

## A Two-Electron Model for the $\text{Li}_2$ Molecule

UGO PINCELLI and BENIAMINO CADIOLI

Istituto di Chimica-Fisica, Università di Modena, Italia

GIUSEPPE DEL RE

Gruppo di Chimica Teorica del C.N.R., Roma, Italia

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The inclusion of complete orthogonalization to the inner shell in the simple non-empirical treatment of Ref. [1] has been studied with special reference to energies. The comparison with experimental data for  $\text{Li}_2$  is also discussed.

In a previous paper [1] a systematic study of a simple two-electron model of a homonuclear bond was given, emphasis being placed on hybridization and "correlation" at different internuclear distances. According to the formal nature of that study, no attempt was made to interpret the results in connection with actual physical systems, but it was remarked that use of a basis of atomic orbitals corresponding to the  $L$ -shell did not ensure a reasonable description of a bond between, say, Lithium atoms; complete orthogonalization to the inner shell MO's [2, 3] was necessary, even intra-atomic orthogonalization being unsatisfactory. The problem of orthogonality to the inner shells is one of two questions peculiar of treatments limited to valence electrons, the other being the choice of an appropriate Hamiltonian. Discussions of both problems can be found in the literature [2–8], but are usually given in the context of very complicated problems. Therefore, we present here a completion of Ref. [1] giving the results obtained when complete orthogonalization is introduced and an interpretation of the model bond treated as an actual (Li–Li) bond. As could be expected for a system where the core and valence electrons are well separated [9, 10], the simple non-empirical treatment is more effective than an all-electron limited-basis SCF calculation.

The choice of the effective Hamiltonian need not be discussed in the present case, because it becomes crucial only with heteronuclear bonds; we have used a hydrogen-like Hamiltonian with an effective nuclear charge of 1.30. The basis used here consists in the set of the four  $2s$  and  $2p$  Slater orbitals (STO) centred on the two nuclei A and B, as in Ref. [1], and in two  $1s$  STO's having the same orbital exponents ( $\alpha$ ) as the  $2s$  and  $2p$  orbitals; these additional orbitals do not increase the size of the basis, because they are used to satisfy additional conditions, in particular intra-atomic orthogonality in one series of calculations ( $B$ ) and complete orthogonality to the inner-shell MO's in another series ( $C$ ). The molecular orbitals used were the normalized sums or differences of atomic orbitals having the forms

$$2s_X + \mu 1s_X, \quad 2p_X + \mu' 1s_X \quad (X = A, B) \quad (1)$$

(or combinations thereof) with appropriate normalization constants. The parameters  $\mu$  and  $\mu'$  are contributions to the given atomic orbital of the  $1s$  Slater orbital having the same exponent. They are zero if the existence of the inner shells is neglected (case *A* of Ref. [1] reported here for comparison) but take non-zero values if orthogonality to the inner atomic or molecular shells (cases *B* and *C*, respectively) is imposed. The calculations have been carried out using the exact integrals on four types of functions: 1) the one determinant function over pure  $s$  orbitals, 2) the one-determinant function over hybrids with different degrees of hybridization, 3) the two-determinant function corresponding to the same hybrids in bonding and antibonding molecular orbitals, and 4) the complete CI function. The molecular orbitals over hybrids depend on a hybridization angle  $\varphi$ . The inner core  $1s$  orbitals – not to be confused with those appearing in Eq. (1) – have been assigned the current orbital exponent 2.70.

Table 1. Approximations of the ground-state electronic energy (a.u.) for two electrons in the field of two equal positive ions with effective charge 1.30 (see text):  $E_1$ , energy for a single determinant over MO's obtained from pure- $s$  AO's;  $E_2$ , idem, with optimum hybrids;  $E_3$ , idem, for best CI on the basis of one hybrid per atom;  $E_4$ , complete CI on the basis of the four AO's. The results are given for the three cases considered in the text: no orthogonality (*A*), intra-atomic orthogonality (*B*), and inter-atomic or "complete" orthogonality (*C*) to the inner core MO's, at different values of  $q = 0.65 R$ ,  $R$  being the internuclear distance in a.u.

	$q$	2.5	3	3.5	4	4.5	6
<i>A</i>	$-E_1$	1.1367	1.0722	1.0131	0.9613	0.9172	0.8244
	$-E_2$	1.2211	1.1189	1.0401	0.9768	0.9262	0.8268
	$-E_3$	1.2212	1.1229	1.0479	0.9912	0.9497	0.8795
	$-E_4$	1.2230	1.1244	1.0493	0.9929	0.9516	0.8813
<i>B</i>	$-E_1$	0.9721	0.8942	0.8480	0.8037	0.7633	0.6688
	$-E_2$	1.1633	0.9878	0.9087	0.8442	0.7913	0.6799
	$-E_3$	1.1643	0.9878	0.9095	0.8468	0.7964	0.7001
	$-E_4$	1.2002	0.9887	0.9108	0.8482	0.7982	0.7019
<i>C</i>	$-E_1$	0.8332	0.8165	0.7943	0.7675	0.7390	0.6614
	$-E_2$	0.8744	0.8601	0.8317	0.7960	0.7603	0.6711
	$-E_3$	0.8759	0.8622	0.8352	0.8014	0.7685	0.6952
	$-E_4$	0.8781	0.8633	0.8365	0.8030	0.7707	0.6970

Table 2. "Hybridization" ( $E_1 - E_2$ ) and "Correlation" effects ( $E_2 - E_4$ ) in cases *A* and *C*, and per cent (*H*) of total correlation accounted for by "partial" correlation  $E_2 - E_3$  in cases *A*, *B*, *C*. The symbols are explained in Table 1

$q$		2	2.5	3	3.5	4	4.5	6
$E_1 - E_2$	<i>A</i>	0.1496	0.0841	0.0467	0.0270	0.0156	0.0090	0.0024
	<i>C</i>	0.0262	0.0412	0.0436	0.0374	0.0285	0.0213	0.0097
$E_2 - E_4$	<i>A</i>	0.0011	0.0019	0.0055	0.0092	0.0161	0.0254	0.0545
	<i>C</i>	0.0030	0.0037	0.0032	0.0048	0.0070	0.0104	0.0259
<i>H</i>	<i>A</i>	47	5	73	85	89	93	97
	<i>B</i>	45	3	0	38	65	74	92
	<i>C</i>	56	41	66	73	77	79	93

The energies obtained for different values of the parameter  $q = \alpha R$  are reported in Table 1, the subscripts 1, 2, 3, 4, referring to the four functions just mentioned. An analysis of Table 1 is presented in the subsequent tables. Table 2 presents an attempt to separate the difference between the "exact" energy ( $E_4$ ) and the reference pure- $s$  energy ( $E_1$ ) into "hybridization" and "correlation" effects. The latter show the expected regular increase with the internuclear distance. The former decrease regularly with  $q$  in case *A*, but show a maximum around  $q = 3$  in case *C*, *i.e.* when orthogonalization taking the inner core completely into account is introduced. This throws some light on the debated question of hybridization in the chemical bond. Mathematically speaking, the existence of a maximum of the hybridization effects only in case *C* is a simple consequence of orthogonalization. In case *A* the lowest molecular orbital obtained from our scheme tends to a  $1s$ -like orbital of the united atom, and, therefore, its  $p$  character increases all the way reaching a maximum at  $R = 0$ ; in case *C* the united-atom limit must be again a  $2s$  orbital, and, therefore, hybridization is not imposed by characteristics of the limits, but must be interpreted as a special physical effect. In the naïve orbital picture, the origin of correlation and hybridization effects can be traced back to the relative positions of the diagonal elements of the one-electron Hamiltonian in the MO basis. Hybridization is more important the closer the elements corresponding to the same symmetry, whereas correlation, as is well-known, properly depends in the same way on the relative positions of elements corresponding to different symmetries.

An analysis of "partial" correlation (obtained from CI over one hybrid per atom) is also given in Table 2. Partial correlation accounts for a minor part of correlation only when the latter is very small; so that, as is illustrated in Table 3, hybridization and partial configuration interaction account for practically all the energy in all the calculations, at all distances [11, 12]. The inaccuracies vary between 0.07 and 0.03 eV. The minimum energy hybrids coincide with the maxi-

Table 3. Per cent of  $E_1$ ,  $E_2$  and  $E_3$  with respect to  $E_4$  in cases *A*, *B* and *C* at selected values of  $q$  (cf. Table 1)

$q$	3			5			7		
<i>A</i>	95.4	99.5	99.9	95.5	96.1	99.8	92.0	92.1	99.9
<i>B</i>	90.5	99.9	99.9	95.9	98.6	99.7	93.5	94.5	99.8
<i>C</i>	94.6	99.6	99.9	95.9	98.0	99.7	93.2	94.1	99.7

Table 4. Differences in overlap between pure orbitals and hybrids corresponding to  $E_2(AS_n)$  and between the latter and maximum-overlap hybrids ( $AS_m$ ), at various values of  $q$

$q$	2.5	3	3.5	4	5	6
$AS_n$ <i>A</i>	0.2321	0.3017	0.2611	0.1677	0.0785	0.0407
<i>B</i>	0.1381	0.2157	0.3219	0.3125	0.2017	0.1163
<i>C</i>	-0.0660	0.1527	0.2760	0.2908	0.2031	0.1152
$AS_m$ <i>A</i>	0.0239	0.0214	0.1047	0.2129	0.2441	0.2185
<i>B</i>	0.0543	0.0515	0.0000	0.0358	0.1247	0.1357
<i>C</i>	0.1600	0.0373	0.0005	0.0384	0.1241	0.1389

mum-overlap ones around  $q = 3$ , which happens to be very close to the equilibrium distance for  $\text{Li}_2$  (Table 4).

The potential energy curves obtained by adding to the electronic energy resulting from our calculations (case C) the nuclear repulsion calculated with the effective nuclear charges used in the electronic Hamiltonian are presented in the figure. In order to discuss them with reference to the  $\text{Li}_2$  molecule, we recall that the experimental data concerning this system are:  $R_e = 5.051$  a.u.;  $D_e = 1.05$  eV;

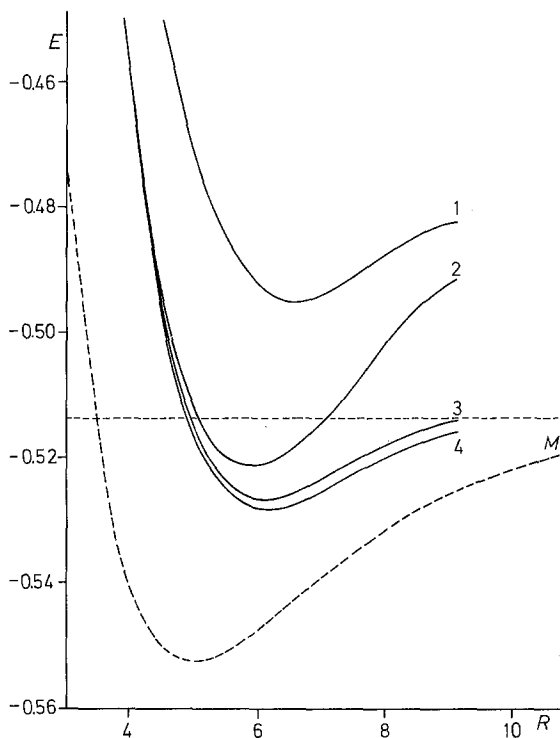


Fig. 1 Potential energy curves obtained from the electronic energies of Table 1 and a nuclear repulsion energy corresponding to nuclei with effective charges 1.30. The empirical Morse curve for  $\text{Li}_2$  is denoted by  $M$

$\omega_e = 351 \text{ cm}^{-1}$  [13]. The distances for which our energy curves show their minima in the four approximations are: 6.69, 6.00, 6.18, 6.23 a.u. respectively. The dissociation energies, calculated as the differences between the energy of the valence electrons in the separated atoms ( $2E_{2s} = -0.5152$  a.u.) and the total energies at the minima are  $-0.54$ ,  $0.17$ ,  $0.32$  and  $0.36$  eV, respectively. This sequence proves that hybridization is already sufficient for inverting the absurd result obtained with pure orbitals. The  $D_e$  value computed with the single-determinant function over hybrids ( $0.17$  eV) corresponds strictly to that found in a SCF all-electron calculation ([14] quoted in [15]). This supports the idea of the separability between core and valence electrons in  $\text{Li}_2$  (see also the results for  $D_e$  and  $R_e$  of a calculation using the pseudopotential method [8]). As could be expected, a much better agreement is obtained when correlation is taken into account; the inclusion

of correlation is also necessary, of course, on order to obtain a satisfactory dissociation limit. The agreement for the quantity  $\omega_e$  is particularly good: the third and fourth trial functions give  $338$  and  $317 \text{ cm}^{-1}$ , respectively.

In conclusion, the most important points suggested or confirmed by the present results are:

1. Hybridization may be just an artificial feature of a special calculation scheme, as in our cases *A* and *B*; but it can be a genuine correction to a first approximation, as in the completely orthogonalized treatment *C*. Even in the latter case, it is a very important effect for first-row atoms.

2. Unless a really sophisticated *ab initio* calculation is carried out (with all the accompanying difficulties of interpretation) a simplified but rigorous scheme may account as satisfactorily for the properties of a single bond as a medium size all-electron calculation.

3. A further simplification of the complete CI scheme used here lies in the fact that only one hybrid per atom is required to give practically precise results for the ground state, if partial CI is allowed.

In order not to complicate the interpretation of the various effects, the orbital exponents of the calculations discussed so far have been kept constant and equal to some "atomic" values. Relaxation of this limitation does improve the agreement with experiment. (The predicted dissociation energy with the orbital exponent treated as a variational parameter at all distances gives about  $0.49 \text{ eV}$ , for an equilibrium distance close to  $5.8 \text{ a.u.}$ ) but does not introduce any novelty as regard to the above conclusions. On the other hand, it may be important for a discussion of the electron densities to which further studies will be devoted.

## References

1. Cadioli, B., U. Pincelli, and G. Del Re: *Theoret. chim. Acta (Berl.)* **10**, 393 (1968).
2. Mulliken, R. S.: *J. chem. Physics* **19**, 912 (1951).
3. Coulson, C. A., and G. R. Lester: *Trans. Faraday Soc.* **51**, 1605 (1955).
4. Slater, J. C.: *Physic. Rev.* **36**, 57 (1930).
5. Goepfert-Mayer, M., and A. L. Sklar: *J. chem. Physics* **6**, 645 (1938).
6. McWeeny, R., and K. A. Ohno: *Proc. Roy. Soc. (London)* **A 255**, 367 (1960).
7. Gombas, P.: *Pseudopotentials*. Berlin-Heidelberg-New York: Springer 1967.
8. Szasz, L., and G. McGinn: *J. chem. Physics* **48**, 2997 (1968).
9. Das, G., and A. C. Wahl: *J. chem. Physics* **44**, 87 (1966).
10. — *J. chem. Physics* **46**, 1568 (1967).
11. Shull, H.: *J. chem. Physics* **30**, 1405 (1959).
12. Davidson, E. R., and L. L. Jones: *J. chem. Physics* **37**, 2966 (1962).
13. Herzberg, G.: *Spectra of diatomic molecules*. New York: van Nostrand 1950.
14. Ransil, B. J.: *Rev. modern Physics* **32**, 245 (1960).
15. Wahl, A. C., P. J. Bertocini, G. Das, and T. L. Gilbert: *Int. J. quant. Chemistry* **1** S, 123 (1967).

Dott. B. Cadioli  
Istit. Chimica-Fisica dell' Università  
Via Campi, 183, Modena, Italy