Chemical Physics 93 (1985) 83–100
North-Holland, Amsterdam

MULTIPLE STATIONARY POINT REPRESENTATIONS IN MC SCF CALCULATIONS

Joseph T. GOLAB, Danny L. YEAGER

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

and

Poul JØRGENSEN

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Received 14 May 1984; in final form 28 September 1984

By using a complete second-order Newton–Raphson multiconfigurational self-consistent field (MC SCF) procedure combined with the Fletcher restricted step constraint algorithm and a modification of the surface walking procedure of Simons et al., an MC SCF energy hypersurface at fixed geometry has been examined in considerably more detail than had been done previously. By calculational example, it is shown that there may exist several MC SCF stationary points which fulfill all four structural criteria we require of a state for being a "good" representation of an exact state. The problem with the existence of several stationary point solutions may be reduced if care is taken in the selection of the MC SCF configuration space. Calculational examples also demonstrate that near-lying stationary points exist which fulfill some, but not all, of these four structural criteria. Hence, stationary points should be obtained with a global MC SCF method which automatically eliminates convergence to as many as possible of these unwanted stationary points. Upon convergence, structural criteria which are not automatically fulfilled should be examined in detail.

1. Introduction

The objective of MC SCF calculations is to obtain a good approximation to the Nth exact state of a certain symmetry [1,2]. A severe problem of MC SCF calculations is that they may not uniquely define an approximate representation of the Nth exact state since the MC SCF calculation optimizes both linear configuration state rotational parameters and non-linear orbital rotational parameters [3,4]. The MC SCF rotational parameters at constant molecular geometry define a very complicated energy hypersurface that contains many stationary points which may or may not be good approximations (representations) of exact eigenstates. It is the purpose of this paper to thoroughly examine an MC SCF energy hypersurface and to demonstrate the existence of multiple MC SCF proper representations of the Nth exact state. We indicate some precautions that may be taken to avoid or at least to make it less likely that the problem of multiple MC SCF stationary point proper representations will be encountered in practical MC SCF calculations.

In order to properly represent the exact Nth state of a certain symmetry, an MC SCF stationary point should fulfill the following four criteria [4,5]:

(1) The stationary point must be variationally correct ($\delta E = 0$);

(2) An MC linear response [also called the multiconfigurational random phase approximation (MC RPA) or the multiconfigurational time-dependent Hartree–Fock (MC TDHF)] calculation [6] for the electronic transitions to states of the same symmetry as the MC SCF stationary point must be stable (give a set of real excitation energies) and have $N-1$ de-excitation (i.e., negative transition) energies;

(3) Criterion 2 implies that the number of negative eigenvalues (index) of the total hessian (the second-derivative matrix) with respect to real vari-

ations of both the orbital and configurational parameters, $(A - B)$, and the index of the total hessian with respect to imaginary variations of both the orbital and configurational parameters, $(A + B)$, must each be equal to $N - 1$;

(4) The MC SCF approximation of the Nth state is the Nth state of a CI calculation using the converged MC SCF orbitals and the same configuration state functions (CSFs) which defined the MC SCF state expansion. This ensures that the energy is an upper bound. We will call this CI the MC SCF CI.

Limited basis sets and the limited number of configuration state functions used to define the MC SCF can lead to cases where there may exist one or more MC SCF stationary points which meet all four of these or where there are MC SCF stationary points which do not consistently fulfill all of these criteria for being a representation of the exact Nth state. When multiple stationary points which fulfill all or some of the above criteria are found, it is often not at all clear which MC SCF stationary point should be chosen over the others as the "best" representation of the Nth exact state.

Until the introduction [3,7–9] of complete second-order MC SCF procedures * (always with suitable constraints which are applied *only* when far from convergence [3–8,10–17] it was well known (but not widely reported) that MC SCF and often SCF calculations were many times very slowly convergent or even divergent. Characteristics of the stationary points were almost never examined. When characteristics were examined, only criteria 1 and 4 were usually considered. Criterion 3 has occasionally been considered in second-order calculations but only for real variations and often only for the orbital subblock of $(A - B)$ rather than the total matrix. Sometimes, even criterion 1 has been violated in supposedly "approximately" converged MC SCF calculations. Since the characteristics of an MC SCF stationary point usually have not been examined, many MC SCF and SCF calculations may have converged (if they really converged at all) to points which are not good representations of the exact Nth eigenstate.

With the introduction [3,7–9,13] and development [4,5,10–17] of complete second-order SCF [13–16] and MC SCF [3–5,7–12,17] procedures, reliable convergence was obtained in MC SCF, and in several cases a surfeit of stationary points [5,18] have been reported which may be considered approximate representations of the Nth exact state. Obviously, these stationary points are present on the energy hypersurface regardless of the method used to converge the MC SCF calculation. Earlier converged calculations may have randomly picked one out of several stationary points dependent on the initial guess of MC SCF orbitals and coefficients and on the MC SCF method used.

When second-order MC SCF procedures are used in connection with the Fletcher constraint technique (applied only when far from convergence), extremely reliable and rapid convergence is obtained in MC SCF. *All* MC SCF procedures, in general, must use constraints of some sort when far from convergence [3–8,10–17]. The Fletcher constraint procedure [19,20] guarantees convergence to a local minimum. It has recently been modified for convergence to excited states [5]. For excited states, convergence is not guaranteed; however, calculations to date indicate that the Fletcher procedure coupled with a second-order procedure is the most efficient, reliable and among the most rapid to use in MC SCF calculations. In fact, both SCF and MC SCF calculations for both ground and excited states using the Fletcher constraint procedure when far from convergence and unconstrained Newton–Raphson (complete second-order) locally are now routinely performed in our laboratory starting from simple symmetrized, orthogonalized basis functions **.

* It is apparently frequently forgotten that many SCF procedures are simplifications and special cases of more general MC SCF techniques. Often, a discussion of a "new" SCF procedure is simply a rehash of a previously discussed MC SCF technique.

** It is often stated that unconstrained Newton–Raphson approaches have smaller radii of convergence than other MC SCF procedures. To our knowledge, this statement has never been proven mathematically. No series of relevant, valid comparison calculations have been presented in the literature supporting this assertion (e.g. often with the other method, constraints were properly used far from convergence and for the "comparison" Newton–Raphson calculation constraints were either not used or improperly used).

"Walking" techniques allow controlled movement with the parameters involving the motion of the nuclei from one stationary point to another [21–23]. Modifications of the Fletcher algorithm have recently been proposed in connection with developing algorithms for "walks" on an energy surface in coordinate space [23] along stream beds. Hence, from a local minimum in coordinate space transition states and then other local minima can be efficiently found.

In order to more thoroughly examine the nature of the MC SCF energy hypersurface, we have made modifications to the procedure for coordinate surface walks of Simons et al. [23], which allow "walks" to be carried out in MC SCF parameter space (fixed geometry) from one MC SCF stationary point to other MC SCF stationary points. With this "walking" algorithm a very large number of other MC SCF stationary points can be found and then these may be characterized using the four criteria above. Hence, an energy hypersurface can be studied in much more detail than was previously possible. From this, a greater understanding is obtained about the importance of the problem of multiple MC SCF representations of the Nth exact state.

To demonstrate these points and to examine in more detail the nature of a complicated MC SCF energy hypersurface, We perform MC SCF calculations on C_2 at 2.70 au. We carry out calculations using three different complete active spaces (CAS). For the two smaller active spaces we have found several different minima by using different initial guesses. Large scale multi-reference CI calculations [24–26] including all single and double excitations from various complete active spaces using the orbitals of the various MC SCF stationary points have also been carried out.

By performing controlled walks on the energy hypersurface starting from MC SCF minima for the largest and smallest CAS we have found stationary points which satisfy all four criteria for being good representations of the first excited state of C_2. For the smallest CAS, this stationary point was also found by our usual (Fletcher constraint algorithm with Newton–Raphson) excited state procedure. By walking, we have also found other near-lying stationary points which fulfil some but not all of the four criteria for representing the ground or first excited state.

In section 2, we review the MC SCF and Fletcher restricted step methods. We also discuss the walking procedure. In section 3, we present our calculations on C_2 at 2.70 au and discuss the results. We end our discussion and draw conclusions in section 4.

2. Theory

In this section, our main focus is directed towards deriving a method to walk in stream beds from one stationary point to another on the energy hypersurface in the parameter space defined by an MC SCF calculation. The algorithm described here follows the scheme proposed by Simons et al. [23] which is a modification of the Fletcher constraint algorithm [5,19,20]. Simons et al. were concerned only about walking in a *coordinate space* from one geometry to another. We use the algorithm to carry out a well-defined walk in the *parameter space* defined by the MC SCF calculations at fixed geometry.

A detailed discussion of the complete second-order Newton–Raphson (NR) MC SCF method of Yeager, Jørgensen and Dalgaard may be found in ref. [4]. A detailed discussion of the Fletcher restricted NR step size constraint procedure (which is in effect only when far from convergence), used in ground and excited state second-order MC SCF calculations, may be found in refs. [20] and [5], respectively. To facilitate the understanding of the present discussion, it is necessary to briefly summarize the concepts contained in these previous papers.

2.1. The Newton–Raphson complete second-order procedure

In an MC SCF calculation, a set of rotational parameters,

$$\lambda = \begin{pmatrix} \kappa \\ S \end{pmatrix}$$

defines a unitary transformation which simultaneously transforms the orbital (κ) and configura-

tion space (S) of a reference state, $|0\rangle$.

$$|\bar{0}\rangle = \exp(i\hat{\kappa}) \exp(i\hat{S})|0\rangle. \quad (1)$$

We have used the nomenclature of ref. [4] and, for convenience, considered only real variations in the orbital optimization and state expansion coefficient parameters. The total energy corresponding to this unitary transformation of the reference state is thus defined in terms of the set of rotational parameters.

$$\begin{aligned} E(\bar{\lambda}) &= \langle \bar{0}|H|\bar{0}\rangle \\ &= \langle 0|\exp(-i\hat{S}) \exp(-i\hat{\kappa}) H \\ &\quad \times \exp(i\hat{\kappa}) \exp(i\hat{S})|0\rangle. \end{aligned} \quad (2)$$

At $\lambda = 0$ a Taylor series expansion of the total energy may be obtained by expanding the exponential operators in eq. (2) and the total energy may then be written in matrix notation as

$$E(\lambda) = E_0 + F^T\lambda + \tfrac{1}{2}\lambda^T G\lambda + \ldots. \quad (3)$$

where all terms through second-order in λ have been written out explicitly. The matrices F and G are identified as the energy gradient and the energy total hessian with respect to real variational parameters and give the slope and curvature of the energy hypersurface, respectively. Since we are considering only real variational parameters, $G = 2(A - B)$; however, $(A + B)$ which is the hessian for imaginary variations can still be easily evaluated and should also have the proper number of negative eigenvalues at convergence, (criteria 3) [5]. (From here on we will use "hessian" and "total hessian" interchangeably. We mean the second derivative matrix including variations with respect to both orbital and configurational state parameters including coupling.)

In the practical implementation of MC SCF calculations, the infinite-order polynomial of eq. (3) is usually truncated at no higher than second-order

$$q(\lambda) = E_0 + F^T\lambda + \tfrac{1}{2}\lambda^T G\lambda. \quad (4)$$

Upon application of the variational principle, eq. (4) yields the NR step

$${}^{NR}\lambda = -G^{-1}F. \quad (5)$$

2.2. The Fletcher constraint algorithm

In deriving the Newton–Raphson step we assumed that the second-order Taylor expansion of the total energy adequately represents the exact energy expansion for the NR step. When far from convergence the NR step may be very large and the second-order Taylor series expansion may not approximate the exact energy expansion very well. The NR step, therefore, cannot be trusted in such a case. In the Fletcher algorithm step-lengths are restricted to fall within a region of trust on the energy hypersurface, that is in the region in which the second-order Taylor series expansion approximates the exact energy expansion reasonably well. This region of trust at the kth iteration point is defined in the Fletcher algorithm in terms of a trust radius $h^{(k)}$, the size of which is determined by the similarity between $q(\lambda)$ and $E(\lambda)$. This similarity can be measured by defining the reduction in $E(\lambda)$ at the kth iteration point ($k+1$st iteration) as

$$-\Delta E^{(k)} = E_0 - E(\lambda^{(k+1)}) \quad (6)$$

and the corresponding predicted reduction as

$$-\Delta q^{(k)} = E_0 - q(\lambda^{(k+1)}), \quad (7)$$

where $\lambda^{(k+1)} = \Delta\lambda^{(k)}$ is the step size of the Fletcher algorithm (which will be defined below) at the kth iteration point ($k+1$st iteration). The ratio

$$r^{(k)} = \Delta E^{(k)}/\Delta q^{(k)} \quad (8)$$

measures the accuracy to which $q(\lambda^{(k+1)})$ approximates $E(\lambda^{(k+1)})$, i.e., the closer $r^{(k)}$ is to unity, the better the agreement. By using eq. (8), the trust radius is updated in each iteration to ensure that maximum "safe" step-lengths are taken. Close to (and sometimes farther from) convergence $r^{(k)}$ is close to unity and the step-length is (unconstrained) Newton–Raphson.

Step sizes can thus be taken with confidence inside the trust region. If the stationary point of $q(\lambda)$ falls inside the trust region and if the index of the hessian with respect to real variations is as desired, the NR step is taken. If no stationary point exists inside the trust region which has the desired index of the hessian with respect to real

variations, the search for stationary points may be restricted to the boundary of the trust region and accomplished by looking for stationary points of the lagrangian function

$$L(\lambda, \nu) = q^{(k)}(\lambda) - \tfrac{1}{2}\nu\left[\lambda^{\mathrm{T}}\lambda - (h^{(k)})^2\right], \tag{9}$$

which is obtained when

$$\partial L(\lambda, \nu)/\partial\lambda|_{\lambda=\lambda^{(k+1)}} = F^{(k)} + \mathbf{G}^{(k)}\lambda^{(k+1)} - \nu\lambda^{(k+1)} = 0, \tag{10}$$

where ν is a lagrangian multiplier, $F^{(k)}$ and $\mathbf{G}^{(k)}$ are the gradient and hessian at iteration point k, and $h^{(k)}$ defines the trust region of the kth iteration point. The solution to eq. (10) is

$$\lambda^{(k+1)}(\nu) = -(\mathbf{G}^{(k)} - \nu\mathbf{1})^{-1}F^{(k)}, \tag{11}$$

where $\mathbf{1}$ is a unit matrix.

The value of ν is determined such that $\lambda^{(k+1)}(\nu^{(k)})$ satisfies

$$\|\lambda^{(k+1)}(\nu^{(k)})\| = h^{(k)}, \tag{12}$$

i.e., the value of $\nu^{(k)}$ ensures step sizes to be on the boundary of the trust region. ($\|\ \|$ denotes the L_2 norm, i.e., $(\sum_i \lambda_i^2)^{1/2}$).

In terms of the eigenvectors $U_i^{(k)}$ and corresponding eigenvalues $b_i^{(k)}$ of the hessian matrix, $\mathbf{G}^{(k)}$, eq. (11) can be expressed as

$$\begin{aligned}\lambda^{(k+1)}(\nu) &= -\sum_i U_i\left(b_i^{(k)} - \nu\right)^{-1}\left(U_i^{\dagger}F^{(k)}\right)\\ &= -\sum_i U_i\left(b_i^{(k)} - \nu\right)^{-1}\left(\bar{F}_i^{(k)}\right)\\ &= \sum_i U_i\bar{\lambda}_i^{(k+1)}.\end{aligned} \tag{13}$$

The direction of the step should be determined from the desired index of the hessian with respect to real variations at the stationary point. There are usually a large number of choices of $\nu^{(k)}$ such that eq. (12) is fulfilled [5,20], and a discussion of these choices for MC SCF ground state and excited state convergence is given in refs. [20] and [5], respectively, and following in section 2.3.

When a stationary point with a desired index in $(\mathbf{A} - \mathbf{B})$ is approached in an MC SCF calculation, $q(\lambda)$ approximates $E(\lambda)$ to within a reasonable tolerance and $\|\lambda\|$ is within some region of trust on the energy hypersurface. This defines the local region where the Fletcher step reduces to the Newton–Raphson step and quadratic convergence is obtained.

2.3. Surface walking along stream beds

We will now discuss how to implement a surface walk within the Fletcher constraint algorithm, so that by carrying out well-defined and controlled walks in stream beds we can more fully investigate the nature of the energy hypersurface.

For example, if all the eigenvalues of the total hessian with respect to real variations at some point on the hypersurface are positive and a stationary point is sought which has a total of one negative eigenvalue in $(\mathbf{A} - \mathbf{B})$, (i.e., a possible representation of the first excited state) it is not appropriate to converge towards a local minimum of $q(\lambda)$. Instead, one could move "uphill" along some one direction defining a "valley floor" away from a local minimum. By maximizing $q(\lambda)$ along the one "valley floor" direction while minimizing $q(\lambda)$ along the $N-1$ other directions, one stays close to a "stream bed" which runs along the direction of uphill movement (provided, of course, that $h^{(k)}$ is sufficiently small so that $\Delta q^{(k)}$ is a good approximation to $\Delta E^{(k)}$).

The value of ν determined from eq. (12) makes the step-length equal to $h^{(k)}$. There are, in general, several choices of ν which give $h^{(k)}$ and which correspond to different directions when searching for a stationary point. To obtain a clearer understanding of how to choose ν, it helps to examine the step-length function [eq. (12)]

$$h^{(k)}(\nu) = \left\| -\sum_i \left(b_i^{(k)} - \nu\right)^{-1}\bar{F}_i^{(k)}\right\|, \tag{14}$$

the linear energy change

$$\begin{aligned}\Delta E_1^{(k)} &= \left(F^{(k)}\right)^{\mathrm{T}}\lambda^{(k+1)}\\ &= -\sum_i \left(b_i^{(k)} - \nu\right)^{-1}\left(\bar{F}_i^{(k)}\right)^2,\end{aligned} \tag{15}$$

and the "quadratic" energy change

$$\begin{aligned}\Delta q^{(k)} &= q\left(\lambda^{(k+1)}(\nu)\right) - E_0\\ &= -\sum_i \left(b_i^{(k)} - \nu\right)^{-2}\left(\bar{F}_i^{(k)}\right)^2\left(\tfrac{1}{2}b_i^{(k)} - \nu\right),\end{aligned} \tag{16}$$

which result when a step given by eq. (13) is taken. Following the discussion of Simons et al., the component of the force vector $\bar{F}$ along the local eigen-direction U_i is denoted $\bar{F}_i (= U_i^\dagger F)$. From eqs. (15) and (16), we see that the linear and quadratic energy contributions from each eigen-direction are uncoupled [3,4,23].

A NR step (see eq. (13) with $\nu = 0$) is directed along the forces with corresponding negative eigenvalues of the total hessian with respect to real variations and in opposition to those forces with corresponding positive eigenvalues of the total hessian with respect to real variations. From eqs. (15) and (16) (with $\nu = 0$), the NR step leads to decreases in both $\Delta E_1^{(k)}$ and $\Delta q^{(k)}$ along directions having positive eigenvalues of the total hessian with respect to real variations and increases in both $\Delta E_1^{(k)}$ and $\Delta q^{(k)}$ for directions with negative eigenvalues.

As an example, let us now state the conditions for choosing ν in the step-length expression of eq. (13) for a surface walk where we want to move from a region with a positive definite hessian with respect to real variations to a stationary point with one negative eigenvalue in $(\mathbf{A} - \mathbf{B})$. To move uphill along the stream bed characterized by the U_1 direction corresponding to the "softest" (smallest magnitude) eigenvalue (b_1) and remain in the "stream bed," ν should be chosen so that [23]:

(1) $(b_1^{(k)} - \nu)^{-1} < 0$. This guarantees that the walk is along the force in this direction and ensures that the linear term of eq. (15) in the U_1 direction is positive.

(2) $(b_i^{(k)} - \nu)^{-1} > 0 \; (i \geq 2)$. This guarantees that the steps along the directions $(i \geq 2)$ oppose the forces $\bar{F}_i$ and therefore given negative linear energy contributions in eq. (15).

(3) $(\frac{1}{2} b_1^{(k)} - \nu) < 0$. This ensures that $\Delta q^{(k)}$ will increase in the U_1 direction [see eq. (16)].

(4) $(\frac{1}{2} b_i^{(k)} - \nu) > 0 \quad (i \geq 2)$. This ensures that $\Delta q^{(k)}$ will decrease along the U_i $(i \geq 2)$ directions.

These conditions allow a walk to be close to the gentlest stream bed. Conditions 1 and 3 require the walk to be energetically uphill along U_1, while conditions 2 and 4 cause movement to be downhill along the other directions. We can conclude from the above analysis that starting from a positive definite hessian ν should be chosen in the range $b_1 < \nu < \frac{1}{2} b_2 < \frac{1}{2} b_3 < \ldots$ when convergence is desired to a representation of the first excited state.

Simons et al. discuss in detail how to deal with the possible problem that the total hessian with respect to real variations may not obey $b_1 < \frac{1}{2} b_2$, for which the above range $b_1 < \nu < \frac{1}{2} b_2$ will not exist, by using a scaling procedure. This same procedure can also be used to develop an algorithm for walking up one of the "stiffer" modes, e.g. to walk and increase the energy along U_2 while decreasing the energy along U_1, U_3,.... This procedure is also useful to enable a walk to remain very near the same "stream bed" on the energy hypersurface since the curvature in the stream bed changes from point to point, e.g. the softest mode may become a stiffer mode as a calculation progresses, etc.

As the walk approaches a near-lying stationary point in which b_1 is negative and b_2 is positive, the range $\frac{1}{2} b_1 < \nu < \frac{1}{2} b_2$ certainly exists. If, in addition, $h^{(k)}$ of eq. (14) is larger than the NR step-length of eq. (5) $(\nu = 0)$, the NR step-length should be taken.

Thus, when walking within the Fletcher constraint modification to the complete second-order MC SCF algorithm as another stationary point is approached the step is not constrained [via eq. (11)] as long as it remains in the region of trust $h^{(k)}$ and there are the desired number of negative eigenvalues of $(\mathbf{A} - \mathbf{B})$. As the new stationary point is approached, complete second-order convergence characteristics are observed.

2.4. "Walking" from one stationary point to another along a stream bed

One final point remains before we finish our discussion of the walking method. Consider the case that the starting point is an MC SCF stationary point with no negative $(\mathbf{A} - \mathbf{B})$ eigenvalues. In order to search the energy hypersurface for the lowest energy "excited state" (i.e., a point where $(\mathbf{A} - \mathbf{B})$ has one negative eigenvalue), a logical way to begin walking is by taking a step of length $h^{(0)}$ along (positive direction) or opposite (negative direction) U_1. Both directions have to be explored when systematically searching for other stationary points. This process can be repeated

until all directions U_2, U_3, U_4,.... have been explored in a positive or negative direction, thus obtaining a detailed search of the energy hypersurface.

Direction $U_i^{(k+1)}$ can be easily identified by examining the overlaps of the eigenvectors with the previous iteration's $U_i^{(k)}$. The appropriate ν can then be chosen and scaling introduced if necessary in order to ensure that a walk can be taken in *the same stream bed from one iteration to another*. Hence by this procedure it is possible to make a systematic controlled "walk" on the energy hypersurface along the same stream bed. The energy can be increased in one direction and decreased in all others by exploiting the properties of the Fletcher constraint algorithm. Close to a stationary point, convergence is second-order.

Once a stationary point is obtained, with, e.g., one negative (**A** − **B**) eigenvalue, other characteristics of the stationary point must be examined to determine if it may be a good representation of the desired exact state. From the new stationary point additional walks may be made to other stationary points, e.g. from a possible representation of the first excited state to local minima or to possible representations of higher excited states.

3. Numerical results

In this section, we report the results of calculations on C_2 at an internuclear separation of 2.70 au. The basis set for all calculations in this paper is a ⟨3s2p1d⟩ contraction of a (10s5p1d) cartesian gaussian basis set on each center [27].

3.1. SCF calculations

Initially, a ground state $^1\Sigma_g^+$ SCF calculation with the single CSF, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ was performed using the Newton–Raphson complete second-order MC SCF procedure with the Fletcher constraint algorithm in use far from convergence. The calculation converged in four iterations starting from simple symmetrized, orthogonalized basis functions. The total SCF energy is −75.416438970048 au.

Two other SCF calculations were performed using this procedure for the configurations $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ and $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$. Each of these calculations converged very rapidly (four iterations) starting from symmetrized, orthogonalized basis functions to −75.356429181641 au and −75.020305915791 au, respectively. The hessian with respect to real variations, (**A** − **B**), and the hessian with respect to imaginary variations, (**A** + **B**), were both positive definite at convergence for all of the above three SCF calculations. In addition there were no instabilities and no negative transition energies to states of $^1\Sigma_g^+$ symmetry in the linear response calculation using the converged SCF orbitals. Hence, all of the criteria are fulfilled by each of these stationary points for being a good representation of the ground state of C_2.

3.2. MC SCF calculations

In this section we examine in detail the MC SCF energy hypersurface at 2.70 au for the lowest state of $^1\Sigma_g^+$ symmetry using three different complete active spaces. The first set of calculations used a small complete active space ($2\sigma_u$, $1\pi_u$, $3\sigma_g$). Three different energy minima were found with this active space. The active space was increased in the second set of calculations to ($2\sigma_u$, $1\pi_u$, $1\pi_g$, $3\sigma_g$). Two energy minima were found using this active space. In the last set of calculations ($2\sigma_g$, $2\sigma_u$, $1\pi_u$, $1\pi_g$, $3\sigma_g$) were used as active orbitals and only one energy minimum was found. This last complete active space is by far the most reasonable of the three to use since the $2\sigma_g$ and $2\sigma_u$ orbitals are close to being degenerate as the dissociation of C_2 is approached. In order to further study the energy hypersurface in more detail, the walking procedure of Simons et al. was used for the smallest and largest CAS MC SCF to walk up the "softest" modes to other stationary points. These walking calculations show the existence of many stationary points which are energetically very close to these minima and may have some characteristics of a proper representation of the ground state but have a (**A** − **B**) index of one. We will now describe the abovementioned calculations in more detail.

Consider initially the smallest active space calculations. Three calculations were carried out

Table 1
MC SCF stationary points for the $X\,^1\Sigma_g^+$ state of C_2 at 2.70 au [a]

Label	Number of configurations	MC SCF complete active space orbitals	Starting point	Number of MC SCF iterations	Final energy (au)	Maximum amplitude configuration state function	Maximum amplitude configuration state function coefficient squared
A	3	$2\sigma_u, 1\pi_u, 3\sigma_g$	SCF MOs [b]	18	−75.431695416508	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	0.9810713
B			Löwdin orthogonalized coefficients [c]	22	−75.425127520205	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	0.9318503
C			SCF MOs [b]	8	−75.417599876869	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.8593182
D	18	$2\sigma_u, 1\pi_u, 3\sigma_g, 1\pi_g$	B	5	−75.569826385118	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.7210440
			C	5	−75.569826385118	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.7210440
			Löwdin orthogonalized coefficients [c]	14	−75.569826385118	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.7210440
E			A	6	−75.501658374802	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	0.8661230
F	44	$2\sigma_g, 2\sigma_u, 1\pi_u, 3\sigma_g, 1\pi_g$	D	6 [d]	−75.574712221969	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.7181273
			E	9 [d]	−75.574712221969	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$	0.3724554
						$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.2019560
						$1\sigma_g^2 1\sigma_u^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$	0.1441340

[a] All stationary points A–F have the same four characteristics: (i) no negative eigenvalues of A − B, (ii) no negative eigenvalues of A + B, (iii) $^1\Sigma_g^+ \rightarrow {}^1\Sigma_g^+$ MC linear response is stable and has no negative transition energies and (iv) the MC SCF root is the lowest root of $^1\Sigma_g^+$ symmetry in a CI using the MC SCF configurations and converged orbitals.

[b] SCF configuration: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$. The difference between A and C is that a different root from the initial CI using the MC SCF configurations and SCF MOs was chosen as an initial guess.

[c] Löwdin orthogonalized [28], symmetry adapted contracted gaussian basis functions [27].

[d] There are an infinite number of equivalent possiblities (related by non-energy changing rotations) for CSF coefficients and final partially occupied orbitals of stationary point F since there is a simple easily handled redundancy among certain state expansion coefficients and orbital optimization parameters. These stationary points are the same since they have exactly the same energy, properties, and overlaps with the other stationary points [4,29]. As an example, two possiblities are given for the CI expansion coefficients for stationary point F.

which lead to three different stationary points which fulfill all the requirements for being a representation of the exact ground state. For two of these, the lowest energy ($1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$) SCF orbitals were used as an initial guess of the orbitals. In the first calculation (labelled A), we used the CI vector corresponding to the lowest root of $^1\Sigma_g^+$ symmetry from a three CSF complete active space CI as an initial guess. In the second calculation (labelled C), we used the second lowest CI root of $^1\Sigma_g^+$ symmetry as an initial guess. In both we used the Fletcher ground state constraint algorithm for lowest states of a certain symmetry to ensure convergence to an energy minimum.

In the third calculation (labelled B), we used symmetrized, Löwdin orthogonalized [28], basis functions [27] and the lowest root of $^1\Sigma_g^+$ symmetry from the three CSF CI as an initial guess. This calculation converged in 22 interactions. These are slightly more iterations than in calculation A and considerably more than in calculation C. Both calculations A and B converged considerably slower than is usual using the Fletcher constraint algorithm [4] indicating that the energy hypersurface is fairly complicated at this geometry with this choice of configurations. Simple symmetrized, orthogonalized basis functions have also been used in our laboratory as a starting point for other MC SCF calculations which used the Fletcher constraint algorithm far from convergence and convergence has been approximately as rapid and reliable as when SCF orbitals were used as the initial guess.

As mentioned above each of these three MC SCF calculations, A, B, and C, converged to different stationary points (local minima) on the energy hypersurface. All three stationary points fulfill the four criteria above for being good approximations to the exact $X\,^1\Sigma_g^+$ state of C_2: each of these stationary points has no negative eigenvalues of **(A + B)** or **(A − B)**, each has no negative excitation energies for $^1\Sigma_g^+ \rightarrow {}^1\Sigma_g^+$ transitions in MC linear response and the MC linear response calculations to states of $^1\Sigma_g^+$ symmetry are stable, and each is the lowest state of the corresponding MC SCF CI. Stationary point C is primarily described by a different CSF than A or B and has the highest MC SCF energy of these three stationary points (see table 1). Furthermore, A and B have relatively large overlaps with the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF stationary point (given in table 2: 0.70031 and 0.68251, respectively) and with each other (given

Table 2
Overlaps of the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$, and $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$ SCF stationary points with the MC SCF stationary points A–M

SCF and MC SCF stationary points	SCF stationary points		
	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$
$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	1.00000		
$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	0.00000	1.00000	
$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$	0.00000	0.00000	1.00000
A	0.70031	−0.00033	−0.10611
B	0.68251	−0.25749	−0.03790
C	−0.05560	0.91910	−0.35749
D	−0.10101	0.83464	−0.23985
E	0.65669	−0.04694	−0.17298
F	−0.06115	0.83409	−0.25986
G	0.66804	−0.32666	0.00000
H	0.69014	−0.20641	−0.06075
I	0.70014	−0.11128	−0.07185
J	−0.23398	0.88222	−0.31174
K	0.39803	0.72932	−0.37387
L	−0.10100	0.83464	−0.23990
M	0.64537	0.06389	−0.23380

Table 3
Overlaps of the MC SCF stationary points for C_2 at 2.70 au

Label	A	B	C	D	E	F	G	H	I	J	K	L	M
A	1.00000												
B	0.96034	1.00000											
C	−0.03976	−0.29888	1.00000										
D	−0.11608	−0.34255	0.88547	1.00000									
E	0.94370	0.91518	−0.06132	−0.16600	1.00000								
F	−0.05647	−0.28727	0.88740	0.99577	−0.09789	1.00000							
G	0.93589	0.99653	−0.37617	−0.40881	0.89404	−0.35529	1.00000						
H	0.97371	0.99823	−0.24290	−0.29366	0.92556	−0.23741	0.98985	1.00000					
I	0.98880	0.98697	−0.15856	−0.22273	0.94152	−0.16499	0.97236	0.99289	1.00000				
J	−0.29447	−0.53462	0.96513	0.87689	−0.30122	0.86323	−0.60236	−0.48443	−0.40706	1.00000			
K	0.59748	0.16986	0.77207	0.61108	0.54803	0.67001	0.29230	0.42316	0.49963	0.58280	1.00000		
L	−0.11607	−0.34255	0.88548	0.99999	−0.16599	0.99577	−0.40880	−0.29365	−0.22272	0.87690	0.63109	1.00000	
M	0.93677	0.87424	0.07073	−0.01151	0.98446	0.05721	0.84221	0.89284	0.91462	−0.17278	0.64874	−0.01150	1.00000

in table 3: 0.96034). Stationary point C has a large overlap (0.91910), with the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ SCF (table 2) and small overlaps (−0.03976 and −0.29888, respectively) with stationary points A and B (table 3).

$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF calculations were also performed using the NR procedure with the Fletcher constraint algorithm starting with orbitals from MC SCF stationary points A, B, and C. All three calculations converged to the same $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF stationary point at −75.416438970048 au. Hence, multiple minima for the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF were not found. If the existence of multiple MC SCF minima (stationary points A, B, and C) were caused only by non-linear orbital rotational parameters, at least two $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF stationary points should have been located. The existence of multiple MC SCF minima may therefore, in this case, be attributed to the coupling between the non-linear orbital rotational parameters and the linear configuration state function rotational parameters.

The three different minima (A, B, and C) are, of course, obtained in a somewhat arbitrary way depending on the starting guess. There may exist other energetically close-lying minima on the energy hypersurface in addition to the three we have located. The NR procedure with the Fletcher constraint algorithm gives reliable and rapid convergence even to stationary points which could not be easily located (if they could be located at all) with other less convergent techniques. In the following we further examine in some detail the importance of the multiple minima problem for practical MC SCF and in section 3.3 for large scale CI calculations.

In the limit of a full CSF expansion the CI and the MC SCF give exactly the same energies [3,4,29,30]. Hence, a solution to the problem of multiple "ground states" may be to expand the complete active space. Using the power of the Fletcher constraint procedure coupled with the NR complete second-order MC SCF, the energy hypersurface of the enlarged CAS MC SCF can also be examined in more detail than was possible previously. We now examine the MC SCF energy hypersurface of C_2 at 2.70 au with the same basis set using complete active spaces ($2\sigma_u$, $1\pi_u$, $1\pi_g$, $3\sigma_g$)

and ($2\sigma_g$, $2\sigma_u$, $1\pi_u$, $1\pi_g$, $3\sigma_g$) to see if the multiple minima problem also occurs for these enlarged complete active spaces.

The complete active space ($2\sigma_u$, $1\pi_u$, $1\pi_g$, $3\sigma_g$) has 18 CSFs of $^1\Sigma_g^+$ symmetry. Four separate calculations were carried out, three of which used the orbitals of stationary points A, B, and C as an initial guess and the fourth used symmetrized, orthogonalized basis functions as an initial guess (see table 1). With an initial guess of molecular orbitals from stationary points B, C, or orthogonalized, symmetrized basis functions and the lowest root of $^1\Sigma_g^+$ symmetry from the respective initial 18 configuration CAS CI, convergence was obtained to stationary point D with energy −75.569826385118 au. An initial guess of molecular orbitals from stationary point A and the lowest root of $^1\Sigma_g^+$ symmetry from the corresponding initial 18 configuration CAS CI converged to stationary point E with energy −75.501658374802 au. Both of these stationary points (D and E) fulfill all four criteria for being a good representation of the $X\,^1\Sigma_g^+$ state for C_2.

There is a large (≈ 0.07 au) difference in energy and a considerably different CSF description of these two stationary points. Stationary point D is essentially $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ and E is largely $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ (see table 1). The overlaps (table 2) of D with the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF and the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ SCF are −0.10101 and 0.83464, respectively, while the overlaps of E with the same SCF states are 0.65669 and −0.04694, respectively. D and E have an overlap with each other of −0.16600 (see table 3). These differences are further demonstrated by the overlaps (see table 3) of D with C (0.88547) and E with A and B (0.94370 and 0.91518, respectively). Compared to the SCFs and the three CSF MC SCF calculations to stationary points A, B, and C, stationary points D and E are reversed in energy order, i.e. MC SCF stationary point D corresponding primarily to the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ configuration is now lower by 0.07 au than MC SCF stationary point E corresponding largely to $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$.

The further enlarged complete active space which included the $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $1\pi_g$, and $3\sigma_g$ orbitals was used in two separate complete active space MC SCF calculations (a total of 44 CSF of $^1\Sigma_g^+$ symmetry, see table 1). The initial guess of molecular orbitals from either stationary point D or E and the lowest root of $^1\Sigma_g^+$ symmetry from the initial 44 CSF CAS CI both converged to the same stationary point, F, with energy −75.574712221969 au. Two possibilities, from an infinite number of possibilities of the amplitudes of CSF of this state [4,29], are given in table 1 for stationary point F. These different CSF amplitudes and orbitals are related by non-energy changing ($2\sigma_g \leftrightarrow 3\sigma_g$) rotations. Since the two descriptions give *exactly* the same energy, properties, and overlaps with the other stationary points, they represent the same stationary point. As expected, the final MC SCF energy of stationary point F is the lowest of all the stationary points because of the larger amount of variational freedom in the calculation. The overlap of stationary point F with D and C is large; 0.99577 and 0.88740, respectively, (since they are mainly described by the same CSF, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$) and small with A, B, and E: 0.05647, −0.28727 and −0.09789, respectively (which are described mainly by another CSF, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$). This is further demonstrated by the overlaps with the SCF stationary points given in table 2, i.e. the overlaps of F with $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ and $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ are −0.06115 and 0.83409 respectively.

By performing multiconfigurational linear response calculations using the stationary points A–F to symmetries other than that of the MC SCF stationary point we can further examine their similarities and differences. These results for electric dipole allowed transitions are summarized in table 4. None of the stationary points A–C have the capability of reliably predicting the low-lying $^1\Sigma_g^+ \rightarrow {}^1\Pi_u$ transition. The $^1\Pi_u$ state is predicted o be much too high in A and B and to lie very slightly below the $X\,^1\Sigma_g^+$ state in C causing a large *negative* frequency-independent polarizability. For stationary points D–F the $X\,^1\Sigma_g^+$ state is lower than all $^1\Pi_u$ states obtained from the respective multiconfigurational linear response calculations. At stationary point E, the lowest $^1\Sigma_g^+ \rightarrow {}^1\Pi_u$ transition (0.067 eV) leads to an anomalously large (26.182 au) frequency-independent polarizability. The excitation energy differences for the same transitions between calculations using stationary

Table 4
Multiconfigurational linear response calculations using stationary points A–F

Stationary point label	Lowest two excitation energies (eV) to $^1\Sigma_u^+$ and $^1\Pi_u$ states		Frequency-independent polarizability (au)
	$^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$	$^1\Sigma_g^+ \rightarrow {}^1\Pi_u$	
A	7.27	12.03	16.08
	9.29	15.27	
B	5.83	11.98	15.52
	10.75	15.45	
C	5.73	−0.09	−182.93
	11.39	11.24	
D	6.39	1.10	17.94
	11.95	11.74	
E	6.02	0.07	26.18
	9.39	9.47	
F	6.03	1.05	18.11
	11.87	11.67	

points C and D compared with D and F seem to indicate the convergence (as expected) of the MC linear response calculations as the size of the complete active space of the stationary point is increased.

So far, we have only been concerned with finding energetically close-lying "good" representations of the ground state on the energy hypersurface. To further investigate the energy hypersurface of C_2 at 2.70 au, we performed several hypersurface walking calculations starting from the three stationary points A, B, and C to find stationary points which have one negative eigenvalue in (A − B). From each stationary point we initially took a step in the direction of the smallest (A − B) eigenvalue of 0.1 in a positive direction and then in a negative direction. For example, A(+0.1) and A(−0.1) respectively represent an energy hypersurface walk starting from stationary point A and initially stepping in the direction corresponding to the lowest eigenvalue of the hessian with respect to real variations by +0.1 or by −0.1. Subsequent MC SCF iterations using the complete second-order NR procedure and Fletcher constraint algorithm modified with the surface walking procedure to ensure that the walk was along the stream bed were performed. The U_1 direction in each iteration was determined by overlap of the hessian eigenvectors with the previous iteration's eigenvectors. These results are given in table 5. Further "walking" along the stream bed from stationary points G–J in the direction initially corresponding to the negative (A − B) eigenvalue took the calculations back to the original starting stationary points A–C.

Also listed in table 5 is the MC SCF calculation starting from the molecular orbitals of stationary point A and the second lowest root in the corresponding MC SCF CI. Our usual excited state Fletcher constraint procedure without walking combined with the NR method [5] was used to converge to the first excited state of $^1\Sigma_g^+$ symmetry. Judged with the criteria 1–4 of the introduction, the stationary point so obtained (labelled K in table 5) may properly represent the $2\,^1\Sigma_g^+$ state of C_2 at 2.70 au.

These walking results clearly demonstrate two important facts about MC SCF calculations. First of all, multiple stationary points which fulfill some of the four criteria may exist nearby stationary points which fulfill all of the four criteria on the hypersurface. Second, unless a careful examination of the characteristics of a stationary point is undertaken when convergence is reached, erroneous results may be reported. Considering the smallest complete active space only one walking calculation, namely C(+0.1), reached a stationary point that fulfills all of the four criteria to properly represent the $2\,^1\Sigma_g^+$ state of C_2. If only criteria 1 and maybe the first part of 3 were used to judge a stationary point, all of the other smallest complete active space stationary points (G–K) in table 5 would be incorrectly considered as the $2\,^1\Sigma_g^+$ state of C_2 since they are all variationally correct and they all have one negative eigenvalue in (A − B).

The energies of stationary points G and H are very close to the energy of B (0.00013 and 0.00002 au, respectively), and the energy of J is very close to the energy of C (0.00081 au). Even though stationary points G–J are the lowest root in the corresponding MC SCF CI, there could be other, similar, unlocated stationary points present in these or other MC SCF calculations which are instead the second root in the MC SCF CI and have one negative (A − B) eigenvalue but do not fulfill the other conditions for being a proper representation

Table 5
MC SCF stationary points obtained by walking on the energy hypersurface of C_2 at 2.70 au

Starting point [a]	Final energy (au)	Label	Characteristics				
			negative eigenvalues		energy order in MC SCF CI	MC linear response [b]	
			(A−B)	(A+B)		number of negative excitation energies	number of instabilities
B(−0.1)	−75.425002343069	G	1	1	1	0	1
B(+0.1)	−75.425111640013	H	1	0	1	0	1
A(+0.1)	−75.423930425981	I	1	0	1	0	1
A(−0.1)							
C(−0.1)	−75.416790067530	J	1	0	1	0	1
C(+0.1)	−75.409581704248	K	1	1	2	1	0
A [c]							
F(±) [d]	−75.569847148164	L	1	1	1	0	2
F(±) [d]	−75.504552744922	M	1	1	2	1	0

[a] An initial step (given in parentheses) was taken from the indicated stationary point in the direction corresponding to the lowest (A−B) eigenvalue.

[b] MC linear response to states of the same spin and spatial symmetry as the MC SCF reference state.

[c] The MC SCF stationary point for the $2^1\Sigma_g^+$ state of C_2 at 2.70 au is obtained by walking or by performing a NR calculation with the Fletcher excited state constraint algorithm used when far from convergence. The second highest root in the CI with the MC SCF configurations and orbitals from stationary point A was used as an initial guess when our ordinary excited state procedure was used.

[d] These stationary points were obtained by walking in several different stream beds starting from stationary point F.

of the first excited state of $^1\Sigma_g^+$ symmetry [5]. Furthermore, the large overlaps of stationary points G, H, and I with those of the $X\,^1\Sigma_g^+$ stationary points A, B, and E (table 3) and the large overlap of stationary point J with the $X\,^1\Sigma_g^+$ stationary points C, D, and F (table 3) suggest that these stationary points G, H, I, and J should be better thought of as very near-lying stationary points which are "almost" representations of the $X\,^1\Sigma_g^+$ state than as good approximations to the $2\,^1\Sigma_g^+$ state of C_2.

We also performed several hypersurface walking calculations starting from the energy minimum, stationary point F, we located with the largest CAS MC SCF. With these walking calculations we were able to obtain two different new stationary points, each with one negative eigenvalue in (A − B) and one negative eigenvalue in (A + B). These results are reported in table 5. The results from the MC linear response indicate that stationary point M is a better representation of the first excited state since there are no instabilities and one negative transition energy while stationary point L has two instabilities and no negative transition energies. M is the second root of the corresponding MC SCF CI and L is the first root of the corresponding MC SCF CI. Overlaps reported in tables 2 and 3 indicate that L is very similar to MC SCF stationary points C, D, and F and has a large overlap with the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ SCF stationary point. Stationary point M is likewise similar to MC SCF stationary points A, B, and E and has a fairly large overlap with the $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$ SCF. It is also interesting to note that stationary point K, a proper representation of the first excited state in the three configuration MC SCF, has almost equal overlap with both points L and M, 0.63109 and 0.64874 respectively.

Although with these C_2 calculations, we have not been able to find a stationary point with the desired number of negative eigenvalues in (A − B) and a larger, different (hence, undesired) number in (A + B), these kinds of stationary points also exist [5]. In recent MC SCF calculations for the ground state of Be atom, using a 54 function set of

contracted gaussian functions, we obtained a stationary point with no negative eigenvalues in (A − B) and one negative eigenvalue in (A + B) [31]. This stationary point was also the lowest root in the corresponding MC SCF CI. Since in previous MC SCF and SCF calculations in the literature the number of negative eigenvalues of *both* (A − B) and (A + B) were not examined, we expect that a substantial fraction of previous ground state calculations may have converged to these kinds of stationary points which are not proper representations of the exact ground state.

These walking calculations show the importance of using an MC SCF algorithm which examines and uses the structural characteristics [e.g., the index of (A − B)] of possible stationary points on the energy hypersurface, thereby avoiding convergence to stationary points which possess some undesired characteristics.

3.3. *Large scale CI calculations*

The problem of multiple stationary points satisfying the same characteristics for representing the Nth exact state may have serious consequences for the use of MC SCF orbitals in large scale CI calculations. In order to analyze these consequences, large scale CI calculations were performed using the molecular orbitals obtained from each $X\,^1\Sigma_g^+$ stationary point (A–F). The CI using the orbitals from stationary points A–C included the complete active space ($2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$) configurations and all single and double excitations from the complete active space into the virtual space for a total of 3239 configurations. The CI using the orbitals from stationary points D–F included the complete active space ($2\sigma_g$, $2\sigma_u$, $1\pi_u$, $1\pi_g$, $3\sigma_g$) configurations and all single and double excitations from the complete active space into the virtual space for a total of 32306 configurations. The results are summarized in table 6. For each different starting guess of molecular orbitals, different CI energies are obtained.

The calculation using the orbitals from MC SCF stationary point C, the stationary point with the highest energy in table 1, gives the lowest large scale CI energy of the three calculations when 3239 configurations are used. Similarly, the calculation using the orbitals from MC SCF stationary point E, the stationary point with the higher energy when using 18 CSF, gives the lower CI energy when 32306 configurations are used compared to the large scale CI calculation with the orbitals from stationary point D. Both MC SCF stationary points C and E might have been disregarded as good approximations to the $X\,^1\Sigma_g^+$ state of C_2 if only the "lower energy is a better approximation" criterion had been used.

The calculation using orbitals from stationary point F gives the lowest large scale CI energy in table 6 which is consistent with the fact that stationary point F also has the lowest MC SCF energy. The largest configuration amplitude squared for the lowest $^1\Sigma_g^+$ large scale CI root using the orbitals from stationary point D is 0.689 corresponding to $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$. It is 0.345 corresponding to $1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$ using the orbitals from stationary point E and 0.354 corresponding to $1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$ using the orbitals corresponding to stationary point F. For MC SCF stationary point F the $2\sigma_g$ and $3\sigma_g$ orbitals may be arbitrarily rotated into each other with the MC SCF energy and properties remaining the same [4,19]. Our choice for stationary point F orbitals is from the second entry in table 1 with CSF amplitude squared 0.372 corresponding to $1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$. A different but equivalent choice of the stationary point F orbitals (such as from the first F stationary point in table 1) would give the same total energy but different amplitudes for $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^1 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$, and $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_u^2$ as well as other configurations, e.g. the amplitude for $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$ may become the largest.

In table 7, the energy order of the large scale 3239 configurations CI results are compared with three configuration MC SCF CI results using MC SCF orbitals from stationary points A, B, and C. Except for the orbitals from stationary point C the large scale CI energy order does not correspond to the MC SCF CI energy order. With the orbitals from stationary point A, the maximum amplitude CSF coefficient for the first and third roots in the large scale CI did not correspond to one of the three original MC SCF CSFs.

In table 8 we give the sums of the squares of the

Table 6
Large scale CI results for C_2 at 2.70 au

Orbitals from stationary point	MC SCF complete active space orbitals	Number of MC SCF CSF	Final MC SCF energy (au) [a]	Large scale $^1\Sigma_g^+$ CI		
				complete active space orbitals	number of CSFs [b]	energies (au) [c]
A	$2\sigma_u, 1\pi_u, 3\sigma_g$	3	−75.431695416508	$2\sigma_g, 2\sigma_u, 1\pi_u, 3\sigma_g$	3239	−75.653473
						−75.633039
						−75.371250
B			−75.425127520205			−75.654471
						−75.624006
						−75.334333
C			−75.417599876869			−75.665521
						−75.626076
						−75.372398
D	$2\sigma_u, 1\pi_u, 3\sigma_g, 1\pi_g$	18	−75.569826385118	$2\sigma_g, 2\sigma_u, 1\pi_u, 1\pi_g, 3\sigma_g$	32306	−75.694033
						−75.639311
						−75.426063
E			−75.501658374802			−75.696188
						−75.652219
						−75.454621
F	$2\sigma_g, 2\sigma_u, 1\pi_u, 1\pi_g, 3\sigma_g$	44	−75.574712221969	$2\sigma_g, 2\sigma_u, 1\pi_u, 1\pi_g, 3\sigma_g$	32306	−75.702500
						−75.650515
						−75.459172

[a] MC SCF $X\,^1\Sigma_g^+$ stationary points (see table 1).
[b] Allowing all single and double excitations from the CI active space orbitals into the virtual orbitals.
[c] Lowest three $^1\Sigma_g^+$ stationary point energies are listed. These energies are converged to 10^{-6} au.

large scale CI coefficients multiplying configurations which are present in the corresponding CAS MC SCF. Stationary points A and E have a large part of the corresponding large scale CI vector outside of the original CAS MC SCF configurations, i.e. 0.81 and 0.63, respectively. Stationary

Table 7
Comparison of $^1\Sigma_g^+$ MC SCF CI stationary points and large scale $^1\Sigma_g^+$ CI stationary points for C_2 at 2.70 au

Orbitals from stationary point	MC SCF CI energy order [b]	Large scale CI [c] energy order	CSF with maximum CI coefficient for MC SCF CI and large scale CI	MC SCF CI energies (au)	Maximum MC SCF CI configuration coefficient squared	Large scale CI energies (au)	Maximum large scale CI configuration coefficient squared
A [a]	1	2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	−75.431695	0.981071	−75.633039	0.723278
B	1	2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	−75.425128	0.931850	−75.624006	0.768960
	2	1	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	−75.393565	0.831456	−75.654471	0.701529
	3	3	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$	−74.944002	0.883162	−75.334333	0.480823
C	1	1	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$	−75.417600	0.859318	−75.665521	0.741430
	2	2	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2$	−75.369055	0.978078	−75.626076	0.791053
	3	3	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 3\sigma_g^2$	−74.898982	0.844703	−75.372398	0.374948

[a] For stationary point A the largest CI coefficient for roots 1 and 3 were outside the MC SCF CI CAS.
[b] MC SCF CI energy order refers to the order in increasing energy of the states from a small CI using converged MC SCF orbitals and the configuration state functions defining the MC SCF calculation.
[c] Allowing all single and double excitations from the CAS $2\sigma_g, 2\sigma_u, 1\pi_u$, and $3\sigma_g$ orbitals into the virtual orbitals.

Table 8
Sums of the squares of the large scale $^1\Sigma_g^+$ CI stationary point coefficients

Orbitals from stationary point	Sum of the squared coefficients of the corresponding large scale CI within the CAS MC SCF configuration space	Sum of the squared coefficients of the corresponding large scale CI within the large scale CI reference space
A	0.192299	0.847436
B	0.846636	0.853698
C	0.849339	0.849916
D	0.951201	0.953012
E	0.370221	0.939815
F	0.947144	0.947144

points D and F instead have a large part of the corresponding large scale CI vector for configurations included in the original CAS MC SCF, i.e. 0.95 for each case.

4. Summary and conclusions

Because of the power of the recently developed complete second-order MC SCF procedures coupled with the Fletcher constraint algorithm, an MC SCF energy hypersurface can be investigated much more thoroughly that was previously possible. The modified algorithm that allows walks to be carried out from one stationary point along stream beds on the energy hypersurface to other "new" stationary points further stresses this fact.

In order to properly classify each of the stationary points, several characteristics of the points must be studied. In previous MC SCF calculations in the literature in which the characteristics were not thoroughly examined, convergence may frequently have been to stationary points which are not proper representations of an exact state.

We have calculationally demonstrated that even in a relatively simple molecule such as C_2, the MC SCF energy hypersurface can be exceedingly complicated. By choosing a small active space we have determined three different stationary points which are energy minima and fulfill all four characteristics for being a representation of the $X\,^1\Sigma_g^+$ ground state. By carrying out walks we have identified many stationary points which are energetically close to these three minima but which have an index of the total hessian with respect to real variations, (A − B), equal to one. These stationary points should, of course, be rejected as proper representations of the $X\,^1\Sigma_g^+$ state. Only MC SCF algorithms that are capable of rejecting such stationary points with an undesired (A − B) index should be used in practical MC SCF calculations. At convergence other characteristics of the obtained stationary point should be examined.

To examine the multiple minima problem further we carried out MC SCF calculations with enlarged complete active spaces. When the complete active space came close to the full valence space, we could not locate more than one energy minimum. It certainly seems that a reasonable MC SCF strategy might be to include all valence orbitals in a CAS for the MC SCF. For all but relatively small systems even with the newly developed direct MC SCF algorithms [4,12,32,33], this is computationally prohibitive. Fortunately, our computational experience has shown that not all energy hypersurfaces are as complicated as the energy hypersurface of C_2 at 2.70 au.

We have further shown that it is sometimes unclear which is the "best" choice of MC SCF orbitals to use when performing a large scale CI when there are several near-lying, equivalent MC SCF stationary points (with each MC SCF having the same CSF) which fulfill all four criteria for being a good representation of an exact state. It may not necessarily be the set of orbitals which yields the lowest MC SCF energy. For example, among stationary points which are proper representations of the ground state for the smallest CAS, i.e. A, B, and C, A has the lowest MC SCF energy but C has the lowest large scale CI energy. C also has the most overlap with MC SCF stationary point F (the only proper representation of the ground state obtained for the largest MC SCF CAS) and C has the biggest sum of the squared coefficients of the corresponding large scale CI within the CAS MC SCF configurations among A, B, and C.

Furthermore, the "best" orbitals to use may not even give the lowest large scale CI energy. For example, a large scale CI calculation using the

orbitals from MC SCF stationary point E gives a lower energy than the large scale CI calculation using the orbitals from stationary point D; however, the MC SCF energy of stationary point E is higher than the MC SCF energy of stationary point D. This may, of course, be somewhat ascribed to inadequacies in the chosen active space. However, D has a large overlap with F and the sum of the squares of the corresponding large scale CI within the CAS MC SCF is much greater than E (0.95 versus 0.37).

The possible adequacy of a chosen MC SCF active space may be checked by comparing the MC SCF CI with a reasonably chosen larger CI using the MC SCF orbitals (see tables 6–8). If the energy order of the MC SCF state in the MC SCF CI compared to the energy order of the corresponding large scale CI stationary point is different or if configurations become important in the larger CI which had small amplitudes or were not included in the MC SCF CI, a larger MC SCF configuration space should be chosen if at all possible. A simple test may be to examine the sum of the squares of the coefficients of the large scale CI within the corresponding CAS MC SCF configurations. If that quantity is greater than ≈ 0.90–0.95 then it may be a good assumption that the MC SCF space was adequate, provided, of course, that the larger scale CI configurations were chosen in a reasonable manner. By this criterion ground state stationary points A, B, C and E may be rejected.

Acknowledgement

We acknowledge research support from the National Science Foundation (Grant CHE-8023352) and the Robert A. Welch Foundation (Grant A-770). We thank W. England, R.C. Raffenetti, I. Shavitt and R. Shepard for the use of their CI programs and R.M. Pitzer for the use of his atomic integral program. JTG thanks R. Shepard for his helpful discussions during the CI phase of this work.

References

[1] D.R. Hartree, W. Hartree and B. Swirles, Phil. Trans. Roy. Soc. London A238 (1939) 229;
G. Das and A.C. Wahl, J. Chem. Phys. 44 (1966) 87;
A. Veillard, Theoret. Chim. Acta 4 (1966) 22;
J. Hinze and C.C.J. Roothaan, Progr. Theoret. Phys. (Kyoto) Suppl. 40 (1967) 37.

[2] A.C. Wahl and G. Das, in: Modern theoretical chemistry, ed. H.F. Schaefer III (Plenum Press, New York, 1977), and references therein.

[3] D.L. Yeager and P. Jørgensen, J. Chem. Phys. 71 (1979) 755; Mol. Phys. 39 (1980) 587.

[4] J. Olsen, D.L. Yeager and P. Jørgensen, Advan. Chem. Phys. 54 (1983) 1.

[5] J.T. Golab, D.L. Yeager and P. Jørgensen, Chem. Phys. 78 (1983) 175.

[6] D.L. Yeager and P. Jørgensen, Chem. Phys. Letters 65 (1979) 77;
E. Dalgaard, J. Chem. Phys. 72 (1980) 816.

[7] E. Dalgaard and P. Jørgensen, J. Chem. Phys. 69 (1978) 3833.

[8] E. Dalgaard, Chem. Phys. Letters 65 (1979) 559.

[9] C.C.J. Roothaan, J.H. Detrich and D.G. Hopper, Intern. J. Quantum. Chem. S13 (1979) 93.

[10] H.-J. Werner and W. Meyer, J. Chem. Phys. 74 (1981) 5794.

[11] D.L. Yeager, D. Lynch, J. Nichols, P. Jørgensen and J. Olsen, J. Phys. Chem. 86 (1982) 2140.

[12] R. Shepard, I. Shavitt and J. Simons, J. Chem. Phys. 76 (1982) 543.

[13] L.G. Yaffe and W.A. Goddard III, Phys. Rev. A13 (1976) 1682.

[14] L.G.J. Douady, J. Ellinger, R. Subra and B. Levy, J. Chem. Phys. 72 (1980) 1452.

[15] J.F. Rico, M. Paniagna, J.I.F. Alonso and P. Fatucci, J. Comput. Chem. 4 (1983) 33; 4 (1983) 41.

[16] G.B. Backskay, Chem. Phys. 61 (1981) 385.

[17] B.H. Lengsfield III and B. Liu, J. Chem. Phys. 75 (1981) 478;
B.H. Lengsfield III, J. Chem. Phys. 77 (1982) 4073;
F.A. Matsen and C.J. Nelin, Intern. J. Quantum Chem. 20 (1981) 861;
P. Siegbahn, J. Almolf, A. Heiberg and B. Roas, J. Chem. Phys. 74 (1981) 2384.

[18] R. Shepard and J. Simons, Generalized Brillouin's Theorem Approaches to Multiconfigurational Self-Consistent Field Theory, preprint.

[19] R. Fletcher, Practical methods of optimization, Vol. 1 (Wiley, New York, 1980);
P.E. Gill, W. Murray and M. Wright, Practical optimization (Academic Press, New York, 1981).

[20] P. Jørgensen, P. Swantstrøm and D.L. Yeager, J. Chem. Phys. 78 (1983) 347.

[21] J. Gerratt and M. Raimondi, Proc. Roy. Soc. A371 (1980) 525.

[22] C.J. Cerjan and W.H. Miller, J. Chem. Phys. 75 (1981) 2800.

[23] J. Simons, P. Jørgensen, H. Taylor and J. Ozment, J. Phys. Chem. 87 (1983) 2746.
[24] I. Shavitt and R.C. Raffenetti, CI program.
[25] R.M. Pitzer, Atomic integral evaluation program;
R.M. Pitzer, J. Chem. Phys. 58 (1973) 3111;
M. Dupuis, J. Rys and H.F. King, J. Chem. Phys. 65 (1976) 111;
R.C. Raffenetti, J. Chem. Phys. 58 (1973) 4452.
[26] R. Shepard and I. Shavitt, Unitary Group CI program;
I. Shavitt, Intern. J. Quantum Chem. S12 (1978) 5;
H. Lischka, R. Shepard, F.B. Brown and I. Shavitt, Intern. J. Quantum Chem. S15 (1981) 91.
[27] T.H. Dunning Jr. and P.J. Hay, in: Modern theoretical chemistry, Vol. 3. Methods of electronic structure theory, ed. H.F. Schaefer III (Plenum Press, New York, 1977).
[28] P.O. Löwdin, J. Chem. Phys. 18 (1950) 365.
[29] J. Olsen, P. Jørgensen and D.L. Yeager, J. Chem. Phys. 76 (1982) 527.
[30] B. Lengsfield III, J. Chem. Phys. 73 (1980) 382.
[31] D.L. Yeager, J. Olsen and P. Jørgensen, Generalizations of the multiconfigurational time dependent Hartree–Fock approach, J. Chem. Soc. Faraday Trans., to be published.
[32] B. Lengsfield III and B. Liu, J. Chem. Phys. 75 (1981) 478;
B. Lengsfield III, J. Chem. Phys. 77 (1982) 4073.
[33] H.J.Aa. Jensen and P. Jørgensen, J. Chem. Phys. 80 (1984) 1204.