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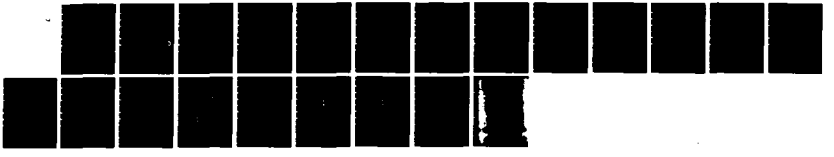

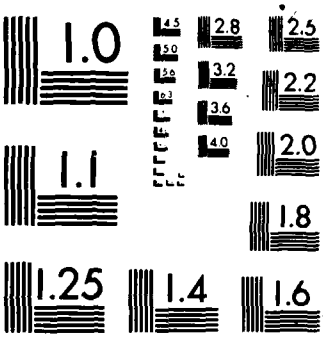

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TECHNICAL REPORT NO. 7

ITERATIVE COUPLING OF PARTITIONED CLUSTERS IN THE SCATTERED-WAVE MOLECULAR-ORBITAL METHOD

by

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ITERATIVE COUPLING OF PARTITIONED CLUSTERS IN THE SCATTERED-WAVE MOLECULAR-ORBITAL METHOD*

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Abstract

The iterative coupling technique is described and applied to the partitioned self-consistent-field Xα scattered-wave method. This technique allows the electronic coupling of a central cluster of atoms to its environment to be calculated iteratively, permitting scattered-wave molecular-orbital calculations to be performed on larger clusters than was previously possible. A test calculation on methanol is reported.

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I. Introduction

The multiple-scattering or scattered-wave method [1], in conjunction with a density-functional approximation to exchange-correlation such as the $X\alpha$ approximation, is a widely used tool for molecular-orbital calculations. This is largely due to its computational efficiency and facility in dealing with large polyatomic molecules, especially those containing heavy atoms (e.g., transition-metal complexes). Nevertheless, there are a wide variety of interesting electronic structure problems that involve a number of atoms greater than that which is practical or possible with the standard scattered-wave method.

Often, the constituents of these large clusters or molecules can be divided into two groups of atoms (i.e., two subclusters): one having the most scientific interest (the "principal" subcluster), and the other (the "environmental" subcluster) having less interest except in modifying the properties of the first group. For example, a biological molecule may have an active enzymatic site consisting of a transition metal and its nearest neighbors. The enzymatic properties of this site might be modified by other subgroups which are physically more distant. In this case it would be desirable to be able to approximate the electronic coupling between the more distance subgroups and the complex consisting of the transition metal and its first nearest neighbors. For a large molecule, such an approximation would allow calculations to be performed which might otherwise be impossible. Another example would be the problem of calculating the electronic structure of a cluster that represents a part of a solid or interface, in which the effects of "embedding" the cluster are to be included.

In this paper, a method for performing this type of approximate calculation is described, and results of numerical calculations are reported. The basis for the calculations is the partitioned form of the scattered-wave method, developed by Kjellander [2-4], in which the atoms of the molecule or cluster are distributed among spherical subclusters. The full secular matrix of the partitioned problem is then contracted, leading to a much simpler secular problem. The molecular orbitals of the approximately coupled scheme are found by an iterative scheme which rapidly converges to the "exact" molecular-orbital energies and wavefunctions; this result is demonstrated by a test calculation using the methanol molecule.

II. Method

In the partitioned form of the scattered-wave method, the atoms of the molecule or cluster are divided into subclusters, and each subcluster is surrounded by a partitioning sphere. While in the standard scattered-wave method the interatomic charge and potential are averaged over the entire interatomic region, in the partitioned case this averaging is performed separately for each subcluster. Thus, in the partitioned method, the constant interatomc potential for each subcluster is different, leading to a more realistic model potential.

Consider a partitioned scattered-wave calculation like the one discussed in the Introduction, in which the cluster can be divided into a principal and an environmental subcluster. The secular

equation of this problem could be written in the following schematic form:

$$\begin{bmatrix} T_a^{-1} & G_{ab} \\ G_{ba} & T_b^{-1} \end{bmatrix} \begin{bmatrix} A_a \\ A_b \end{bmatrix} = 0 \qquad (1)$$

In this equation, the matrix T_a^{-1} represents the scattering matrix for the principal subcluster (including scattering from the sphere surrounding it), and T_b^{-1} represents the scattering matrix for the environmental subcluster; G_{ab} and G_{ba} are matrices which represent the Green's function that describes the propagation of the electrons between the two subclusters; and A_a and A_b are column vectors containing the atomic and partitioning sphere coefficients of the wavefunction. (The detailed definitions of these matrices and column vectors will be given in a future paper, or can be found by studying Refs. [1] and [2].) Note that (1) is a linear system for the coefficients A_a and A_b; solutions are found by varying the energy (all matrix elements are energy dependent) until a zero in the determinant of the full secular matrix is found.

The most severe approximation to the electronic coupling interaction between the principal and environmental subclusters of (1) would be to assume that there is no electronic coupling at all, i.e., that G_{ab} and G_{ba} vanish. This would put (1) in block diagonal form so that molecular orbitals could be found for T_a^{-1} and T_b^{-1} separately. However, these

orbitals differ from those found by calculations of the isolated subclusters because the atomic potentials used to create the matrix elements of T_a^{-1} in (1) are assumed to include the electrostatic effects of the atoms in the environmental subcluster. We call this level of approximation the "molecular-field" approximation.

To go beyond the molecular-field approximation, the effects of electronic coupling between the subclusters must be considered as well as the electrostatic coupling. The method presented here is called "iterative" coupling. There are two components of this approximation: first, contraction of the secular matrix; second, evaluation of the matrix elements of the environment only at certain trial energies (to be discussed further below).

Contraction of the full secular matrix is accomplished using a simple property of linear algebra [5]. For example, the linear system of (1) can be re-written in a way that eliminates the A_b coefficients. To see this, the matrix multiplication of (1) is explicitly written out to obtain the following two matrix equations:

$$T_a^{-1} A_a + G_{ab} A_b = 0 \tag{2}$$

$$G_{ba} A_a + T_b^{-1} A_b = 0 \tag{3}$$

Solving (3) for A_b and substituting into (2),

$$[T_a^{-1} - G_{ab} T_b G_{ba}] A_a = 0 \tag{4}$$

where T_b is the matrix inverse of T_b^{-1}. Here the order of the secular matrix has been reduced, i.e., the matrix has been "contracted"; solutions to the linear system of (4) are obtained only when the determinant of the matrix in brackets in (4) vanishes. Once the column vector A_a has been obtained, A_b can be found using (3). Thus, solution of the contracted linear system of (4) is equivalent to solution of (1), with the exception of cases in which the matrix inverse of T_b^{-1} does not exist (i.e., when det (T_b^{-1}) vanishes).

Taking the determinant of the smaller matrix of (4) is certainly more computationally efficient than calculating the determinant of the larger matrix of (1); however, (4) was obtained by taking the matrix inverse of T_b^{-1}, so there is probably no overall computational advantage in following this procedure. However, consider a state which is primarily localized in the principal subcluster (T_a^{-1}); for such a state, the molecular-field energy should be close to the corresponding full secular matrix energy. This suggests the following iterative prescription for an approximate coupling method:

(1) First, an energy eigenvalue (E_o) is found from submatrix T_a^{-1} using the molecular-field approximation.

(2) The matrix elements of G_{ab}, T_b^{-1}, and G_{ba} are calculated using E_o as the trial energy; the matrix inverse of T_b^{-1} is found.

(3) Determinants of the matrix

$$T_a^{-1}(E) - G_{ab}(E_o)T_b(E_o)\, G_{ba}(E_o) \tag{5}$$

are calculated at various values of E until a zero is found. This value of E (call it E_1) is assumed to be an approximate solution of (1) (or (4)). If E_1 differs considerably from E_o, the process is repeated from step 2, using

$$E = \beta E_o + (1 - \beta)\, E_1 \tag{6}$$

as the next trial energy ($0.0 < \beta < 1.0$).

Note that in the third step of this procedure, the matrix elements of G_{ab}, T_b^{-1}, and G_{ba} are unchanged, so they must be calculated only once per iteration. Similarly, the matrix inverse need be taken only once per iteration. Thus, this procedure can lead to very substantial improvements in computational efficiency, particularly for systems in which the matrix T_b^{-1} is large. The crucial questions, of course, are the accuracy and speed of convergence of this method. These questions will be investigated using methanol as an example.

III. Results

The electronic structure of methanol can be easily calculated using the partitioned scattered-wave method without contraction; thus, it can

serve as an example with which to test the validity of the iterative coupling procedure. Furthermore, as an organic molecule, methanol is a prototype for molecules which might need the iterative coupling procedure such as large biological molecules, polymers, or embedded clusters.

The partitioning of the methanol molecule is shown schematically in Fig. 1. The single partitioning sphere containing the carbon and oxygen atoms is treated as the principal subcluster, while the four hydrogen atoms collectively form the environment. The starting potentials for the iterative calculation were obtained from a fully converged, partitioned scattered-wave calculation.

The second column of energy levels in Fig. 2 shows the results of the molecular-field calculation for the C-O subcluster, in which all scattering from the four hydrogen atoms is neglected. Note that two pairs of levels are degenerate: the 1a", 3a' pair and the 2a", 5a' pair. This degeneracy is due to the fact that the true symmetry of the CO subcluster is $C_{\infty v}$, so that the degenerate pairs correspond to π levels of an isolated CO molecule. Even though the potentials in this molecular-field calculation include the electrostatic effects of the hydrogen atoms, the spherical averaging process in the C and O atomc spheres precludes any symmetry breaking.

For purposes of comparison, a standard scattered-wave calculation of an isolated CO molecule was performed using the C-O bond distance of methanol. The energy levels are very similar to those of the molecular-

field calculation, except that they are shifted lower by about 0.05-0.09 rydbergs. This shift is explained by the donation of charge from the hydrogen to the carbon and oxygen atoms in the methanol molecule. Because the molecular-field calculation uses potentials from a converged partitioned scattered-wave calculation, the energy levels reflect the charge transfer but not the stabilization energy associated with the interaction with the hydrogen atoms.

The third column of Fig. 2 shows the energy levels of the f ;t iteration of the iterative coupling method. The initial enviror ;t energies (E_0 in (5)) were taken from the molecular-field results Comparing these approximately coupled results to the "exact" or fully coupled results in the fifth column, it is seen that although the energy levels have the correct ordering, they have a tendency to "overshoot" the fully coupled values. In the fourth column of Fig. 2 are the energy levels of the second iteration; these used initial environment energies obtained from the average of the molecular-field and first iteration energies, corresponding to $\beta = 0.5$ in (6). The energy levels resulting from the second iteration are in remarkably good agreement with those of the fully coupled case.

Plots of the wavefunctions of the 3a' level from molecular-field and first iteration calculations are shown in Fig. 3 and Fig. 4. These can be compared with the corresponding wavefunction of the fully coupled calculation, which is shown in Fig. 5. The wavefunction from the second iteration calculation is not shown because it is virtually identical with that from the fully coupled calculation.

IV. Summary

For the example of methanol, the iterative coupling method successfully reproduces the energies and wavefunctions found in the fully coupled ("exact") calculation. Yet, the iterative coupling method involves substantially less computational effort. For example, the fully coupled calcuation of the methanol a' state uses a secular matrix of order 93, while that of the approximate calculation has order 68. Because the numerical calculation of the determinant dominates the use of computer time, the reduction of the order of the secular matrix takes on increasing importance as the cluster size increases. (Calculations involving larger clusters have been performed and will be reported in future papers.)

Although fully self-consistent starting potentials were used, the iterative coupling calculations reported here are not in themselves self-consistent; however, there is, in principle, no obstacle to extending the method in order to perform self-consistent calculations.

In summary, the iterative coupling method has been shown to be an effective way to drastically reduce the computational effort involved in scattered-wave molecular-orbital calculations. Thus, this method has the potential of opening up new areas of application of the scattered-wave method, applications which were previously impractical or impossible due to cluster size. These include biological macromolecules, polymers, and microstructured electronic materials.

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Figure Captions

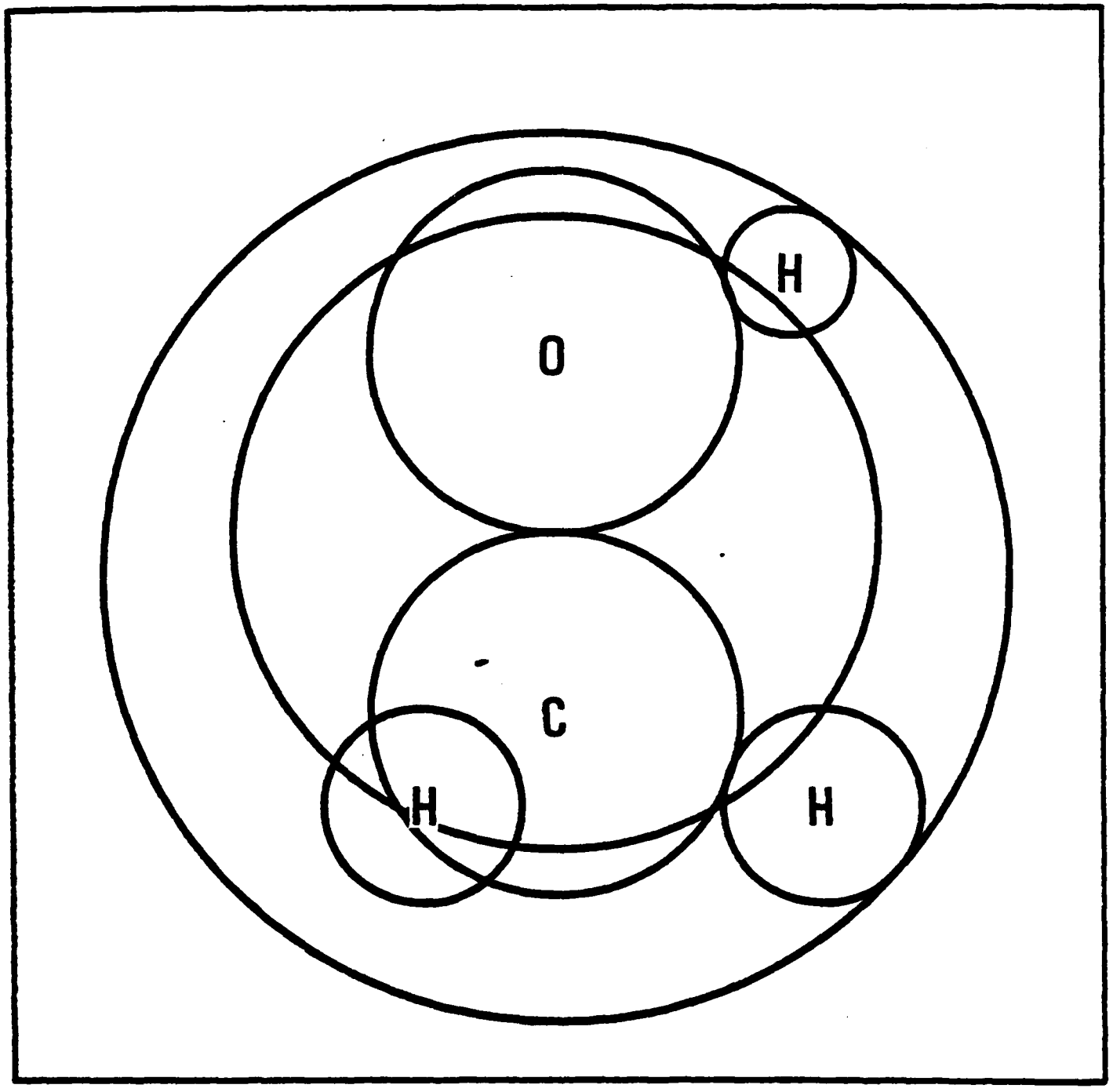
Fig. 1. Diagram of the partitioning of the methanol molecule. The single partitioning sphere containing the carbon and oxygen atoms is treated as the principal subcluster, while the four hydrogen atoms collectively constitute the environment.

Fig. 2. Molecular-orbital energy levels from iteratively coupled scattered-wave calculation for methanol using the subcluster partitioning of Fig. 1, compared with a standard SCF-Xα-SW calculation for an isolated CO molecule on the left and the "exact" partitioning results on the right. The second column shows the molecular-field energies for CO. The third and fourth columns show the first and second iteration approximate coupling results for methanol.

Fig. 3. Contour map of the 3a'(π) molecular-orbital wavefunction for CO in the molecular-field limit. The solid and dashed contours represent positive and negative values, respectively, of the wavefunction.

Fig. 4. Contour map of the 3a' molecular-orbital wavefunction for methanol after the first iteration in the coupling of the hydrogen environment to the CO subcluster. Note the formation of incipient C-H "σ bonds".

Fig. 5. Contour map of the 3a' molecular-orbital wavefunction for methanol in the fully-coupled partitional SCF-Xα-SW calculation.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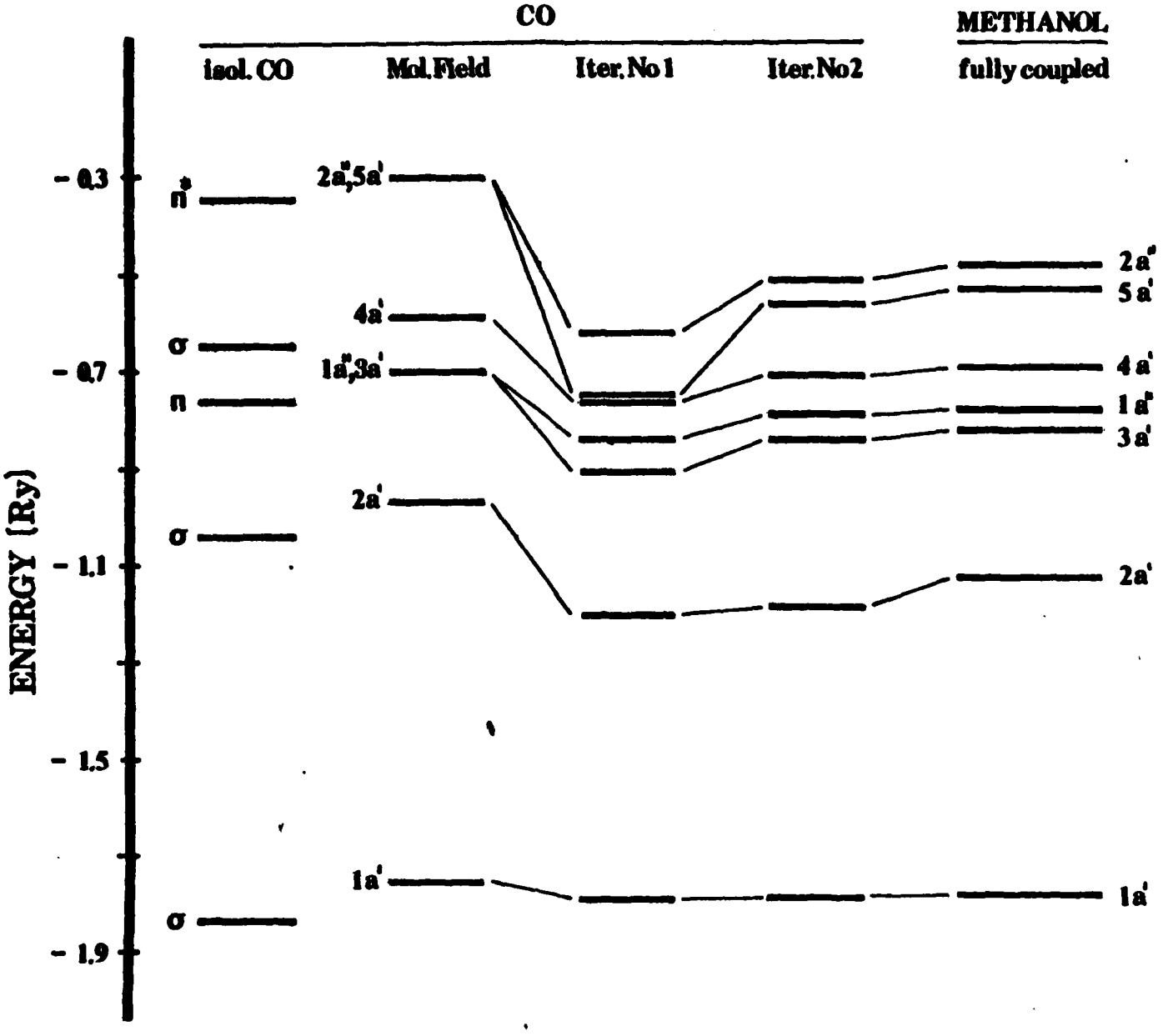
CO
METHANOL
isol. CO
Mol.Field
Iter.No1
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fully coupled
ENERGY (Ry)
- 0.3
- 0.7
- 1.1
- 1.5
- 1.9
π*
σ
π
σ
σ
2a",5a'
4a'
1a",3a'
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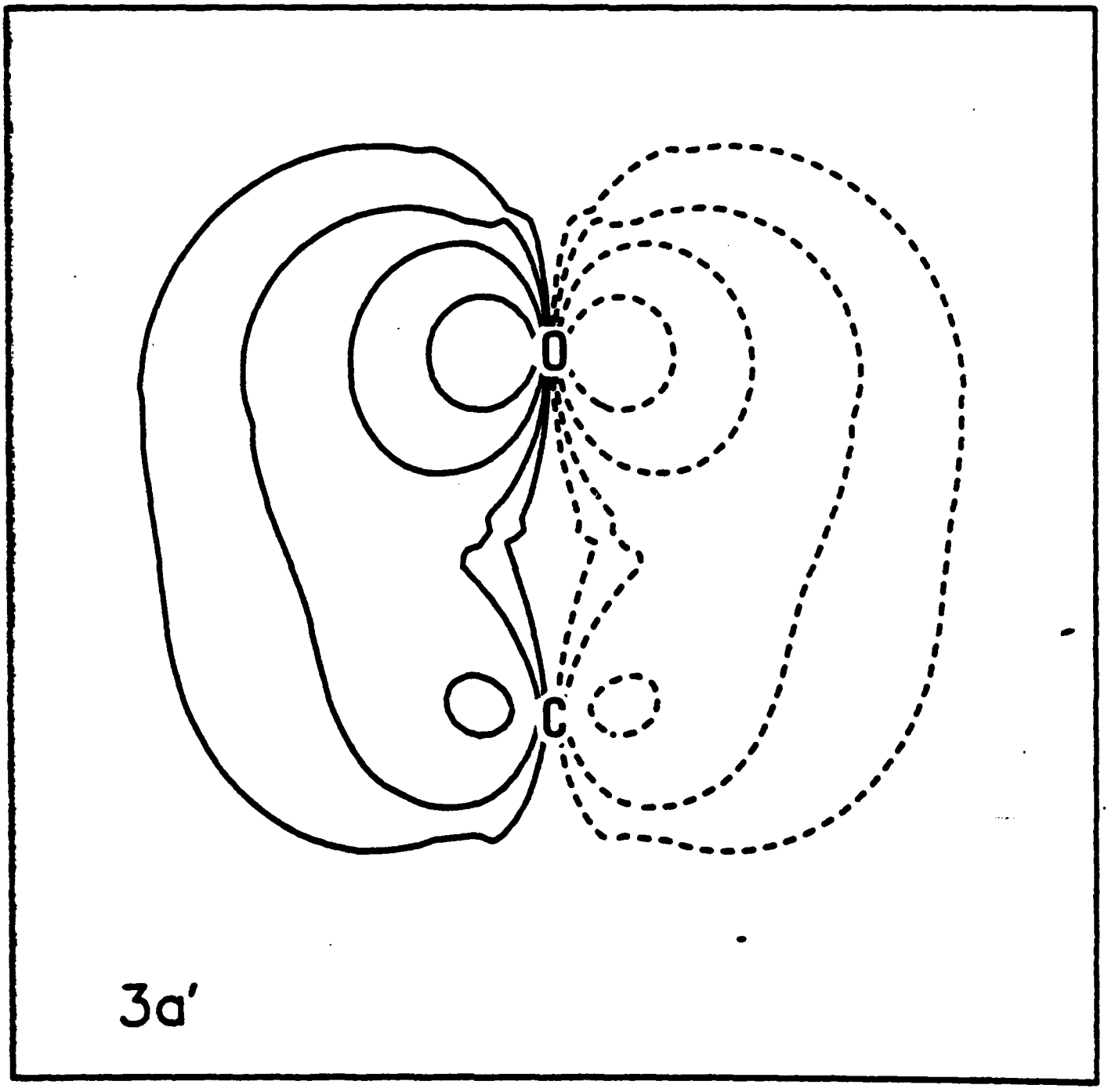
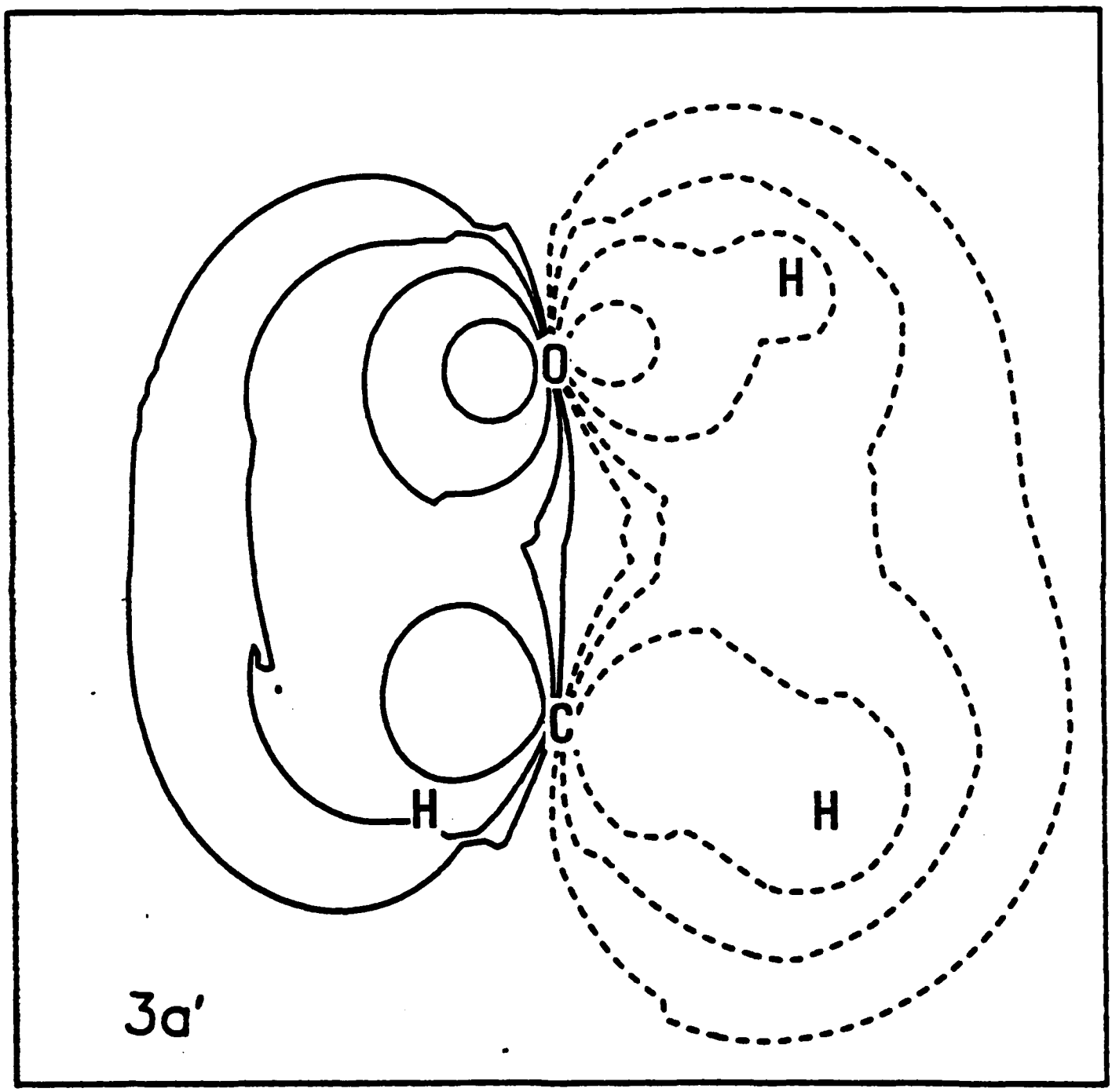


3a'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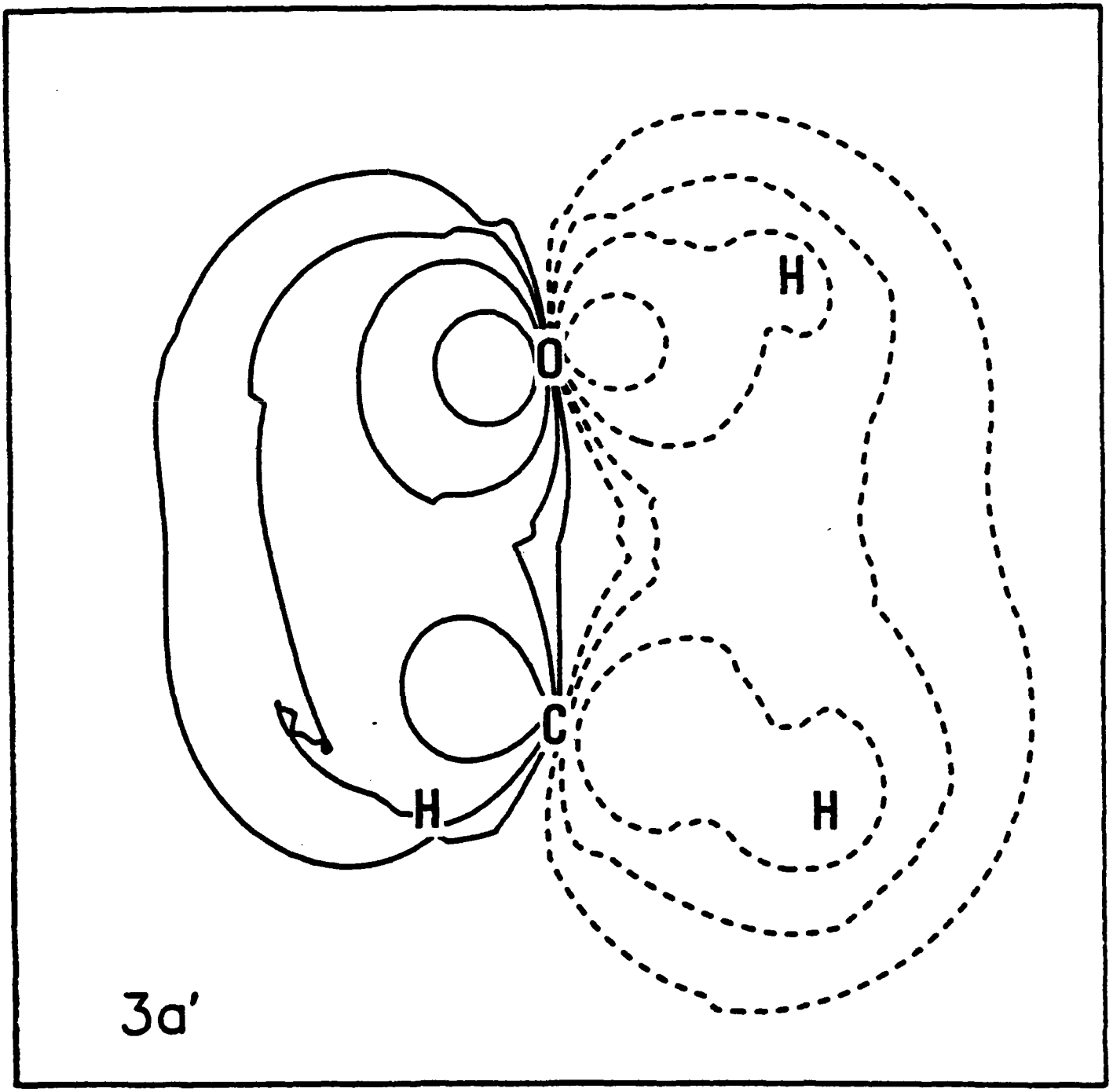

3a'

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