 eV.

In this paper we will present the results of theoretical calculations on the Li_2 $B^1\Pi_u$ state to show the nature of the full potential energy curve and the electronic structure of this state.

II. DESCRIPTION OF THE Li_2 $B^1\Pi_u$ STATE

The Hartree-Fock (HF) configuration for the $B^1\Pi_u$ state is

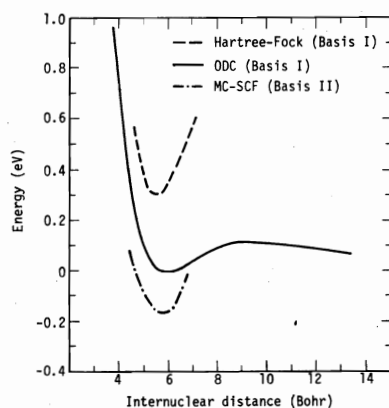


FIG. 1. Potential curves for the HF, ODC, and MCSCF wavefunctions of the $B^1\Pi_u$ state of Li₂.

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g 1\pi_u \quad (2)$$

Although this simple form of the wavefunction gives a reasonable description of the electronic state near the equilibrium distance, it does not correlate correctly with the separated atoms limit, Li(²S) + Li(²P). For large internuclear separations the correct configuration is the valence bond configuration

$$1s_L^2 1s_R^2 (2s_L 2p_R + 2s_R 2p_L) \quad (3)$$

where $1s$, $2s$, and $2p$ are just Li atomic orbitals, and the subscripts L and R refer to the atom (left or right) on which the orbital is localized. The localized atomic orbitals are related to the molecular symmetry orbitals as follows:

$$(2\sigma_g + \lambda 2\sigma_u) - 2s_L \quad (4a)$$

$$(1\pi_u - \lambda 1\pi_g) - 2p_R \quad (4b)$$

$$(2\sigma_g - \lambda 2\sigma_u) - 2s_R \quad (4c)$$

$$(1\pi_u + \lambda 1\pi_g) - 2p_L \quad (4d)$$

where $\lambda = 1$ for infinite separation. Substituting these relations into (3) gives the optimized double configuration (ODC) form of the wavefunction,¹¹

$$1\sigma_g^2 1\sigma_u^2 (2\sigma_g 1\pi_u - \lambda^2 2\sigma_u 1\pi_g) \quad (5)$$

where the mixing coefficient and the molecular orbitals are to be variationally optimized.

The ODC wavefunction contains just the "left-right" electron correlation effects that allow for proper dissociation (the GVB configurations). Near equilibrium the description of the state is not significantly improved compared to the HF wavefunction. The potential curves for the ODC and HF wavefunctions calculated with a $(1s1s'2s2s'2s''2p2p'2p''3d)$ Slater basis set,¹² optimized for the ²S and ²P states of the Li atom, are compared in Fig. 1. The ODC curve correctly approaches the separated atoms limit of -14.7978 hartree and exhibits the potential barrier predicted by King and Van Vleck⁵ and Mulliken.⁷ The calculated barrier height is 0.115 eV, but the calculated binding energy is only 0.0065 eV relative to the separated atoms.¹³

In order to improve the binding energy it is necessary to include configurations to describe other correlation

effects. In the ground state calculation of Das,⁴ the major contributions to binding arise from the $2\sigma_u^2$, $3\sigma_g^2$, and $1\pi_u^2$ configurations, describing "left-right," "in-out," and "angular" types of electron correlation. "In-out" correlation can be included in the B state wavefunction by the configuration

$$3\sigma_g 2\pi_u \quad (6)$$

Adding this configuration to the HF configuration we obtain

$$2\sigma_g 1\pi_u - \lambda^2 3\sigma_g 2\pi_u = \frac{1}{2} \{ (2\sigma_g + \lambda 3\sigma_g)(1\pi_u - \lambda 2\pi_u) + (2\sigma_g - \lambda 3\sigma_g)(1\pi_u + \lambda 2\pi_u) \} \quad (7)$$

In the right-hand side of relation (7) we see that in the first term the new molecular orbital $(2\sigma_g + \lambda 3\sigma_g)$ becomes more diffuse than the $2\sigma_g$ orbital, while concurrently the $(1\pi_u - \lambda 2\pi_u)$ molecular orbital becomes contracted in relation to the $1\pi_u$ orbital, and vice versa for the second term.

"Angular" type of correlation can be introduced into the ODC wavefunction (5) by adding $\delta\pi$ -like configurations, such as

$$1\delta_g 1\pi_u \quad (8)$$

and

$$1\delta_g 2\pi_u \quad (9)$$

Although (8) is a single excitation with respect to the Hartree-Fock wavefunction, it cannot be eliminated in this case by use of Brillouin's theorem.¹⁴ This is because the variational condition on the $2\sigma_g$ orbital in the ODC wavefunction is not exactly the Brillouin condition

$$\langle \delta 2\sigma_g 1\pi_u | H | \Psi \rangle = 0 \quad (10)$$

but rather it is [Eq. (10)] subject to the constraint that the variations in $2\sigma_g$ be in the σ_g space, i.e., the field due to the $1\pi_u$ orbital is cylindrically averaged in Eq. (10). Thus, the $1\delta_g 1\pi_u$ configuration has the dual role of allowing for the polarization of the $2\sigma_g$ orbital in the variational field of the $1\pi_u$ orbital, and of allowing simultaneous distortion of both orbitals off the line of the nuclei, or "angular" correlation.

One might presume that including the $1\delta_g 1\pi_u$ configuration would eliminate the need for the explicit consideration of the $1\delta_g 2\pi_u$ configuration, Eq. (9). However, the variational condition arising from optimizing the $1\pi_u$ with Eq. (8) presently is

$$\langle (2\sigma_g - C1\delta_g) \delta 1\pi_u | H | \Psi \rangle = 0 \quad (11)$$

therefore,

$$\langle 1\delta_g 2\pi_u | H | \Psi \rangle = 0 \quad (12)$$

is not necessarily satisfied and a new term (9) must be added to the wavefunction.

The $1\delta_g 2\pi_u$ configuration introduces solely "angular" correlation. In an analogous manner it allows the $2\sigma_g$ orbital to incorporate $1\delta_g$ character and distort off of the line of the nuclei while allowing the $1\pi_u$ orbital to use $2\pi_u$ character and adjust its shape in a manner corresponding to the changes in the $2\sigma_g$ orbital.

Finally, for the sake of completeness we included the

TABLE I. Calculated energies with the two and seven configuration wavefunctions in basis set III.^a All quantities are in Hartree atomic units.^b

R	$E^{(2)}$	$E^{(2)} - E(\infty)$	$E^{(7)}$	$E^{(7)} - E(\infty)$
5.0	-14.79753	0.00027	-14.80474	-0.00694
5.5	-14.80044	-0.00264	-14.80718	-0.00938
5.75	-14.80076	-0.00296	-14.80718	-0.00938
6.0	-14.80059	-0.00279	-14.80670	-0.00890
6.5	-14.79937	-0.00157	-14.80499	-0.00708
8.0	-14.79494	0.00286	-14.79842	-0.00062
9.0	-14.79386	0.00394	-14.79602	0.00178
10.0	-14.79388	0.00392	-14.79510	0.00270
11.0	-14.79434	0.00346	-14.79501	0.00279
12.0	-14.79488	0.00292	-14.79526	0.00254
13.0	-14.79588	0.00432	-14.79560	0.00220
15.0	-14.79615	0.00165	-14.79623	0.00157

^aSee Ref. 17.^bSee Ref. 2.

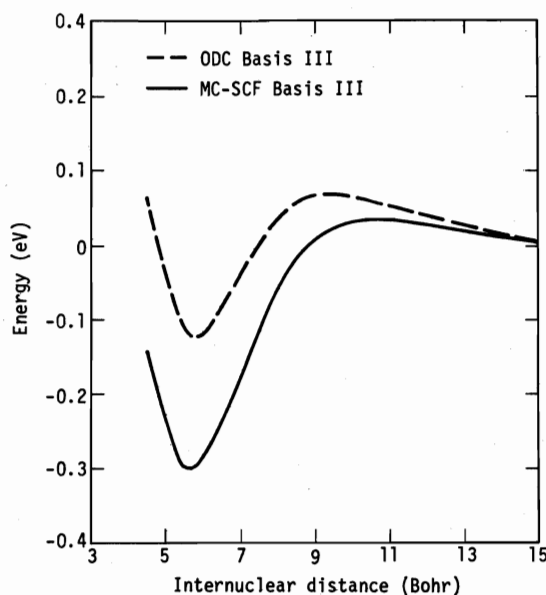
configurations $1\delta_u 1\pi_g$ and $1\delta_u 2\pi_g$, which also describe angular correlation although we expected their contributions to be minor in relation to the others. All linear coefficients and orbitals are then variationally optimized for this multiconfiguration self-consistent field MC SCF wavefunction.¹⁵

Two $3d\delta$ Slater functions on each center were added to basis set I (we call this basis set II).¹⁶ The results of the seven-configuration MCSCF calculations with basis set II are also shown in Fig. 1 along with the HF and ODC results. We see that although there is a marked improvement in the binding energy, now 0.00677 hartree or 0.184 eV, we still account for less than 50% of the experimental binding energy.

In order to further improve the accuracy of the wavefunction it is important to consider the completeness of our basis set. The Be(2^1P) atom has an electronic structure closely resembling that of the Li₂ $B^1\Pi_u$ state with the $2s2p$ singlet-coupled open shell of the atom analogous to the $2\sigma_g 1\pi_u$ configuration of the molecule. A CI calculation on Be(2^1P) by Dunning and Bender,¹⁷ which we have used as a guide in the choice of additional configurations, reveals an anomalous situation similar to the one we find for Li₂ $B^1\Pi_u$. These authors find that

TABLE II. Relative contributions of the terms in the seven configuration wavefunction in basis set III.^a All quantities are in hartree atomic units.^b

R	$2\sigma_g 1\pi_u$	$2\sigma_u 1\pi_g$	$1\delta_g 1\pi_u$	$1\delta_g 2\pi_u$	$1\delta_u 1\pi_g$	$1\delta_u 2\pi_g$	$3\sigma_g 2\pi_u$
5.0	0.96746	-0.16677	-0.14393	-0.10152	-0.01036	-0.00539	0.05896
5.5	0.96496	-0.19064	-0.14196	-0.09435	-0.00993	-0.00539	0.05764
5.75	0.96294	-0.20420	-0.13869	-0.09079	-0.00944	-0.00532	0.05873
6.0	0.95978	-0.22136	-0.13607	-0.08670	-0.00906	-0.00525	0.06062
6.5	0.95129	-0.26044	-0.13000	-0.07809	-0.00784	-0.00500	0.06428
8.0	0.90079	-0.41423	-0.10020	-0.04794	-0.00262	-0.00315	0.06807
9.0	0.86071	-0.49844	-0.07742	-0.03238	0.00292	-0.00137	0.06060
10.0	0.82048	-0.56638	-0.05624	-0.02128	0.00588	-0.00057	0.04877
11.0	0.78727	-0.61395	-0.04009	-0.01413	0.00774	-0.00074	0.03745
12.0	0.76320	-0.64477	-0.02885	-0.00965	0.00842	-0.00116	0.02841
13.0	0.74569	-0.66553	-0.02113	-0.00666	0.00841	-0.00139	0.02141
15.0	0.72545	-0.68801	-0.01212	-0.00333	0.00717	-0.00137	0.01234

^aSee Ref. 17.^bSee Ref. 2.FIG. 2. The ODC and MCSCF potential curves for the $B^1\Pi_u$ state of Li₂.

with a ($4s3p$) Slater basis optimized for the Hartree-Fock configuration and augmented with $3d$ - and $4f$ -functions, a full valence electron CI accounted for only 62% of the valence correlation energy (of 0.029 Hartree). A recent CI calculation on the Be(2^1P) state of Tatewaki, Taketa, and Sasaki,¹⁸ although employing fewer contributions than the previous work, yielded a much improved result, accounting for 86% of the valence correlation energy. The essential difference in the two calculations is the use of a $3p$ Slater function with its exponent optimized for the CI wavefunction. It would thus appear that a $3p$ Slater function plays an essential role in the CI wavefunction for the Be(2^1P) state.

Consequently a $3p\pi$ Slater function was added to basis set II, the orbital exponent being chosen on the basis of the beryllium calculations.¹⁹ In addition, the tightest $2p\sigma$ function was deleted since previous calculations had shown that this function made a negligible contribution. We call this basis set III.²⁰ Using this basis set with the two and seven configuration wavefunction, we ob-

TABLE III. Calculated energies with the seven configuration wavefunction in basis set IV.^a All quantities are in Hartree atomic units.^b

<i>R</i>	<i>E</i> ⁽⁷⁾	<i>E</i> ⁽⁷⁾ - <i>E</i> (∞)
5.5	-14.80888	-0.01108
11.0	-14.79514	0.00266

^aSee Ref. 18.^bSee Ref. 2.

tained the results shown in Fig. 2 and tabulated in Tables I and II. There is a marked improvement in the region about the equilibrium geometry. The seven configuration wavefunction now yields a binding energy of 0.26 eV, which is 68% of the experimental binding energy. Although the two configuration potential curve is also shifted down by a similar amount as the seven configuration curve, it is still a rather poor representation for the Li₂ B¹Π_u state, accounting for only 21% of the experimental binding energy. In going from the two configuration result to the seven configuration result, there is a marked change in the over-all shape of the curve, with a significant lowering of the height of the potential hump from 0.11 eV to 0.077 eV, as well as a shift in the position of the maximum from 9.4 bohr to 10.6 bohr.

Finally, in order to assess the convergence of our results in terms of basis set III, we enlarged our basis set even further by: (1) adding both 3*s*- and 3*p*-functions to the σ-basis and (2) splitting the 3*p*-function in the II set into two functions. We call this basis set IV.²¹ In terms of this basis and with the seven configuration wavefunction, we calculated the Li₂ B¹Π_u energy at *R* = 5.5 bohr and *R* = 11.0 bohr. The results are given in Tables III and IV. From these calculations we find our best binding energy to be 0.3015 eV, or 78% of experimental binding energy. In magnitude this error (0.08 eV) is approximately the same error (0.04 eV) as found in the MCSCF calculations by Das⁴ for the ground state (see Tables III and IV for the results). It is important to note that the energy lowering at *R* = 11.0 bohr with respect to the results with basis set III is minimal (just 0.005 eV). Thus we expect the shape about the hump to be insensitive to any further refinements in the wavefunction.

The accuracy of the potential energy curves about the equilibrium distance is best shown by a comparison of theoretical and experimental spectroscopic constants. These are given in Table V for the ODC and MCSCF wavefunctions. Even the ODC values are in good agreement with experiment, except for the dissociation energy. It should be noted that the experimental values in-

TABLE V. Calculated and experimental spectroscopic constants for the B¹Π_u state of Li₂.^a Basis set III.

	<i>R</i> _e (Å)	<i>D</i> _e (eV)	ω _e (cm ⁻¹)	x _e ω _e (cm ⁻¹)	<i>B</i> _e (cm ⁻¹)	α _e (cm ⁻¹)	<i>k</i> _e × 10 ⁶ (dyn/cm)
ODC	3.05	0.081	240	5.7	0.52	0.01	1.19
MCSCF	2.97	0.26	260	3.8	0.54	0.01	1.39
MCSCF ^b	...	0.302
Exptl ^c	2.934	0.362	269.69	2.74	0.557	0.008	...

^aAll units are defined in Ref. 2.^bBasis set IV.^cSee Ref. 1.

cluding *D*_e are from the older work of Loomis and Nussbaum,¹ and do not represent the best values.⁹

III. LONG RANGE INTERACTION OF Li(²S) AND Li(²P)

At internuclear separations sufficiently large that overlap of the atomic wavefunctions is negligible, the interaction energy for two like atoms in different electronic states can be determined from the first-order dispersion forces.⁵⁻⁷

For Li(²S) + Li(²P) the leading term can be written

$$V(R) = \frac{|\langle {}^2S|x|{}^2P \rangle|^2}{R^3}$$

The transition moment $\langle {}^2S|x|{}^2P \rangle$ was determined to be 2.378 a. u. by Weiss²² using a Hartree-Fock wavefunction of comparable accuracy to the present calculations. The potential *V*(*R*) is compared to the calculated potential in Fig. 3. As expected, the dispersion forces overestimate the potential energy in the region of the barrier due to the neglect of the overlap or bonding effects beginning to appear at this internuclear distance. However, for *R* > 15 bohr the calculated potential and the first-order interaction agree remarkably well. Weiss²² has also determined the transition moment from an accurate CI wavefunction. The more accurate value for $\langle {}^2S|x|{}^2P \rangle$ is 2.355 a. u., which is a negligible difference on the scale of our plot in Fig. 3.

IV. THE ORBITALS OF THE Li₂ B¹Π_u STATE

In order to examine the changes in the wavefunction as we bring the two atoms together, the σ and π open-shell orbitals are plotted in Fig. 4 at internuclear separations of 15, 9, and 6 bohr.²³ From the figure we see that the σ-orbital delocalizes slowly onto the opposite center until the barrier is reached. After this, the σ-orbital hybridizes significantly toward the other center to form a stronger one-electron bond (as in Li₂⁺). In turn, the π-orbital adjusts to these changes in the σ-orbital [with which it interacts via a repulsive (*J* + *K*)-po-

TABLE IV. Relative contributions of the terms in the seven configuration wavefunction in basis set IV.^a All quantities are in Hartree atomic units.^b

<i>R</i>	2σ _g 1π _u	2σ _u 1π _g	1δ _g 1π _u	1δ _g 2π _u	1δ _u 1π _g	1δ _u 2π _g	3σ _g 2π _u
5.5	0.96852	-0.18139	-0.12587	-0.09596	-0.00995	0.00520	0.06240
11.0	0.78944	-0.16054	-0.04297	-0.01480	0.00810	-0.00068	0.04355

^aSee Ref. 18.^bSee Ref. 2.

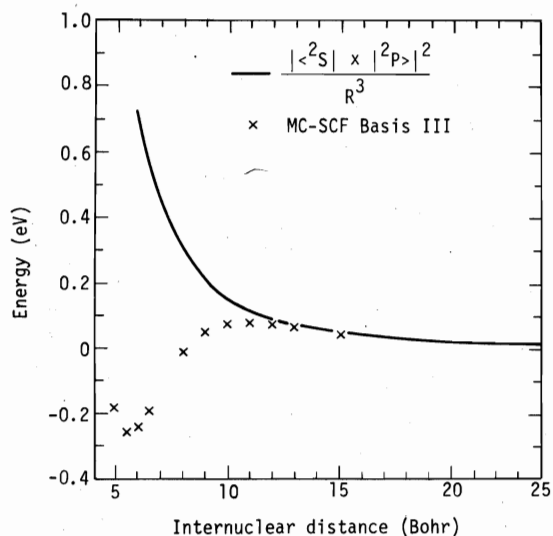


FIG. 3. Comparison of the long range behavior of the MCSCF potential curve (crosses) with that predicted by dispersion forces (solid line).

tential] by becoming more diffuse. It is here that the $3p\pi$ function is important. It allows amplitude near the internuclear axis to diminish, thus reducing the σ - π repulsion.

V. SUMMARY

We find that the barrier in the $B^1\Pi_u$ potential curve has its maximum at $R=10.6$ bohr and that the height is 0.00266 hartree or 0.0724 eV. While this value is outside the range of error for the experimental value of 0.115 ± 0.036 eV, as given by Velasco *et al.*,⁸ the final experiment value depends on the accuracy of the dissociation energy for the Li₂ $B^1\Pi_u$ state. Upon reanalyzing the experimental data of Loomis and Nusbaum,¹ Gaydon²⁴ suggests that perhaps larger error bounds would be safer. Alternatively, because the correlation errors remaining in our wavefunction should increase with decreasing R , we expect the theoretical value of the height of the barrier to be an upper bound on the experimental value.

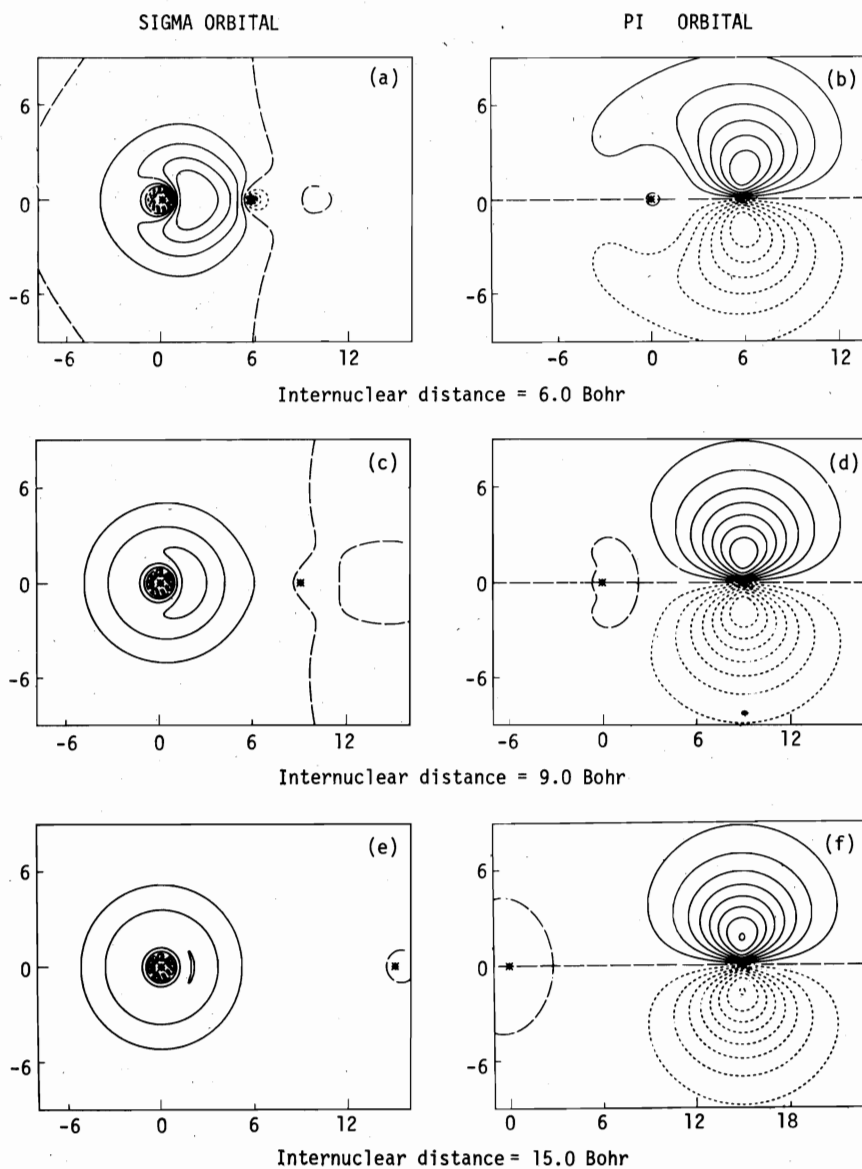


FIG. 4. Orbital contour plots of the open shell σ - and π -orbitals at internuclear distances of 6, 9, and 15 bohr. Long dashes indicate zero amplitude; other contours are separated by increments of 0.05 a.u.

The recent work of Hessel and Vidal⁹ has confirmed this prediction, finding a barrier height of 0.065 eV with error limits of ± 0.0025 eV. In a recent study of the dissociation energy of Li₂, Stwalley²⁵ suggests 1.046 ± 0.012 eV as a best value for the dissociation energy of Li₂. From this he obtains 0.074 ± 0.042 eV as the barrier in the potential curve for the B state.

After the present calculations were completed,¹⁰ Olson and Konowalow²⁶ carried out calculations on the B¹Π_u state using an ODC wavefunction and what they call a partial optimized valence configuration (POVC) wavefunction. Their ODC calculation predicts a barrier height of 0.11 eV, in agreement with our ODC results; their POVC calculation gives a barrier of 0.087 eV. Their best value for the dissociation energy was only 42% of the experimental value. The trend is quite clear. As the wavefunction is improved so as to approach the exact wavefunction for the B¹Π_u state, the value of the barrier decreases, with the best value being 0.0724 eV given by our MCSCF calculation.

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¹²Basis set I: 1s(4.699, 2.478), 2s(1.770, 0.810, 0.643), 2pσ(2.869, 1.203, 0.512), 3dσ(0.70), 2pπ(2.869, 1.203, 0.512), 3dπ(0.70).

¹³We define the binding energy D_e as the energy difference between the separated-atoms energy and the energy at the minimum in the potential energy curve.

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¹⁶Basis set II consists of basis set I plus 3dδ(1.32, 0.60).

¹⁷T. H. Dunning and C. F. Bender (unpublished results).

¹⁸H. Tatewaki, H. Taketa, and F. Sasaki, *Int. J. Quant. Chem.* **5**, 335 (1971).

¹⁹The 3pπ orbital exponent was chosen to be in the same ratio to the most diffuse 2pπ exponent, as found for Be(¹P).

²⁰Basis set III: 1s(4.699, 2.478), 2s(1.770, 0.810, 0.643), 2pσ(1.203, 0.512), 3dσ(0.70), 2pπ(2.869, 1.203, 0.512), 3pπ(0.61), 3dπ(0.70), 3dδ(1.32, 0.60).

²¹Basis set IV: 1s(4.699, 2.478), 2s(1.770, 0.810, 0.643), 2pσ(1.203, 0.512), 3s(0.56), 3pσ(0.61), 3dσ(0.70), 2pπ(2.869, 1.203, 0.512), 3pπ(1.12, 0.51), 3dπ(0.70), 3dδ(1.10, 0.50).

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²⁴By σ-orbitals we mean the localized orbitals ($2\sigma_g + \lambda 2\sigma_u$) and by π-orbitals we mean the localized orbital ($1\pi_u - \lambda 1\pi_g$) from the ODC wavefunction.

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