

MODEL AB-INITIO CALCULATIONS AND THE FOUNDATION OF THE MO—LCAO METHOD*

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A use of *ab initio* calculations that seems to have been largely overlooked because of its simplicity is the construction and analysis of simple models of the chemical bond. Such models may render enormous services both in clarifying previously known results and in suggesting new ones, and in making possible a detailed discussion of interpretation schemes and approximations. Treatments using the LCAO scheme over the valence electrons may be seriously at fault when effects like inter-shell orthogonalization are neglected. Such effects are consequences of the approximations used; nevertheless, they may be physically significant because the corresponding approximations may be essential in order to reach an understanding of the molecular reality. They include changes of the AO's with molecular geometry. The realization that a certain type of modification of the AO basis is important must be followed by a very careful analysis of the way in which such a correction should be introduced in order to preserve simplicity and physical significance.

The present article is part of a discussion of the theory of molecules started several years ago with a study of the connection between hybridization and localization [1] and continued later in various directions. The attempt will be made here to draw attention on some more points regarding the use and limitations of the molecular orbital method, in its simple LCAO versions, as a tool of theoretical physics rather than as an interpolation technique useful for chemical problems.

The fact that such pioneers as MULLIKEN [2], PAULING [3], GOMBÁS [4] have devoted much work to single-particle treatments and related aspects of the quantum theory of molecules is sufficient indication of the importance of our subject. Nevertheless, we recall some of the considerations that justify a renewed interest in methods avowedly incapable of giving exact numerical results.

One can expect two kinds of information from a theoretical treatment: very good quantitative predictions and/or an explanation of facts in the sense of a correlation of various details in a general scheme. Contrary to what was once the case, the domains where the two uses of the theory do not exclude each other are nowadays very rare. This is because the equations that govern the behaviour of most systems are very complicated, and very accurate treatments are seldom amenable to a clear physical interpretation. In fact, quali-

* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

tative and even semi-quantitative understanding is often reached by simple schemes connecting the phenomena to be interpreted with some specially significant features of the general theory of matter; such in the case, for instance, with the interpretation of the excitation potentials of conjugated molecules in terms of the allowed energies of a single particle confined in a limited region of space.

Various reasons, among which the advent of large computers is very important, have led to much emphasis on the quantitative side, so that an enormous effort has been made to obtain better and better solutions of the (electronic) Schrödinger equations for larger and larger molecules. It is curious that, instead of insisting on the undeniable importance of such calculations for testing and reference purposes, many authors have defended that effort by claiming that no attempt should be made to understand molecular phenomena unless very accurate wavefunctions are available. To many a physicist, this claim must sound as a condemnation of most of theoretical physics, both pure and applied; suffice it to think of problems like particle scattering or transport phenomena in solids to realize what broad fields are based on comparatively rough approximations of the 'rigorous' equations.

I. Correlation and the MO—LCAO method in a simple model calculation

In a first part of the present article, we shall consider the above questions in some more detail, the reason being that one must somehow know where one stands when one tries to use an approximation for strictly theoretical purposes. There are two kinds of objections put forth against physical considerations on molecules based on single-particle (i.e., orbital) methods. One regards the fact that such methods are usually approximate versions of the ideal one-electron treatment given by the Hartree—Fock equations; the other is more directly concerned with the shortcomings of the one-electron scheme. We shall consider first the latter point, which goes under the name of "the correlation problem" [5].

Although there is a growing suspicion that this problem may have been overemphasized by some authors, there is no doubt that it has a perfectly sound origin. Any independent-particle treatment of a many-electron system must involve averages over all the electrons but one, thus replacing them by charge clouds. As has been known for a long time, this contradicts the inherent dualism in the nature of an electron, whose interactions are all to be described by point-particle potentials. The corrections that should be introduced in order to take into account the corpuscular nature of all the electrons are the so-called correlation corrections; evidently, they must be studied and their

importance assessed before accepting even qualitative conclusions drawn from treatments neglecting them. Now, an examination of the available data suggests that the correlation correction to the energy of a molecule is indeed very small; however, it is comparable with the dissociation energies of ordinary chemical bonds. Therefore, the argument runs, the independent-particle model is not reliable in connection with molecular physics. Of course, there is a weak point in the last part of the above considerations, because the fact that dissociation energies and correlation energies are of the same order of magnitude does not imply that one cannot obtain the former without knowing the latter; as a matter of fact, dissociation energies are differences, and, in principle, can be obtained to a good approximation from (more or less equally) incorrect quantities. This remark leads to further arguments in favour and against the supporters of correlation, all based on quantitative considerations involving mainly the expectation values of the energy. The question is how far such quantitative arguments, usually limited to energies, are significant.

With very few exceptions, highly accurate molecular calculations with correlation are not available; moreover, calculations claimed to include correlation are very complicated, and this is a serious hindrance in discussions of aspects other than energy expectation values.

Attempts to introduce simple indices of the importance of correlation for various observables, especially those using the so-called "correlation coefficients", appear to be quite promising [6], but several difficulties have still to be overcome especially as regards the application to molecules. The best alternative to rough estimates and dubious analyses of complicated situations consists in following the traditional approach of theoretical physics, namely to have recourse to a model, where the main features of the actual problem are present.

Although much has been done using the hydrogen molecule as a model, a better way of simulating very simply an ordinary chemical bond is probably to treat the states of two electrons in the field of two positive first-row ions (say, Li ones) by an LCAO-MO-CI method with a limited basis set [7, 8]. In fact, the coefficients of the linear combinations of atomic orbitals used to construct the molecular orbitals are the variational parameters which must be determined in order to reach an "optimum" one-electron description, just as the coefficients of an expansion in a complete set of orthogonal functions can be taken as the variational parameters to be determined in order to get the best one-electron scheme, namely the Hartree—Fock orbitals for the given system; and the coefficients of the linear combinations of the Slater determinants that can be constructed from the given molecular orbitals correspond to the coefficients of the expansion in a complete set of configurations obtained from the Hartree—Fock orbitals, and thus describe correlation. The definition of the latter adopted here amounts to the statement that correlation is whatever

cannot be taken into account by a single-configuration treatment carried out within the given scheme. In order to use our model for the purpose of assessing the importance of correlation in the qualitative description of bonds, we have to compare results obtained with and without single-configuration mixing.

To illustrate the above considerations, take the basis set formed by the $2s$ and $2p$ orbitals of lithium, centred on two different nuclei at a distance R [8]. Let us postpone for the moment a discussion of the importance of the existence of the inner core, and assume that the given orbitals depend on R only through their centres; this is in full accordance with the spirit of the simplest MO—LCAO method, as used by theoretical chemists. Then, the results for the ground-state energy are those summarized in Table I, where the single-

Table I

Ground-state energies of a two-electron bond between equal nuclei having effective charge 1.30 when the trial function is: (b) a single determinant over $2s$ STO's with orbital exponent 0.65; (c), a single determinant over $2s-2p$ hybrids with the same orbital exponent and an optimized s -character; (d), a linear combination of the two determinants corresponding to the bonding and antibonding MO's formed by the same hybrids. Line (e) is the percent difference between (c) and (d). All the energies are in a.u.; the distances in a.u. multiplied by 0.65 are given in line (a)

(a)	2	3	4	5	6
(b)	1.2020	1.0722	0.9613	0.8803	0.8244
(c)	1.3515	1.1199	0.9768	0.8857	0.8268
(d)	1.3519	1.1228	0.9912	0.9194	0.8795
(e)	0.03	0.26	1.45	3.63	6.00

determinant (SC) and configuration interaction (CI) approximations are compared, the SC function being optimized with respect to the degree of hybridization of the atomic orbitals, and the SC function being a linear combination of the two g determinants constructed with the bonding and antibonding bond orbitals resulting from the optimum hybrids.

Table II shows that the model used leads to the same results as analyses of the hydrogen molecule and *ab initio* all-electron calculations. In particular, the internuclear distance can be divided into three ranges: one, where the correlation effects are relatively unimportant; one, where they are very important; and one where an intermediate situation takes place. The question we are interested in is whether the picture given by the correlation energies must be understood as an indication that interpretations of facts based on the SC function are not reliable.

There is no doubt that the electron density distribution is a more sensitive and convenient quantity for assessing the validity of a given description. Therefore, we present Table II, where, in addition to the actual changes in

Table II
Analysis of electron densities for the model of Table I

(a)	2	3	4	5	6
(b)	.0004	.0029	.0144	.0337	.0527
(c)	.005	.203	.283	.341	.231
(d)	.0001	.0007	.0002	.0000	.0000
(e)	-.001	-.006	-.083	-.261	-.401
(f)	-.0001	-.0004	-.0032	-.0054	-.0043
(g)	.998	.994	.917	.740	.599

Explanation:

- (a) same as line (a) of Table I;
- (b) 'correlation' energies (line (d)-line(c) of Table I);
- (c) and (d), relative and absolute changes in the electron densities at the nuclei;
- (e) and (f), idem at the centre of the bond of Table I;
- (g) corresponding weights of the ground-state configurations.

energies, the changes in the one-electron densities associated with the nuclei and the centre of the bond for various internuclear distances are compared. The changes in density at the nuclei, even though they are large fractions of the density itself, are not very important. The situation at the centre is different: the correlation correction (which tends, of course, to separate the electrons) is lower than 10% for internuclear distances R lower than ca. 6.5 a.u., but then increases rapidly, thus deepening the well between the atoms. In Table II, therefore, the three regions mentioned above appear to be for R less than 6 a.u., R larger than 8 a.u., R comprised between 6 and 8 a.u.; this partition is quite clear in the weights of the SC ground-state function in the CI functions.

In short, Table II confirms and even emphasizes the importance of correlation at large internuclear distances, but indicates that, around the internuclear equilibrium distance, that correction is relatively unimportant both on energies and on the electron densities. This conclusion can be generalized to most bonds in a very easy way, if we assume that they can be treated by at most two determinants — as is strongly indicated by the example of Li_2 and some other examples. In order to see this point, consider the secular equation associated with the Hamiltonian matrix over two configurations, and suppose that the configurations in question are determinants over bonding and antibonding orbitals, respectively. In the homonuclear case, the energies E_1, E_2 associated with the two configurations become equal when the internuclear distance tends to infinity, and, moreover, the contribution of hybridization becomes very small. Now, when the diagonal elements of a second-order matrix are nearly degenerate, the first perturbation term is proportional to the interaction element B_{12} ; moreover, the coefficients of the linear combination associat-

ed with it become equal each other. On the other hand, for small internuclear distances, the separation between E_1 and E_2 is large (at least if the bond is very stable), and the first-order perturbation correction is proportional to $B_{12}^2/(E_2 - E_1)$ and the contribution of the excited-state configuration is proportional to $B_{12}/(E_2 - E_1)$. This result is valid for any homonuclear bond, provided the difference $E_2 - E_1$ is large compared with B_{12} ; this is the condition one can assume as a condition for the possibility of describing a bond by means of an MO picture [2].

The case of heteronuclear bonds involves a number of novel features. For instance, it does not necessarily require configuration mixing as a means of ensuring the correct limit at large distances. A study of these cases is rather complicated because simplifications provided by equal nuclear charges are lacking. It is very important, however, that a close similarity can be introduced between the two cases by taking into account the screening effect of the electrons: at large internuclear distances, an electron on atom A tends to see B as a singly-charged positive ion, and vice versa; therefore, as far as binding effects are concerned, the situation should be very much the same as for the homonuclear case (cfr. [9]). Further work on simple models for heteronuclear cases is in progress.

We shall assume from now on that the picture provided by the one-electron density associated with an SC (MO) calculation is sufficient for interpretation purposes in the vicinity of the equilibrium distance. The fact that correlation pushes some charge away from the centre of the bond cannot be considered very important if the corresponding change is almost negligible from a quantitative point of view. The numerical examples given above show, on the other hand, that the real shortcoming of MO 'theories' is still in the dissociation limits, as was pointed out by MOFFITT a long time ago [10]. A very urgent task of quantum chemistry seems to be, therefore, that of combining the exceptional simplicity and heuristic power of the single-electron picture at distances near the equilibrium ones with some convenient picture of the situation when the atoms are far apart; the more so, as already the interactions between non-bonded atoms in a polyatomic molecule would seem to fall in the category of molecular features not describable by an MO theory, at least as such theories stand now.

There have been suggestions that the two-particle density is a more significant function as regards the importance of correlation. As a matter of fact, the ratios between the values of $P(1, 2)$ as obtained from a configuration interaction calculation and the corresponding values for a single-determinant approximation are all very close to unity in the case of formaldehyde in the equilibrium configuration [11]; the only important correlation appears to be 'spin' or Fermi correlation, which is already included in the single-determinant function.

II. Choice of the basis and physical significance of simple LCAO treatments. Radial distortion

The brief discussion given above may be completed by the remark that the very concept of correlation implies that the single-particle description of a molecule should be well understood and brought to its extreme consequences, so that one may be sure that certain facts cannot be explained within any consistent orbital scheme. We shall now try to indicate some of the points that must still be clarified in that connection on the basis of very simple models, especially with LCAO 'theories' [18].

The introduction of the latter answers, as was pointed out by MULLIKEN [2], to a need of simplicity and physical significance of the interpretation scheme. It may seem at first sight that the best orbital scheme is a Hartree—Fock one, where the variational principle has been used to obtain the best energy compatible with a single-particle treatment. It is now becoming clearer and clearer that the word "best" used in an ambiguous way has been the source of many difficulties. From the point of view adopted in the present article, the most important function of a theory of molecules is to make possible a complete and consistent interpretation of molecular properties, by tracing them back to very few basic statements and pictures; this goal is to be reached, if necessary, at the expense of high accuracy. Now, among other things, the pure Hartree — Fock scheme does not provide a built-in reference to the fact that atoms are the building blocks of a molecule; and much less that bonds exist at all: so that the analysis of its results requires a large amount of work to find out the way in which atoms and bonds are concealed in them [12]. This consideration is sufficient to show that the choice of atomic orbitals is a most important point in the progress toward a consistent theory of molecules [13]. The usual choice of an (AO) basis is well-known, and corresponds closely to that considered above for the Li_2 molecule: one assumes that the AO's are fixed functions of the atoms forming a molecule, and can only adjust to the specific situation through hybridization. This starting point is sound as long as the basis is complete and the treatment involves all the electrons; but we are interested precisely in the case when a limited basis is used and only a few electrons are treated, in order to keep the results as easy to interpret as possible. Under these conditions, at various internuclear distances, as can be seen when one considers a specific example (*vide infra*), a choice of AO's adjusted in a special way to the molecular situation is required by strictly physical considerations.

In short, if simplified schemes are necessary for interpreting molecular phenomena, and if a limited-basis MO—LCAO treatment must be taken as such a scheme (thus deserving the name of theory), a careful study of the dependence of the basis AO's on molecular geometry is essential. Of course, it would be particularly satisfying if the forms of the AO's could be left invariant; but the

very example of hybridization indicates that this is not possible. What we can (and should) do in order to put some order in our analysis is to make reference to some standard AO's to be interpreted as the entities that represent, as it were, the undisturbed atoms; and introduce corrections on them, trying to interpret them as physical effects.

Let us come back to the simple model (the two-electron model of the Li_2 molecule) which we have introduced in order to consider a case where a number of features arising from the use of a complicated basis is eliminated. Here, the reference fixed AO's are the $2s$ Slater orbitals of lithium, and a first step shows that hybridization is very important for obtaining reasonable results. Further analysis indicates that modifications of the radial parts of the AO's are necessary — still with four AO's as a basis — among other things, in order to ensure orthogonality to the inner shell [14, 15]. Finally, variation of the orbital exponents is necessary in order to satisfy the virial theorem. These modifications are not introduced just as improvements of the calculations; they must be considered as essential features of an LCAO calculation, to be added to those already discussed in [13]. We shall call them radial distortion (or, sometimes, 'promotion' [13]) and 'scaling', respectively. We emphasize that they are introduced with the tacit assumption that the unmodified AO is of the s type (in our model), although — as will be seen presently — not necessarily a regular Slater orbital.

The simplest kind of radial distortion in an atomic orbital participating in a bond orbital is connected with orthogonalization to the inner core. The necessity of introducing this modification in the basis orbitals was pointed out long ago [14], but has not been stressed too much in recent years, because it arises only when the valence electrons are treated separately, and becomes really evident when such a treatment is carried out at various distances; moreover, it may be very small when the inner core has a very high orbital exponent. To emphasize the importance of the condition of orthogonality to the inner shell suffice it to mention that, in its absence, the united atom limit of bond orbitals resulting from two ($2s$, $2p$) hybrid AO's would be essentially $1s$ orbitals [8]. Therefore, in a consistent orbital theory, the corresponding modification of the atomic orbitals should be introduced as a standard effect to be treated before actual energy calculations, as could be done with hybridization [1, 15], because it is part of the preparation of the atomic orbital basis.

The problems arising in this connection are easily illustrated in the model at hand. For simplicity, suppose a treatment using only one s -type orbital per atom is to be carried out for the valence electrons. Then, orthogonalization to the MO to which the inner core electrons are assigned requires the introduction of atomic orbitals of the form

$$|2s_m\rangle = N(|1s\rangle - m|2s\rangle), \quad (1)$$

Table III

Analysis of orthogonalization to the inner shell in a two-electron model of the Li_2 molecule for three values of the internuclear distance R .

Column (a) gives the values of $\rho = \alpha R$, with $\alpha = 0.65$ and R in a. u. Columns (b) and (c) report the energies obtained from a Slater determinant over pure- s orbitals corresponding to Equ. (1) of the text with $m = 0$ and m such as to ensure orthogonality of the $2\sigma_g$ to the $1\sigma_g$ orbital, respectively. The corresponding values of m are given in column (d). Column (e) contains the values of m ensuring the same orthogonality condition when the Slater $2s$ orbital is replaced by an sp^3 hybrid, the values for hybrids with a lower p character being intermediate. Column (f) gives the values of the parameter m' for a pure- p orbital of the type of Equ. (6)

(a)	(b)	(c)	(d)	(e)	(f)
3	1.0722	.8165	2.849	2.585	.3499
4	.9613	.7675	2.923	2.859	.2614
5	.8244	.6614	2.941	2.939	.1725

where N is an appropriate normalization factor, m is a positive quantity used for ensuring orthogonality to the inner core MO (which is given by the normalized sum of the Slater $1s$ orbitals associated with the inner core of the two atoms, having exponent 2.70). The two Slater orbitals appearing in (1) are assigned the same orbital exponent, say 0.65. Some indications about the results are given in Table III, which shows that the contribution of the $1s$ orbitals is not negligible. The changes in energy reported in Table III support the physical interpretation of orthogonalization as a repulsion tending to increase the energy of the outer electrons, especially at small internuclear distances [15]. As is well known, this interpretation can be translated into a rigorous mathematical formalism by introducing appropriate pseudopotentials [4].

The kind of orthogonalization suggested here — which corresponds to forming hydrogen-like orbitals — is equivalent to the usual Schmidt orthogonalization. A study of such hydrogen-like orbitals in free atoms has been carried out [16], and has given results comparable with those of the usual Slater orbitals, thus removing the only serious objection to the use of hydrogenlike orbitals. Of course, the ‘best-atom’ orbital exponents are no longer very close to those given by the Slater rules. Nevertheless, they are close enough for most practical calculations.

The modification brought about by the addition of $1s, 3s, \dots$ terms to the Slater orbital may be called “promotion”; here, at variance with [13], we use the term “radial distortion” because the word ‘promotion’ recalls the physical interpretation of the additional terms as higher-energy orbitals of the free atom, which is not possible here (see also [2]). A physical interpretation of this distortion can only be founded on a redefinition of the reference

free-atom orbital and on a discussion of the way in which an analysis of the electron density should be carried out.

We consider now some more aspects of the question of orthogonalization to the inner shell. Suppose that, instead of considering pure- s orbitals, we wish to consider hybrids. We are then faced with two possibilities. First of all, we can write a hybrid in the form

$$|h\rangle = N[|1s\rangle - m(|2s\rangle + g|2p\rangle)] \quad (2)$$

(where g is a hybridization parameter and N a normalization factor), and then it is impossible to decide whether, by introducing the $1s$ contribution, we have modified the $2s$ or the $2p$ orbital; so that we have no longer a right to distinguish between hybridization and radial distortion. In other words, the procedure based on (2) leads to an m value which depends both on the inner core and on the degree of hybridization, but, as we have just said, it must be interpreted as a distortion of the s orbital. This point of view is perfectly reasonable, and should be completed by the decision that radial distortion of the $2p$ orbital will be introduced only if orthogonalization to orbitals resulting from p orbitals is to be carried out, as would happen in the case of, say, the Na_2 molecule. However, this leads to ambiguities in the general case of bond orbitals formed by hybrid AO's which must be orthogonalized to bond orbitals also formed by hybrid AO's. We consider here, therefore, the other possibility, namely that of orthogonalizing separately the pure- s orbital and the pure- p bond orbital to the inner core orbitals, and then building the required hybrids. The situation becomes particularly interesting when this criterion is to be applied to the general case. Let s_1, s_2, p_1, p_2 denote the subsets formed by a $1s$, a $2s, \dots$ orbital with the same orbital exponent on atom 1, same on atom 2, and the subsets formed by a $1p$, a $2p, \dots$ orbital on atom 1, same on atom 2, respectively. A molecular orbital $|\chi_1\rangle$ will be written in terms of a column vector C which is defined as follows

$$|\chi_1\rangle = \begin{matrix} (s_1, s_2, p_1, p_2) \\ \left| \begin{array}{c} C_{11} \\ C_{21} \\ C_{31} \\ C_{41} \end{array} \right. \end{matrix} \quad (3)$$

and another orbital $|\chi_2\rangle$ will be expressed through the same basis set and another column vector with subvectors C_{12}, C_{22} , etc. By definition, a mixing of orbitals of the same subset is a radial distortion or 'promotion', whereas a mixing of subsets s_i and p_i is hybridization. Now, the requirement that $|\chi_1\rangle$ and $|\chi_2\rangle$ be orthogonal to one another leaves such a freedom that we can require at the same time that only promotion be used to satisfy it. Let us assume that

$|\chi_1\rangle$ is given, and that only $|\chi_2\rangle$ must be determined. Let us denote by S_{11} , S_{12} , etc. the overlap matrices associated with the four subsets of the given AO basis. Then, the conditions we find on C_{12} , C_{22} , etc., are:

$$\sum_j C_{i2}^+ S_{ij} C_{j1} = 0. \quad (4)$$

This equation defines one element of each C_{i2} , and thus, when there is only one inner-shell orbital to which orthogonality must be ensured, the C_{i2} vectors need have only two elements. A particular case is that of the pure- s orbitals considered above. Another interesting case is that of pure- p orbitals, where the possibility of including the $1p$ orbitals in the atomic p subset has been considered explicitly. We comment briefly on this point because it illustrates one of the most delicate aspects of the problem at hand. There are two ways of looking at our new s orbitals. One, as has been mentioned, consists in assuming that we replace Slater orbitals by strictly hydrogen-like orbitals; the other consist in assuming that we have granted a certain degree of flexibility to the radial parts of our orbitals, and replaced the factor r of the Slater $2s$ orbital by a more general first-degree polynomial involving one parameter to be used for the orthogonality requirements. From the former point of view, the introduction of a $1p$ orbital does not appear to be justified; from the latter point of view, on the contrary, it would seem reasonable to modify the radial part of a p orbital exactly as has been done for its s counterpart. Now, it is important to keep in mind that the $1s$ orbital introduced by us in the s_i subset cannot be interpreted as something physically significant by itself, because it is not one of the functions of the basis set actually used for the calculations, but belongs to a basis set from whose *contraction* the final physically significant set is obtained; the $1p$ orbital would play the same rôle, and hence it seems advisable to use it. In short, Equ. (1) can be rewritten as

$$|2s_m\rangle = \sqrt{\frac{\alpha^3}{\pi}} N(m) \left(1 - \frac{m}{\sqrt{3}} \varrho\right) e^{-\varrho}, \quad (5)$$

where α is the orbital exponent, and $\varrho = \alpha r$ is the scaled distance from the nucleus; and, so far, it seems that the most reasonable p partner of the orbital (5) should be

$$|2p_{m'}\rangle = \sqrt{\frac{3\alpha^3}{\pi}} N(m') \left(1 - \frac{m'}{\sqrt{3}} \varrho\right) e^{-\varrho} \cos \vartheta \quad (6)$$

(m' being determined from the condition of orthogonality to the inner core MO) rather than a p orbital having in the radial part a second-degree polynomial in ϱ .

A simple calculation gives the values of m' reported in the last line of Table III. These data reveal that there is a weakness in the above reasoning, because they show (as can be proven algebraically) that the limit of the orbital (6) when the internuclear distance goes to infinity is a $1p$ orbital rather than the expected $2p$ orbital. This makes a physical interpretation of the orbital (6) quite difficult, and one may conclude that inclusion of a $3p$ orbital is a better choice.

A point not apparent in our simple model is that orthogonalization to the inner core involves, in principle, a doubling of the orbitals. In the homonuclear case, if one had to introduce the antibonding valence MO's one should take care that, say, the $2s$ orbitals participating in the $2\sigma_u$ MO be modified so as to make it orthogonal to the $1\sigma_u$ inner-shell orbital. This condition is not equivalent to that associated with the g symmetry. More generally, let the 1σ molecular orbitals be given as

$$1\sigma = (\bar{1}s_1, \bar{1}s_2) \begin{vmatrix} q_{11} & q_{12} \\ q_{21} & q_{22} \end{vmatrix} = 1s \cdot Q(1\sigma) \quad (7)$$

and the 2σ molecular orbitals are given as

$$2\sigma = (s_1, s_2) \begin{vmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{vmatrix} \cdot Q(2\sigma), \quad (8)$$

where s_1 and s_2 contain, say, n elements each. Calling S the $2 \times 2n$ overlap matrix between the set $1s$ and the set $2s \equiv (s_1, s_2)$, we obtain, for the condition that 2σ be orthogonal to 1σ whatever $Q(2\sigma)$ may be,

$$Q^+(1\sigma) \cdot S \cdot C = T \cdot C = 0, \quad (9)$$

where T has been introduced as a $2 \times 2n$ matrix. As C is a $2n \times 2$ matrix, we have four conditions to be satisfied by $4n-2$ unknowns, and this is clearly possible with $n = 2$, as would be if we used Equ. (1). The difficulty is that we have to accept non-zero elements in C_{21} and C_{12} , thus entering the long dispute about the significance of multi-centre basis orbitals. If we wish to stay in the frame of a simple MO—LCAO scheme, it is better to require that C_{21} and C_{12} should vanish, in which case we have only $2(n-1)$ unknowns. This means that we must have $n \geq 3$, if we wish to keep the basis set completely independent of $Q(2\sigma)$. An intermediate situation, where we can use a double basis [different values of m in (1) for the bonding and the antibonding MO's] arises if one tries to take advantage of some general property of $Q(2\sigma)$. A case in point is that of homonuclear two-centre bonds, where it is easy to define different $2s_n$ orbitals for the g and the u 2σ MO's. If this is not done, one must use

a general form:

$$|2s_{\text{ortho}}\rangle = N(l, lm) (|1s\rangle - m|2s\rangle + l|3s\rangle) \quad (10)$$

exactly as would be done in the non-symmetrical case.

Conclusion

The example of radial distortion required by the orthogonality condition is a good illustration of an effect which must be included in an approximate treatment lest one should lose any hope of giving a theoretical interpretation of them. The physical significance of orthogonality originates from the fact that the limits for very large and very small internuclear distances are to satisfy certain conditions known from the theory of atoms. It is interesting to note that, as a byproduct of inter-shell orthogonalization, one can distinguish between two kinds of hybridization. When no orthogonality to the inner shell is required, an SC calculation with hybrids where the s character is a variational parameter will always give as close as possible an approximation to the 1σ molecular orbital; consequently, the s character tends to zero for the united-atom limit. On the other hand, at very large internuclear separations, the s character is maximum; continuity then implies an increasing p contribution as the internuclear distance tends to zero [8]. This kind of hybridization is so to say 'essential', and disappears as soon as orthogonality to the inner shell is ensured; only then whatever hybridization is found is really a feature leading to a better approximation of the actual physical situation, and hence has a real physical significance.

We shall not discuss here in detail scaling as a further modification of the basis; we only point out that it is very close to radial distortion because it is not expressible as a linear combination of the basis elements, and affects directly the radial forms of the atomic orbitals. We prefer to close the present remarks with a few words regarding the analysis of charge densities and the reference free-atom orbitals. It is clear that no theory of chemistry is possible if one has no way of comparing the molecular situation with an ideal, free-atom situation. The problem of the reference free-atom orbitals arises all the time whenever we speak of modifications of the basis AO's. In the above discussion, we have assumed that the reference orbitals in question are essentially Slater orbitals, except for the $2s$ orbital, which is supposed to be orthogonalized to the corresponding $1s$ orbital by an appropriate choice of m in Equ. (1). The path to be followed in using these reference orbitals is exemplified in our studies of the model mentioned above, where one of the intermediate calculations is over a Slater determinant with pure- s spinorbitals in no way adjusted to the molecular situation. There are several delicate points in the choices implicit in this kind of comparison, and the question is by no means settled.

Once the reference orbitals have been chosen, the question of the analysis of electron densities ceases to be meaningless. Why one should consider electron densities is nowadays clear: the analyses in terms of single indices like the various kinds of populations are much too arbitrary to be relied upon in drawing physical interpretations, and it seems that, if such indices have to be introduced, it will be best to start all over again. The analysis of electron densities could follow RUEDENBERG's very good treatment [17]. As regards the basis orbitals, one might separate the density associated with a single atomic orbital into a contribution identical with that of the free atom and an 'interference' contribution associated with each successive modification.

The questions just mentioned deserve a separate study. As a conclusion of the present article, we shall briefly summarize the main points illustrated in it [18].

First, a use of *ab initio* calculations that seems to have been largely overlooked because of its simplicity is the construction and analysis of simple models of the chemical bond. Such models may render enormous services both in clarifying previously known results and in suggesting new ones, and in making possible a detailed discussion of interpretation schemes and approximations.

Second, treatments using the LCAO scheme over the valence electrons may be seriously at fault when effects like inter-shell orthogonalization are neglected. Such effects are consequences of the approximations used; nevertheless, they may be physically significant because the corresponding approximations may be essential in order to reach an understanding of the molecular reality. They include changes of the AO's with molecular geometry.

Third, the realization that a certain type of modification of the AO basis is important must be followed by a very careful analysis of the way in which such a correction should be introduced in order to preserve simplicity and physical significance.

We hope that considerations like those given above will help to bridge the apparent gap between the work of researchers devoted to highly sophisticated *ab initio* calculations and the work of researchers interested in a simple if approximate understanding of facts.

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МОДЕЛЬ АВ INITIO ВЫЧИСЛЕНИЙ И ОБОСНОВАНИЕ МЕТОДА МО—LCAO

ДЖУЗЕППЕ ДЭЛ РЕ

Резюме

Применение ab initio вычислений, которое оказывается тщательно проверенным благодаря его простоте, является истолкованием и анализом простых моделей химической связи. Такие модели могут оказывать огромную помощь, как при уточнении заранее известных результатов, так и при исследовании новых, далее сделают возможным подробную дискуссию интернациональных схем и приближений. Приемы, применяющие LCAO схему в случае валентных электронов, могут давать серьезно ошибочный результат, если пренебречь эффектами, обусловленными ортогонализацией внутренних оболочек. Такие эффекты следуют из примененного приближения, хотя они могут быть физически важными, так как соответствующие приближения иногда необходимы с целью обеспечения понятности молекулярной реальности. Они включают в себя изменения атомных орбит с молекулярной геометрией. За реализацией, в которой модификация базиса атомных орбит определенного типа важна, обязательно должен следовать очень тщательный анализ приема, в рамках которого имеется возможность для введения данной коррекции с целью сохранения простоты и физических характеристик.