Revista Mexicana de Física **42**, *No. 6 (1996) 911–923*

Localized orbitals for molecular calculations

A. RAMÍREZ-SOLÍS* AND RAMÓN HERNÁNDEZ-LAMONEDA
Facultad de Ciencias, Universidad Autónoma de Morelos
62210 Cuernavaca, Morelos, México

Recibido el 10 de abril de 1996; aceptado el 10 de junio de 1996

ABSTRACT. We present an overview of the existing localization algorithms which have been or are being used to perform quantum chemical molecular calculations that take into account electronic correlation effects. The natural distinction between intrinsic and extrinsic localization methods is explained and developed. The advantages and drawbacks of specific methods are discussed in terms of CPU time required to obtain the (in most cases) almost identical localized molecular orbitals. Finally, we show using a specific example of a second order multireference perturbational calculation, the enormous gain in computer time that the use of localized molecular orbitals can bring. We also show explicitly the "concentration" of second order Möller-Plesset correlation energy into a much smaller perturbed space.

RESUMEN. Se presenta una revisión de los métodos de localización de orbitales usados para realizar cálculos moleculares químico-cuánticos que toman en cuenta efectos de correlación electrónica. La distinción natural entre métodos de localización intrínsecos y extrínsecos es explicada y desarrollada en detalle. Las ventajas y desventajas de métodos específicos son discutidas comparativamente en términos del tiempo de CPU requerido para obtener, en la mayoría de los casos, los orbitales localizados prácticamente idénticos. Finalmente mostramos, usando un ejemplo específico de un cálculo perturbativo multirreferencial de segundo orden, la enorme ganancia en tiempo de máquina que el uso adecuado de orbitales localizados puede proporcionar respecto al uso de orbitales canónicos SCF o CAS-SCF. También se hace explícita la gran "concentración" de energía de correlación de segundo orden Möller-Plesset en un número mucho menor de determinantes.

PACS: 71.10.+x

1. INTRODUCTION

Two opposite views appear when one considers the molecular aspect of matter. The first one is the delocalized picture which has its natural roots in the concept of electronic configurations in atoms. This concept has been confirmed by the surprisingly accurate results of atomic spectroscopy.

The idea of electronic configurations in atoms leads naturally to molecular delocalization. This stems from the fact that, since the selection rules that take into account the molecular symmetry play the main role in molecular spectroscopy, it is straightforward to imagine a set of closed shells, filled with paired electrons, which reflect the symmetry properties of the nuclear skeleton.

The unescapable conclusion is that these electronic shells will therefore be delocalized among the equivalent atoms in a given molecule.

---

[*] Email: alex@alpha.fc.uaem.mx.

On the other side, the localized approach has its origin in pure and applied chemical experience. This can immediately be seen in the deep meaning of chemical formulae. These formulae implicitly suggest the existence of couples of localized electrons since these electrons should, in general, remain close to the nuclei between which they form a chemical bond.

At this point there is no reason to choose one point of view or the opposite, since each approach can help to understand many phenomena of rather different nature. For instance, the delocalized approach can successfully explain molecular ionization or excitation processes, while the localized view is better suited to deal with real chemical problems.

Nevertheless, these localized and delocalized views can be used as starting points of two series which converge to the same result. We see this idea clearly illustrated in the mathematical equivalence of two molecular wave functions described by Slater determinants, the first one built using delocalized molecular orbitals (MO) and the second one built using localized MOs which have been obtained from the delocalized set by a unitary transformation; this means that the localized and the delocalized MOs are the same, up to a phase factor.

Here it should be said that the mathematical equivalence of the previously mentioned molecular wave functions has deeper implications; the electronic density matrices calculated using one set of MO or the other are exactly the same. For this reason all the molecular properties which can be calculated using these density matrices will be the same, regardless of whether the localized or the delocalized set of MOs has been used.

It is very interesting to note that, in spite of the rather common idea that it was through the delocalized picture that the first quantum chemical calculations were made, it was through the localized approach that they were performed. Millié *et al.* [1] made an interesting historic review which showed that the first molecular wave functions were built using bielectronic functions centered on only one or two atoms [2].

The generalized use of delocalized MOs did not a appear until after their application to some specific problems such as the aromatic Hückel compounds or the successful study of excited molecular states by Mulliken.

Without a doubt, the work of Pauling had a great impact on the theoretical milieu. Electronic delocalization ceased to be a mere curiosity which appeared as a particular property of some specific molecules which had "moving electrons" and became a universal feature of all electronic systems bound to a nuclear framework.

In the 60's, the application of the Hückel theory to all problems dealing with valence electrons as well as the discovery of the Woodward-Hoffman rules for concerted reactions are clear examples of this general delocalized approach by theoreticians.

Very soon after the formulation of the molecular orbital theory, one of its proponents, Coulson, noticed that an N-electronic wave function made using a set of delocalized MO could be analyzed in terms of quasi-localized MO and *viceversa* without any effect on the global electronic structure of the molecule. He carefully looked at a few examples [3] and showed that the delocalized MO set of Mulliken was equivalent to the Hund localized set except for the effect of the orthogonalization tails.

Some years later, the mathematical proof of Coulson's idea was given by Lennard-Jones and two of his students, Hall and Pople [4–6]. They showed that the occupied MO which are solutions of the closed shell Hartree-Fock equations are determined up to a unitary transformation. This result is of utmost importance since, it yields the mathematical basis upon which one can propose the relocalization theories which aim at recovering the local character of the molecular orbitals using the previously mentioned transformation.

In this way we can transform the canonical molecular orbitals (those which satisfy the Hartree-Fock equations) to obtain an **equivalent** set of localized MO, in the sense that these localized MO have their largest coefficients corresponding to the orbitals centered on two chemically bound atoms (bonds) or centered on a single atom (lone pairs).

The concept of localized MO equivalent to the delocalized canonical MO set has also been extended to multiconfigurational self-consistent field (SCF) methods [7] and to configuration interaction (CI) algorithms [8].

Once we know that is possible to obtain a unitary transformation that allows one to find equivalent localized MO starting from the delocalized MO set (canonical or other), it should be said that there are great many ways of determining the precise form of this transformation.

Ruedenberg [9] has classified the resulting localization methods in two categories, according to the nature of the unitary transformation used in each method: extrinsic and intrinsic algorithms.

2. EXTRINSIC LOCALIZATION METHODS

In this section we do not attempt to give a full account of all the existing extrinsic localization methods, since there is an enormous number of possible choices. We will further impose another constraint in this section since we will only consider methods which use molecular orbitals as developed in the linear combination of atomic orbitals (LCAO) approach, that is, orbitals which can be written as

$$|\phi_i\rangle = \sum_{\mu}^{N} C_i^{\mu} |\chi_\mu\rangle. \tag{1}$$

The extension of these localization algorithms towards more general MO, such as numeric Hartree-Fock orbitals, is not straightforward at all.

2.1. Truncation of delocalization tails

This seems to be the most natural method when constructing one (or many) MO centered on one atom or on a particular domain of the entire molecule.

Given a set of delocalized MO, it is possible to construct a series of unitary transformations such as

$$\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix},$$

where the first one is determined by an angle θ which insures that one of the molecular orbitals does not have any components outside a certain number of atoms, generally one or two of them. Unfortunately this method has a serious drawback: the remaining molecular orbitals will have even larger delocalization tails in some of the unwanted atoms. The father of this idea is Pople [10] who used it to build localized lone pairs. Some years later this method was generalized by Peters [11] and Stamper [12].

2.2. *Homogeneous localization by Mulliken population*

A more democratic alternative to the previous method will be given here. Instead of choosing a particular MO to be localized, one could impose the more egalitarian condition that all the elements (bonds and lone pairs) of the chemical formula play the same role. In order to achieve this goal, Magnasco and Perico [15] proposed to maximize the overlap Mulliken populations, that is, to maximize

$$P_i^{\mathrm{A,B}} = \sum_{\alpha \in \mathrm{A}} \sum_{\beta \in \mathrm{B}} C_i^{\alpha} C_i^{\beta} \langle \chi_\alpha | \chi_\beta \rangle, \tag{2}$$

where i is the transformed localized molecular orbital associated to atoms A-B in the overall chemical formula. Atoms A and B will then be chemically bound and a lone pair will be produced if $\mathrm{A} = \mathrm{B}$. This method yields almost the same results as those produced by the intrinsic algorithms or those of the following method.

2.3. *Projection methods*

The construction of MO that have a clear chemical meaning by projection of the appropriate mono- or bicentric orbitals is undoubtedly the most simple way, both from the computational point of view or from the conceptual point of view.

We should note here that this method is also the most versatile, since it allows us to use "group" orbitals instead of only mono or bicentric MO as projection tools; for instance, with these group orbitals we could recover all the local (polarization, local excitations, etc.) effects due to a monomer in a polymer.

The basic principle underlying all projection techniques is rather simple: one projects a set of completely localized (on one or more atoms) orbitals $|\chi\rangle$ on the subspace spanned by the delocalized set $|\phi\rangle$; this produces a new set of localized orbitals $|\phi'\rangle$. Finally one has to perform an orthonormalization process on this set, either by applying the symmetric ($S^{-1/2}$) orthogonalization of Löwdin or by applying the Schmidt method.

It has been proved [2] that this method is equivalent to the minimization of

$$\sum_i (|\chi_i\rangle - |\phi_i\rangle)^2, \tag{3}$$

or to the maximization of the sum of the scalar products

$$\sum_i \langle \chi_i | \phi_i \rangle. \tag{4}$$

We will see that these methods are comparatively, rather efficient, since they produce almost identical localized MO as those obtained using methods which require the computation of many monoelectronic or bielectronic integrals of a given operator and are, therefore, much more time consuming. This CPU time is proportional to N^3 or N^4 where N is the dimension of the atomic basis set in Eq. (1).

Here we will briefly mention the basic ideas of the method developed and used in our group, which is an improvement of a program [13] based on the original proposal of Chambaud *et al.* [14]; this algorithm allows one to localize any subset B of a set A of delocalized orbitals by projecting one or more sets of fragment orbitals on the space spanned by A. In particular A could represent the doubly occupied canonical HF orbitals, the open-shell orbitals and some or all of the virtual orbitals. For the interested reader, the full details of the algorithm are carefully given in the original article [16]. Let us start by considering a molecule A composed of, for the sake of simplicity, only two fragments. This restriction is only imposed for brevity and many fragments can formally and practically be treated in the same way. Let us denote by $\mathbf{V}_i$ and $\mathbf{V}_i^*$ (i=1,2) the occupied and virtual orbitals of fragment i and let

$$\hat{P} = \sum_{k\in \mathrm{A}}^{\mathrm{occ}} |\phi_k\rangle\langle\phi_k| \tag{5}$$

be the projection operator on the Fock space of the molecule A (note that the sum goes over all the occupied orbitals of A). Then

$$\hat{Q} = \hat{1} - \hat{P} = \sum_{k\in \mathrm{A}}^{\mathrm{virt}} |\phi_k^*\rangle\langle\phi_k^*| \tag{6}$$

is the projector on the virtual SCF orbitals. The elements of the atomic overlap matrix are given by

$$\mathbf{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle. \tag{7}$$

If N_1 and N_2 are the dimensions of the basis sets of fragments 1 and 2, then $N = N_1 + N_2$ is the dimension of the basis set in which the SCF orbitals $|\phi_k\rangle$ are expanded. Let us denote by OSB the open-shell and bonding orbitals and by NMV the non-modified virtual orbitals of the whole molecule A.

With these conventions we can now construct an orbital array as in Fig. 1. Each subset represented there has N rows since orbitals are expressed as columns in the overall basis set. Clearly, the complete set of vectors has approximately twice the dimension ($2N$) of the original SCF (occupied and virtual) orbitals. The first subset is composed by the open-shell and bonding orbitals which we may not want to change. The second and third subsets represent the projection of the occupied orbitals of fragments 1 and 2 on the Fock space of the molecule. The fourth subset is given by the occupied SCF orbitals of the complete molecule minus those orbitals already appearing in the first subset. The fifth subset consists of the non-modified virtual orbitals which, in some cases, may already

OSB	PSV$_1^{occ}$	PSV$_2^{occ}$	SCF^{occ}-OSB	NMV	QSV$_1^*$	QSV$_2^*$	SCF*

FIGURE 1. OSB: Open-shell and bonding orbitals; V$_n^{occ,*}$ stand for the occupied and virtual orbitals of fragment n in its reduced basis set; SCF^{occ,*} are the occupied and virtual orbitals the whole molecule; NMV are the non modified virtual orbitals; P and Q are the projector operators defined in the text.

be localized. The sixth and seventh subsets are the projections of the virtual orbitals of fragments 1 and 2 onto the $\hat{Q}$ space of A. Finally, the eighth subset are the SCF virtual orbitals of the molecule.

As we have said, since the whole orbital matrix has about twice the number of original SCF orbitals, one has to find a sensible way to get rid of the extra N linearly dependent orbitals. This poses some serious technical problems when dealing with an actual calculation. The overall elimination process we use now is based on an overlap criterion and treats molecular orbitals within each subset in an equivalent manner while, at the same time, keeps the i-th orbital of the j–th subset orthogonal to all the previously orthogonalized MOs of the $j-1$ preceding subsets through a Schmidt orthogonalization.

At this point we should say that there are two main strategies to eliminate redundant virtual orbitals. The first one is to Schmidt orthogonalize a given virtual MO to the already chosen (occupied and virtual) MOs and then symmetrically-orthogonalize ($S^{-1/2}$) the remaining orbitals within each virtual subset. This has proven to be rather effective especially for cases in which the two fragments (which can in turn be composed of many sub-fragments) are equivalent as far as the symmetry of the molecule concerns. The second strategy is to simply Schmidt-orthogonalize all the virtual MOs with respect to the previous orbitals, again occupied and virtual. In Ref. [16] an example of the application of this localization method has been given to deal with the CuF molecule. In that case the localized orbitals were used to perform second order multireference Möller-Plesset calculations and an impressive gain was obtained regarding the number of generated perturbed determinants. For instance, for the $^3\Pi$ and $^1\Pi$ states, with a reference wave function containing 340 Slater determinants and using the non localized SCF orbitals of the ground state, the multireference second order Möller-Plesset (MR-MP2) algorithm produced more than 25 million perturbed determinants; if one uses instead the localized orbitals resulting from the previously described method, the number of perturbed determinants decreases to only 7.9 million; this represents a significant reduction of CPU time used in the perturbational part of the CIPSI [17] calculation. Of course, we get exactly the same MP2 energetic contribution from both calculations.

Other cases have also been treated which differ from the previous one in that there were more than two fragments and that there were zero or one open-shell per fragment. In this respect we have observed that, depending on these two variables (the number of fragments and the number of open-shells per fragment), sometimes the Schmidt elimination-orthogonalization method for the virtual orbitals or the symmetric $S^{-1/2}$ method are better suited to deal with each case. We present in Table I the results regarding some of the possible combinations of these factors and the best method to eliminate redundant virtual orbitals.

TABLE I. Elimination-orthogonalization method best suited for some cases including up to three fragments.

Number of fragments	Number of open shells per fragment	Elimination-orthogonalization method
2	(1, 1)	Schmidt
2	(0, 0)	$S^{-1/2}$
2	(1, 0)	Schmidt
3	(1, 1, 0)	$S^{-1/2}$
3	(0, 0, 0)	$S^{-1/2}$
3	(1, 1, 1)	Schmidt

3. INTRINSIC LOCALIZATION TECHNIQUES

As a general rule, these methods employ spatial extension or energetic criteria to perform the localization of the original input orbitals. This means that two electrons belonging to two different molecular orbitals are said to be well localized if the mean distance between them is as large as possible or if their interaction energy is as low as possible. Using Dirac's notation, an extremely elegant operational definition of all the intrinsic localization techniques exists, since these methods can be defined as those searching for an extremum of the functional

$$W(|i\rangle) = \sum_{i}^{N} \langle ii|\Omega^{W}|ii\rangle, \tag{8}$$

where N is the number of occupied orbitals and Ω^W is the operator which defines the functional W.

Let us review each one of the best known algorithms following their chronological order. We shall therefore start with the method developed by Boys.

3.1. Boys' localization method

Actually, the method we are about to describe is but one among many algorithms proposed by Boys and coworkers [18–20], but the present method is the best known because of its simplicity. As previously mentioned, in this case Boys' idea was to search for the minimum spatial extension of the occupied orbitals. This is equivalent to search for the minimization of the functional

$$B(|i\rangle) = \sum_{i}^{N} \langle ii|\Omega^{B}|ii\rangle, \tag{9}$$

where Boys' operator is given by

$$\Omega^{B}(\mathbf{r}_i, \mathbf{r}_2) = \|\mathbf{r}_1 - \mathbf{r}_2\|^2. \tag{10}$$

Two equivalent equations can be derived for the functional B:

$$B(|i\rangle) = -\frac{2}{N}B^1(|i\rangle) + 2\,\mathrm{tr}(\mathbf{r}^2) - \frac{2}{N}[\mathrm{tr}(\mathbf{r})]^2 \tag{11}$$

or

$$B(|i\rangle) = -2B^2(|i\rangle) + 2\,\mathrm{tr}(\mathbf{r}^2), \tag{12}$$

where

$$B^1(|i\rangle) = \sum_i^N \sum_{j\leq i}^N [\langle i|\mathbf{r}|i\rangle - \langle j|\mathbf{r}|j\rangle]^2, \tag{13}$$

$$B^2(|i\rangle) = \sum_i^N [\langle i|\mathbf{r}|i\rangle]^2. \tag{14}$$

One must note here that since the unitary transformation we are looking for leaves unchanged the traces in Eqs. (11) and (12), the search for a minimum of the functional B is equivalent to the maximization of the distance between centroids (functional B^1) or to the maximization of the sum of the squares of the centroids' distance to the origin (functional B^2). We should also stress the fact that, besides the SCF calculation which generates the delocalized orbitals, one has to calculate N^2 dipolar integrals. Finally, notice that the functional B^2 is the only one which is not invariant under origin translations.

3.2. Edmiston-Ruedenberg method

We know that the structure of the Hartree-Fock self consistent field theory insures that each component of the total energy (kinetic, nuclear, Coulomb and exchange) is conserved under the application of a unitary transformation of the occupied orbitals. For this reason, the structure of the electronic interaction part has been suggested as a measure of the degree of electronic localization or delocalization. A very interesting idea was proposed by Edmiston and Ruedenberg in 1963 [21–23] which is based in the fact that the quantity

$$\sum_i^N \sum_j^N J_{ij} = \sum_i^N J_{ii} + 2\sum_{i\leq j}^N \sum_j^N J_{ij} \tag{15}$$

remains constant before and after the unitary transformation has been applied to the molecular orbitals, that is

$$\sum_i^N \sum_j^N J_{ij} = \sum_{i'}^N \sum_{j'}^N J_{i'j'}, \tag{16}$$

where the primed quantities indicate that they are calculated using the transformed molecular orbitals. Therefore, as a reasonable localization condition we could impose that the sum of the interorbital Coulomb interactions be a minimum; that implies the minimization of

$$\sum_{i\leq j}^{N}\sum_{j}^{N} J_{ij}. \tag{17}$$

The Edmiston-Ruedenberg operator that should be substituted in Eq. (8) is then

$$\Omega^{\mathrm{ER}}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\|\mathbf{r}_1-\mathbf{r}_2\|}, \tag{18}$$

and we want to maximize the functional

$$\mathrm{ER}(|i\rangle)=\sum_{i}^{N}\langle ii|\|\mathbf{r}_1-\mathbf{r}_2\|^{-1}|ii\rangle. \tag{19}$$

Unfortunately there is simply no way to decrease the N^4 dependence on the number occupied orbitals. Of course, one has to calculate also the Coulomb bielectronic integrals in the molecular basis set (which implies another N^5 transformation); this, however, is not a problem at all if the SCF (or complete active space-SCF, CAS-SCF) orbitals were only the starting point to perform anyway correlated molecular calculations that imperatively need these integrals.

3.3. Von Niessen's method

One of the latest localization proposals was the one given by von Niessen [24] who suggested to maximize the charge density overlap functional

$$N(|i\rangle)=\sum_{i}^{N}\langle ii|\Omega^{N}|ii\rangle, \tag{20}$$

where the operator Ω^N is

$$\Omega^{N}=\delta(\mathbf{r}_1-\mathbf{r}_2). \tag{21}$$

We should point out that the dependence of the last two localization schemes on the number of occupied orbitals is N^4 whereas Boys' method's dependence is only N^2.

There have been several works comparing the localized orbitals obtained using the various localization algorithms. The interested reader can find such comparisons for diatomic and small polyatomic molecules in Refs. [24, 25]; for molecules containing a large number of atoms refer to [26]. The important thing regarding these comparative works is that they show that all the localization techniques (both extrinsic and intrinsic) produce, qualitatively and quantitatively, almost identical localized orbitals regardless of the methods used to obtain them, except for the delocalization tails. The small variations observed between the resulting localized orbitals always concern minute details of these delocalization tails.

Another remark that should be made here is that the intrinsic localization methods based on energetic criteria can, of course, only be applied to the occupied orbitals; they will therefore be unable to produce reasonably well localized virtual orbitals; these virtual orbitals will be of no use when one is trying to get a better description of the molecule through the construction of correlated wave functions, variationally and/or perturbationally. We see here that, besides being a lot faster to perform, the projection methods have the important advantage over the intrinsic algorithms that they can produce well localized virtual orbitals.

4. ADVANTAGES OF USING LOCALIZED ORBITALS

Although we have mentioned all along this report some of the most obvious advantages of using localized orbitals, we will here explicitly discuss the most important advantages one gets by using localized MO. We can summarize these advantages in two specific areas:

1) Localized orbitals allow a coherent treatment of electronic correlation effects; and

2) when multireference perturbational methods are used to deal with these correlation effects, an impressive speed-up is obtained for the calculation of the perturbational contribution to both the energy and the wave function. We shall illustrate these points using a particular example.

By the year 1986 the molecular structure of the silver trimer was a debated subject. Walch *et al.* [27] found that the ground state was the $^2B_2$ component arising from the Jahn-Teller stabilization of the doubly-degenerate 2E' electronic state in D_{3h} symmetry (an equilateral triangle); this $^2B_2$ component had an "obtuse"-triangled ($\theta = 69°$) geometry while the first excited state ($^2A_1$) had an acute-triangle ($\theta = 53°$) geometry. However, a previous work using the delocalized canonical MO of the ground state of Ag_3 and the variational + 2nd order multireference perturbational CIPSI scheme [28] showed that the most stable structure of this trimer was the almost linear ($\theta = 175.2°$) geometry and not the Jahn-Teller distorted geometry reported by Walch *et al.*, this latter obtuse isosceles structure lying only 2.7 kcal/mol higher in the potential energy surface of Ag_3. The problem arising here was that, using delocalized molecular orbitals, one cannot assess the relative quality of the correlated descriptions of the wave functions corresponding to very different nuclear geometries. A slight difference in the quality of these correlated wave functions can give rise to artifactual energy differences which are larger in magnitude than the real energy differences we are looking for. So, in this case, a wrong treatment of the differential electronic correlation effects as a function of the angle θ could easily yield completely unreliable results.

For this reason we decided to apply a localization algorithm in order to be able to control the interatomic and intra-atomic excitations appearing in the variational and the perturbational energy contributions. This allowed us to identify the corresponding equivalent excitations of the almost-linear, the equilateral and the obtuse-triangled geometries of the silver trimer and thus to perform a coherent treatment of the electronic correlation effects.

TABLE II. Comparative distribution of the multireference MP2 correlation energy using localized molecular orbitals (MO) *vs.* non-localized MO.

Coefficient range	Non localized MO		Localized MO	
	Number of determinants	MR-MP2 energy (a.u.)	Number of determinants	MR-MP2 energy (a.u.)
0.01–0.05	83	−0.0110	541	−0.2234
0.002–0.01	11 664	−0.1944	4 396	−0.0958
0.0004–0.002	91 894	−0.1507	37 815	−0.0522
0.00008–0.0004	307 587	−0.0211	132 985	−0.0085
Total	11.7×10^6	−0.3828	2.4×10^6	−0.3822

Special care had to be taken in order to have the same ratios of perturbational/variational energy contributions since minute differences in the variational quality of the wave functions could produce errors greater than the Jahn-Teller stabilization energy (δJT) for this trimmer. This δJT is the energy difference between the equilateral doubly-degenerate state and the Jahn-Teller distorted triangular geometry. The use of the localized orbitals allowed us to obtain differences of less than 0.1% in the ratios of perturbative/variational contributions for these two particularly stable Ag_3 structures. Applying this method it was found out that the most stable structure was the obtuse-angled trimer lying only 328 cm^{-1} (δJT) below the totally symmetric (doubly degenerate) equilateral triangle and that the almost linear arrangement was 1610 cm^{-1} above the absolute minimum. Here we can see that only because we used localized orbitals we could give credit to these rather small energy differences and consider them as reliable figures. To show how the use of localized orbitals "concentrates" the perturbational energy contributions into a much smaller number of perturbed determinants, we present our results in Table II for the case of Ag_3 given above.

This table was obtained using a basis with 72 molecular orbitals (no f orbitals) and using only four determinants in the zeroth order reference space. It is clear that the ratio

$$\frac{E^{\mathrm{MP2}}(\text{correlation})}{1000\ \text{determinants}} \tag{22}$$

as a function of the coefficient range is much more favorable for the localized calculation than for the delocalized case. This is a very important remark from the practical point of view, since it gives an answer to the question of how much CPU time is needed to recover, variationally, a certain amount of the overall MP2 correlation energy. For instance, in order to recover variationally 85% of the MP2 correlation energy of the example given above, in the localized case it is enough to diagonalize a CI matrix of dimension 5000, whereas for the delocalized case it would be necessary to diagonalize a matrix of dimension 70,000 to obtain the same result. Of course, nowdays, nobody winks an eye at such "small" diagonalizations since they can be performed rather swiftly on any low-priced workstation. However, when one needs a reasonable number of energies using this variational-perturbational scheme in order to construct a potential energy surface (or a non negligible part of it) using a localized scheme provides important time savings.

This comparison of localized *vs.* delocalized multireference MP2 calculations becomes even more dramatic when the dimension of the molecular basis set is increased. We performed equivalent calculations with 93 molecular orbitals (this time with 7 f orbitals per silver atom) using the same four reference determinants as before. Using the localized orbitals, the multireference MP2 CIPSI scheme produced 3.5 million perturbed determinants whereas, using the delocalized HF-SCF orbitals, we obtained more than 27 million perturbed determinants. This meant that the delocalized calculation took 8 times the CPU time required for the localized calculation, producing, of course, equivalent results.

ACKNOWLEDGMENT

This work has been supported through A. Ramírez-Solís Research grant number 4061-E from CONACYT.

REFERENCES

1. Ph. Millié, B. Lévy and G. Berthier, *Localization and Delocalization in Quantum Chemistry*, Ed. O. Chalvet, R. Daudel, S. Diner and J.P. Malrieu. Reidel Pub. Co, Dordrecht (1975).
2. W.G. Penney, *The Quantum Theory of Valence*, Methnen, London (1935); H. Hellmann, *Einführung in die Quantenchimie*, F. Deuticke, Leipzig und Wien (1937).
3. C.A. Coulson, *Trans. Faraday Soc.* **38** (1942) 433; *J. Chim. Phys.* **46** (1949) 198.
4. J.E. Lennard-Jones, *Proc. Roy. Soc.* **198** (1949) 1.
5. G.G. Hall and J.E. Lennard-Jones, *Proc. Roy. Soc.* **A 202** (1950) 155.
6. J.E. Lennard-Jones and J.A. Pople, *Proc. Roy. Soc.* **A 202** (1950) 166.
7. B. Lévy, *Chem. Phys. Lett.* **4** (1969) 17.
8. D.L. Wilhite and J.L. Whitten, *J. Chem. Phys.* **58** (1973) 948.
9. K. Ruedenberg, *Modern Quantum Chemistry*, Ed. O. Sinanoĝlu Vol. I. Academic Press, New York (1965).
10. J.A. Pople, *Proc. Roy. Soc.* **202** (1950) 323.
11. D. Peters, *J. Chem. Soc. A.* (1963) 2003.
12. J.G. Stamper and N. Trinajstic, *J. Chem. Soc. A.* (1967) 782.
13. R. Caballol (private communication).
14. G. Chambaud, M. Gerard-Ain, B. Lévy, E. Kassab and P. Pernot, *Chem. Phys.* **90** (1984) 271.
15. V. Magnasco and A. Perico, *J. Chem. Phys.* **47** (1967) 971.
16. A. Ramírez-Solís and J.P. Daudey, *Chem. Phys.* **134** (1989) 111.
17. B. Huron, P. Rancurel and J.P. Malrieu, *J. Chem. Phys.* **58** (1973) 5745.
18. S.F. Boys, *Rev. Mod. Phys.* **32** (1960) 296.
19. J.M. Foster and S.F. Boys, *Rev. Mod. Phys.* **32** (1960) 300.
20. S.F. Boys, in *Quantum Theory of Atoms, Molecules and the Solid State*, Ed. P.O. Löwdin, Academic Press, New York (1966) p. 253.
21. C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35** (1963) 457.
22. C. Edmiston and K. Ruedenberg, *J. Chem. Phys.* **43** (1965) S97.
23. C. Edmiston and K. Ruedenberg, in *Quantum Theory of Atoms, Molecules and the Solid State*, Ed. P.O. Löwdin, Academic Press, New York (1966) p. 263.
24. W. von Niessen, *J. Chem. Phys.* **56** (1972) 4290.

25. W. von Niessen, *Theoret. Chim. Acta* **27** (1972) 9; **29** (1973) 29; **33** (1974) 185.
26. D.A. Kleier, T.A. Halgren, J.H. Hall and W.N. Lipscomb, *J. Chem. Phys.* **61** (1974) 3905.
27. S.P. Walch, C.W. Bauschlicher, S.R. Langhoff, *J. Chem. Phys.* **85** (1986) 5900.
28. A. Ramírez-Solís, M.Sc. Thesis, Facultad de Ciencias, Universidad Nacional Autónoma de México (1986).
29. A. Ramírez-Solís, J.P. Daudey, O. Novaro and M.E. Ruíz, *Z. Phys. D* **15** (1990) 71.