Theoret. chim. Acta (Berl.) 31, 111—135 (1973)

A Theory of Molecules in Molecules

II. The Theory and Its Application to the Molecules Be–Be, Li_2–Li_2, and to the Internal Rotation in C_2H_6

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Received February 20, 1973/May 23, 1973

A theory of molecules in molecules is presented, which permits the computation of the wave function of a molecule from the wave functions of fragment molecules by transferring some of the localized molecular orbitals of the fragments and recalculating the orbitals in the region of interaction. A projection operator is used to obtain orthogonality of the orbitals to be determined to the transferred and fixed orbitals. Additional approximations allow the reduction of the dimension of the matrices to be diagonalized and the neglect of a part of the basic integrals, which can lead to a considerable saving in the computation time. The justification of these approximations will be investigated for the case of the molecules Be – Be, $Li_2 - Li_2$, and for the calculation of the rotational barrier in C_2H_6.

Key words: Localized orbitals, transferability of ~ – Be_2 – Li_4 – C_2H_6 – Molecules in molecules

1. Introduction

The Schrödinger equation is the fundamental equation of molecular quantum mechanics; it is an exact equation, if relativistic effects are neglected. The equation itself as well as its solutions describe nature in a very abstract way and the connection to the terms used to describe molecular structure as there are atoms, bonds, inner shells or lone pairs of electrons etc. can only indirectly be established. A similar statement can be made of the most frequently used approximation to the solution of the Schrödinger equation, the Hartree-Fock (HF) approximation. The HF equation and its solutions are abstract and lack the direct interpretability in the terms mentioned above. But it is possible to reformulate the Schrödinger equation and the HF equation so that their solutions can be interpreted more directly in familiar terms and thus appeal stronger to physical and chemical intuition. It is possible to make this reformulation in such a way that the solutions to the new equations are equivalent to the solutions of the original ones. Solving the new equations – which depend on the introduction of a model – does consequently not necessarily involve a loss in rigour. In most cases the reformulated equations are more difficult to solve than the original ones. From a mathematical point of view it is only in the cases where convergence difficulties arise that the new equations can be preferable, because the starting point is known. The main advantage of the reformulation is that physical and chemical intuition can be used to find solutions to the equations and to establish approximations to them. These approximations should be physically appealing and intelligible, be justifiable in a precise manner, and the approximated equations should be easier to solve than the equations which formed the starting point. Quite a significant amount of work has been done in this direction. A number of approaches, which are of concern to the present work, will be shortly mentioned.

Pseudopotential theory [1–4] has been developed to remove orthogonality constraints in the calculation of wave functions for some subsystem of the electrons (e.g. the calculation of the valence electron wave function which must be orthogonal to the core electron wave function). It gives ample opportunity to introduce model potentials which simplify the calculations. The theory of atoms in molecules [5] is based on the idea that the relative ease with which atomic wave functions can be calculated can be used to construct molecular wave functions from these fragments. Related is the semiempirical method of diatomics in molecules [6] and the work of Adams on the solution of the Schrödinger and the HF equation in terms of wave functions which are least distorted from products of atomic wave functions [7–9]. The recent article of Ohno [10] *et al.* should also be mentioned in this context. The theory of the separability of many-electron systems in the case of the pi-electron approximation has been examined among others by McWeeny [11] and by Lykos and Parr [12]. This problem has been in general treated by Huzinaga and Cantu [13]. The author has in a previous article presented a method which allows the construction of a wave function of a molecule starting from the wave functions of fragment molecules [14].

One of the most important concepts in the context of the present work is the concept of the localized molecular orbitals (LMO's) and their transferability property. LMO's closely correspond to the classical chemical concepts of inner shells and lone pairs of electrons and bonds linking the atoms in a molecule. They bridge the gap between these concepts and the rigorous description of molecules by wave functions. A wave function constructed from LMO's is equivalent to a wave function constructed from the delocalized canonical molecular orbitals, i.e. all expectation values of totally symmetric operators calculated with these wave functions are identical. LMO's can be obtained directly as solutions of the HF or multiconfiguration equations using a pseudopotential method [7, 15–19]. Peters has developed a different approach for the direct calculation of LMO's [20, 21]. These methods correspond to a reformulation of the HF equation, which can then be used to introduce approximations. (See e.g. Ref. [20]). But in most cases LMO's are obtained by a unitary transformation of the molecular orbitals (MO's) resulting as solutions of the HF equation in their standard form. LMO's have been introduced and examined mainly by Lennard-Jones and coworkers, by Boys, and by Edmiston and Ruedenberg and they have proved to be extremely useful [22–29]. The aspect of the LMO's which is of greatest concern to the present work is their approximate transferability property. LMO's can be expected to be transferable among molecules having chemically related structures because they are maximally separated from each other and because they are themselves restricted to a minimal spatial region (for a discussion see Ref. [25]). Transferable orbitals have been the subject of a number of investigations [14, 24, 25, 29–37], although few calculations have been performed which calculate an atomic or molecular wave function by an actual transfer of LMO's [14, 33, 34]. Shull *et al.* were to the knowledge of the author the first ones to report such a transfer of LMO's (in their case geminals) [33]. The detailed examination of the structure of the LMO's and an energy analysis based on them has also contributed to an understanding in this respect [24, 36]. The study of molecular momentum distributions and Compton profiles both by experimental and theoretical methods yields information on the transferability of LMO's and deserves notice in this context [37].

The transfer of LMO's or geminals and the transfer of parameters associated with them is only one aspect of the problem, although it constitutes the most frequently used path. Different approaches are possible. Lipscomb and coworkers made investigations in which they transferred matrix elements of the HF operator from smaller molecules to larges ones in order to calculate the wave function of the larger molecule [38]. Bader *et al.* defined a spatial partitioning of total molecular charge distributions independent of an orbital concept and discussed the transferability of molecular energies [39]. Christoffersen and coworkers transfer elements of the one-particle reduced density matrix between structurally related molecules, but use it only as a starting point for a SCF calculation [40]. Nelander discusses the partitioning of the first order density matrix and its use for bond energy schemes [41].

There are other constructive ways to generate molecular wave functions, which do not or which do not necessarily involve the variation principle. These methods start in general from the hybridization concept. The first step is the construction of hybrids which are combined to form one- or two-center localized bond orbitals using polarity parameters. These bond orbitals are then used to build the molecular wave function. Chemical experience and experimental data on the one hand or the variation principle on the other hand determine the necessary parameters. There are many variants of this method [42–44]. The wave function can surpass HF wave functions in quality, if the correlation energy is taken into account by perturbation theory [45]. The fundamental concept in these approaches is besides the concept of hybrids again the one of localized orbitals.

As mentioned above a method has been introduced which permits the computation of the wave function of a molecule from the wave functions of fragment molecules by transferring some of the LMO's of the fragments and recalculating the orbitals in the region of interaction [14]. In the present article this topic will be pursued and the method generalized. The formal theory will be presented in Sect. 2 together with a brief outline of the physical background. The application of the method to study the interaction of two Be atoms, the interaction of two Li_2 molecules and to calculate the barrier to internal rotation in ethane is discussed in Sect. 3.

2. Theory

If one introduces a change in some part of any "large" molecule by a substitution or an isomerization, the effects of this change on the electronic distribution will be important mainly in its immediate neighbourhood. By allowing for the electronic rearrangement in this immediate neighbourhood, which will be called the region of interaction, it should be possible to obtain a good approximation to the actual process in many cases. There will certainly be an electronic rearrangement in the far distant parts of the molecule too, but this should be only of minor importance for many practical questions. To take advantage of this one has to look for molecular fragments which allow to construct new molecules from these fragments such that the wave function of this new molecule constructed from the fragment wave functions is a good approximation to the wave function calculated by an ab initio method. For the general case of a molecule A – B being formed from two molecules A – X and B – Y (where A, X, B, and Y are any molecular fragments):

$$\mathrm{A-X+B-Y=A-B+remainder}$$

one would distinguish three different spatial regions in each of the molecules A – X and B – Y: a region which will be discarded, a region of interaction, and a fixed core which will be transferred unaltered. This approach should open a general path to the calculation of approximate wave functions of molecules from molecular fragments.

The considerations will be restricted to the closed shell case of the wave functions constructed from real orbitals for all of the molecules A – X, B – Y, and A – B [46]. Let

$$\begin{aligned}&\langle \boldsymbol{r}_1, s_1, \cdots, \boldsymbol{r}_{2n_A}, s_{2n_A} | \Psi^{\mathrm{A}} \rangle\\ &= (2n_{\mathrm{A}}!)^{\frac{1}{2}} A^{\mathrm{A}} \{ \langle \boldsymbol{r}_1, s_1 | 1+ \rangle \langle \boldsymbol{r}_2, s_2 | 1- \rangle \cdots \langle \boldsymbol{r}_{2n_A}, s_{2n_A} | n_{\mathrm{A}} - \rangle \}\end{aligned}$$

in short

$$|\Psi^{\mathrm{A}}\rangle = (2n_{\mathrm{A}}!)^{\frac{1}{2}} A^{\mathrm{A}} \left\{ \prod_{i=1}^{n_A} |i+\rangle |i-\rangle \right\} \tag{1}$$

be the wave function for molecule A – X with $2n_{\mathrm{A}}$ electrons. A^{A} is the antisymmetric projection operator for this case. The MO's $|i\rangle$ are determined from the HF equations for A – X

$$F^{\mathrm{A}} |i\rangle = \sum_{i'} \varepsilon_{ii'} |i'\rangle\,, \tag{2}$$

where

$$F^{\mathrm{A}} = h^{\mathrm{A}} + \sum_i 2J_i^{\mathrm{A}} - K_i^{\mathrm{A}}\,. \tag{3}$$

$h^{\mathrm{A}}(1) = -\frac{1}{2}\nabla_1^2 - \sum_\lambda Z_\lambda^{\mathrm{A}}/R_{\lambda 1}$ and J_i^{A} and K_i^{A} are Roothaan's Coulomb and exchange operators [46]

$$\begin{aligned} J_i^{\mathrm{A}} &= \langle i | r_{12}^{-1} | i \rangle\\ K_i^{\mathrm{A}} &= \langle i | r_{12}^{-1} | \rangle | i \rangle\,. \end{aligned} \tag{4}$$

$|+\rangle$ and $|-\rangle$ denote the two possible spin states of a spin 1/2 system. The product is over all occupied MO's of molecule A − X. In the same way let

$$|\Psi^{\mathrm{B}}\rangle = (2n_{\mathrm{B}}!)^{\frac{1}{2}} A^{\mathrm{B}} \left\{ \prod_{j=1}^{n_B} |j+\rangle |j-\rangle \right\} \tag{5}$$

be the wave function of molecule B − Y with similar definitions for the operator and quantities appearing in (5). The letter i will be used for the MO's of molecule A − X and the letter j for the MO's of molecule B − Y. The MO's $|j\rangle$ are solutions of the HF equations for molecule B − Y:

$$F^{\mathrm{B}}|j\rangle = \sum_{j'} \varepsilon_{jj'} |j'\rangle\,, \tag{6}$$

where

$$F^{\mathrm{B}} = h^{\mathrm{B}} + \sum_{j} 2J_j^{\mathrm{B}} - K_j^{\mathrm{B}}\,. \tag{7}$$

For a proper description of the different regions in the molecules it is necessary to construct the wave functions from LMO's. The orbitals $|i\rangle$ and $|j\rangle$ are thus the LMO's describing inner shells and lone pairs of electrons and bonds in the two molecules. LMO's can be defined as solutions of the HF equations corresponding to a non-diagonal matrix of Lagrangian multipliers [24]. This is why this form of the equations has been given in (2) and (6).

The following ansatz is made for the wave function of molecule A − B in this theory of molecules in molecules (MIM):

$$\begin{aligned} |\Psi\rangle &= (2n!)^{\frac{1}{2}} A \{ \textstyle\prod_i' |i+\rangle\, |i-\rangle \prod_j' |j+\rangle |j-\rangle \prod_m |m+\rangle\, |m-\rangle \} \\ &= (2n!)^{\frac{1}{2}} A \{ \textstyle\prod_k |k+\rangle\, |k-\rangle \prod_m |m+\rangle\, |m-\rangle \} \end{aligned} \tag{8}$$

A is the antisymmetric projection operator for the entire molecule containing $2n$ electrons. Note that $2n \neq 2n_{\mathrm{A}} + 2n_{\mathrm{B}}$ in general! The prime on the product sign indicates that a number of LMO's is left out to be deleted completely or to be recalculated in the region of interaction. The remaining LMO's (for which the letters k and l will be used) are transferred unaltered. They form the fixed core. These orbitals are nonorthogonal because they result from calculations on different molecules. The MO's $|m\rangle$ are to be determined for the description of the new bonds formed and of their neighbourhood. They will be required to be orthogonal to the fixed orbitals $|k\rangle$. This can be done by using the projection operator for orthogonality

$$P = 1 - \sum_{k,l} |k\rangle\, S_{kl}^{-1} \langle l|;\ P^2 = P,\ P^+ = P\,, \tag{9}$$

where S^{-1} is the inverse matrix of the overlap matrix $S = \{\langle k|l\rangle\}$ [47]. An outer projection by P of the operator determining the MO's $|m\rangle$ gives orbitals exactly orthogonal to the MO's $|k\rangle$ [47]. If the MO's $|k\rangle$ can be regarded as approximately orthogonal (e.g. because of spatial separation) this projection operator simplifies to

$$P = 1 - \sum_k |k\rangle\langle k| \,. \tag{10}$$

The approach suggested by Huzinaga and Cantu [13] is identical in the ansatz, and differs only by the use of the coupling operator technique [48, 49] instead of the present method of outer projections, if no further approximations are introduced.

The MO's $|m\rangle$ are to be determined such that the total energy of the system is minimized. The total energy is calculated as the expectation value of the Hamiltonian operator H of the entire molecule A – B with the wave function of equation (8). The expression for the total energy in the case of nonorthogonal orbitals is given by

$$\begin{aligned}\langle\Psi|H|\Psi\rangle = &\sum_{n_1,n_2} \langle n_1|h|n_2\rangle\, D(n_1|n_2)\\ &+\frac{1}{2}\sum_{n_1,n_2,n_3,n_4} [n_1 n_2|n_3 n_4]\, D(n_1 n_3|n_2 n_4)\,,\end{aligned} \tag{11}$$

where the $|n_i\rangle$ are any MO's,

$$[ij|kl] := \iint \langle i|\boldsymbol{r}_1\rangle\langle\boldsymbol{r}_1|j\rangle\, r_{12}^{-1}\, \langle k|\boldsymbol{r}_2\rangle\langle\boldsymbol{r}_2|l\rangle\, d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2\,, \tag{12}$$

and $D(i|j)$ and $D(ij|kl)$ are minors of the determinant

$$D = \det\{\langle i|j\rangle\}\,. \tag{13}$$

A clear discussion of MO theory for nonorthogonal orbitals can be found in a series of papers by Löwdin [50]. Variation of the orbitals $|m\rangle$ to get the minimum energy in the restricted subspace created by the projection operator P leads to the equations

$$PFP|m\rangle = \varepsilon_m|m\rangle\,, \tag{14}$$

where the matrix of Lagrangian multipliers is diagonal, because the MO's $|m\rangle$ are not required to be LMO's. Note that the operators P and F in (14) do not commute because the MO's $|k\rangle$ are not eigenfunctions of the operator F! The HF operator F in (14) is given by

$$F = F_{\text{core}} + \sum_m 2J_m - K_m \tag{15}$$

$$F_{\text{core}} = h + \sum_{k,l} (2\langle k|r_{12}^{-1}|l\rangle - \langle k|r_{12}^{-1}|\rangle|l\rangle)\, S_{kl}^{-1}\,. \tag{16}$$

If the MO's $|k\rangle$ are orthogonal or if their nonorthogonality is neglected, (16) simplifies to

$$F_{\text{core}} = h + \sum_k 2J_k - K_k\,, \tag{17}$$

where the familiar Coulomb and exchange operators appear. Since the projection is done prior to diagonalization optimal orthogonal MO's $|m\rangle$ are obtained – optimal with respect to the fixed core.

The ansatz (8) and (14) represents an approximation to the exact HF wave function and HF equation. But the theory can be made exact by extending the work of Lykos and Parr [12] on the pi-electron approximation to the present case, where the orthogonality of the orbitals is not garanteed by symmetry. (See also Ref. [13]). Above, the $|m\rangle$-electron approximation has been taken. If the MO's $|k\rangle$ are now determined with the MO's $|m\rangle$ held fixed, the $|k\rangle$-electron approximation is taken. This process can be continued until self-consistency is reached. The procedure is a generalization of the usual SCF procedure. The orthogonality of the orbitals is garanteed by employing the method of outer projections, which corresponds to making the variations in a restricted subspace [47]. The MIM method can be made "exact" still in another way. If the region of interaction is the entire molecule, the wave function calculated is identical with the SCF wave function. This is again not the aim of the present approach, but it offers the possibility of obtaining wave functions differing in quality from the SCF wave function to more approximate ones. This method is thus capable of providing in a relatively nonarbitrary way an information on which MO's can be transferred, i.e. which MO's are not appreciably affected by the formation of the new bonds. Simultaneously it can give information on the energy contributions of the individual inner shells and lone pairs of electrons and bonds to the total energy change of a process.

The total SCF energy is always a lower limit to the energy expectation value in the MIM approximation, if the nonorthogonality of the MO's is properly taken into account. No general statement can be made if this nonorthogonality is neglected. But because the sets of transferred orbitals $\{|i\rangle\}$ and $\{|j\rangle\}$ are spatially well separated such an approximation should frequently be justified and give reliable answers.

The method discussed so far appears to be a reasonable approach which can be expected to give reliable answers. Applications made so far justify it [14, 51]. But it must be mentioned that the transfer of LMO's for some part of the molecule together with the redetermination of the MO's in the region of interaction does not lead to a considerable saving in the computation time. All integrals over the basis functions have to be evaluated, only the iteration part of the calculation might be shortened. This is not the final aim. A theory of molecules in molecules is desired which permits a significant saving in the computation time, i.e. gives the possibility to circumvent the "N^4 law" of the computational expense (where N is the number of particles or basis functions) at least in some part of the integral calculation. It is consequently necessary to proceed from the above ansatz and introduce further approximations.

Since only the MO's in the region of interaction are going to be redetermined and since the interest is in "larger" molecules, it might be acceptable to restrict the expansion of the MO's $|m\rangle$ to a subset Γ of the total set of basis functions (a LCAO expansion form for the MO's is assumed from now on):

$$|m\rangle = \sum_{p \in \Gamma} |p\rangle C_{pm} \,. \tag{18}$$

In mathematical terms this is an outer projection of the operator *PFP* of equation (14) by the projector on the manifold spanned by the basis functions in the set Γ according to

$$O_\Gamma PFP\, O_\Gamma\,, \tag{19}$$

where the projection operator O_Γ is given by

$$O_\Gamma = \sum_{p,q\in\Gamma} |p\rangle\, S^{-1}_{pq}\, \langle q|\,;\, O^2_\Gamma = O_\Gamma,\, O^+_\Gamma = O_\Gamma\,. \tag{20}$$

S^{-1} is the inverse matrix of the overlap matrix $S = \{\langle p|q\rangle\}$, p, $q\in\Gamma$. Such an approach reduces the dimension of the matrices to be diagonalized, but it does not affect the number of integrals which have to be evaluated. If this number is to be reduced as well, still another approximation must be made.

The basis functions whose centers are distant from the region of interaction should play only a minor role for the orthogonality of the MO's $|m\rangle$ to the transferred LMO's $|k\rangle$. The LMO's $|k\rangle$ to which orthogonality can be expected on spatial ground could be left out from the projection operator P and the basis functions which mainly contribute to these LMO's could be taken out from the entire set of basis functions for the expansion of the orbitals in the projection operator. This means the operator P in equation (9) is replaced by

$$P' = 1 - \sum_{k,l}{}' |k\rangle\, S^{-1}_{kl} \langle l|\,, \tag{21}$$

where the prime on the summation sign indicates the deletion of some of the orbitals. Then an outer projection of the operator P' is made according to

$$O_\Delta P' O_\Delta\,, \tag{22}$$

where

$$O_\Delta = \sum_{r,s\in\Delta} |r\rangle\, S^{-1}_{rs}\, \langle s|\,;\, O^2_\Delta = O_\Delta,\, O^+_\Delta = O_\Delta \tag{23}$$

is the projection operator on the manifold of the basis functions in the set Δ, which are to be included in the operator P'. This approximation results in a reduction of the number of integrals which have to be evaluated. For the success of the method it is essential that this approximation works. The final operator determining the MO's $|m\rangle$ is given by

$$O_\Gamma O_\Delta P' O_\Delta F O_\Delta P' O_\Delta O_\Gamma \tag{24a}$$

Note: Γ must always be a subset of $\Delta{:}\Gamma \subseteqq \Delta$! The other case is physically meaningless. The operator therefore simplifies to

$$O_\Gamma P' O_\Delta F O_\Delta P' O_\Gamma \tag{24b}$$

because

$$O_\Gamma O_\Delta = O_\Delta O_\Gamma = O_\Gamma\,. \tag{25}$$

This operator permits to save computational time, but it has acquired a relatively complicated structure. One main disadvantage is that the additional approximations introduced by the projections result in a nonorthogonality of the MO's

$|m\rangle$ to the transferred LMO's $|k\rangle$. The final justification of the approach can only be done by calculations.

Although these equations have been derived for the case of two fragments joined together, it is easily extended to any number of fragments. In fact the final equations are valid for the general case.

A few more points have to be discussed in this context. If one wants to avoid the calculation of all integrals, which is one intention of the theory of molecules in molecules, the nonorthogonality of the MO's has to be neglected – otherwise all integrals will appear again. The expression for the electronic energy then takes the well-known form

$$E_{el} = 2\sum_{n} \langle n|h|n\rangle + \sum_{n_1,n_2} 2J_{n_1n_2} - K_{n_1n_2}, \tag{26}$$

where $J_{n_1n_2}$ and $K_{n_1n_2}$ are the Coulomb and exchange integrals between any orbitals $|n_1\rangle$ and $|n_2\rangle$. In this expression the interaction terms J_{ij} and K_{ij} between an orbital transferred from molecule $A-X$ and another orbital transferred from molecule $B-Y$ appear. These terms necessitate the calculation of the integrals over all basis functions, if one is not willing to approximate some of these integrals or to approximate the energy terms J_{ij} and K_{ij} directly. The simplest method would be to make a point charge approximation for every orbital, which would be justified for large distances:

$$\begin{aligned} K_{ij} &= 0 \\ J_{ij} &= |\boldsymbol{r}_i - \boldsymbol{r}_j|^{-1}, \end{aligned} \tag{27}$$

where $\boldsymbol{r}_i = \langle i|\boldsymbol{R}|i\rangle$ is the charge centroid of LMO $|i\rangle$.
This particular approximation is not necessary and more refined procedures can be used. All two-electron integrals have then to be evaluated exactly except the integrals between the basis functions in the two fixed cores; this will be an appreciable part for larger molecules.

Equation (24) for the operator defining the MO's $|m\rangle$ is complicated and because of the multiple projection the question arises, whether it is still possible to give bounds to the eigenvalues and energy expectation values as in the case of a simple projection. The HF operator is projected according to Q^+FQ by an operator $Q = O_\Delta P' \, O_\Gamma \cdot Q$ is a product of projection operators, but itself is not a projection operator due to the fact that the projection operators O_Γ and O_Δ do not commute with P' (i.e. $Q^2 \neq Q$ and $Q^+ \neq Q$). However, it is still possible to derive bounds. Löwdin [47] has shown that for an outer projection of a self-adjoint operator A, which is bounded from below, by an arbitrary projection operator O

$$OAO = \bar{A} \quad \text{with} \quad O^2 = 0,\, O^+ = 0 \tag{28}$$

the eigenvalues of $\bar{A}$ are upper bounds to the eigenvalues of A in order

$$a_k \leqq \bar{a}_k, \tag{29}$$

where

$$A|k\rangle = a_k|k\rangle \quad \text{and} \quad \bar{A}|\bar{k}\rangle = \bar{a}_k|\bar{k}\rangle. \tag{30}$$

$|k\rangle$ and $|\bar{k}\rangle$ are normalized eigenfunctions. (See also Ref. [52]). Let P be another projection operator

$$P^2 = P,\ P^+ = P \tag{31}$$

which does not commute with O

$$[P, O] \neq 0\,. \tag{32}$$

According to the definition the operator

$$P\bar{A}P = \bar{\bar{A}} \tag{33}$$

is an outer projection of $\bar{A}$ with respect to P. The eigenvalue equation for $\bar{\bar{A}}$ is

$$\bar{\bar{A}}|\bar{\bar{k}}\rangle = \bar{\bar{a}}_k|\bar{\bar{k}}\rangle \tag{34}$$

and – applying Löwdin's theorem again – the eigenvalues $\bar{\bar{a}}_k$ are upper bounds to the eigenvalues of $\bar{A}$ in order. Using equation (29) one obtains

$$a_k \leqq \bar{a}_k \leqq \bar{\bar{a}}_k\,. \tag{35}$$

This result applies in the following form to the projected HF operator of the theory of molecules in molecules:

$$\begin{aligned}&\varepsilon_m(F) \leqq \varepsilon_m(O_\Delta F O_\Delta) \leqq \varepsilon_m(P' O_\Delta F O_\Delta P') \leqq \varepsilon_m(O_\Delta P' O_\Delta F O_\Delta P' O_\Delta)\\ &\leqq \varepsilon_m(O_\Gamma O_\Delta P' O_\Delta F O_\Delta P' O_\Delta O_\Gamma)\,,\end{aligned} \tag{36}$$

where the ε_m are the eigenvalues of the operators given in brackets. The same series of inequalities can be written down for the energy expectation value. (The operators are given in brackets.)

$$\begin{aligned}&E(F) \leqq E(O_\Delta F O_\Delta) \leqq E(P' O_\Delta F O_\Delta P') \leqq E(O_\Delta P' O_\Delta F O_\Delta P' O_\Delta)\\ &\leqq E(O_\Gamma O_\Delta P' O_\Delta F O_\Delta P' O_\Delta O_\Gamma)\,.\end{aligned} \tag{37}$$

This result will be taken up again in the applications.

Another important bound can be derived in a similar way as above. Let the sets Γ' and/or Δ' be obtained from Γ and/or Δ by subtracting some functions (subject to the restriction that $\Gamma' \subseteq \Delta'$ whatever members the two sets have). For the projection operators $O_{\Gamma'}$ and $O_{\Delta'}$ the following relations hold

$$O_{\Gamma'} O_\Gamma = O_\Gamma O_{\Gamma'} = O_{\Gamma'} \tag{38}$$

and

$$O_{\Delta'} O_\Delta = O_\Delta O_{\Delta'} = O_{\Delta'}\,. \tag{39}$$

The reduction of the number of basis functions can thus be written as another outer projection

$$O_{\Gamma'} O_\Gamma P' O_\Delta F O_\Delta P' O_\Gamma O_{\Gamma'} = O_{\Gamma'} P' O_\Delta F O_\Delta P' O_{\Gamma'} \tag{40}$$

and

$$O_\Gamma P' O_{\Delta'} O_\Delta F O_\Delta O_{\Delta'} P' O_\Gamma = O_\Gamma P' O_{\Delta'} F O_{\Delta'} P' O_\Gamma\,. \tag{41}$$

Because of this fact one can immediately write down the following inequalities:

$$\varepsilon_m(O_\Gamma P' O_\Delta F O_\Delta P' O_\Gamma) \leqq \varepsilon_m(O_{\Gamma'} P' O_\Delta F O_\Delta P' O_{\Gamma'}) \tag{42}$$

$$\varepsilon_m(O_\Gamma P' O_\Delta F O_\Delta P' O_\Gamma) \leqq \varepsilon_m(O_\Gamma P' O_{\Delta'} F O_{\Delta'} P' O_\Gamma) \tag{43}$$

and for the energy expectation value

$$E(O_\Gamma P' O_\Delta F O_\Delta P' O_\Gamma) \leqq E(O_{\Gamma'} P' O_\Delta F O_\Delta P' O_{\Gamma'}) \tag{44}$$

$$E(O_\Gamma P' O_\Delta F O_\Delta P' O_\Gamma) \leqq E(O_\Gamma P' O_{\Delta'} F O_{\Delta'} P' O_\Gamma). \tag{45}$$

This supplies the rigorous basis for the statement made before concerning the quality of the approximated wave functions. The physical argument is that one is working in more and more restricted subspaces which consequently raises the energy.

In the applications the justification of the four approximations introduced by 1) O_Γ, 2) O_Δ together with the approximation of P by P', 3) the neglect of the nonorthogonality of the MO's, and 4) the point charge approximation in the calculation of the total energy will be examined.

3. Applications

3.A. Be–Be

Wave functions have been calculated for the Be_2 molecule for various distances in the range from 2 to 12 a.u. On each atom a basis set of 9 *s*-type Gaussian functions [53], which are left completely uncontracted, is used to expand the MO's. For the Be atom the resulting total SCF energy is $E^{SCF} = -14.572068$ a.u. This compares with the value calculated by Clementi using a Slater-type basis: $E^{SCF} = -14.573020$ a.u. [54]. The energy values calculated for the Be_2 molecule by the *ab initio* method are given in Table 1, the potential curve is a repulsive curve. The calculated wave functions serve as a simple laboratory to test the approximations introduced in Sect. 2. The canonical MO's are transformed to LMO's by the method of Edmiston and Rueden-

Table 1. Total SCF energies for the Be_2 molecule (all values in atomic units)

R	E^{SCF}
2.0	−28.457626
3.0	−28.937517
4.0	−29.072896
6.0	−29.134913
8.0	−29.143207
12.0	−29.144131
∞	−29.144137

Table 2. Total energies for the Be_2 molecule calculated in the MIM approximation (all values in atomic units, for notation see text)

R	$E^{MIM}a$	$E^{MIM}b$	$E^{MIM}a$	$E^{MIM}b$
	Approximation Γ 18 Δ 18		Approximation Γ 16 Δ 18	
2.0	−28.450985	−28.451053	−28.450818	−28.453928
3.0	−28.932477	−28.934408	−28.932356	−28.937243
4.0	−29.070994	−29.071620	−29.070897	−29.074349
6.0	−29.134804	−29.134818	−29.134730	−29.137385
8.0	−29.143202	−29.143195	−29.143135	−29.145732
12.0	−29.144131	−29.144131	−29.144066	−29.146664
	Approximation Γ 14 Δ 18		Approximation Γ 12 Δ 18	
2.0	−28.449401	−28.480178	−28.446801	−28.577635
3.0	−28.931497	−28.960672	−28.929688	−29.050076
4.0	−29.070222	−29.096477	−29.068847	−29.179064
6.0	−29.134170	−29.158525	−29.133064	−29.232825
8.0	−29.142623	−29.166574	−29.141584	−29.238986
12.0	−29.143565	−29.167444	−29.142538	−29.239556
	Approximation Γ 16 Δ 16		Approximation Γ 14 Δ 16	
2.0	−28.450814	−28.450853	−28.449345	−28.473663
3.0	−28.932354	−28.934262	−28.931457	−28.954868
4.0	−29.070895	−29.071501	−29.070189	−29.091052
6.0	−29.134728	−29.134723	−29.134145	−29.153459
8.0	−29.143133	−29.143108	−29.142602	−29.161601
12.0	−29.144064	−29.144045	−29.143544	−29.162488
	Approximation Γ 12 Δ 16		Approximation Γ 14 Δ 14	
2.0	−28.446708	−28.573309	−28.449091	−28.448388
3.0	−28.929626	−29.046714	−28.931284	−28.932593
4.0	−29.068796	−29.176071	−29.070045	−29.070129
6.0	−29.133022	−29.230020	−29.134037	−29.133534
8.0	−29.141545	−29.236234	−29.142508	−29.141982
12.0	−29.142500	−29.236815	−29.143453	−29.142933
	Approximation Γ 12 Δ 14		Approximation Γ 12 Δ 12	
2.0	−28.445775	−28.534407	−28.441889	−28.434050
3.0	−28.928968	−29.014654	−28.925911	−28.921521
4.0	−29.068250	−29.147044	−29.065682	−29.060888
6.0	−29.132577	−29.203173	−29.130656	−29.125515
8.0	−29.141140	−29.209981	−29.139443	−29.134258
12.0	−29.142104	−29.210677	−29.140453	−29.135264

a nonorthogonality of the MO's taken into account
b nonorthogonality neglected

berg [24]. The approximations are applied in the following way. The inner shell LMO's will be transferred and the outer shell orbitals recalculated. A series of calculations has been made with different numbers of basis functions in the sets Γ and Δ. The following notation will be used to define the individual calculations. For both sets Γ and Δ the total number of functions which they

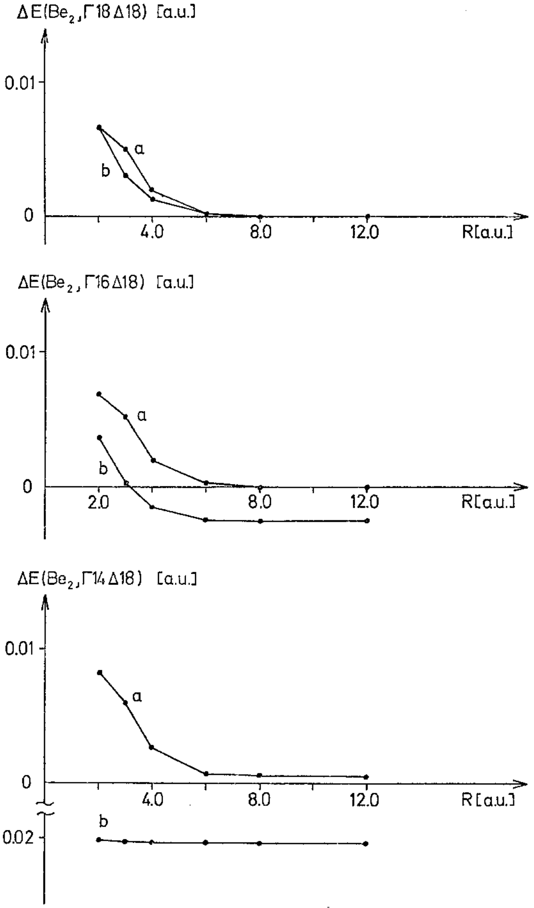

Fig. 1. Energy difference between MIM and SCF result for Be_2: $\Delta E = E^{MIM} - E^{SCF}$; approximations $\Gamma 18\, \Delta 18$, $\Gamma 16\, \Delta 18$, $\Gamma 14\, \Delta 18$ (for notation see text). a: nonorthogonality of the MO's taken into account, b: nonorthogonality neglected

contain is written behind the respective symbol. $\Gamma 18\, \Delta 18$ e.g. means that all basis functions are included. For the other approximations functions are excluded stepwise from the two sets, where the deletion is done in the sequence of decreasing exponential parameter of the functions. The calculations performed are defined by the symbols $\Gamma 18\, \Delta 18$, $\Gamma 16\, \Delta 18$, $\Gamma 14\, \Delta 18$, $\Gamma 12\, \Delta 18$, $\Gamma 16\, \Delta 16$, … and finally $\Gamma 12\, \Delta 12$. In addition the letter *a* denotes that the energy expectation value is calculated taking the nonorthogonality of the MO's into account, the letter *b* denotes the neglect of this nonorthogonality. For the orthogonalization the method of Löwdin has been used [55]. The total energies, which have been computed for all the approximations, are given in Table 2. In Fig. 1 the energy differences $\Delta E = E^{MIM} - E^{SCF}$ are plotted for some examples which are representative for the whole set of calculations: the curve for $\Gamma 12\, \Delta 18$ is similar to the one for $\Gamma 14\, \Delta 18$; $\Gamma 16\, \Delta 16$ corresponds to $\Gamma 18\, \Delta 18$, from which it differs

Table 3. Interaction energy between the two sets of transferred LMO's for Be_2 calculated exactly (X_{ex}) and by a point charge approximation (X_{pc}). The nonorthogonality of the MO's is neglected. (All values in atomic units)

R	X_{ex}	X_{pc}	$\Delta X = X_{pc} - X_{ex}$
2.0	1.989410	2.0	0.010590
3.0	1.330469	1.333333	0.002864
4.0	0.999347	1.0	0.000653
6.0	0.666638	0.666667	0.000029
8.0	0.499999	0.5	0.000001
12.0	0.333333	0.333333	0.0

very little; $\Gamma 14 \Delta 16$ is similar to $\Gamma 14 \Delta 18$ etc. Considering the figure the following statements can be made. The curves *a* and *b* do not meet in general for $R \to \infty$ and do in general not approach the limiting value zero, but they run parallel to the abscissa for interatomic distances larger than approximately 6 a.u. (for some cases — the poorer approximations — 8 a.u.). This then corresponds to a parallel shift of the potential curves, which is the result one would like to obtain. If a number of basis functions is completely excluded from the expansion of the outer shell MO's — which is the case for most of the approximations — the limiting value zero for the energy difference ΔE can no longer be reached and further on the curves *a* and *b* can no longer meet. It is the nonorthogonality of the outer shell MO on any Be atom to the inner shell MO on the same atom which causes this. The first conclusion to be drawn is that it is advisable to keep the sets Γ and Δ identical, which will be done in the subsequent investigations. The difference between curves *a* and *b*, which determines the reliability of the calculations where the nonorthogonality is neglected in the computation of the energy expectation value, is minimal for this case. There is in fact little computational advantage in allowing the sets Γ and Δ to differ. The operator defining the MO's $|m\rangle$ thus simplifies to ($O_\Gamma = O_\Delta = O$):

$$OP'OFOP'O. \tag{46}$$

In Table 3 the energy values for the exactly calculated interaction energy of the transferred LMO's, for the point charge approximation to it, and their difference $\Delta X = X_{pc} - X_{ex}$ is given. This approximation seems to be justified for distances greater than about 6 a.u.

3.B. Li_2–Li_2

The interaction of two Li_2 molecules is more interesting than the interaction of two Be atoms. 9 *s*-type functions contracted to 6 *s*-type functions [53] augmented by $2p\sigma$-type Gaussian lobe functions were used on every Li atom. The parameters for the *p*-type functions are: $\eta_1 = 0.5$, $R_1 = \pm 0.075$ a.u. and $\eta_2 = 2.0$, $R_2 = \pm 0.065$ a.u. For the experimental bond length $R = 5.0504$ a.u. the calculated total SCF energy is $E^{SCF} = -14.862665$ a.u. This compares with the result of

Table 4. Total SCF energies for the linear geometry of the Li_4 molecule (the bond distance of the two Li_2 molecules is kept fixed at its experimental value of 5.0504 a.u.; all values in atomic units)

R	E^{SCF}
3.0	−29.645618
4.0	−29.699425
5.0504	−29.720226
6.0	−29.725574
8.0	−29.726184
12.0	−29.725281
20.0	−29.725316
∞	−29.725330

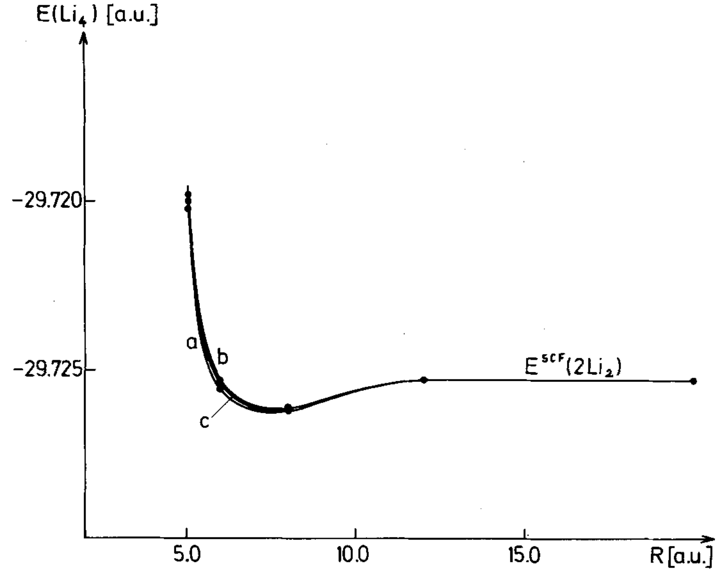

Fig. 2. Potential energy curve for $Li_2 - Li_2$; approximation 1, 1, 4 Γ 32 (for notation and definition of *a*, *b*, *c* see text)

Ransil and Sinai: $E^{SCF} = -14.87152$ a.u. [56]. The bond distance of the two Li_2 molecules is held fixed at $R = 5.0504$ a.u., only the distance between the two molecules is varied for the linear configuration in the range from $R_{LiLi'} = 3.0$ a.u. to $R_{LiLi'} = 20.0$ a.u. The energy values are given in Table 4 and the potential curve is plotted in Fig. 2, curve *a*. It is interesting to observe that the Li_4 molecule is bound relative to two Li_2 molecules with a binding energy of approximately 0.54 kcal/mole at a distance of about 7.5 a.u. At a distance of about 12 a.u. there is an extremely small maximum of approximately 0.03 kcal/mole in the potential curve, but this value is too small to be interpretable. The MO's have been localized by the method of Edmiston and Ruedenberg [24].

Table 5. Total Energies for the linear geometry of the Li_4 molecule calculated in the MIM approximation. The energy values are given for the exact calculation (E_{ex}^{MIM}) and for the calculation involving the point charge approximation (E_{pc}^{MIM}) both for the neglect of the nonorthogonality (*b*) and taking it into account (*a*). (All values in atomic units, for notation see text)[a]

R	E_{ex}^{MIM} (*a*)	E_{ex}^{MIM} (*b*)	E_{pc}^{MIM} (*a*)	E_{pc}^{MIM} (*b*)
	Approximation 1, 1, 4 Γ 32			
3.0	−29.644888	−29.644876	−29.645150	−29.645136
4.0	−29.698830	−29.698818	−29.699034	−29.699021
5.0504	−29.719834	−29.719825	−29.719994	−29.719984
6.0	−29.725334	−29.725328	−29.725464	−29.725457
8.0	−29.726116	−29.726114	−29.726203	−29.726201
12.0	−29.725278	−29.725278	−29.725323	−29.725324
20.0	−29.725316	−29.725316	−29.725333	−29.725333
	Approximation 1, 1, 4 Γ 30			
3.0	−29.638803	−29.635818	−29.639110	−29.636078
4.0	−29.693411	−29.690324	−29.693644	−29.690526
5.0504	−29.714923	−29.711548	−29.715098	−29.711706
6.0	−29.720727	−29.717065	−29.720863	−29.717194
8.0	−29.721801	−29.717732	−29.721888	−29.717819
12.0	−29.721022	−29.716755	−29.721064	−29.716800
20.0	−29.721037	−29.716749	−29.721053	−29.716766
	Approximation 2, 2, 2 Γ 30			
3.0	−29.636990	−29.634395	−29.643269	−29.640672
4.0	−29.692931	−29.689996	−29.696687	−29.693735
5.0504	−29.714643	−29.711327	−29.717108	−29.713778
6.0	−29.720555	−29.716899	−29.722317	−29.718656
8.0	−29.721774	−29.717687	−29.722721	−29.718642
12.0	−29.721059	−29.716779	−29.721426	−29.717153
20.0	−29.721078	−29.716778	−29.721182	−29.716884
	Approximation 2, 2, 2 Γ 28			
3.0	−29.629013	−29.619032	−29.634952	−29.625309
4.0	−29.686023	−29.676296	−29.689619	−29.680035
5.0504	−29.709180	−29.700053	−29.711548	−29.702504
6.0	−29.715760	−29.706846	−29.717455	−29.708603
8.0	−29.717376	−29.708449	−29.718291	−29.709404
12.0	−29.716747	−29.707682	−29.717102	−29.708056
20.0	−29.716796	−29.707719	−29.716896	−29.707826
	Approximation 3, 3, 0 Γ 32			
3.0	−29.623096	−29.800562	−29.629370	−29.797858
4.0	−29.687252	−29.787452	−29.739871	−29.847213
5.0504	−29.713562	−29.762680	−29.778986	−29.835688
6.0	−29.721609	−29.746389	−29.784926	−29.814538
8.0	−29.724955	−29.730399	−29.772598	−29.778947
12.0	−29.725239	−29.725417	−29.747492	−29.747632
20.0	−29.725316	−29.725316	−29.731914	−29.731914

[a] The bond distance of the two Li_2 molecules is kept fixed at its experimental value of $R = 5.0504$ a.u.

A number of calculations have been made applying the method of molecules in molecules in various approximations. They will be described in the sequence of decreasing accuracy. The inner shell MO's on the two outer Li atoms are transferred and the set Γ includes all basis functions (i.e. altogether 32) in the first application. This approximation is denoted as $1, 1, 4\,\Gamma 32$; the notation gives the number of LMO's transferred for the first and the second Li_2 molecule and the number of MO's redetermined in the region of interaction (4). By excluding the contracted *s*-type function on both outer Li atoms approximation $1, 1, 4\,\Gamma 30$ results. If the inner shell MO's on the two inner Li atoms are transferred as well, the approximations $2, 2, 2\,\Gamma 30$ and $2, 2, 2\,\Gamma 28$ are obtained, where $\Gamma 28$ means that the contracted *s*-type function is excluded on all four Li atoms from the expansion of the bonding orbitals. In the crudest approximation all LMO's are transferred $(3, 3, 0\,\Gamma 32)$. The energy values for all approximations are listed in Table 5. The potential curves for approximation $1, 1, 4\,\Gamma 32$ are plotted in Fig. 2, curves *b* and *c* (*b*: interaction energy between the transferred LMO's calculated exactly, *c*: interaction energy calculated by the point charge approximation). Both curves *b* and *c* are in excellent agreement with the potential curve *a* calculated by the *ab initio* SCF method. The nonorthogonality of the MO's causes nearly no error in this case as can be seen from Table 5. The corresponding potential curves coincide with curves *b* and *c*, respectively. The difference

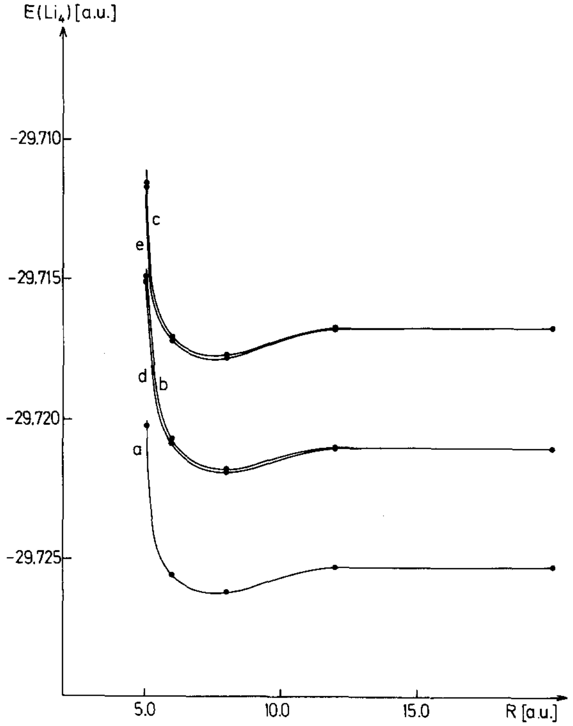

Fig. 3. Potential energy curve for Li_2-Li_2; approximation 1, 1, $4\,\Gamma 30$ (for notation and definition of *a*, *b*, *c*, *d*, *e* see text)

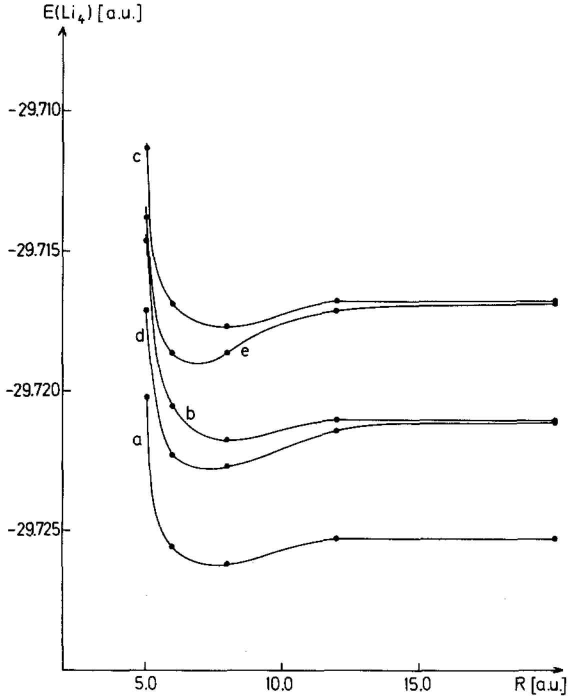

Fig. 4. Potential energy curve for Li_2-Li_2; approximation 2, 2, 2 Γ 30 (for notation and definition of *a*, *b*, *c*, *d*, *e* see text)

$\Delta E = E^{MIM} - E^{SCF}$ is nearly zero for all R. For approximation 1, 1, 4 Γ30 the potential curves are plotted in Fig. 3 (curve *a*: SCF result, *b*: energy value calculated exactly, nonorthogonality of the MO's taken into account [55], *c*: as *b* but nonorthogonality neglected, *d*: energy value calculated including point charge approximation, nonorthogonality taken into account [55], *e*: as *d* only with nonorthogonality neglected). Curves *b* and *c* are nearly parallelly shifted from the exact SCF curve and curves *d* and *e* are good approximations to them.

The agreement deteriorates slightly for approximation 2, 2, 2 Γ30 (Table 5 and Fig. 4, the letters *a*, *b*, *c*, *d* and *e* have the same meaning as above). Curves *b* and *c* are still fairly parallel to *a*. But the point charge approximation in the calculation of the energy leads to a small shifting of the minimum to smaller R values and to a deeper minimum. This tendency is found as well for approximation 2, 2, 2 Γ28 (Table 5 and Fig. 5 with *a*, *b*, *c*, *d*, *e* as defined above). For a good agreement with the SCF result (parallel shift of the potential curve) R must be larger than about 6–8 a.u.

The approximation 3, 3, 0 Γ32, in which all MO's have been transferred, is unreasonable because the minimum in the potential curve is not reproduced (Table 5). It is concluded that it is the modification of the bonding orbitals in the two Li_2 molecules which leads to bonding in Li_4.

Table 6 summarizes the effect of the point charge approximation on the interaction energy between the nonorthogonal transferred MO's: *a* is a very good

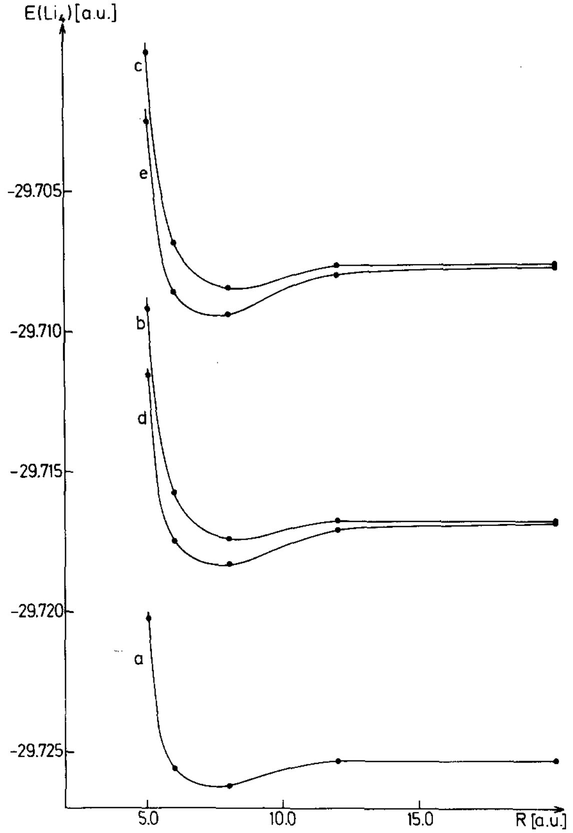

Fig. 5. Potential energy curve for $Li_2 - Li_2$; approximation 2, 2, 2 Γ 28 (for notation and definition of *a*, *b*, *c*, *d*, *e* see text)

Table 6. Difference between the exactly calculated interaction energy between the two sets of transferred LMO's and the result of the point charge approximation for Li_4 ($\Delta X = X_{pc} - X_{ex}$). The nonorthogonality of the MO's is neglected. (All values in atomic units; for notation see text)

R	a	b	c
	ΔX (1, 1, 4 Γ 32 and 1, 1, 4 Γ 30)	ΔX (2, 2, 2 Γ 30 and 2, 2, 2 Γ 28)	ΔX (3, 3, 0 Γ 32)
3.0	− 0.000260	− 0.006277	0.002704
4.0	− 0.000202	− 0.003739	− 0.059761
5.0504	− 0.000158	− 0.002451	− 0.073009
6.0	− 0.000129	− 0.001757	− 0.068149
8.0	− 0.000087	− 0.000955	− 0.048548
12.0	− 0.000045	− 0.000374	− 0.022214
20.0	− 0.000017	− 0.000106	− 0.006599

Table 7. Approximate bond distance and binding energy B of the Li_4 molecule relative to two Li_2 molecules (kept at their experimental bond length of $R = 5.0504$ a.u.). (For an explanation of the notation see the text)

Method	$R_{LiLi'}$ [a.u.]	B [kcal/mole]
SCF	7.5	0.54
1, 1, 4 Γ 32 b	7.5	0.5
1, 1, 4 Γ 32 c	7.5	0.55
1, 1, 4 Γ 30 b	7.5	0.49
1, 1, 4 Γ 30 c	7.5	0.62
1, 1, 4 Γ 30 d	7.5	0.52
1, 1, 4 Γ 30 e	7.5	0.66
2, 2, 2 Γ 30 b	7.5 – 8.0	0.44
2, 2, 2 Γ 30 c	7.5 – 8.0	0.57
2, 2, 2 Γ 30 d	7.0	1.0
2, 2, 2 Γ 30 e	7.0	1.1
2, 2, 2 Γ 28 b	8.0	0.36
2, 2, 2 Γ 28 c	8.0	0.46
2, 2, 2 Γ 28 d	7.0 – 7.5	0.88
2, 2, 2 Γ 28 e	7.0 – 7.5	0.99
3, 3, 0 Γ 32	∞	0.0

result, b is satisfactory for $R > 8.0$ a.u. and c is completely useless, but this is not surprising.

In Table 7 the approximate bond distance $R_{LiLi'}$ and binding energy of the Li_4 molecule with respect to two Li_2 molecules are given as a summary on the quality of the various approximations investigated.

3.C. Barrier to Internal Rotation in Ethane

The basis set used in the calculation of the barrier to internal rotation in ethane consists of 7 s-type functions and 3 p-type Gaussian lobe functions on every C atom [57] contracted to 5 s-type and 2 p-type functions and of 3 s-type functions on every H atom contracted to 2 s-type functions [53]. For the p-type functions the distances from the center have been chosen to be $R_1 = \pm 0.1$ a.u. for $\eta_1 = 0.1992$, $R_2 = \pm 0.08$ a.u. for $\eta_2 = 0.8516$ and $R_3 = \pm 0.05$ a.u. for $\eta_3 = 4.1829$. The experimental geometry has been used for both the staggered and the eclipsed conformation of the ethane molecule. The total energy calculated for the staggered form is $E^{SCF} = -79.090587$ a.u. and for the eclipsed form $E^{SCF} = -79.085792$ a.u., which results in a rotational barrier of 3.01 kcal/mole. The best wave function for C_2H_6 has been calculated by Veillard, who obtained $E^{SCF} = -79.2377$ a.u. for the staggered form and a rotational barrier of 3.07 kcal/mole [58]. The experimental value is 2.928 kcal/mole [59].

The theory of molecules in molecules is applied in the following way. Two CH_4 molecules in the appropriate geometry serve as fragments for the C_2H_6 molecule. One of the H atoms and its associated C–H bond orbital is taken out from each of the two CH_4 molecules. The inner shell MO's and the remaining 6 C–H bond orbitals are transferred. Thus only the C–C bond orbital has to be determined. The different approximations, which have been investigated, are described as follows: 1) $\Gamma 34$: all basis functions are included in Γ, 2) $\Gamma 28$: the contracted *s*-type function on all of the H atoms is taken out, 3) $\Gamma 22$: all basis functions on the H atoms are taken out, 4) $\Gamma 20$: in addition to 3) the contracted *s*-type functions used mainly to describe the inner shell MO's on the C atoms are taken out. The exact calculation of the energy with the nonorthogonality of the MO's taken into account is denoted by *a* [55], if the nonorthogonality is neglected, *b* is obtained; *c* and *d* are the corresponding results when the interaction energy between the two sets of LMO's transferred from the fragments is calculated by the point charge approximation. The transfer has been done for the energy localized MO's of Edmiston and Ruedenberg [24] (ELMO), the LMO's of Boys [23], the LMO's of Magnasco and Perico [26] and the density localized MO's of the author [29]. It turns out that the results for the different LMO's are nearly the same throughout in agreement with the fact that the LMO's themselves do not differ significantly [29]. Only the data for the ELMO's will be given. It further on turns out that the approximations denoted by $\Gamma 34$, $\Gamma 28$, $\Gamma 22$, and $\Gamma 20$ all give nearly the same value for the rotational barrier and it is only of importance whether one is dealing with case *a*, *b*, *c* or *d* of the calculations. The results for the rotational barrier are (in kcal/mole): $\Delta E(a) = 2.38$, $\Delta E(b) = -2.06$, $\Delta E(c) = 3.34$, and $\Delta E(d) = 1.52$. (The values are given for approximation $\Gamma 34$, the values for the other cases differ by less than 0.1 kcal/mole). It is seen that the nonorthogonality of the MO's is important causing result *b* to have the incorrect sign. If the nonorthogonality is properly taken into account, the rotational barrier is about 20% smaller than the *ab initio* value, which is satisfactory. The point charge approximation gives an acceptable result in both cases and result *c* is quite a good approximation to *a*, which is surprising if one considers how unjustified this point charge approximation in the energy evaluation looks for such a small molecule as ethane. The fact that the other approximations (indicated by the notation $\Gamma 28$, $\Gamma 22$, $\Gamma 20$) do not remarkably affect the value of the rotational barrier is somewhat surprising in view of the crudeness of some of the approximations made. Karplus and coworkers [60] have analyzed the rotational barrier in ethane. They were able to show that nearly any wave function gives an acceptable value for the barrier, if it is only antisymmetric. From the present investigation one can in addition conclude that the antisymmetry with respect to the two CH_3 fragments does not play a crucial role, because this has been neglected in the calculation of E^{MIM} by the point charge approximation, but only the antisymmetry within each CH_3 group taken together with the C–C bond orbital.

The approximations made for C_2H_6 can lead to a considerable saving in the computation time. For the approximation denoted by $\Gamma 28$ a saving of about 47% in the integral computation could be achieved, for $\Gamma 22$ and $\Gamma 20$ a saving of about 59% and 60%, respectively, would be possible. These numbers are given only as an orientation. They have to be taken with great care, because many integrals would anyway be zero or negligible and secondly the necessity of taking the nonorthogonality of the MO's into account modifies this result.

4. Conclusions

The following conclusions can be drawn from these applications. The construction of the wave function of a molecule from the wave functions of fragment molecules by transferring some of the LMO's and redetermining the MO's in the region of interaction is a justified approach which gives results in close agreement with those obtained by the *ab initio* method. In particular it has been shown for the cases considered to what extent LMO's are transferable between structurally related molecules, if the total energy is taken as the measure of transferability. Additional approximations have been suggested: a) the truncation of the basis set for the expansion of the MO's in the region of interaction, b) the similar approximation for the projection operator for orthogonality, c) the neglect of the nonorthogonality of the MO's in the calculation of the energy expectation value, and d) the point charge approximation for the calculation of the interaction energy between the two sets of transferred LMO's. These additional approximations can be justified too.

Because these approximations acquire validity for distances between the atomic centers involved of the order of two normal bond lengths, the sets Γ and Δ must be chosen with care. Except for the molecule C_2H_6 the approximation of truncating the basis set has been examined for the case of the basis functions which have large exponential parameters and are mainly used to construct the inner shell MO's. In this case the distance between the centers must be about 6 a.u. for the Li and Be atoms in order to obtain a parallel shift of the potential curves relative to the exact SCF result to within 10^{-3} to 10^{-4} a.u. or 0.6 to 0.06 kcal/mole. (It has been stated at which distances agreement with the SCF result is obtained; in many practical questions, however, such stringent conditions might be unnecessary.) The same approximation can certainly be made for any type of basis function and any type of LMO, only the distance between the centers or centroids, respectively, must be greater to obtain equally good results. It is possible that in larger molecules this situation might improve, because the MO's in the region of interaction can serve as a kind of buffer.

It has been found that the sets Γ and Δ are best chosen to be identical. It proves to be disadvantageous to allow in the set Δ degrees of freedom which are not allowed in the set Γ. In other words the projection operators O_Γ and O_Δ should project into the same subspace. This result could have been anticipated from the bounds in Eq. (37). The operator determining the MO's in the region of interaction is consequently given by Eq. (46).

Two different sources exist for the nonorthogonality of the MO's. The transferred LMO's of the two fragments are nonorthogonal because they result from calculations on different molecules and because their expansion might have been truncated due to the deletion of some basis functions in each of the two fragments. The MO's in the region of interaction are nonorthogonal to the transferred LMO's due to the projection effected by the operator O. The neglect of the nonorthogonality in the calculation of the total energy seems to be valid for the same distances between the atomic centers as the truncation of the basis set becomes valid. That this approximation works reliably, i.e. introduces essentially only a parallel shift of the potential curves is vital for the aim of saving computational time.

The point charge approximation for the calculation of the interaction energy between the two sets of transferred LMO's in the two fragments can only be valid for large distances where quantum mechanical effects of bonding play no role. It seems to be valid for distances equal to or larger than the ones necessary for the validity of the other approximations discussed above. It should be mentioned that this approximation can easily and in various ways be refined. A rather crude but extremely simple version has been examined in this work, which allows to reduce the computational expense to a "N^2 law", where N is the number of basis functions, for a significant part of the calculation leaving the "N^4 law" only in the region of interaction. The present version of the approximation has given reasonable results in most cases considered, but its reliability in more complicated cases still remains to be demonstrated [51].

The theory of molecules in molecules discussed in the present article appears to be a promising starting point for reliable and time saving computations on larger molecules, but more experience is necessary with the approximations involved. This will supply the information where the method has to be ameliorated.

Acknowledgement. The calculations were performed on an IBM 360/91 computer while the author was at the Max-Planck-Institut für Physik und Astrophysik, München. The author would like to thank Professor Dr. L. Biermann and Dr. G. Diercksen for the opportunity of working in the institute and for using its facilities. Financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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