

# Hybridization and Correlation in a Model Calculation of a Two-Electron Bond

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The paper presents a quantitative examination of some aspects of the molecular two-electron problem, using a calculation for a two-electron homonuclear bond based on a restricted set of one  $2s$  and one  $2p$  orbital per nucleus. The single-determinant approximations with pure  $2s$  STO's and with hybrid AO's are considered, as well as "partial" configuration mixing (CI) over MO's involving one hybrid per atom and "complete" CI over the whole four-orbital basis. The calculations simulate an exact calculation as regards hybridization and (left-right) correlation effects. These are studied, for the lowest state, at various distances, introducing the axial electron density as a means for interpreting quantitatively the various effects. The importance of orthogonalizing the  $2s$  AO's to the corresponding  $1s$  AO's and the MO's used to the MO formed by  $1s$  AO's is reviewed, pending further numerical analysis.

Eine Untersuchung des molekularen 2-Elektronenproblems wird vorgenommen, wobei die 2-Elektronenbindung zwischen gleichen Molekülen mit einem beschränkten Satz eines  $2s$ - und eines  $2p$ -Orbitals pro Kern berechnet wird. Es wird sowohl die Eindeterminantennäherung mit reinen  $2s$ -STO's und Hybrid AO's als auch „partielle“ CI mit einem Hybrid pro Atom und schließlich „vollständige“ CI über die gesamte 4-Orbitalbasis durchgeführt. In bezug auf die Hybridisierung und die Korrelationseffekte (links-rechts) simulieren die Rechnungen eine exakte Berechnung. Für den tiefsten Zustand werden diese Effekte bei verschiedenen Abständen untersucht, wobei die axiale Elektronendichte zur quantitativen Interpretation der verschiedenen Effekte eingeführt wird. Die Notwendigkeit der intra- und interatomaren Orthogonalisierung bezüglich der Rumpfindegrale wird diskutiert.

On présente une analyse quantitative de quelques aspects du problème moléculaire, à partir d'un calcul pour une liaison homonucléaire à deux électrons avec une base limitée d'une orbitale  $2s$  et une orbitale  $2p$  par noyau. On prend en considération les approximations à un seul déterminant avec des orbitales  $2s$  de Slater pures et avec des hybrides; et l'interaction des configurations «partielle» (une hybride par atome) et «complète» (toute la base mentionnée). Les calculs simulent un calcul exact en ce qui concerne les effets d'hybridation et de corrélation (left-right). Ceux-ci sont étudiés, pour l'état le plus bas, à différentes distances, la densité électronique axiale servant pour interpréter quantitativement les différents effets. On discute l'importance de l'orthogonalisation intra-atomique et interatomique par rapport aux orbitales du coeur.

## Introduction

In recent years, the attempts to treat complicated saturated molecules have largely centered on the idea that a good starting point should be provided by functions describing electron pairs localized between two nuclei – fully in line with the classical theory of Lewis. Several points in this approach deserve further analysis and illustration. They reduce essentially to the question: how should an electron pair be treated, as a first approximation, or, better, as an idealization of

a bond, in order to give a satisfactory starting point for a reliable calculation, and, at the same time, in order to satisfy the need for visualization that especially the theoretical organic chemist feels so deeply?

To a large extent, the question thus posed amounts to asking, on one hand, that the pair function introduced should include as much as possible of the *intra-bond* contributions to the molecular properties, and hence contain correlation; on the other hand, that it be practically a single determinant built out of simple LCAO MO's, so that the usual interpretation and visualization be applicable to it (or that some picture having more or less the same advantages, and not requiring a complete revision of previous studies, be introduced in its place).

The two requirements are contradictory to a large extent: for correlation corrections are just called in, by and large, to denote important effects that cannot be accounted for by an orbital picture – the latter being the only visualizable picture in so far as it introduces three space coordinates at a time. A general study of the whole problem arising in this way has been given by Mulliken [1], with several numerical examples. However, some aspects of it (especially hybridization and correlation at varying distances) cannot be effectively illustrated on existing calculations, because the latter relate either to diatomic molecules with all their electrons [2], or to approximations whose effect cannot be easily predicted [3], or, finally, to the hydrogen molecule, where one has in fact one electron pair, but the atoms come into play essentially with their  $1s$  functions, certain corrections like hybridization [4] being relatively unimportant.

In the absence of further information, we have considered it worth the while to study systematically the simplest form of the two-electrons-two-nuclei problem in an idealized and simplified but *internally rigorous and consistent* way. More precisely, we have considered a system of two electrons in the field of two equal nuclei, treated on a basis of  $2s$  and  $2p\sigma$  orbitals with partial and 'complete' configuration mixing (CI). The very simplicity of the problem makes a systematic study of it very instructive; the more so, because CI can simulate the introduction of correlation, while the fact that we have  $2s$  and  $2p\sigma$  orbitals allows a study of hybridization in a case where it should not be so small as in the hydrogen molecule. A study somewhat complementary to ours has been recently published [5].

### General Comments on the Calculations

In a model calculation like ours it is advisable to start by ignoring the  $1s$  core orbitals; therefore, the  $2s$  orbitals have not been made orthogonal to the  $1s$  orbitals, nor, which is more important, to the  $1\sigma$  bond orbitals of the core. The consequences of this will be discussed below.

We call our calculation a model in the following sense: given the four Slater orbitals mentioned above,  $2s_A$ ,  $2s_B$ ,  $2p\sigma_A$ ,  $2p\sigma_B$ , with A and B equal atomic cores having some appropriate effective charge, we consider this minimal set formally as a complete set and consider all the singlet configurations symmetric with respect to the centre of symmetry of the system, thus carrying out formally a complete calculation for the states of the given symmetry. Using the letters  $s$  and  $p$  to denote the kind of orbitals, and the letters  $g$  and  $u$  to denote their symmetry with respect to an inversion of the nuclei, we can denote the four basic molecular orbitals by

$$sg, su, pg, pu, \quad (1)$$

where, *e.g.*,  $sg$  stands for  $\frac{1}{\sqrt{2(1+S_{ss})}} (2s_A + 2s_B)$ , (2)

and  $S_{ss}$  is the overlap integral between the  $2s_A$  and  $2s_B$  AO's.

The configurations that can be built from the orbitals (1) with  $g$  symmetry are evidently six, which we shall denote as follows:

$$\begin{aligned} V_1 &= \frac{1}{\sqrt{2}} \{sg(1), \overline{sg}(2)\}, \\ V_2 &= \frac{1}{\sqrt{2}} \{pg(1), \overline{pg}(2)\}, \\ V_3 &= \frac{1}{2} [\{sg(1), \overline{pg}(2)\} + \{pg(1), \overline{sg}(2)\}], \\ V_4 &= \frac{1}{\sqrt{2}} \{su(1), \overline{su}(2)\}, \\ V_5 &= \frac{1}{\sqrt{2}} \{pu(1), \overline{pu}(2)\}, \\ V_6 &= \frac{1}{2} [\{su(1), \overline{pu}(2)\} + \{pu(1), \overline{su}(2)\}]. \end{aligned} \quad (3)$$

Here, as is conventional, different spins are denoted by the presence or the absence of a bar; only the main diagonal is given to represent each Slater determinant, and all the determinants are normalized; however, the set of the six configurations is not orthonormal. The reason for this is, of course, that the pairs of orbitals  $sg$ ,  $pg$  and  $su$ ,  $pu$  are not orthogonal to one another. Of course, they can be made so by suitable hybridization, but this involves an elaboration unnecessary for the calculations as such. The overlap matrix of the set chosen is given by:

$$\begin{aligned} (V_1, V_1) &= (V_2, V_2) = (V_4, V_4) = (V_5, V_5) = 1; \\ (V_3, V_3) &= 1 + t_g^2; \quad (V_6, V_6) = 1 + t_u^2; \\ (V_1, V_3) &= (V_2, V_3) = (V_3, V_1) = (V_3, V_2) = \sqrt{2} t_g; \\ (V_3, V_6) &= (V_4, V_6) = (V_6, V_3) = (V_6, V_4) = \sqrt{2} t_u, \end{aligned} \quad (4)$$

where the parentheses denote integration over the whole configuration-spin space, and

$$\begin{aligned} t_g &= (sg, pg), \\ t_u &= (su, pu), \end{aligned}$$

are overlap integrals between molecular orbitals. All the  $(V_i, V_j)$  integrals not given in (4) are zero.

Coming now to the actual computational work, we point out that, granted the double idealization consisting in treating only two electrons with a four-orbital basis, no approximations need be introduced, for all the required integrals can be found in the literature [6], or calculated quite easily, including exchange integrals. Of course, there are some parameters (not considered as variational ones) on which the various quantities depend; they are:

- the orbital exponent  $\alpha$ ;
- the internuclear distance  $R = \frac{\rho}{\alpha}$ ;
- the effective nuclear charge  $Z$ .

The latter parameter has forced us to refer to actual atoms in choosing  $\alpha$  and  $Z$ . We have done so, referring to Lithium ( $\alpha = 0.65$ ,  $Z = 1.30$ ). Therefore, our model is strictly related to a real bond, even though we have allowed  $\rho = \alpha R$  to vary over a wide range of values; however, we have ascertained that our general conclusions hold also for bonds with different  $Z$  and  $\alpha$  values.

So far, we have not mentioned hybridization. It is a common tenet that hybridization reduces the importance of configuration mixing. A discussion of this statement has been given in Ref. [1], but, again, further numerical analysis of the matter is desirable, especially as regards  $L$ -shell orbitals.

Mathematically speaking, the relation between hybridization and CI can be seen very easily by remarking that the introduction of hybrids with use of just one Slater determinant corresponds to a special reduced CI. For instance, considering the  $g$  molecular orbitals between hybrids of parameter  $\lambda = \text{tg } \phi$ , we have:

$$N\{a\,s\bar{g}(1) + b\,p\bar{g}(1), a\,s\bar{g}(2) + b\,p\bar{g}(2)\} = N\{a^2 V_1 + b^2 V_2 + ab\sqrt{2} V_3\}, \quad (5)$$

where

$$a = \sqrt{2(1 + S_{ss})} \cos \phi, \quad b = \sqrt{2(1 + S_{pp})} \sin \phi, \quad N = \frac{1}{2(1 + S_{hh})}, \quad (6)$$

with  $S_{ss}$ ,  $S_{pp}$ , and  $S_{hh}$  the overlap integrals between the orbitals indicated as subscripts, on atoms A and B, respectively ( $h$  denotes the hybrid AO  $\cos \phi(2s) + \sin \phi(2p\sigma)$ ). It is clear that for hybridization to account for most of the properties of our model very special circumstances must take place. In the general case the coefficients of  $V_1$ ,  $V_2$ ,  $V_3$  in the wave function will not be related in this simple way with vanishing coefficients of  $V_4$ ,  $V_5$ ,  $V_6$ . We are, of course, interested in the conditions under which this is at least approximately so.

It is easily seen that the situation here is entirely parallel to the situation one has in connection with correlation proper, the hybrids playing the rôle of the Hartree-Fock orbitals (expanded as LCAO MO's), our 'complete' configuration mixing on the four AO's given playing the rôle of actual CI.

## Results and Discussion

In the following, we shall consider only results relating to the ground states, unless otherwise stated.

### 1. Effect of Hybridization

We can consider as the reference calculation, in our model, a single-determinant calculation involving only the  $2s$  orbitals. We shall then assign to hybridization the differences between that simplest description of the two-electron bond and the description obtained by replacing the  $2s$  orbitals by hybrids with  $\sin \phi$  varying from 1 to  $-1$ . The energies obtained in this way are given as functions of  $\rho = \alpha R$  and of the hybridization parameter  $\lambda = \text{tg } \phi$  (see Eq. (5)) in Table 1.

One sees immediately that the energy of the one-determinant approximation is very sensitive to changes in hybridization. In every case, hybrids pointing towards one another give a lower energy than hybrids pointing away from the bond; but only for low  $\rho$ 's does hybridization result in a significant stabilization of the bond, the value of  $\lambda$  for which the energy is lowest tending to 0 quite rapidly for increasing  $\rho$ 's. Although we shall not discuss here cases with  $Z$  and  $2\alpha$  other

Table 1. *Electronic energies<sup>a</sup> in a single determinant approximation over hybrids with different p-characters and different values of  $\varrho$  (see text)*

$\varrho$ tg $\phi$	1	2	3	4	5	6	7
$+\infty$	-1.598	-1.117	-0.867	-0.727	-0.638	-0.576	-0.528
4.83	-1.747	-1.247	-0.949	-0.780	-0.675	-0.603	-0.550
2.31	-1.705	-1.320	-1.017	-0.833	-0.717	-0.639	-0.583
1.33	-1.617	-1.350	-1.071	-0.885	-0.766	-0.686	-0.630
0.75	-1.513	-1.342	-1.110	-0.939	-0.824	-0.748	-0.696
0	-1.301	-1.202	-1.072	-0.961	-0.880	-0.824	-0.768
-0.75	-1.030	-0.857	-0.761	-0.707	-0.671	-0.644	-0.624
-1.33	-0.858	-0.699	-0.648	-0.617	-0.591	-0.568	-0.547
-2.31	-0.784	-0.740	-0.679	-0.627	-0.584	-0.549	-0.519
-4.83	-1.100	-0.928	-0.771	-0.673	-0.606	-0.556	-0.517
$-\infty$	-1.598	-1.117	-0.867	-0.727	-0.638	-0.576	-0.528

<sup>a</sup> in a. u.

than 1.30, we repeat that this behaviour is typical of other values of  $Z$  and  $\alpha$  – i.e., takes place also for the corresponding models of bonds like C–C, N–N, etc.: for larger  $\varrho$ 's an isolated bond is described, in a single determinant approximation, by a combination of pure  $2s$  orbitals. Considering the important rôle assigned to hybridization in the current qualitative theory of the chemical bond, one can reconcile the latter with this result by concluding that the equilibrium distances usually correspond to low values of  $\varrho$ , and/or that hybridization is mainly an *inter-bond* effect characteristic of polyatomic molecules. The first conclusion is supported by the circumstance that, if our calculations are referred to the  $\text{Li}_2$  molecule, the equilibrium distance corresponds to  $\varrho = 3.28$ ; around this value not only is hybridization a major factor in the stabilization of the system, but the hybrids for which the electronic energy is at a minimum are maximum-overlap hybrids. As regards the second remark, one need just recall that the situation corresponding to the minimum of energy for a fictitious isolated two-electron bond at a given  $\varrho$  does not correspond necessarily to the situation of the same bond in a polyatomic molecule.

Coming back to Table 1, one may wonder why should hybridization be important only at low values of  $\varrho$  (see also Table 2). The explicit calculation of the appropriate limit gives answer to this: for  $\varrho \rightarrow 0$ , one tends to the united atom, for which, as we have not imposed any orthogonality with respect to  $1\sigma g$  MO, the lowest state is the limit of a  $pg$  molecular orbital, i.e. essentially a  $1s$  orbital. Thus, we find again a well-known result, that the  $sg$  orbital for the atoms at large distances goes over to an  $s$  orbital of the united atom; our results illustrate the fact that this takes place through a gradual increase in the  $p$ -character of the two AO's forming the bond, which become pure  $2p\sigma$  orbitals at very low values of  $\varrho$ .

Shifting our point of view, we can imagine that changes in  $\varrho$  correspond to an actual physical process of slow motion of the atoms involved. In this perspective we have interest in formulating some sort of mechanism for the important "orbital adaptation" that takes place especially around small values of  $\varrho$ .

A number of quantities associated with the minimum-energy hybrids for different values of  $\varrho$  are given in Table 2. The optimum-hybrid energies for the

various  $q$ 's are not strongly correlated with the overlap integrals (while the  $sg$  energies are); one can only add to a previous remark that just around the equilibrium distance of  $\text{Li}_2$ , where  $q = 3.28$ , the difference between the overlap corresponding to the optimum hybrids and the overlap for pure  $2s$  orbitals is at a maximum.

A very important index of the effect of hybridization is perhaps a quantity  $d$  defined as the ratio between the squares of the  $g$  hybrid ( $hg$ ) and  $sg$  MO's along the internuclear axis *between* the nuclei:

$$d = \frac{1 + S_{ss}}{1 + S_{hh}} \cos^2 \phi (1 + \sqrt{3} \operatorname{tg} \phi)^2, \quad (7)$$

this quantity is independent of the position considered, and follows a trend indicating that hybridization tends to concentrate the charge between the nuclei, with respect to a pure- $s$  MO as the nuclei come closer to each other, without changing the shape of the curve axial density *vs.*  $q$ . A more detailed analysis further shows the expected fact that, for low  $q$ 's, the density along the axis has a pronounced maximum at the centre of the bond, whereas, for higher  $q$ 's, two maxima roughly corresponding to the maxima of the  $2s$  orbitals appear, even though the density at the centre of the bond remains higher than at the nuclei (Table 2). Note also that, whereas the peak at the centre of the bond is highest when  $q = 2$  for a pure- $s$  MO, it becomes higher and higher for  $q \rightarrow 0$  when hybridization is introduced.

Table 2. Analysis of the one-determinant approximation

$q$	1	2	3	4	5	6	7
$c_s$	0.217	0.662	0.909	0.975	0.992	0.997	0.998
$\lambda$	4.498	1.132	0.459	0.228	0.127	0.078	0.063
$S_{ss}$	0.9483	0.8150	0.6373	0.4563	0.3025	0.1879	0.1106
$S_{hh}$	-0.5404	0.6905	0.9450	0.6308	0.3950	0.2237	0.1286
$d$	15.422	4.123	2.271	1.650	1.366	1.231	1.215
$E_{ss}$	-1.3005	-1.2020	-1.0722	-0.9613	-0.8803	-0.8244	-0.7859
$E_{hh}$	-1.7474	-1.3515	-1.1199	-0.9786	-0.8857	-0.8268	-0.7872
$x_m$	0	0	0	0	$\pm 1.290$	$\pm 1.914$	$\pm 2.478$
$P_0(0)$	0.0220	0.0348	0.0318	0.0212	0.0180	0.0162	0.0154
$P_\phi(0)$	0.3394	0.1434	0.0722	0.0350	0.0245	0.0200	0.0187

*Explanation.* The symbols  $c_s$  denotes the coefficient of the  $2s$  orbitals in the hybrids giving the minimum energies for the values of listed;  $\lambda = \operatorname{tg} \phi = \sqrt{1 - c_s^2}/c_s$  is the corresponding hybridization parameter;  $S_{ss}$  and  $S_{hh}$  are the overlap integrals for pure  $2s$  AO's and for the hybrids specified above;  $d$  is the ratio between the electron densities for the MO's formed by the hybrids and by pure  $2s$  AO's along the internuclear axis;  $E_{ss}$  and  $E_{hh}$  are the calculated energies with  $2s$  AO' and optimum hybrids, resp., in a.u. Finally,  $x_m$  denotes the position of the maximum density along the axis (in units of  $q$  counted from the centre of the bond) between the nuclei;  $P_0(0)$  and  $P_\phi(0)$  are the values of the density at the maxima for the non-hybridized and the hybridized case.

## 2. Partial Correlation

As has been said, in our model calculations we shall call "correlation" effects what cannot be accounted for by hybridization – even though the latter corresponds already to partial configuration mixing; this point of view is strictly parallel to calling correlation effects all those effects that cannot be reproduced by a single determinant approximation no matter what combinations of Slater

AO's one chooses as "predetor" functions (which is to say, all that goes beyond an exact HF calculation [7]). However, we can think now of two steps in the configuration mixing going beyond the hybridization step: one, where a restricted basis of one hybrid per atom is used, the other where all the configurations (of appropriate symmetry) arising from the four-orbital basis chosen are used. We shall call the former "partial correlation", and investigate it before studying the latter. Here again, we find some well-known and some less well-known results illustrated in our calculation.

First of all, partial correlation leads to energies that have a minimum practically for the same hybrids as those giving a minimum-energy one-determinant function, a very slight increase in *s*-character being noticeable for high *q*'s. Second, as appears from Table 3, the effect of partial correlation becomes more and more important as *q* increases, following a trend opposite to hybridization effects. In other words, we deal here with a really new effect whose importance becomes greater and greater as the atoms come apart. This is evidently due to the fact that correlation is indeed an inter-electronic effect. Except at very low *q*'s, the energy correction compares in magnitude with that due to hybridization.

Table 3. Successive corrections to the energy of a single determinant wave functions over 2*s* orbitals (a), after optimum hybridization (b), CI with one hybrid per atom (c), CI with two pure Slater AO's per atom (d), for increasing values of  $q = \alpha R$

<i>q</i>	(a)	(b)	(c)	(d)
1	-1.3005	-0.4469	-0.0002	-0.0059
2	-1.2020	-0.1495	-0.0004	-0.0006
3	-1.0722	-0.0477	-0.0029	-0.0016
4	-0.9613	-0.0155	-0.0144	-0.0017
5	-0.8803	-0.0054	-0.0337	-0.0022
6	-0.8244	-0.0024	-0.0527	-0.0018
7	-0.7859	-0.0013	-0.0663	-0.0010

Note. The minimum energy after "complete" CI is obtained by summing the contributions (a), (b), (c), (d). Energies in a.u.

An idea of what the new effect means in terms of electron density can again be given as a ratio along the internuclear axis. In general, given two MO's *hg* and *hu*, corresponding to the sum and to the difference of two hybrids of parameter  $\lambda = \text{tg } \phi$ , respectively, we can write the CI function as

$$\psi = \cos \omega \{hg, \overline{hg}\} + \sin \omega \{hu, \overline{hu}\}. \quad (8)$$

Calling  $P_\phi(\omega)$  the one-electron density associated with  $\psi$  (so that  $P_\phi(0)$  corresponds to a single determinant over *hg* MO's, and  $P_0(0)$  to the reference case of a single determinant over *sg* MO's), the ratio  $P_\phi(\omega)/P_\phi(0)$  may be used to represent the relative change in the electron density with respect to the single-determinant approximation (Fig. 1). Using the standard elliptical coordinates  $\xi$  and  $\eta$ , we have, along the axis between the nuclei ( $\xi = 1$ )

$$d_\phi^\omega(1, \eta) = \frac{P_\phi(\omega|1, \eta)}{P_\phi(0|1, \eta)} = 1 + \left[ \frac{1 + S_{hh}}{1 - S_{hh}} \left( \frac{\eta - \tanh \frac{\alpha \eta}{2}}{1 - \eta \tanh \frac{\alpha \eta}{2}} \right)^2 - 1 \right] \sin^2 \omega. \quad (9)$$

In particular, at the centre of the bond, where  $\eta = 0$ , and at the nuclei ( $\eta = \pm 1$ ):

$$d_{\phi}^{\omega}(1, \eta) = \cos^2 \omega; \quad d_{\phi}^{\omega}(1, \pm 1) = 1 + \frac{2S_{hh}}{1 - S_{hh}} \sin^2 \omega. \quad (10)$$

These results provide an illustration of the fact that the CI tends to decrease the electron density at the centre of the bond while increasing that at the nuclei, thus producing an effect qualitatively different from that of hybridization, which left the shape of the density along the internuclear axis unchanged, while multiplying the values by a factor larger than unity. The two effects, however, are related to each other, because both depend on  $S_{hh}$ ; only at the centre of the bond the change in density produced by CI is independent of  $S_{hh}$ , and, for small values of  $\omega$ , is quite small. At the nuclei, the density relating to a single determinant may be multiplied by a very large factor, if  $S_{hh} \sim 1$  (as happens, in our calculations, for  $\varrho \sim 3$ ). This means that, the higher the overlap, the higher the effect tending to restore the electrons on the nuclei. How large this effect can be is shown by the detailed numerical study given in Table 4. For  $\varrho = 1$ , where the two nuclei are very close to each other,  $d_{\phi}^{\omega}$  is everywhere very slightly lower than 1; this is in agreement

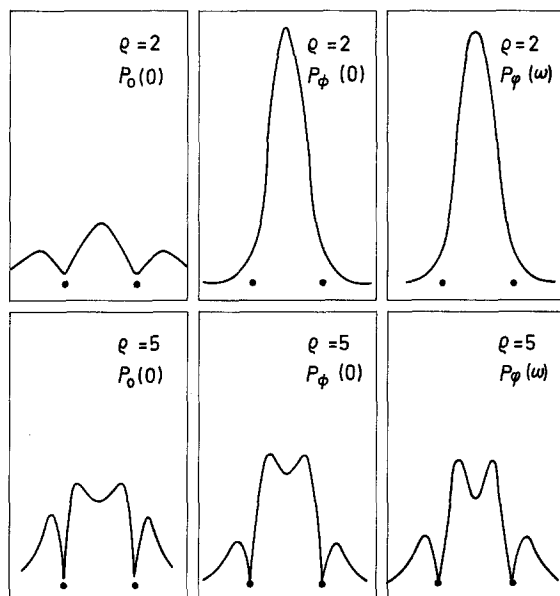


Fig. 1. One-electron densities along the internuclear axis associated with a single-determinant function over *sg* MO's [ $P_0(0)$ ], with a single-determinant function over *hg* MO's [ $P_{\phi}(0)$ ], and with a CI function over *hg* and *hu* MO's [ $P_{\phi}(\omega)$ ], for  $\varrho = 2$  and  $\varrho = 5$

with the fact that we are quite close to the united atom. When  $\varrho$  increases, more and more charge is pushed away from the centre toward the nuclei, as the one-determinant wave-function becomes less and less reliable [1]. Around  $\varrho = 5$  the charge density at the centre of the bond is reduced by 25% with respect to the one-determinant approximation, so that the CI compensates the effect of hybridization, giving again the same density as the *sg* MO. At the same time, however, the density at the nuclei increases by over 30% with respect to the *hg* case, *i.e.* by



Table 4. Values of the coefficient  $\cos\omega$  of the CI over one hybrid per atom (with parameter  $\lambda = \text{tg}\phi$ , see Table 2) and ratios  $d_{\frac{1}{2}}^0$  of the corresponding electron densities to those of the one-determinant approximation over hybrids. The parameter  $\eta$  is  $2/R$  the distance from the centre of the bond

$\varrho$	$\eta$ $\cos\omega$	0	0.2	0.4	0.6	0.8	1.0
1	0.999	1.000	1.000	1.000	1.000	1.000	1.000
2	0.999	0.999	0.999	0.999	0.999	0.999	1.005
3	0.997	0.994	0.996	1.000	1.003	0.996	1.203
4	0.958	0.917	0.931	0.964	0.997	0.996	1.283
5	0.860	0.739	0.789	0.902	1.007	1.048	1.341
6	0.774	0.599	0.689	0.867	1.006	1.069	1.231
7	0.733	0.536	0.663	0.875	1.009	1.061	1.137

over 80% with respect to the reference  $sg$  case. At the maximum of  $P_0(0)$ , the change is quite variable (see also figure). This is an illustration, in the case of  $L$ -shell hybrids, of a well-known correlation effect.

### 3. Complete Configuration Mixing

In our model, the equivalent of an exact calculation is the determination of the linear combination of all the six configurations  $V_1, \dots, V_6$  of Eq. (2) which minimizes the corresponding energy. The new corrections to the total ground-state energy for various  $\varrho$ 's are given in Table 3. They are very small everywhere, thus proving that a single hybrid per atom is sufficient, at least in the case of homonuclear bonds, to give energies accurate to 0.05 eV, except for very low values of  $\varrho$ , where the correction rises to 0.2 eV. From the chemical point of view, these corrections may be important for quantities like rotational barriers, but are already minor corrections.

The meaning of the small effect of complete CI is difficult to analyze; the only thing we can say off-hand is that apparently the elements of the eigenvectors of the complete Hamiltonian over  $V_1, \dots, V_6$  are related among themselves so that the two variational parameters on which the partial CI depends are sufficient to give practically the correct result.

A way for seeing how far this is true can be found as follows. We have seen that

$$W_{gg}(\lambda) \equiv \frac{1}{\sqrt{2}} \{hg, \overline{hg}\} = (a^2 V_1 + b^2 V_2 + \sqrt{2}ab V_3)N\sqrt{2} \quad (11)$$

with  $a, b, N$  given by Eq. (6) and all functions of  $\lambda = \text{tg}\phi$ , the hybridization parameter. Let us introduce the new hybrids  $l = \cos\chi 2s_X + \sin\chi 2p\sigma_X$  (with  $X = A, B$ ), letting  $\mu = \text{tg}\chi$  be the new hybridization parameter.

We can then write a new expression for the ground-state complete-CI wavefunction

$$\psi = \Sigma a_i V_i = \alpha W_{gg}(\lambda) + \beta W_{uu}(\lambda) + \gamma W_{gg}(\mu) + \delta W_{uu}(\mu), \quad (12)$$

which is particularly instructive in the light of the actual values of  $\lambda, \mu, \alpha, \beta, \gamma, \delta$ , derived from the values of the  $a_i$ 's. As could be expected, one configuration over hybrids pointing one towards the other ( $\lambda > 0$ ) is always predominant, but the corresponding value of  $\lambda$  (or of  $\cos\phi$ ) may be quite different from that found by the one-determinant calculation. The reason for this is, of course, that the Ritz method is not a perturbation method, and, by extending the basis, one modifies

the coefficients of every element. In addition, it is found that sometimes (for  $q$  close to 1) the most important contribution after that of  $W_{gg}(\lambda)$  (with  $\lambda$  close to the  $\lambda$  of Table 2) is that of  $W_{uu}(\mu)$ , whereas in other cases (for  $q \geq 4$ ), it is that of  $W_{uu}(\lambda)$ . This again corresponds to the qualitative difference between the limiting cases  $q \rightarrow 0$  and  $q \rightarrow \infty$ . Table 5 gives some results obtained by the above analysis of  $\psi$ .

Table 5. Analysis of the "complete" CI in terms of non-orthogonal hybrids

$q$	$\cos \phi$	$\cos \chi$	$\alpha$	$\beta$	$\gamma$	$\delta$
1	0.2286	0.9767	0.9970	0.0107	-0.0212	-0.4538
3	0.9317	0.7298*	1.0079	-0.0756	-0.0611	-0.0196
5	0.9823	0.7813	1.0828	-0.8111	-0.2749	0.3122

Note. For the meaning of the symbols, see Eqs. (11) and (12). The values of  $\cos \phi$  and  $\cos \chi$  are given instead of  $\lambda$  and  $\mu$  because the latter are tangents, and emphasize too much slight differences between  $\cos \chi$  of this table and  $c_s$  of Table 2. The starred value of  $\cos \chi$  corresponds to a hybrid pointing away from the bond, all the other hybrids point one towards the other.

#### 4. Effect of Orthogonalization

In this article we have not considered explicitly the question of orthogonalization; however, some remarks on the importance of the latter are in order.

There are three kinds of orthogonalizations important in our problem: the orthogonality  $1s$ ,  $2s$  for the same atom, the orthogonality of the  $L$ -shell MO's used to the  $K$ -shell MO's, in particular  $N(1s_A + 1s_B)$ , and the orthogonality of the  $L$ -shell MO's to one another.

The latter is clearly unimportant, because the calculations take account of the non-vanishing overlap between the orbitals used. The other two are important in so far as they affect the input data.

The *intra-atomic* orthogonality between  $L$ -shell and  $K$ -shell orbitals is qualitatively different from the corresponding *inter-atomic* condition, for it leads to important effects at all distances, and affects only the  $2s$  AO's. What should be expected from this orthogonalization? In order to answer this question we have to consider the limiting cases of very low and very high values of  $q$ . For the latter, only the *intra-atomic* integrals are affected by the orthogonalization, for the  $1s_A$  contribution on terms of the energy expression relating to B (and vice versa) is negligible. Therefore, as regards the energies for the atoms very far apart, *intra-atomic* orthogonalization to the  $1s$  orbitals is equivalent only to a shift in zero-point.

In order to discuss the situation when the atoms are very close to each other, we consider the form of an  $s'g$  orbital (where the prime denotes orthogonality of each  $2s$  orbital to the  $1s$ , or  $k$ , orbital of the same atom)

$$s'g = n \sqrt{\frac{1 + S_{ss}}{1 + S_{s's'}}} \left( sg - \lambda \sqrt{\frac{1 + S_{kk}}{1 + S_{ss}}} kg \right), \quad (13)$$

where  $\lambda$  is the  $2s-1s$  orthogonalization parameter and  $n$  the corresponding normalization factor. We can thus expand the configuration  $1/\sqrt{2} \{s'g, \bar{s}g\} = V'_1$  in the form (5)

$$V'_1 = \sqrt{2}N(V_1 + b^2V_7 + b\sqrt{2}V_8), \quad (14)$$

with the conventions

$$N = \frac{n^2(1 + S_{ss})}{\sqrt{2}(1 + S_{s's'})}; \quad b' = \lambda \sqrt{\frac{1 + S_{kk}}{1 + S_{ss}}}; \quad (15)$$

and

$$\begin{aligned} V_1 &= \frac{1}{\sqrt{2}} \{sg, \overline{sg}\} \\ V_7 &= \frac{1}{\sqrt{2}} \{kg, \overline{kg}\} \\ V_8 &= \frac{1}{2} |\{kg, \overline{sg}\} + sg, \overline{kg}\}|. \end{aligned} \quad (16)$$

Clearly, only if  $b'$  is very small can  $V_1$  replace  $V'_1$ , but that can happen only if  $\lambda$  is small. Consequently, we must presume that the effect of *intra-atomic* orthogonalization will be quite large at short distances. Table 6 illustrates the above remarks, and further shows that this type of orthogonalization leads to an increase in energy of the  $V'_1$  configuration with respect to  $V_1$ . This corresponds to a sort of repulsion of the core electrons on the binding electrons [8].

This kind of correlation does not apply, of course, to the  $2p\sigma$  orbitals. Keeping in mind that, as we have seen, the latter AO's predominate when  $\varrho$  decreases, as far as the minimum-energy situation is concerned, we may conclude that the effect of *intra-atomic* orthogonalization on minimum energies is roughly constant, as is brought out in Table 6, where one can see also that the optimum hybrids follow the same trend as in Table 2, but tend more rapidly to pure  $p$ 's when  $\varrho \rightarrow 0$ .

The other type of orthogonalization we must consider is a much more important one, discussed by Coulson and Lester in connection with the hydrogen molecule [9]. We have already mentioned it in the discussion of the effect of hybridization, when we have pointed out that our variational procedure gives

Table 6. *Effect of intra-atomic orthogonalization*

$\varrho$ tg $\phi$	1	2	3	4	5	6	7
$S$	0.9376	0.8185	0.6741	0.5143	0.3621	0.2370	0.1457
$\Delta S$	0.0107	-0.0035	-0.0368	-0.0580	-0.0596	-0.0691	-0.0351
$E_{s's'}$	-1.0045	-0.9722	-0.8916	-0.8010	-0.7249	-0.6700	-0.6228
$\Delta E(s')$	0.2960	0.2298	0.1806	0.1603	0.1554	0.1554	0.1631
$c_{s'}$	0.090	0.410	0.730	0.890	0.950	0.970	0.980
$E_{H'H}$	-1.6321	-1.2162	-0.9857	-0.8422	-0.7455	-0.6807	-0.6298
$\Delta E(H)$	0.1153	0.1373	0.1342	0.1364	0.1402	0.1461	0.1574

Notes. a) The orthogonalized  $s'$  orbitals used here were taken in the form  $N(r-k)e^{-ar}$  and not as linear combinations of the  $1s$  and  $2s$  orbitals. This procedure is slightly worse, from an atomic point of view, than the current one, but presents several advantages, in particular as regards the introduction of exchange integrals; nor is it much less justified than the usual Schmidt orthogonalization [10, 11].

b) The symbols have the following meanings:  $S$  is the overlap integral for the  $s'$  AO's, and  $\Delta S$  its difference from  $S_{ss}$ ;  $E_{s's'}$  is the single-determinant energy over  $s'$  AO's;  $E_{H'H}$  is the corresponding energy over optimum hybrids whose  $s'$  coefficient is  $c_{s'}$ ;  $\Delta E(s')$  and  $\Delta E(H)$  are the differences between these energies given and those without *intra-atomic* orthogonalization.

c) The energies are given in a.u.

a ground state converging practically to a  $1s$  orbital of the united atom. Now, the usual correlation diagrams assume that an  $sg$  MO of separated atoms goes into a  $2s$  orbital of the united atom, thus having a node on the nucleus, not a peak. Yet, our results are fully consistent with a correct variational procedure, for, as our  $sg$ ,  $pg$ , and  $su$ ,  $pu$  MO's are not orthogonal to the  $kg$  and  $ku$  MO's, respectively, they must necessarily tend to the lowest state of the united atom, and, in general, to a  $1\sigma_g$  state of the two electrons. Here again, the fact that a modified nuclear charge has been used is very important, for the energy obtained can never attain the values of a true  $1\sigma_g$  MO; but the electron distribution found can come close to that corresponding to MO's of this type.

The effect of inter-shell *inter-atomic* orthogonalization can be seen again as a sort of inter-shell correlation. In this case, however, the behaviour of the energy at different values of  $\varrho$  is qualitatively different from that seen for the previous case, especially because now also the  $pg$  and  $pu$  orbitals must be modified, and in fact it is the latter modification that becomes important at low values of  $\varrho$ .

The overlap integrals between the MO's (1) and  $kg$ ,  $ku$  are:

$$\begin{aligned}(sg, kg) &= 2(S_0 + S_{ks}), \\(su, ku) &= 2(S_0 - S_{ks}), \\(pg, kg) &= 2S_{kp}, \\(pu, ku) &= -2S_{kp}.\end{aligned}\tag{17}$$

From the actual values of these integrals for an orbital exponent of the  $1s$  AO equal to 2.70, one finds that indeed the correction for orthogonalization does not alter significantly the qualitative behaviour of the results as long as  $\varrho$  is larger than 3; for a lower  $\varrho$ , it does, so much that a  $pg$  MO made orthogonal to the  $kg$  orbital tends to a  $2s$  AO of the united atom, whereas, as has been mentioned, normally it tends to  $1s$ -like AO.

We shall take up this question quantitatively in subsequent work. Here we note only that the configuration  $V_2$  is everywhere orthogonal to  $V_1$  and so is the excited state function obtained by partial CI with respect to the ground state one. Thus, we can have an idea of the effect of *inter-atomic* orthogonalization just by considering the excited states. Referring to calculations where the *intra-atomic* orthogonalization has been performed, we find indeed not only much higher energies, but, for appropriate  $\varrho$ 's, energies close to those one should expect from existing calculations on the  $Li_2$  molecule.

### Conclusion

The results and remarks presented here are only a first step in a new analysis of the two-electron problem. In fact, notwithstanding the deep pioneering work of Slater, Mulliken, Coulson and others [12], it seems that the rise of large computers has led people to attack directly more complicated problems, without laying the ground for an analysis of their results by simpler calculations, so that new interest in simpler basic questions has arisen only quite recently. Of course, many aspects of the present analysis are discussed in other publications; in particular, as regards hybridization, in Ref. [13]; however, as has been said, a model calculation like ours has the great advantage of representing a simple faithful parallel to more complicated problems concerning the chemical bond, and

especially hybridization and correlation. Therefore, we intend to deepen and complete the above analysis in further work.

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