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# PROPER CHARACTERIZATION OF MC SCF STATIONARY POINTS

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We discuss several characteristics that an MC SCF stationary point should fulfill in order to be a proper representation of the exact $N$th state in energy of a certain symmetry. We derive an MC SCF iterative scheme that invokes some of these characteristics directly as conditions on the iterative algorithm. Numerical examples demonstrate that convergence is obtained rapidly and reliably to a stationary point with this algorithm. Numerical examples also demonstrate one main point of this paper, i.e. the importance of carefully examining the characteristics of an MC SCF stationary point before assigning it to be an approximate representation of a state. Several different stationary points have been determined for BeO that satisfy some or all of the conditions for being an approximate representation of the same state and it is often not at all clear which stationary point should be chosen as a representative of the desired state. This difficulty may be present in all current and previous MC SCF calculations.

## 1. Introduction

A multiconfigurational self-consistent field (MC SCF) stationary point is variationally correct in both the orbital and configuration space [1], i.e. the first derivative with respect to both orbital and state parameter variations is zero. An MC SCF optimization scheme may be described in terms of a set of rotational parameters (step-length amplitudes) in the orbital and in the configuration state space [2]. The state-expansion coefficients are linear variational parameters whereas the orbital parameters are non-linear variational parameters [3]. Because an MC SCF calculation is optimized with respect to both linear and non-linear variational parameters, many stationary points may be determined that are not approximate representations of exact eigenstates.

In this paper we discuss two primary objectives that may be used to decide whether an MC SCF stationary point is a good approximate representation of the $N$th exact state in energy. Primary characteristics we consider are:

(1) the state has to be variationally correct [1], and,

(2) when an external frequency-dependent one-electron perturbation is applied to the state the linear-response calculation must be stable (give a set of real excitation energies) and give $N-1$ negative excitation energies [2–7].

Objective (2) implies that the sum of the hessian $(\mathbf{A}-\mathbf{B})$ index (number of negative hessian eigenvalues) and the index of the second-derivative matrix with respect to imaginary variations [7], $(\mathbf{A}+\mathbf{B})$, is $2N-2$. The matrix of second derivatives with respect to real variations is called the *hessian* and the matrix of second derivatives with respect to both real and imaginary variations is called the *total hessian*. For the

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lowest and first excited state of a certain symmetry, fulfillment of primary objective (2) implies as a necessary condition that each of the matrices, $(\mathbf{A}-\mathbf{B})$ and $(\mathbf{A}+\mathbf{B})$, has an index $N-1$. For higher excited states, we also require in general that the hessian $(\mathbf{A}-\mathbf{B})$ index is $N-1$ even though in this case objective (2) only implies that the sum of the indices $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ is $2N-2$.

It has previously been suggested [2,4,8,9] to use as a requirement on the MC SCF approximation to the $N$th state that its hessian index is $N-1$. This criterion was then justified because the hessian index of the $N$th exact state is $N-1$.

It has also been suggested [1,2,8–11] to require the MC SCF approximation to the $N$th state to be the $N$th state of a configuration-interaction (CI) calculation using the configuration state functions which are used to define the MC SCF state expansion. (We will occasionally call this the MC SCF CI.) This condition guarantees the MC SCF state to be an upper bound to the $N$th state [12] (Hylleraas–Undheim–McDonald theorem). Certainly this characteristic is desirable. However, if this condition is forced, an MC SCF calculation may be unnecessarily constrained and convergence of the calculation to the correct stationary point may be impossible [6]. For example, an MC SCF calculation where root-flipping naturally occurs cannot converge if an upper-bound criterion is invoked as a constraint in the iterative procedure. Root-flipping frequently occurs in MC SCF calculations, e.g. near avoided crossing [6,10]. Such "root-flipping" states may be good approximations to exact states since they may satisfy both primary objectives (1) and (2).

Furthermore, the upper-bound criterion is not a very well-defined property of an MC SCF calculation. In some MC SCF calculations there is a freedom of choice between state and orbital variables [6]. The converged MC SCF calculation with the largest state-expansion (MC SCF CI) space may satisfy an upper-bound criterion while the calculation using the smallest state-expansion (MC SCF CI) space may have root-flipping [6]. However, the two stationary points have exactly the same energy and properties and may have exactly the same orbitals and configuration-expansion coefficients (the configuration amplitudes may then be zero for the configurations that are added in the calculation of the largest configuration space). The calculation of largest configuration space then may show the upper-bound criterion is satisfied, whereas it is not clear from the MC SCF calculation using the smallest configuration space that the MC SCF state satisfies an upper-bound criterion [6].

Although the upper-bound condition is often neither a very well-defined property of an MC SCF calculation nor applicable in all cases, it is usually a desirable property. The deficiency of the upper-bound criterion originates from the fact that it is related only to the configurational part of the variational space. However, characteristics of an MC SCF state should refer to the total variational space of an MC SCF calculation to avoid unnecessary constraints and ambiguities in identifying an approximation to the exact $N$th state. Primary objective (2) is such a characteristic. Objectives (1) and (2) strongly limit the number of MC SCF states that are candidates for being approximate representations of the $N$th exact state.

However, a very important question arises whether primary objectives (1) and (2) uniquely define the MC SCF approximation to the $N$th state. The MC SCF calculations we report *clearly show* this is not always the case. In several cases, we have found two or more stationary points of different energy that satisfy objectives (1) and (2). In this paper, we report calculations on the $^1\Sigma^+$ excited states of BeO as an example of the ambiguities that may arise in choosing a stationary point as the representation of a state. We note that these ambiguities may be present in *all* MC SCF calculations. So far in our calculations, we have always found that these several stationary points are close in energy and have overlaps close to unity. Even so, the orbitals and the configuration-expansion coefficients have been very different in some cases. Even though the energy is often similar and the overlap is close to unity for the MC SCF stationary points that are candidates for being the approximate representation of the same exact state, it is *not at all satisfactory* to arbitrarily select one of them over another for being the approximate representation of the state.

The difficulties in uniquely selecting an MC SCF stationary point as a representation of the $N$th exact

state is a very severe problem of MC SCF theory and of all previous and current MC SCF calculations which we feel deserves much more attention. Previous calculations have not either monitored the number of negative eigenvalues of $(\mathbf{A}+\mathbf{B})$ or the multiconfigurational linear response. Previous MC SCF calculations would usually only consider the energy ordering of the MC SCF stationary point in the CI calculation which uses the MC SCF configuration state expansion functions [1]. More recent calculations have occasionally also monitored the number of negative eigenvalues of $(\mathbf{A}-\mathbf{B})$ [2–4,8–11], but have not considered the index of $(\mathbf{A}+\mathbf{B})$ or the multiconfigurational linear response.

Fulfillment of primary objectives (1) and (2) requires that the $N$th MC SCF state has a hessian matrix with index $N-1$. An MC SCF calculation may be carried out to first locate a stationary point and then the stationary point may be investigated to determine if it has the hessian $(\mathbf{A}-\mathbf{B})$ index $N-1$ [and also $N-1$ negative excitation energies in multiconfigurational linear response and index $N-1$ in $(\mathbf{A}+\mathbf{B})$]. However, such an approach is very inefficient and many stationary points may be determined before the desired solution is found. A much more efficient approach is to directly introduce into the MC SCF iterative procedure the condition that the hessian matrix has the index $N-1$. In this communication we describe an MC SCF iterative scheme that has such a feature. We do note, however, that this condition does not guarantee that at convergence $(\mathbf{A}+\mathbf{B})$ has index $N-1$ or that the multiconfigurational linear response will have no instabilities and give $N-1$ negative excitation energies. At convergence, the number of negative eigenvalues of the second-derivative matrix with respect to imaginary variations $(\mathbf{A}+\mathbf{B})$ needs to be determined and the multiconfigurational linear-response calculation needs to be performed in order to properly characterize the stationary point.

The MC SCF algorithm we describe is a natural excited-state extension of the Fletcher algorithm [13]. The Fletcher algorithm has previously been successfully used in ground-state MC SCF calculations [14] where it can be proven to guarantee convergence. Excited-state extensions of the Fletcher algorithm have not been proven mathematically to guarantee convergence. Other MC SCF algorithms in current use have not been proven mathematically to guarantee convergence for either ground- or excited-state calculations [1–3,8–11]. The basic features of the Fletcher algorithm for ground states are used in our excited-state extensions of the algorithm. Consequently, convergence is generally rapid and extremely reliable to a stationary point with hessian index $N-1$.

The idea behind the Fletcher algorithm is to carry out a controlled walk on the energy hypersurface. The controlled walk is defined to be one that is restricted to be within a *trust region* of the energy hypersurface. This is the region in which the second-order Taylor series expansion, $q(\lambda)$, is a good approximation to the total Taylor series expansion, $E(\lambda)$. In an actual excited-state implementation of the Fletcher algorithm, a stationary point of $q(\lambda)$ is determined subject to the constraint that the norm of the step length has to be smaller than or equal to a positive value, $h$. The parameter, $h$, defines the trust region and $h$ is updated in each iteration according to the measured agreement between $q(\lambda)$ and $E(\lambda)$. The stationary point of $q(\lambda)$ is also chosen to be within the area that ensures that the converged hessian matrix has the desired index. Hence, the convergence cannot occur to any nearby stationary point with too many or too few negative hessian eigenvalues using the Fletcher algorithm.

Close to convergence (the local region), the Fletcher algorithm will give a sequence of unconstrained Newton–Raphson iterations [13] and thus show second-order convergence characteristics. For ground-state calculations, the controlled walk within the trust region ensures that a sequence of monotonically decreasing total energies is obtained. The monotonic decrease in the total energies is one essential feature which is necessary to guarantee convergence in ground-state calculations. In excited-state calculations, we also carry out a controlled walk within the trust region. However, the total energy of each iteration cannot be ensured to bound the final energy either from above or below. For that reason convergence cannot be guaranteed. Even so, the controlled walk within the trust region ensures that the information content of the second-order Taylor series expansion is optimally used in the iterative procedure. The second-order Taylor series expansion contains no further reliable information on the structure of the exact energy hypersurface

than what is contained in the trust region.

In section 2 we will briefly describe how a unitary transformation may be carried out in the orbital and state space and how to perform a Taylor series expansion of the total energy. Both real and imaginary variations are considered. This development is necessary to fully understand how to properly characterize an MC SCF stationary point. It is thus different but parallels previous derivations [2,3,15,16] where only real variations were considered. In section 3 we show that if a linear-response calculation [objective (2)] for the MC SCF approximation to the $N$th exact state is stable and has $N-1$ negative excitation energies then the sum of the hessian $(\mathbf{A}-\mathbf{B})$ and $(\mathbf{A}+\mathbf{B})$ indices is $2N-2$. Section 4 describes how the Fletcher algorithm may be extended so as to be applicable to excited-state calculations. Section 5 contains some numerical results to illustrate the previous developments. First we present calculations which show that the Fletcher-algorithm calculations converge rapidly and reliably to a stationary point with hessian index $N-1$. In the second part of section 5 we give examples that demonstrate the important points that several MC SCF stationary points may be approximate representation of the same exact state. These calculations also show the necessity of examining both the $(\mathbf{A}+\mathbf{B})$ index and multiconfigurational linear response at convergence as well as the $(\mathbf{A}-\mathbf{B})$ index. The last section contains some concluding remarks.

## 2. Taylor series expansion of the total energy

In this section we derive the expression for the energy of a state where we allow both real and imaginary variations in the orbital and configurational parameters. This derivation is necessary to understand our subsequent discussion of characterization of a stationary points. Since both real and imaginary variations are allowed, this derivation is different even though paralleling previous derivations where only real variations have been considered [2,3,7].

### *2.1. Unitary transformation in state and orbital space*

The multiconfigurational Hartree–Fock (MC SCF) reference state $|0\rangle$ may be regarded as a member of the set of states $\{|j\rangle\}$

$$|0\rangle=\sum_g|\Phi_g\rangle C_{g0},\qquad |j\rangle=\sum_g|\Phi_g\rangle C_{gj}, \tag{1}$$

where the coefficient matrix $\mathbf{C}$ forms a unitary matrix. The configuration state functions $\{|\Phi_g\rangle\}$ are composed of simple linear combinations of determinants $\{|\Phi_f^{\mathrm{D}}\rangle\}$

$$|\Phi_f^{\mathrm{D}}\rangle=\prod_{r\in f}a_r^+|\mathrm{vac}\rangle, \tag{2}$$

where $\prod_{r\in f}a_r^+$ refers to an ordered product of creation operators.

A unitary transformation of the state $|0\rangle$ among the states $|j\rangle$ may then be described [2,3,15,16] as

$$\exp(\mathrm{i}\hat{S})|j\rangle=\sum|k\rangle[\exp(\mathrm{i}\mathbf{S})]_{kj}=\sum|k\rangle X_{kj}, \tag{3}$$

where

$$\hat{S}=\sum_{k=0}\left(S_{k0}|k\rangle\langle 0|+S_{k0}^*|0\rangle\langle k|\right)=\sum_{k=0}\left[N_{k0}\left(|k\rangle\langle 0|+|0\rangle\langle k|\right)+\mathrm{i}P_{k0}\left(|k\rangle\langle 0|-|0\rangle\langle k|\right)\right]. \tag{4}$$

$\mathbf{T}=\exp(\mathrm{i}\mathbf{S})$ is a unitary matrix and $\mathbf{S}=\mathbf{N}+\mathrm{i}\mathbf{P}$ is a hermitean matrix (where $\mathbf{N}$ and $\mathbf{P}$ are real matrices) with elements $S_{k0}$ and $S_{0k}(=S_{k0}^*)$ and zero elsewhere. Alternatively, the non-zero elements of $\mathbf{S}$ may be

rewritten as a vector $\boldsymbol{S}$. We consider in the following the real and imaginary parts of $S_{k0} = N_{k0} + iP_{k0}$ as variational parameters.

A unitary transformation of the orbitals may be similarly be described as [7,15,16]

$$\tilde{a}_r^+ = \exp(i\hat{\kappa}) a_r^+ \exp(-i\hat{\kappa}), \tag{5}$$

where

$$\hat{\kappa} = \sum_{r=s} \kappa_{rs} a_r^+ a_s = \sum_{r>s} (\kappa_{rs} a_r^+ a_s + \kappa_{rs}^* a_s^+ a_r) = \sum_{r>s} [\gamma_{rs}(a_r^+ a_s + a_s^+ a_r) + i\beta_{rs}(a_r^+ a_s - a_s^+ a_r)]. \tag{6}$$

From eqs. (5) and (6) we get

$$\tilde{a}_r^+ = \sum a_s^+ [\exp(i\kappa)]_{sr} = \sum a_s^+ X_{sr}, \tag{7}$$

where $\mathbf{X} = \exp(i\boldsymbol{\kappa})$ is a unitary matrix and $\boldsymbol{\kappa} = \boldsymbol{\gamma} + i\boldsymbol{\beta}$ a hermitean matrix (where $\boldsymbol{\gamma}$ and $\boldsymbol{\beta}$ are real matrices) with the elements $\kappa_{rs}$ and $\kappa_{sr} (= \kappa_{rs}^*)$ of eq. (6) and zero elsewhere. Alternatively, the non-zero elements of $\boldsymbol{\kappa}$ may be rewritten as a vector $\boldsymbol{\kappa}$. We consider in the following the real and imaginary parts of $\kappa_{rs}$ as additional variational parameters.

A unitary transformation of the reference state $|0\rangle$ which performs simultaneously a unitary transformation in the orbital and the configuration space may therefore be described as

$$|\tilde{0}\rangle = \exp(i\hat{\kappa}) \exp(i\hat{S})|0\rangle. \tag{8}$$

The set of excitation operators $\{a_r^+ a_s\}$ in $\hat{\kappa}$ and $\{|k\rangle\langle 0|\}$ in $\hat{S}$ may be linearly dependent. This linear dependency may be removed by eliminating redundant operators $a_r^- a_s$. The elimination of redundant operators for a specific choice of configurations in the MC SCF reference state has been described in detail in ref. [2].

### 2.2. *Variations in the total energy*

The total energy corresponding to the unitary transformation of the reference state given in eq. (8) may be written as [2,3,15,16]

$$E(\boldsymbol{\lambda}) = E(\boldsymbol{\kappa}, \boldsymbol{S}) = \langle\tilde{0}|H|\tilde{0}\rangle = \langle 0|\exp(-i\hat{S}) \exp(-i\hat{\kappa}) H \exp(i\hat{\kappa}) \exp(i\hat{S})|0\rangle. \tag{9}$$

The total energy is thus defined in terms of a set of rotational parameters $\{\boldsymbol{\kappa}, \boldsymbol{S}\}$. A Taylor series expansion may be carried out in these rotational parameters at $\{\boldsymbol{\kappa}, \boldsymbol{S}\} = (\boldsymbol{0}, \boldsymbol{0})$ (the parameter set characterizing $|0\rangle$). At this point the partial derivatives of the total energy may be evaluated by expanding the exponential operators

$$\begin{aligned} E(\boldsymbol{\kappa}, \boldsymbol{S}) &= \langle\tilde{0}|H|\tilde{0}\rangle = \langle 0|\exp(-i\hat{S}) \exp(-i\hat{\kappa}) H \exp(i\hat{\kappa}) \exp(i\hat{S})|0\rangle \\ &= E(0) - i\langle 0|[\hat{S} + \hat{\kappa}, H]|0\rangle - \tfrac{1}{2}\langle 0|[\hat{S}, [\hat{S}, H]]|0\rangle - \tfrac{1}{2}\langle 0|[\hat{\kappa}, [\hat{\kappa}, H]]|0\rangle \\ &\quad - \langle 0|[\hat{S}, [\hat{\kappa}, H]]|0\rangle + \ldots . \end{aligned} \tag{10}$$

All terms through second order in $\boldsymbol{\kappa}$ and $S$ in eq. (10) are written out explicitly.

Using the super-matrix notation, where the variational parameters $\{\gamma_{rs}\}$, $\{N_{k0}\}$, $\{\beta_{rs}\}$ and $\{P_{k0}\}$ and the excitation operators

$$\boldsymbol{Q}^+ = \{a_r^+ a_s\}, \quad r > s; \qquad \boldsymbol{R}^+ = \{|k\rangle\langle 0|\} \tag{11}$$

both form vectors,

$$\boldsymbol{\lambda} = \begin{pmatrix} \boldsymbol{\gamma} \\ \boldsymbol{N} \\ \boldsymbol{\beta} \\ \boldsymbol{P} \end{pmatrix}, \qquad \boldsymbol{T} = \begin{pmatrix} (\boldsymbol{Q}^+ + \boldsymbol{Q}) \\ (\boldsymbol{R}^+ + \boldsymbol{R}) \\ i(\boldsymbol{Q}^+ - \boldsymbol{Q}) \\ i(\boldsymbol{R}^+ - \boldsymbol{R}) \end{pmatrix}, \tag{12}$$

allows us to write the total energy in eq. (10) in matrix notation

$$E(\lambda) = E_0 + \boldsymbol{F}^{\mathrm{T}}\boldsymbol{\lambda} + \tfrac{1}{2}\boldsymbol{\lambda}^{\mathrm{T}}\mathbf{G}\boldsymbol{\lambda} + \ldots, \tag{13}$$

where the matrices $\boldsymbol{F}$ and $\mathbf{G}$ are identified to be

$$\boldsymbol{F} = -\mathrm{i}\langle 0|[\boldsymbol{T}, H]|0\rangle, \qquad \mathbf{G} = -\langle 0|[\boldsymbol{T}, \boldsymbol{T}, H]|0\rangle. \tag{14}$$

The double commutator for the operators $C$ and $D$ is defined as

$$[C, D, H] = \tfrac{1}{2}([C[D, H]] + [D, [C, H]]). \tag{15}$$

The terms in the double commutator in eq. (15). that couple the orbital and configurational space are here defined such that the hamiltonian always operates first on the orbital space excitation operators and then on the configuration space excitation operators (see below).

The energy gradient $\boldsymbol{F}$ and the energy *total hessian* $\mathbf{G}$ may be decomposed to component form. Using eq. (14) we may write the gradient as

$$\boldsymbol{F} = \begin{pmatrix} -\mathrm{i}\langle 0|[\boldsymbol{Q}^+ + \boldsymbol{Q}, H]|0\rangle \\ -\mathrm{i}\langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, H]|0\rangle \\ \langle 0|[\boldsymbol{Q}^+ - \boldsymbol{Q}, H]|0\rangle \\ \langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, H]|0\rangle \end{pmatrix} = 2\begin{pmatrix} \mathrm{Im}\langle 0|[\boldsymbol{Q}^+, H]|0\rangle \\ \mathrm{Im}\langle 0|[\boldsymbol{R}^+, H]|0\rangle \\ \mathrm{Re}\langle 0|[\boldsymbol{Q}^+, H]|0\rangle \\ \mathrm{Re}\langle 0|[\boldsymbol{R}^+, H]|0\rangle \end{pmatrix}, \tag{16}$$

or

$$\boldsymbol{F} = 2\begin{pmatrix} \mathrm{Im}\boldsymbol{W} \\ \mathrm{Re}\boldsymbol{W} \end{pmatrix}, \quad \text{where} \quad \boldsymbol{W} = \begin{pmatrix} \langle 0|[\boldsymbol{Q}^+, H]|0\rangle \\ \langle 0|[\boldsymbol{R}^+, H]|0\rangle \end{pmatrix}. \tag{17}$$

The energy total hessian can similarly be written as

$$\mathbf{G} = \begin{bmatrix} \langle 0|[\boldsymbol{Q}^+ + \boldsymbol{Q}, \boldsymbol{Q}^+ + \boldsymbol{Q}, H]|0\rangle & \langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, [\boldsymbol{Q}^+ + \boldsymbol{Q}, H]]|0\rangle & \mathrm{i}\langle 0|[\boldsymbol{Q}^+ + \boldsymbol{Q}, \boldsymbol{Q}^+ - \boldsymbol{Q}, H]|0\rangle & \mathrm{i}\langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, [\boldsymbol{Q}^+ + \boldsymbol{Q}, H]]|0\rangle \\ \langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, [\boldsymbol{Q}^+ + \boldsymbol{Q}, H]]|0\rangle & \langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, \boldsymbol{R}^+ + \boldsymbol{R}, H]|0\rangle & \mathrm{i}\langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, [\boldsymbol{Q}^+ - \boldsymbol{Q}, H]]|0\rangle & \mathrm{i}\langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, \boldsymbol{R}^+ - \boldsymbol{R}, H]|0\rangle \\ \mathrm{i}\langle 0|[\boldsymbol{Q}^+ - \boldsymbol{Q}, \boldsymbol{Q}^+ + \boldsymbol{Q}, H]|0\rangle & \mathrm{i}\langle 0|[\boldsymbol{R}^+ + \boldsymbol{R}, [\boldsymbol{Q}^+ - \boldsymbol{Q}, H]]|0\rangle & -\langle 0|[\boldsymbol{Q}^+ - \boldsymbol{Q}, \boldsymbol{Q}^+ - \boldsymbol{Q}, H]|0\rangle & -\langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, [\boldsymbol{Q}^+ - \boldsymbol{Q}, H]]|0\rangle \\ \mathrm{i}\langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, [\boldsymbol{Q}^+ + \boldsymbol{Q}, H]]|0\rangle & \mathrm{i}\langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, \boldsymbol{R}^+ + \boldsymbol{R}, H]|0\rangle & -\langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, [\boldsymbol{Q}^+ - \boldsymbol{Q}, H]]|0\rangle & -\langle 0|[\boldsymbol{R}^+ - \boldsymbol{R}, \boldsymbol{R}^+ - \boldsymbol{R}, H]|0\rangle \end{bmatrix} \tag{18}$$

or

$$\mathbf{G} = 2\begin{pmatrix} \mathrm{Re}(\mathbf{A}+\mathbf{B}) & \mathrm{Im}(-\mathbf{A}+\mathbf{B}) \\ \mathrm{Im}(\mathbf{A}+\mathbf{B}) & \mathrm{Re}(\mathbf{A}-\mathbf{B}) \end{pmatrix}, \tag{19}$$

where the $\mathbf{A}$ and $\mathbf{B}$ matrices are defined as

$$\mathbf{A} = -\begin{pmatrix} \langle 0|[\boldsymbol{Q}, \boldsymbol{Q}^+, H]|0\rangle & \langle 0|[\boldsymbol{R}^+, [\boldsymbol{Q}, H]]|0\rangle \\ \langle 0|[\boldsymbol{R}, [\boldsymbol{Q}^+, H]]|0\rangle & \langle 0|[\boldsymbol{R}, \boldsymbol{R}^+, H]|0\rangle \end{pmatrix}, \quad \mathbf{B} = -\begin{pmatrix} \langle 0|[\boldsymbol{Q}, \boldsymbol{Q}, H]|0\rangle & \langle 0|[\boldsymbol{R}, [\boldsymbol{Q}, H]]|0\rangle \\ \langle 0|[\boldsymbol{R}, [\boldsymbol{Q}, H]]|0\rangle & \mathbf{0} \end{pmatrix}. \tag{20}$$

The energy gradient gives the slope and the energy total hessian gives the curvature of the energy hypersurface.

Optimized MC SCF states are variationally correct in the orbital and configuration spaces and therefore represent stationary points on the energy hypersurface of eq. (13), that is points where $\boldsymbol{F} = \boldsymbol{0}$. The condition

that $\boldsymbol{F}=\boldsymbol{0}$ is often referred to as the generalized Brillouin theorem (GBT). At a stationary point, the two terms in the symmetric double-commutator expressions in the total hessian in eq. (18) become identical, since for example

$$\langle 0|[Q^+,[Q,H]]|0\rangle - \langle 0|[Q,[Q^+,H]]|0\rangle = \langle 0|[[Q^+,Q],H]|0\rangle = 0, \tag{21}$$

because the GBT is valid. The full hessian matrix may therefore be written as an ordinary double-commutator expression at a stationary point.

The index of the total hessian matrix (the number of negative total hessian eigenvalues) characterizes the stationary point as being a minimum, a saddle point or a maximum. In the next section, we show that the index of the total hessian matrix may also be used to ensure that the MC SCF state is a proper representation of the desired state.

## 3. Characteristics of an MC SCF stationary point

An MC SCF stationary point satisfies the generalized Brillouin theorem (GBT). However, the fulfillment of the GBT does not guarantee that the MC SCF stationary point is an approximate representation of the desired $N$th state. To ensure an MC SCF state really is an approximate representation of the $N$th state, other characteristics of the state have to be analyzed in more detail. One requirement for an MC SCF stationary point to be an acceptable representation of the $N$th state is that the linear response [5,7] of the stationary point to a frequency-dependent one-electron perturbation is stable and gives a set of real excitation energies among which $N-1$ are negative [4]. This requirement is intuitively and physically sound. The requirement of having stability and $N-1$ negative excitation energies implies that only stationary points need to be determined that have a total hessian index $2N-2$ (see below for a proof). The condition that the hessian with respect to real variations in orbitals and configurations $(\mathbf{A}-\mathbf{B})$ has index $N-1$ is *not* the same as the condition requiring $N-1$ negative excitation energies in a linear response calculation. In fact, if $(\mathbf{A}-\mathbf{B})$ has index $N-1$, the linear response may not give $N-1$ negative excitation energies and may show instabilities.

The system of equations that determine the linear response of the MC SCF state to a frequency-dependent one-electron perturbation has previously been derived [5]. The result of this derivation is given in the following equations:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}\begin{pmatrix} Z_\lambda \\ Y_\lambda \end{pmatrix} = \omega_\lambda \begin{pmatrix} \mathbf{S} & \Delta \\ -\Delta^* & -\mathbf{S}^* \end{pmatrix}\begin{pmatrix} Z_\lambda \\ Y_\lambda \end{pmatrix}. \tag{22}$$

The matrices $\mathbf{A}$ and $\mathbf{B}$ are defined in eqs. (20), and $\binom{Z_\lambda}{Y_\lambda}$ is the eigenvector corresponding to the excitation energy $\omega_\lambda = E_\lambda - E_0$. The matrices $\mathbf{S}$ and $\Delta$ are defined as

$$\mathbf{S} = \begin{pmatrix} \langle 0|[Q,Q^+]|0\rangle & \langle 0|[R^+,Q]|0\rangle \\ \langle 0|[R,Q^+]|0\rangle & \langle 0|[R,R^+]|0\rangle \end{pmatrix}, \quad \Delta = \begin{pmatrix} \langle 0|[Q,Q]|0\rangle & \langle 0|[R,Q]|0\rangle \\ \langle 0|[R,Q]|0\rangle & \mathbf{0} \end{pmatrix}. \tag{23}$$

The eigenvectors of eq. (22) are normalized to unity

$$(Z_\lambda^+ Y_\lambda^+)\begin{pmatrix} \mathbf{S} & \Delta \\ -\Delta^* & -\mathbf{S}^* \end{pmatrix}\begin{pmatrix} Z_\lambda \\ Y_\lambda \end{pmatrix} = 1. \tag{24}$$

Eq. (22) has a paired solution

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}\begin{pmatrix} Y_\lambda^* \\ Z_\lambda^* \end{pmatrix} = -\omega_\lambda \begin{pmatrix} \mathbf{S} & \Delta \\ -\Delta^* & -\mathbf{S}^* \end{pmatrix}\begin{pmatrix} Y_\lambda^* \\ Z_\lambda^* \end{pmatrix}. \tag{25}$$

which satisfies the normalization condition

$$(Y_\lambda^\dagger Z_\lambda^\dagger)\begin{pmatrix}\mathbf{S} & \Delta \\ -\Delta^* & -\mathbf{S}^*\end{pmatrix}\begin{pmatrix}Y_\lambda^* \\ Z_\lambda^*\end{pmatrix} = -1. \tag{26}$$

Eq. (22) is often referred to as the multiconfigurational random phase approximation (MC RPA) or the multiconfigurational time-dependent Hartree–Fock approximation (MC TDHF) [5]. For a physical acceptable linear response [4], the set of eigenvectors of eqs. (22) and (25) form a complete set of orthogonal eigenvectors that are normalized in the sense of eqs. (24) and (26). A comparison of eqs. (22), (24), (25) and (26) and the spectral representation of the polarization propagator [3] shows that the eigenfrequencies corresponding to the positive norm solutions give the excitation energies of the system. The positive norm solutions of a multiconfigurational linear-response calculation [eq. (22)] therefore are expected to give a set of real excitation energies (positive norm solutions) of the dimension of the **A** or **B** matrices. $N-1$ of these excitation energies should be negative to ensure the MC SCF reference state $|0\rangle$ is an approximate representation of the $N$th exact state. It should be noted that for this linear-response calculation, the converged MC SCF stationary point is the reference state, $|0\rangle$.

Since eq. (22) is a non-hermitean eigenvalue problem, it cannot be guaranteed to give only real eigenfrequencies. Complex excitation energies are known as instabilities. A calculation has to be carried out in each case to decide if a converged MC SCF state really satisfies condition (2) for being an approximate representation of the $N$th state.

We show in the following that a necessary condition for obtaining $N-1$ negative excitation energies in a linear-response calculation is that the full hessian index is $2N-2$. To prove this, it is convenient to define matrices **K** and **J** and vectors $\nu_\lambda$

$$\mathbf{K} = \begin{pmatrix}\mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^*\end{pmatrix}, \qquad \mathbf{J} = \begin{pmatrix}\mathbf{S} & \Delta \\ -\Delta^* & -\mathbf{S}^*\end{pmatrix}; \tag{27}$$

$$^{+}\nu_\lambda = \begin{pmatrix}Z_\lambda \\ Y_\lambda\end{pmatrix}, \qquad ^{-}\nu_\lambda = \begin{pmatrix}Y_\lambda^* \\ Z_\lambda^*\end{pmatrix}. \tag{28}$$

and to define the functions

$$K(\nu_\lambda, \nu_{\lambda'}) = \nu_\lambda^\dagger \mathbf{K} \nu_{\lambda'}, \qquad J(\nu_\lambda, \nu_{\lambda'}) = \nu_\lambda^\dagger \mathbf{J} \nu_{\lambda'}. \tag{29}$$

Multiplying eqs. (22) and (25) from the left with $\nu_\lambda^\dagger$, gives using eq. (29)

$$K(\nu_{\lambda'}, \nu_\lambda) = \omega_\lambda J(\nu_{\lambda'}, \nu_\lambda). \tag{30}$$

Since

$$J(\nu_{\lambda'}, \nu_\lambda) = 0, \qquad \text{for } \lambda' \neq \lambda, \tag{31}$$

we obtain from eq. (30)

$$K(\nu_{\lambda'}, \nu_\lambda) = 0, \qquad \text{for } \lambda \neq \lambda'. \tag{32}$$

The eigenvectors of the MC RPA equation [eqs. (22) and (25)] therefore diagonalize the matrix **K**. It is easy to show that

$$K(^{-}\nu_\lambda, ^{-}\nu_\lambda) = K(^{+}\nu_\lambda, ^{+}\nu_\lambda). \tag{33}$$

The positive norm solution in eq. (22) gives the excitation energies of the linear response calculation. Eq. (30) becomes for the positive norm solution

$$K(^{-}\nu_\lambda, ^{-}\nu_\lambda) = \omega_\lambda. \tag{34}$$

Eqs. (33) and (34) show that if $N-1$ negative excitation energies are determined in a linear-response calculation then the matrix $\mathbf{K}$ must have an index $2N-2$. The index of a matrix is independent of the set of eigenvectors used to diagonalize the matrix [17]. Since the matrix $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}$ is just a unitary transformation of the total hessian matrix in eq. (23)

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} = \tfrac{1}{2}\begin{pmatrix} 1 & \mathrm{i} \\ 1 & -\mathrm{i} \end{pmatrix}\begin{pmatrix} \mathrm{Re}(\mathbf{A}+\mathbf{B}) & \mathrm{Im}(-\mathbf{A}+\mathbf{B}) \\ \mathrm{Im}(\mathbf{A}+\mathbf{B}) & \mathrm{Re}(\mathbf{A}-\mathbf{B}) \end{pmatrix}\begin{pmatrix} 1 & 1 \\ -\mathrm{i} & \mathrm{i} \end{pmatrix}. \tag{35}$$

the total hessian matrix must have an index $2N-2$ to give $N-1$ negative excitation energies in a linear-response calculation.

Let us now consider the usual case of real orbitals and restrict variations to be within the real space [2,3]. The $N$ and $\lambda$ parameters of eqs. (4) and (7) respectively become equal to zero and $W$, $\mathbf{A}$ and $\mathbf{B}$ of eqs. (17) and (20) become real. The $F$ in eq. (17) and total hessian matrix in eq. (19) reduce to

$$F = \begin{pmatrix} 0 \\ W \end{pmatrix}, \quad \mathbf{G} = 2\begin{pmatrix} \mathbf{A}+\mathbf{B} & 0 \\ 0 & \mathbf{A}-\mathbf{B} \end{pmatrix}. \tag{36}$$

Since variations are restricted to the real space only the $(\mathbf{A}-\mathbf{B})$ block of the hessian enters directly in an MC SCF optimization algorithm involving real orbitals. $N-1$ negative excitation energies and no instabilities can therefore only be obtained in a linear-response calculation using the converged MC SCF stationary point as a reference state if the $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ matrices have totally $2N-2$ negative eigenvalues. A calculation on the lowest state of a given symmetry which fulfills primary characteristic (2) therefore requires both $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ to be positive definite. A calculation on the first excited state of a given symmetry which fulfills primary characteristic (2) requires a total of two negative eigenvalues in $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$. In ref. [4], it is shown that complex excitation energies (instabilities) are encountered if either $(\mathbf{A}+\mathbf{B})$ or $(\mathbf{A}-\mathbf{B})$ are positive definite while the other matrix is not. The distribution of negative eigenvalues in a calculation on the first excited state thus has to be such that one is in $(\mathbf{A}-\mathbf{B})$. For higher excited states, instabilities are definitely encountered [4] if there are $2N-2$ total negative hessian eigenvalues and if either $(\mathbf{A}-\mathbf{B})$ or $(\mathbf{A}+\mathbf{B})$ is positive definite.

Since the eigenvalues of the $\mathbf{A}$ matrix in general are much larger than those of the $\mathbf{B}$ matrix we expect an equal distribution of negative eigenvalues in $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$. Such a distribution cannot, of course, be guaranteed and has to be checked in each calculation. An equal distribution of negative eigenvalues in $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ may be justified for some additional reasons. In the limit of an MC SCF with the full configuration space, all orbital operators are redundant and only variations with respect to configurational parameters are considered, the matrix $\mathbf{B}$ is a zero matrix; and $\mathbf{A}$, when diagonalized, has the diagonal elements $\{E_n - E_0,\ n \neq 0\}$, where $E_0$ is the energy of the MC SCF reference state and $\{E_n - E_0\}$ are the energy differences between the reference state and the other states in the orthogonal complement space. Hence, in the limit of a full MC SCF, both $(\mathbf{A}-\mathbf{B})$ and $(\mathbf{A}+\mathbf{B})$ will each have $N-1$ negative eigenvalues. In the limit of a single configuration calculation (random phase approximation), perturbation arguments show that we also have an equal distribution of negative eigenvalues in $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$.

Thus, as a further condition, we expect that in an MC SCF calculation which yields a good approximate wavefunction for the exact $N$th state in energy [i.e. fulfills primary characteristics (1) and (2)], the $2N-2$ negative eigenvalues in the total hessian $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}$ are equally distributed with $N-1$ negative eigenvalues in each of $(\mathbf{A}-\mathbf{B})$ and $(\mathbf{A}+\mathbf{B})$ (even for the second, third,... excited states of a certain symmetry). As shown above, it is only with $2N-2$ total negative eigenvalues of $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ that there may be $N-1$ negative excitation energies and no instabilities in the multiconfigurational linear-response calculation.

In summary then, the two primary objectives for an MC SCF state to be a proper representation of the $N$th exact state are: (1) that the state is variationally correct and (2) that the multiconfigurational linear-response calculation is stable and has $N-1$ negative excitation energies. For the ground and first

excited states the second primary characteristic implies that the hessian $(\mathbf{A}-\mathbf{B})$ and the $(\mathbf{A}+\mathbf{B})$ matrices both have $N-1$ negative eigenvalues. For higher excited states objective (2) implies that $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ have a total of $2N-2$ negative eigenvalues. For higher excited states we require as a constraint that cannot be justified through primary characteristic (2) that $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ each have $N-1$ negative eigenvalues.

An additional objective, but one which is not as well-defined, is that the MC SCF state is the $N$th root of a CI which uses the configurations of the MC SCF calculation [2]. If this objective is fulfilled, the MC SCF stationary point energy will be an upper bound to the exact energy. This is certainly desirable, however, the upper bound may be considerably above the exact energy. If only an upper bound is ensured, the MC SCF stationary point often may not have other important characteristics, i.e. the index of each of $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ should be $N-1$ and the multiconfigurational linear response should have $N-1$ negative excitation energies and no instabilities.

## 4. Excited state optimization with the Fletcher procedure

An MC SCF optimization algorithm locates stationary points of the energy hypersurface. An efficient MC SCF algorithm further distinguishes between the stationary points by searching only for the one(s) that really represent the desired (say $N$th) state. In section 3, we showed that the one condition for a stationary point to be an approximate representation of the $N$th exact state is that the hessian matrix [$(\mathbf{A}-\mathbf{B})$ of eq. (36)] for real variations has an index $N-1$. In this section, we show one way this condition may be built into an iterative procedure as a constraint, thereby ensuring the converged stationary point satisfies at least one condition to be an approximate representation of the $N$th state. Further examination of the characteristics of the stationary point, of course, have to be carried out to really ensure that the stationary point is a good approximate representation of the $N$th state, i.e. that the MC TDHF is stable and has $N-1$ negative excitation energies and that $(\mathbf{A}+\mathbf{B})$ has index $N-1$ (see section 3).

The algorithm we propose is an extension to excited states of the Fletcher algorithm [13] for the lowest state of a certain symmetry. We consider in this section only real orbitals and sates. The Fletcher algorithm has previously been successfully applied to the MC SCF calculations for the lowest state of a certain symmetry where it is guaranteed to converge [14]. The Fletcher algorithm uses the information content of the second-order Taylor expansion

$$q(\boldsymbol{\lambda}) = q(\boldsymbol{\lambda}^{(k)} + \Delta\boldsymbol{\lambda}) = E(0) + \boldsymbol{F}^{\mathrm{T}}\boldsymbol{\lambda} + \tfrac{1}{2}\boldsymbol{\lambda}^{\mathrm{T}}\mathbf{G}\boldsymbol{\lambda}, \tag{37}$$

to determine the step of the iterative algorithm. In eq. (37) since we are considering only real orbitals and states $\boldsymbol{F} = \boldsymbol{W}$ and $\mathbf{G} = 2(\mathbf{A}-\mathbf{B})$, where $\boldsymbol{W}$, $\mathbf{A}$ and $\mathbf{B}$ are all real [2], that is $\boldsymbol{F}$ and $\mathbf{G}$ are of half the dimension of eqs. (17) and (18) and $\mathbf{G}$ is the hessian (*not* the full hessian) for real variations. The minimum of $q(\boldsymbol{\lambda})$ may be reached in one iteration using a Newton–Raphson algorithm. However, the Newton–Raphson step may be so large that no similarity exists between $q(\boldsymbol{\lambda})$ and $E(\boldsymbol{\lambda})$ [see eq. (10)] for step sizes of the magnitude of the Newton–Raphson step. Furthermore, if the hessian matrix $\mathbf{G}$ has an undesired index the Newton–Raphson approach may also result in steps in undesired directions. The Newton–Raphson step therefore cannot be trusted under such conditions. However, in the neighborhood of the origin for the Taylor series expansion, the second-order truncated form $q(\boldsymbol{\lambda})$ and the total Taylor series expansion $E(\boldsymbol{\lambda})$ simulate each other closely. This neighborhood defines the *trust region* of $q(\boldsymbol{\lambda})$. The Fletcher algorithm is designed to only take steps that are justified through the information content of this trust region. The Fletcher algorithm therefore carries out a constrained and well-defined walk on the energy hypersurface when far from convergence to a stationary point with index $N-1$.

Exact information about the trust region is not readily available and requires, in principle, evaluation of

function values $q(\lambda)$ and $E(\lambda)$ at a very large number of points. However, a rather accurate estimate of the trust region of the $(k+1)$th iteration (at iteration point $k$) may relatively easily be obtained as will be described later in this section. For now we assume that the trust region $\Omega^{(k)}$ is defined by a radius $h^{(k)}$ that is specific for iterative point $k$

$$\Omega^{(k)} = \{\Delta\lambda : \|\lambda - \lambda^{(k)}\| \leqslant h^{(k)}\}, \tag{38}$$

where $\| \|$ denotes the $L_2$ norm, i.e. $(\Sigma\lambda_i^2)^{1/2}$, $\lambda^{(k)}$ is the origin of the Taylor series expansion, and $\lambda = \lambda^{(k)} + \Delta\lambda$. The step length $\Delta\lambda^{(k)}$ of Fletcher iteration $k+1$ is determined through optimizing $q(\lambda)$ within the trust region of $q(\lambda)$ that is

$$\mathrm{opt}_{\Delta\lambda} q(\lambda^{(k)} + \Delta\lambda) \quad \text{subject to} \quad \|\lambda - \lambda^{(k)}\| \leqslant h^{(k)}. \tag{39}$$

Eq. (39) is satisfied by

$$\Delta\lambda^{(k)} = \lambda^{(k+1)} - \lambda^{(k)}, \tag{40}$$

which then becomes the step of the Fletcher algorithm. Note that for the usual non-linear MC SCF procedures [2], $\lambda^{(k)} = 0$ so that $\lambda = \Delta\lambda$.

Many points may be determined that satisfy eq. (39). The stationary point to choose depends on the desired characteristics of the converged state. The condition that the hessian matrix of the $N$th state has an index $N-1$ decides which stationary point to choose as will be described below.

To determine the $(k+1)$th step with the Fletcher algorithm we initially examine if the hessian matrix at iteration point $k$, $\mathbf{G}^{(k)}$, has an index $N-1$ and if the Newton–Raphson step [which optimizes $q(\lambda)$]

$$\Delta^{\mathrm{NR}}\lambda = -(\mathbf{G}^{(k)})^{-1} F^{(k)}, \tag{41}$$

satisfies

$$\Delta^{\mathrm{NR}}\lambda \leqslant h^{(k)}. \tag{42}$$

If these two conditions are met, then eq. (39) is satisfied by the Newton–Raphson step and the Newton–Raphson step becomes the step of the Fletcher algorithm, i.e. $\Delta\lambda^{(k)} = \Delta^{\mathrm{NR}}\lambda$.

Otherwise the constraint in eq. (39) becomes active and eq. (39) can be written as

$$\mathrm{opt}_{\Delta\lambda} q^{(k)}(\lambda) \quad \text{subject to} \quad (\Delta\lambda)^{\mathrm{T}}\Delta\lambda = h^{(k)^2}. \tag{43}$$

Eq. (43) may be solved by introducing a lagrangian multiplier $\nu$ and a lagrangian function

$$L(\Delta\lambda, \nu) = q^{(k)}(\lambda) + \tfrac{1}{2}\nu\left[(\Delta\lambda)^{\mathrm{T}}\Delta\lambda - h^{(k)^2}\right]. \tag{44}$$

The stationary points of the lagrangian function are determined from the equation

$$\partial L(\Delta\lambda, \nu)/\partial\Delta\lambda = F^{(k)} + \mathbf{G}^{(k)}\Delta\lambda + \nu\Delta\lambda = 0. \tag{45}$$

A solution to eq. (45) becomes

$$\Delta\lambda^{(k)}(\nu) = -(\mathbf{G}^{(k)} + \nu\mathbf{I})^{-1} F^{(k)}, \tag{46}$$

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

With the Fletcher algorithm, at iteration point $k$ the matrices $\mathbf{G}^{(k)}$ and $F^{(k)}$ are evaluated and a $\nu^{(k)}$ determined which satisfies

$$\|\Delta\lambda(\nu^{(k)})\| = h^{(k)}. \tag{47}$$

As pointed out previously, many $\nu^{(k)}$ exist that satisfy eq. (47). To determine which one to choose we analyze the structure of the function $\|\Delta\lambda(\nu)\|$. It is easily seen that $\|\Delta\lambda(\nu)\|$ is a positive valued function that has asymptotes at the negative of the hessian eigenvalues. Furthermore, $\|\Delta\lambda(\nu)\| \to 0$ when $\nu \to \pm\infty$. A plot of the function $\|\Delta\lambda(\nu)\|$ as a function of $\nu$ is given in fig. 1. The hessian eigenvalues in fig. 1 are assumed to be ordered $\epsilon_1 < \epsilon_2 < \ldots < \epsilon_p$ ($p$ is the dimension of the hessian). The plot of $\|\Delta\lambda(\nu)\|$ in fig. 1 clearly demonstrates that several values of $\nu$ satisfy eq. (45). However, the hessian of the lagrangian function

$$\mathbf{G} + \nu\mathbf{I}, \tag{48}$$

may be used to decide the value of $\nu$ to choose in a particular calculation. In ground-state calculations we are interested in determining the step length that gives the minimum value of the lagrangian function. We therefore choose the $\nu$ value that ensures that the hessian matrix of the lagrangian function is positive definite (giving the minimum value of the lagrangian function), that is $-\epsilon_1 < \nu < \infty$. Since $\|\Delta\lambda(\nu)\|$ is a monotonically decreasing function in this $\nu$ interval, $\nu$ is uniquely determined for the minimization problem. If we are interested in the first excited state of a given symmetry we require the hessian of the state upon convergence to have one negative hessian eigenvalue. This is achieved if we consistently choose, in the iterative procedure, the value of $\nu$ to be in the interval $-\epsilon_1 > \nu > -\epsilon_2$. The value of $\nu$ can then smoothly and continuously approach zero as the calculation is approaching convergence. When $\nu$ becomes zero the Fletcher algorithm proceeds in this case as a Newton–Raphson sequence of iterations with a hessian $(\mathbf{A} - \mathbf{B})$ matrix of index one.

In the interval $-\epsilon_1 > \nu > -\epsilon_2$ there are two values of $\nu$ that satisfy eq. (43) provided $h^{(k)}$ is larger than the minimum value of $\|\Delta\lambda(\nu)\|$. Which value to choose is not obvious and depends on the problem under consideration. Some understanding of which value to choose may be obtained by analyzing the structure of $\|\Delta\lambda(\nu)\|$ in a typical initial iteration on a first excited state. Such a plot is given in fig. 2. The plot in fig. 2 shows one relatively large negative hessian eigenvalue and further, several very small negative (and positive) hessian eigenvalues. The very small negative hessian eigenvalues are spurious and may arise because of very small (close to zero) or large (close to two) occupations in one or more of the orbitals [2]. The large negative hessian eigenvalue $\epsilon_1$ is relatively accurate in its location and is not important for the convergence of the calculation. However, the small negative hessian eigenvalues are spurious and have to be removed before the calculations can converge. These spurious negative eigenvalues can only be removed by carrying out rotations in the orbitals of small or large occupations. Rotations in these orbitals will be predominant if we choose the value of $\nu$ that is closest to $-\epsilon_2$.

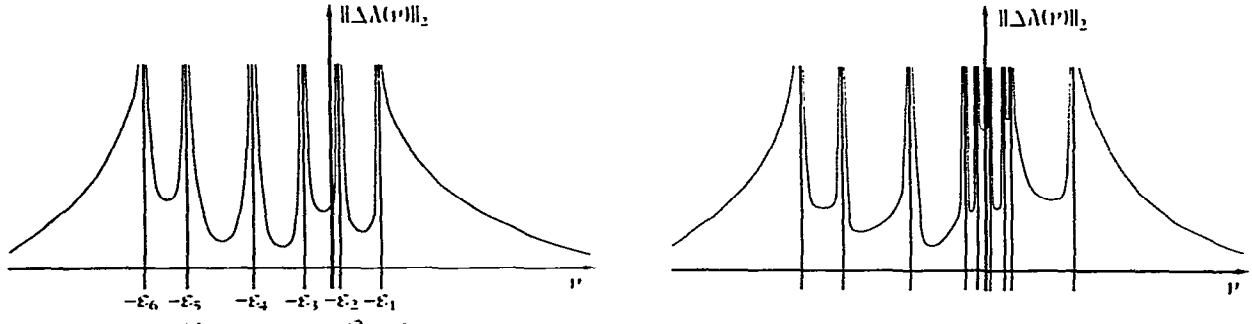


Fig. 1. A plot of $\|\Delta\lambda(\nu)\|$ versus $\nu$. $\Delta^2(\nu)$ has asymptotes at the negative eigenvalues of the hessian matrix.

Fig. 2. The structure of $\|\Delta\lambda(\nu)\|$ in a typical initial iteration on a first excited state.

In choosing $\nu$ to be in the interval $-\epsilon_1 > \nu > -\epsilon_2$ we force our calculation to proceed in a direction as if the hessian matrix had the index of the converged state. By doing this, the hessian matrix gradually improves, thus requiring smaller and smaller modifications (i.e. the adding of a smaller level-shift parameter) to be of the correct structure. Since the $\nu$ value closest to $-\epsilon_2$ is much smaller in magnitude than the $\nu$ value closer to $-\epsilon_1$ the number of iterations required to get the hessian to be of the correct structure is expected to be fewer by persistently choosing the smallest value of $\nu$.

If it happens that the minimum value of $\|\Delta\lambda(\nu)\|$ is greater than $h^{(k)}$ then we take $\nu = (-3\epsilon_2 - \epsilon_1)/4$ and scale the vector down to have a norm $h^{(k)}$. The last procedure is, of course, rather arbitrary. However, since we are carrying out an iterative procedure in which a controlled walk is performed on the energy hypersurface in consecutive iterations such a scaling procedure will allow us to reach the set of variational parameters corresponding to the original unscaled parameter set if in subsequent iterations the algorithm decides that a route to this unscaled parameter set is optimal.

MC SCF calculations on the higher states of a given symmetry may be carried out similarly to the one for the second state. The range of the $\nu$ parameter for the MC SCF approximation to the $N$th state is $-\epsilon_{N-1} > \nu > -\epsilon_N$ and the preferential choice of $\nu$ is the one closest to $-\epsilon_N$.

We have now described the $\nu$ value to select in a Fletcher calculation on the $N$th state. The actual determination of the $\nu$ value has to be performed using an iterative algorithm. An efficient algorithm to find $\nu$ has been proposed by Hebden and is described in detail in ref. [13].

The last problem of the Fletcher algorithm we address is how to efficiently define and update the trust region during the iterative procedure. The first question is how to choose $h^{(k)}$. To prevent undue restriction of the steps (which may unnecessarily slow convergence), $h^{(k)}$ should be chosen as large as possible subject to a certain measure of agreement of $q(\lambda^{(k)} + \Delta\lambda^{(k)})$ with $E(\lambda^{(k)} + \Delta\lambda^{(k)})$. The agreement between $q(\lambda^{(k)} + \Delta\lambda^{(k)})$ and $E(\lambda^{(k)} + \Delta\lambda^{(k)})$ can be quantified by defining the actual reduction in $E(\lambda)$ at the $k$th iteration point as

$$\Delta E^{(k)} = E(\lambda^{(k)}) - E(\lambda^{(k)} + \Delta\lambda^{(k)}). \tag{49}$$

and the corresponding predicted reduction

$$\Delta q^{(k)} = E(\lambda^{(k)}) - q(\lambda^{(k)} + \Delta\lambda^{(k)}). \tag{50}$$

The ratio

$$r^{(k)} = \Delta E^{(k)} / \Delta q^{(k)} \tag{51}$$

measures the accuracy to which $q(\lambda^{(k)} + \Delta\lambda^{(k)})$ approximates $E(\lambda^{(k)} + \Delta\lambda^{(k)})$, i.e. the closer $r^{(k)}$ is to unity, the better the agreement.

Fletcher [13] gives a model algorithm for changing $h^{(k)}$ during the iterative procedure. The $(k+1)$th iteration of the Fletcher algorithm for the lowest state of a certain symmetry has previously been described [14]. Since convergence to excited states may be difficult when the energy hypersurface is particularly complicated, and since positive and negative energy contribution may cancel each other in excited-state calculations we have slightly modified steps (4) and (5) below from our lowest-state procedure.

(1) Given $\lambda^{(k)}$ ($\lambda^{(k)}$ is zero in the usual non-linear MC SCF iterative procedure [2]) and $h^{(k)}$, calculate the energy gradient and hessian matrix for real variations.

(2) Solve eq. (43) for $\Delta\lambda^{(k)}$.

(3) Evaluate $E(\lambda^{(k)} + \Delta\lambda^{(k)})$ and hence $r^{(k)}$.

(4) If $r^{(k)} < 0.70$ or $r^{(k)} > 1.30$ set $h^{(k+1)} = 0.66\|\Delta\lambda^{(k)}\|$. If $0.70 < r^{(k)} \leqslant 0.85$ or $1.15 \leqslant r^{(k)} < 1.30$ set $h^{(k+1)} = h^{(k)}$. If $0.85 < r^{(k)} < 1.15$ and $h^{(k)} \leqslant \|\Delta\lambda^{(k)}\|$ set $h^{(k-1)} = 1.2\, h^{(k)}$.

(5) If $r^{(k)} \leqslant 0.50$ or $r^{(k)} \geqslant 1.50$, $\lambda^{(k+1)} = \lambda^{(k)}$ (i.e. repeat this step) else $\lambda^{(k+1)} = \lambda^{(k)} + \Delta\lambda^{(k)}$.

The ranges for $r^{(k)}$ are somewhat arbitrary. Fletcher argues that the algorithm is quite insensitive to

changes in these values and to the use of more refined extrapolation schemes. However, because the energy function is periodic in the rotational parameters $\lambda$, slight modifications of the original algorithm may improve the convergence characteristics of the algorithm when applied in MC SCF. We have found that 0.50 is a reasonable initial choice for $h$.

For geometry optimization, Cerjan and Miller [18] have used an optimization algorithm that contains some of the ideas of the Fletcher algorithm to determine transition states. Cerjan and Miller consider a second-order Taylor series expansion of the total energy and the way in which they chose their step length so that the calculation converges to a stationary point is very similar to the Fletcher algorithm. However, Cerjan and Miller do not introduce a trust region for the second-order Taylor series expansion. Therefore, the Cerjan and Miller steps may be arbitrary and may lead to undesired convergence characteristics.

Gerratt and Raimondi [19] have used a technique very similar to the Fletcher algorithm for minimizing the total energy of valence bond wavefunctions. The working equations of the Fletcher algorithm and those of Gerratt and Raimondi are very similar. However, the derivation of Gerratt and Raimondi is rather ad hoc and does not stress that step sizes are constrained to be within the trust region of the second-order Taylor series expansion. The convergence characteristics of the calculation of Gerratt and Raimondi may be improved if more explicit use is made of this fact, e.g. through updating the trust region more efficiently during the iterative procedure as is done in the Fletcher algorithm.

Camp and King [20] have recently introduced a technique which they feel will be computationally efficient. Their overall technique is a scheme to combine approximate second-order procedures far from convergence with first-order conjugate gradient techniques closer to convergence. With their procedure a calculation is "restarted" if the energy obtained from a first-order Hestenes conjugate gradient technique differs considerably from the energy obtained from a fit by a two-dimensional quadratic function using the known energies and gradient vectors at two points. They do not introduce the concept of a trust region and an exact versus second-order energy expansion. Their algorithms are designed only for the lowest state of a certain symmetry and, unlike the Fletcher procedure, do not guarantee convergence for the lowest state of a certain symmetry. Our own experience has been that approximate second-order [9,16] and first-order techniques are adequate only for extremely simple MC SCF problems. Our experience has shown that it is generally much better to use exact second-order procedures with properly applied constraints when far from convergence since convergence is much more reliably ensured [2,,21]. Approximate second-order and first-order schemes may save some computational effort per iteration but often converge very slowly (if at all!) and then more often to a stationary point which is not a good representation of an exact state.

## 5. Calculations

In section 5.1 we present some calculational studies for excited states where we apply the Fletcher algorithm and make comparisons with calculations where the mode-controlling [6] procedure is used. We show that the Fletcher algorithm for excited states converges rapidly and reliably to a stationary point with hessian index $N-1$. Results are presented for the $2\,^1A_1$ state in $CH_2$ and for the $E\,^3\Sigma_u^-$ state in $O_2$. We also examine and discuss characteristics of the converged stationary points.

In section 5.2 we present some results for the lowest three $^1\Sigma^+$ states of BeO. In the BeO case we have found two or more stationary points which have many (or all) of the desired primary characteristics for being an approximate representation of the desired excited states. Both for the $2\,^1\Sigma^+$ and the $3\,^1\Sigma^+$ states it is difficult or even impossible to prefer one stationary point over another as a better approximation to the desired state. This is an important and previously overlooked difficulty which may be present in many MC SCF calculations. In previous MC SCF calculations all of our discussed characteristics for a stationary point to be a proper representation of a state have not been examined and detailed searches of the energy hypersurface have not been performed [1,2].

Section 5.2 also contains a discussion of a stationary point of $^1\Sigma^+$ symmetry that has been determined

which has two negative (**A** − **B**) eigenvalues and has one negative (**A** + **B**) eigenvalue. Hence, calculations which monitor the hessian index only would probably assign this stationary point as a representation of the third $^1\Sigma^+$ state. However, it is found to have a small overlap with other stationary points which have more of the desired characteristics for the $3\,^1\Sigma^+$ state and it has large overlap with the stationary points which have been characterized as being approximate representations of the $2\,^1\Sigma^+$ state.

Since all primary characteristics have not been examined for most other calculated MC SCF stationary points we believe that many previous calculations [1] have converged to stationary points which may be a very poor or even incorrect representation of the states of interest.

Comparison calculations will be reported between the Fletcher and the mode-controlling [2,6] procedures. Mode controlling [2,6] has been shown to be an efficient and generally reliable procedure to obtain global convergence of a MC SCF calculation [21]. Mode control modifies individual step-length amplitudes in the basis where the hessian matrix is diagonal. The mode-control procedure constrains the magnitude of individual step-length amplitudes and monitors and possibly changes the signs of the hessian eigenvalues. We have previously demonstrated [2,6,9,21] that difficulties in Newton–Raphson optimization are generally caused by small eigenvalues of the hessian. Hence a complete hessian diagonalization is not required with mode controlling. Comparison calculations have demonstrated [21] that for both ground- and excited-state convergence, mode controlling, the norm-constrained augmented hessian approach of Shepard et al. [11] and the "infinite-order" procedure with level shifting of Werner and Meyer [10] all converge at approximately the same rate, i.e. the same number of iterations. In the procedures of Werner and Meyer [10] and Shepard et al. [11] as well as mode-controlling [6] constraints are applied only when far from convergence. Locally, in all of these procedures, convergence is quadratic.

### *5.1. Convergence characteristics for excited states using the Fletcher procedure*

In this section we report the results of calculations on two systems: the $2\,^1A_1$ state of $CH_2$ at the previously reported $^3B_1$ geometry [22] and the $E\,^3\Sigma_u^-$ state of $O_2$ at internuclear separation 2.3 au. The basis set for the $CH_2$ calculations is the 29 contracted gaussian functions previously reported in ref. [22]. The configuration list is given in table 1. For $O_2$ the basis set is a (3s2p1d) contraction of a (10s5p1d) cartesian gaussian basis set [23]. In addition, two diffuse $p_x$ and two $p_y$ functions are included on each center with exponents 0.0887 and 0.0163. The configuration list is given in table 2. This configuration list is the same as for previously reported calculations [6]. However, the calculations reported here utilize a gaussian basis set while the previously reported calculations utilize a set of 34 STOs.

Table 1
The configurations for the $2\,^1A_1 CH_2$ calculations

| | |
|---|---|
| $1a_1^2 2a_1^2 1b_2^2 3a_1^2$ | $1a_1^2 2a_1^2 3a_1^2 1b_1^2$ |
| $1a_1^2 2a_1^2 1b_2^2 4a_1^2$ | $1a_1^2 1b_2^2 3a_1^2 1b_1^2$ |
| $1a_1^2 2a_1^2 3a_1^2 4a_1^2$ | $1a_1^2 2a_1^2 1b_2^2 2b_2^2$ |
| $1a_1^2 1b_2^2 3a_1^2 4a_1^2$ | $1a_1^2 2a_1^2 3a_1^2 2b_2^2$ |
| $1a_1^2 2a_1 1b_2^2 3a_1 4a_1^2$ | $1a_1^2 1b_2^2 3a_1^2 2b_2^2$ |
| $1a_1^2 2a_1^2 1b_2^2 1b_1^2$ | |

Table 2
The configurations for the $E\,^3\Sigma_u^-$ $O_2$ calculations

| | Configuration | Number of states |
|---|---|---|
| $v_\pi$ | core $3\sigma_g^2 1\pi_u^3 1\pi_g^3$ | 1 |
| $v_o$ | core $3\sigma_g^1 1\pi_u^3 1\pi_g^2 3\sigma_u^1$ | 2 |
| $v_o'$ | core $3\sigma_g^1 1\pi_u^2 1\pi_g^4 3\sigma_u^1$ | 2 |
| $R_y$ | core $3\sigma_g^2 1\pi_u^4 1\pi_g^1 2\pi_u^1$ | 1 |

Table 3
Convergence characteristics of a Fletcher MC SCF calculation on the $2^1A_1$ state of $CH_2$ at the geometry $R_{C-H} = 2.04$ au and $\angle HCH = 134°$

| Iteration point [a] | $E - E^{conv}$ [b] | Negative eigenvalues | | $r$ | $\nu$ | $h$ |
|---|---|---|---|---|---|---|
| | | (A−B) | (A+B) | | | |
| 0 | 0.0367222014 | 9 | 6 | | 0.0279 | 0.5 |
| 1 | 0.0258854916 | 5 | 2 | 0.789 | 0.0385 | 0.5 |
| 2 | 0.0126341820 | 1 | 1 | 0.825 | 0.0197 | 0.5 |
| 3 | 0.0025732876 | 1 | 1 | 0.855 | | |
| 4 | 0.0000707290 | 1 | 1 | 0.998 | | |
| 5 | 0.0000000664 | 1 | 1 | 1.006 | | |
| 6 | 0.0000000000 | 1 | 1 | 1.000 | | |

[a] At iteration point $n$, iteration $n+1$ is performed.
[b] $E - E^{conv}$ is the difference in total energy between the current energy and the converged energy ($E^{conv} = -38.8302870376$ au).

The results of a Fletcher calculation on the $2^1A_1$ state of $CH_2$ at the $^3B_1$ geometry are given in table 3 and the corresponding mode-controlled results are given in table 4. The initial guess of orbitals in both the Fletcher and mode-controlled calculations were a set of SCF orbitals for the $1^1A_1$ state with IVO virtuals. The Fletcher procedure reaches the region on the energy hypersurface with the proper number of negative eigenvalues of both $(\mathbf{A} - \mathbf{B})$ and $(\mathbf{A} + \mathbf{B})$ after two iterations (at iteration point 2). Constraints are applied in the first three iterations. Subsequently the Fletcher approach results in a sequence of Newton–Raphson steps since the proper number of negative eigenvalues are present in $(\mathbf{A} - \mathbf{B})$ and the norm of $\lambda$ is less than 0.5. The calculation with the Fletcher procedure converges after seven iterations with the norm of $\lambda$ less than $10^{-10}$. Convergence in the energy to $< 10^{-10}$ occurs after six iterations.

The mode-controlled results for $CH_2$ are given in table 4. The region on the energy hypersurface with the proper number of negative eigenvalues in $(\mathbf{A} - \mathbf{B})$ is reached after 5 iterations (at iteration point 5). However, at iteration point 5 there are two negative eigenvalues of $(\mathbf{A} + \mathbf{B})$. At iteration point 6 there are the correct number of negative eigenvalues of both $(\mathbf{A} + \mathbf{B})$ and $(\mathbf{A} - \mathbf{B})$. No reduction in step-length amplitudes is required after iteration point 5. Convergence to $\|\lambda\| < 10^{-10}$ occurs after 11 iterations and convergence in the energy to less than $10^{-10}$ occurs after 9 iterations.

Hence, in this case the Fletcher procedure for excited states saves approximately 4 iterations. This

Table 4
Convergence characteristics of a mode-controlled MC SCF calculation on the $2^1A_1$ state of $CH_2$

| Iteration point [a] | $E - E_{conv}$ [b] | Negative eigenvalues | |
|---|---|---|---|
| | | (A−B) | (A+B) |
| 0 | 0.0367222014 | 9 | 6 |
| 1 | 0.0300442455 | 4 | 3 |
| 2 | 0.0226187698 | 3 | 1 |
| 3 | 0.0156645430 | 2 | 1 |
| 4 | 0.0089511774 | 2 | 2 |
| 5 | 0.0056377176 | 1 | 2 |
| 6 | 0.0009891699 | 1 | 1 |
| 7 | 0.0000475219 | 1 | 1 |
| 8 | 0.0000001095 | 1 | 1 |
| 9 | 0.0000000000 | 1 | 1 |

[a] At iteration point $n$, iteration $n+1$ is performed.
[b] $E - E^{conv}$ is the difference in total energy between the current energy and the converged energy ($E^{conv} = -38.8302870376$ au).

behavior is typical, although perhaps somewhat more optimal than can usually be expected from the use of the Fletcher procedure. A saving of $\approx 1$–5 iterations over other constraint procedures normally occurs since the Fletcher procedure for excited states is a modification and extension of a similar procedure for energy minima (lowest states of a certain symmetry). The Fletcher procedure for energy minima is guaranteed to converge and is based on solid mathematical principles [13]. Although convergence is not guaranteed in excited-state calculations the Fletcher procedure for excited states is expected generally to more rapidly and more reliably converge than other MC SCF constraint procedures.

The $CH_2$ $2\,^1A_1$ stationary point fulfills all our other conditions in addition to having the proper number of negative eigenvalues in $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ for being a good representation of the first excited state of $^1A_1$ symmetry. The CI with the configurations defining the MC SCF state and MC SCF orbitals (MC SCF CI) gives one eigenstate with lower energy (−38.90113550 au) than the MC SCF stationary point (−38.83028704 au). The MC TDHF/MC RPA (linear-response) calculation using the converged $2\,^1A_1$ stationary point as a reference state has no instabilities and only one negative excitation energy (positive norm) of −2.42 eV. All other MC TDHF/MC RPA excitation energies (positive norm solutions) are positive. Hence this stationary point is a good approximation to the $2\,^1A_1$ state.

The convergence of the Fletcher and mode-controlled approach for the $E\,^3\Sigma_u^-$ state of $O_2$ at 2.3 au is reported in table 5. Both calculations converge to $\|\lambda\| < 10^{-10}$ after 6 iterations. Convergence in energy ($\Delta E < 10^{-10}$ au) occurs after 4 iterations for the Fletcher procedure and after 5 iterations for the mode-controlled scheme. The local region (where $\Delta\lambda$ is not constrained) is reached in 1 iteration for both procedures. Although the Fletcher procedure converges slightly more rapidly, i.e. at iteration point 5 $\|\lambda\| < 10^{-10}$ for the Fletcher versus $1 \times 10^{-6}$ for mode controlling, the convergence rate for this fairly easy case must be viewed as essentially the same. For relatively simple cases such as this one, probably most reasonable constraint procedures would converge at approximately the same rate (as the local region is reached in only 1 iteration). For slightly more difficult cases, such as for the $2\,^1A_1$ state in $CH_2$, the Fletcher procedure is expected to most rapidly and reliably converge to a stationary point with hessian index $N-1$ on the energy hypersurface.

Again, this excited state fulfills all our other criteria for a good representation of the $E\,^3\Sigma_u^-$ state. There is one MC SCF orthogonal complement CI eigenvector (MC SCF CI) with lower energy (−149.2994487 au) than the converged MC SCF state (−149.2379241 au). The MC TDHF/MC RPA (linear response) has no instabilities, and one negative excitation energy. The remaining MC TDHF/MC RPA excitation energies are positive.

Table 5
Convergence characteristics of a Fletcher and a mode-controlled MC SCF calculation on the $E\,^3\Sigma_u^-$ state of $O_2$ at 2.3 au

| Iteration point [a] | Fletcher | | | Mode controlled | | |
|---|---|---|---|---|---|---|
| | $E - E^{conv}$ [b] (au) | negative eigenvalues | | $E - E^{conv}$ [b] (au) | negative eigenvalues | |
| | | (A−B) | (A+B) | | (A−B) | (A+B) |
| 0 | 0.0579201092 | 1 | 2 | 0.0579201092 | 1 | 2 |
| 1 | 0.0022379149 | 1 | 1 | 0.0037129492 | 1 | 1 |
| 2 | 0.0001438010 | 1 | 1 | 0.0004929823 | 1 | 1 |
| 3 | −0.0000001853 | 1 | 1 | 0.0000012858 | 1 | 1 |
| 4 | 0.0000000000 | 1 | 1 | 0.0000000024 | 1 | 1 |
| 5 | | | | 0.0000000000 | 1 | 1 |

[a] At iterative point $n$, iteration $n+1$ is performed.
[b] $E - E^{conv}$ is the difference in total energy between the current energy and the converged energy ($E^{conv} = -149.2379241716$ au).

### 5.2. Difficulties in proper characterization: The $^1\Sigma^+$ states of BeO

For the lowest three $^1\Sigma^+$ states of BeO we obtained some very interesting results using the configuration list reported in table 6. The starting orbitals in all calculations were $X\,^1\Sigma^+$ SCF orbitals and IVO virtuals. For comparison purposes, we chose the basis set and MC SCF configuration list to be the same as the one previously used by Bauschlicher and Yarkony [24]. For both the $2\,^1\Sigma^+$ and $3\,^1\Sigma^+$ states, we found two stationary points that fulfill some or all of the criteria for being approximate representatives of these states. In addition we have found another stationary point with two negative eigenvalues in $(\mathbf{A}-\mathbf{B})$ and one in $(\mathbf{A}+\mathbf{B})$. This stationary point has large overlaps with the $2\,^1\Sigma^+$ states and small overlaps with the $1\,^1\Sigma^+$ and $3\,^1\Sigma^+$ states. Its primary characteristics indicate that it can be rejected as a proper representation of the $2\,^1\Sigma^+$ state.

In the ground-state $X\,^1\Sigma^+$ calculation (table 7), the Fletcher procedure reached the local region at iteration point 7. At iteration points 4 and 5 negative $r$ values [see eq. (51)] were found and the only effect of using the Fletcher procedure in these iterations was therefore to reduce the trust region of the calculation. At iteration points 4 and 5 no step on the energy hypersurface is therefore taken. Using mode controlling, the local region is not reached until iteration point 11. This is atypical for mode controlling since the local region is usually reached in fewer iterations. The Fletcher procedure for the lowest states of a certain symmetry for this case is even more efficient since for two iterations no step is taken. These results reported in table 7 again demonstrate the effectiveness of the Fletcher procedure for the lowest state of a

Table 6
The configurations for the $^1\Sigma^+$ BeO calculations

| | | | |
|---|---|---|---|
| $c_1$: | $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$ | $c_3$: | $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^3 2\pi^1$ |
| $c_2$: | $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 5\sigma^1 1\pi^4$ | $c_4$: | $1\sigma^2 2\sigma^2 3\sigma^2 5\sigma^2 1\pi^4$ |

Table 7
Convergence characteristics of a Fletcher and a mode-controlled MC SCF calculation on the $X\,^1\Sigma^+$ state of BeO at 2.5 au

| Iteration point [a] | Fletcher | | | Mode controlled | | |
|---|---|---|---|---|---|---|
| | $E-E^{\mathrm{conv}}$ [b] (au) | negative eigenvalues | | $E-E^{\mathrm{conv}}$ [b] (au) | negative eigenvalues | |
| | | (A−B) | (A+B) | | (A−B) | (A+B) |
| 0 | 0.0840448281 | 9 | 7 | 0.0840448281 | 9 | 7 |
| 1 | 0.0521441669 | 3 | 1 | 0.0834801536 | 4 | 3 |
| 2 | 0.0227064109 | 0 | 0 | 0.0818084092 | 3 | 2 |
| 3 | 0.0092087267 | 0 | 1 | 0.0777264967 | 3 | 2 |
| 4 | 0.0021414225 | 0 | 0 | 0.0719454851 | 2 | 2 |
| 5 | 0.0021414225 | 0 | 0 | 0.0700048938 | 3 | 2 |
| 6 | 0.0021414225 | 0 | 0 | 0.0690730920 | 2 | 1 |
| 7 | 0.0002644535 | 0 | 0 | 0.0634936112 | 1 | 1 |
| 8 | 0.0000108774 | 0 | 0 | 0.0509323218 | 1 | 0 |
| 9 | 0.0000000249 | 0 | 0 | 0.0347170991 | 1 | 0 |
| 10 | 0.0000000000 | 0 | 0 | 0.0167429783 | 0 | 0 |
| 11 | | | | 0.0035853879 | 0 | 0 |
| 12 | | | | 0.0002619965 | 0 | 0 |
| 13 | | | | 0.0000012549 | 0 | 0 |
| 14 | | | | 0.0000000002 | 0 | 0 |
| 16 | | | | 0.0000000000 | 0 | 0 |
| 17 | | | | | | |

[a] At iteration point $n$, iteration $n+1$ is performed.
[b] $E-E^{\mathrm{conv}}$ is the difference in total energy between the current energy and the converged energy ($E^{\mathrm{conv}} = -89.5071645303$ au).

certain symmetry [14]. In fact, we have recently performed several MC SCF calculations which rapidly converge using orthogonalized atomic orbitals as a starting guess of orbitals [25]. The MC SCF stationary point we converge to is the same as the one determined by Bauschlicher and Yarkony [24].

In table 8 the results of the MC TDHF/MC RPA and the CI with the configurations defining the MC SCF state and MC SCF orbitals (MC SCF CI) are given. It is seen that there are no negative excitation energies or instabilities. In addition, the stationary point is the lowest eigenvalue from a CI using the MC SCF configurations and orbitals. Hence this converged point meets all the criteria for being a good representation of the exact ground state. Bauschlicher and Yarkony [24] did not previously examine the indices of $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ or the linear response of this stationary point. However, they did monitor the position of the MC SCF stationary point in the CI with the MC SCF configurations and orbitals.

The situation for the excited states of $^1\Sigma^+$ symmetry in BeO is more intersting as well as more complex. For the $2\,^1\Sigma^+$ state the convergence characteristics of a Fletcher and mode-controlled calculation are reported in tables 9 and 10, respectively. The MC TDHF/MC RPA and CI results with the MC SCF configurations and orbitals are given in table 11. The Fletcher and mode-controlling procedures converge to two different stationary points on the energy hypersurface which meet our primary criteria for a proper representation of the first excited state. The MC TDHF/MC RPA (linear-response) calculation with the stationary point obtained with the Fletcher procedure has no instabilities and one negative excitation energy (−2.66 eV). The MC TDHF/MC RPA calculation for the mode-controlled state also has no instabilities and one negative excitation energy (−2.52 eV). The CI calculation with the MC SCF configurations and orbitals shows that there is a small root-flipping for the stationary point obtained with

Table 8
$^1\Sigma^+$ MC TDHF/MC RPA excitation energies (positive norm), CI energies, using the MC SCF configurations for the $X\,^1\Sigma^-$ state of BeO at 2.5 au

| Ordered MC TDHF/MC RPA excitation energies ($^1\Sigma^+$): | MC SCF configuration CI energies ($^1\Sigma^-$): |
|---|---|
| 3.34 eV | −89.50716450 au [a] |
| 8.15 eV | −88.85121540 au |
| 10.25 eV | −88.22912020 au |
| 11.20 eV | −87.87088450 au |
| ⋮ | |

[a] Converged MC SCF stationary point.

Table 9
Fletcher calculation of the $2\,^1\Sigma^+$ state of BeO at 2.5 au

| Iteration point [a] | $E-E^{conv}$ [b] (au) | Negative eigenvalues | | $r$ | $\|\|\lambda\|\|$ | |
|---|---|---|---|---|---|---|
| | | (A−B) | (A+B) | | unconstrained | constrained |
| 0 | 0.1296084733 | 4 | 4 | | 0.927 | 0.500 |
| 1 | 0.0195257055 | 2 | 2 | 0.754 | 2.227 | 0.600 |
| 2 | 0.0195257055 | 2 | 2 | 0.151 | 2.227 | 0.396 |
| 3 | 0.0195257055 | 2 | 2 | 0.418 | 2.227 | 0.261 |
| 4 | 0.0051390398 | 3 | 1 | 0.655 | 20.971 | 0.173 |
| 5 | 0.0018904136 | 2 | 1 | 0.949 | 0.234 | 0.207 |
| 6 | 0.0011334382 | 2 | 1 | 0.852 | 0.494 | 0.248 |
| 7 | 0.0005422654 | 1 | 1 | 0.892 | 0.940 | 0.298 |
| 8 | 0.0000341773 | 1 | 1 | 0.766 | 0.050 | |
| 9 | 0.0000000814 | 1 | 1 | 0.933 | 0.001 | |
| 10 | 0.0000000000 | 1 | 1 | 0.996 | 0.000 | |

[a] At iteration point $n$, iteration $n+1$ is performed.
[b] $E-E^{conv}$ is the difference in total energy between the current energy and the converged energy ($E^{conv}=-89.4000631808$ au).

Table 10
Mode-controlled calculation of the $2^1\Sigma^+$ state of BeO at 2.5 au

| Iteration point [a] | $E - E^{conv}$ [b] (au) | Negative eigenvalues | |
|---|---|---|---|
| | | (A−B) | (A+B) |
| 0 | 0.1281764516 | 4 | 4 |
| 1 | 0.0092423264 | 2 | 1 |
| 2 | 0.0006669335 | 2 | 1 |
| 3 | 0.0000901488 | 2 | 1 |
| 4 | 0.0000038019 | 1 | 1 |
| 5 | 0.0000004786 | 1 | 1 |
| 6 | 0.0000000002 | 1 | 1 |
| 7 | 0.0000000000 | 1 | 1 |

[a] At iteration point $n$, iteration $n+1$ is performed.
[b] $E - E^{conv}$ is the difference in total energy between the current energy and the converged energy ($E^{conv} = -89.3986311591$ au).

the Fletcher procedure since the converged state of total energy (−89.40006310 au) is the lowest root of the CI using the MC SCF configurations and orbitals. The second root has a total energy of −89.38696250 au (see table 11). The stationary point obtained with the mode-controlling procedure is the second state in the CI with the MC SCF configurations and orbitals with a total energy of −89.39863110 au. The lowest root is slightly lower in energy (−89.42136540 au). Hence, this stationary point is not root-flipped and the energy is an upper bound by the Hylleraas–Undheim–MacDonald theorem.

In addition, Bauschlicher and Yarkony [24] report another stationary point on the energy hypersurface with energy −89.398552 au. Comparisons with the MC SCF state (CI) expansion coefficients of Bauschlicher and Yarkony and our states are given in table 12. Bauschlicher and Yarkony use a super-CI procedure and do not report convergence data. The super-CI procedure is a linear (not quadratic) procedure. Hence, they may not be sufficiently close to the stationary point for a comparison with the configuration amplitudes we have obtained. Bauschlicher and Yarkony do not consider the number of negative eigenvalues of (A − B) and (A + B) or the MC TDHF stability and excitation energies. Since Bauschlicher and Yarkony do not analyze characteristics of their stationary point it is very difficult to judge whether their stationary point is a good representation of the $2^1\Sigma^+$ state, that is, if it meets some or all of the criteria discussed in this paper.

Table 11
$^1\Sigma^+$ MC TDHF/MC RPA results and CI (with the MC SCF configuration state functions and orbitals) results for the $2^1\Sigma^+$ and $3^1\Sigma^+$ states of BeO at 2.5 au

| State | MC TDHF/MC RPA ($^1\Sigma^+$) (eV) | | MC SCF CI ($^1\Sigma^+$) (au) | |
|---|---|---|---|---|
| | Fletcher | mode control | Fletcher | mode control |
| $2^1\Sigma^+$ | −2.66 | −2.52 | −89.40006310 [a] | −89.42136540 |
| | 7.01 | 5.91 | −89.38696250 | −89.39863110 [a] |
| | 7.26 | 7.17 | −88.87834250 | −88.82297060 |
| | 8.37 | 8.35 | −88.67190470 | −88.75105630 |
| | ⋮ | ⋮ | | |
| $3^1\Sigma^+$ | 4 instabilities | 4 instabilities | −89.30764740 | −89.32555120 |
| | 2.88 | 2.94 | −89.19013440 [a] | −89.19298010 [a] |
| | 6.79 | 6.62 | −87.16964600 | −87.87242030 |
| | 11.46 | 11.40 | −85.22644807 | −86.47269651 |
| | ⋮ | ⋮ | | |

[a] Converged MC SCF energy.

As a further consideration, we report in table 13 the overlaps of our two $2\,^1\Sigma^+$ stationary points with each other, with the ground state, and with our converged $3\,^1\Sigma^+$ states. The overlap between these two $2\,^1\Sigma^+$ states is 0.997 even though the two states have different configuration amplitudes (see table 12). The overlaps with both the $X\,^1\Sigma^+$ and $3\,^1\Sigma^+$ states are small (less than 0.1). Thus, the two converged stationary points representing the $2\,^1\Sigma^+$ state appear to be approximate representations of this same state, even though without the examination of the overlaps of these states it would be difficult to see. The state obtained by the Fletcher procedure *appears* to be much more highly correlated, i.e. $c_1$ is 0.63 and $c_2$ is $-0.58$ in table 12 versus $c_1 = -0.09$ and $c_2 = -0.91$ for the mode-controlled procedure even though the overlap of 0.997 shows that they are essentially the same state.

In table 14 we give the overlap between the occupied orbitals for these two stationary points. The $4\sigma$ and $5\sigma$ orbitals appear to be quite different between these two stationary points. This may be rationalized as follows. For both the Fletcher and the mode-controlled stationary point the coefficient $c_3$ is approximately the same and relatively small ($\approx 0.2$). If this configuration is neglected, there is a redundancy [2] among configurations $c_1$, $c_2$ and $c_4$ and the excitation $4\sigma \rightarrow 5\sigma$. Hence in the latter case there is an arbitrariness in the configuration amplitudes for $c_1$, $c_2$ and $c_4$, i.e. the $4\sigma$ and $5\sigma$ orbitals may be rotated between each other and exactly the same stationary point with different configuration amplitudes is obtained [6]. This

Table 12
Configuration amplitudes of converged $^1\Sigma^+$ states of BeO

| State | $c_1$ | $c_2$ | $c_3$ | $c_4$ |
|---|---|---|---|---|
| $X\,^1\Sigma^+$ | 0.8370 | 0.2254 | −0.4974 | −0.0346 |
| Bauschlicher et al. [a] $X\,^1\Sigma^+$ | 0.8370 | 0.2254 | −0.4974 | −0.0346 |
| Fletcher $2\,^1\Sigma^+$ | −0.6280 | −0.5839 | 0.2363 | −0.4569 |
| mode control $2\,^1\Sigma^+$ | −0.0886 | −0.9131 | −0.2130 | 0.3363 |
| Bauschlicher et al. [a] $2\,^1\Sigma^+$ | 0.2471 | −0.9466 | −0.2043 | −0.0345 |
| Fletcher $3\,^1\Sigma^+$ | −0.2884 | −0.0002 | −0.9575 | 0.0089 |
| mode control $3\,^1\Sigma^+$ | −0.2833 | 0.0504 | −0.9577 | 0.0070 |
| Bauschlicher et al. [a,b] $3\,^1\Sigma^+$ | −0.2915 | 0.0012 | −0.9550 | 0.0012 |
| $^1\Sigma^+$ [c] | 0.1396 | −0.9654 | −0.2038 | −0.0832 |

[a] This state was determined by Bauschlicher and Yarkony in ref. [24].
[b] This calculation is not converged since no orbital excitation operators from $5\sigma$ were included [24].
[c] Stationary point with two negative eigenvalues in **A**−**B** and one in **A**+**B** (see text).

Table 13
Overlaps of the $^1\Sigma^+$ MC SCF stationary points for BeO

| State | $X\,^1\Sigma^+$ | $2\,^1\Sigma^+$ | | $3\,^1\Sigma^+$ | | $^1\Sigma^+$ [b] |
|---|---|---|---|---|---|---|
| | | Fletcher [a] | mode controlled [a] | Fletcher [a] | mode controlled [a] | |
| $X\,^1\Sigma^+$ | 1.00 | | | | | |
| $2\,^1\Sigma^+$ Fletcher [a] | 0.059 | 1.00 | | | | |
| $2\,^1\Sigma^+$ mode controlled [a] | 0.105 | 0.997 | 1.000 | | | |
| $3\,^1\Sigma^+$ Fletcher [a] | 0.066 | 0.038 | 0.061 | 1.000 | | |
| $3\,^1\Sigma^+$ mode controlled [a] | 0.057 | 0.042 | 0.066 | 0.999 | 1.00 | |
| $^1\Sigma^+$ [b] | 0.081 | 0.998 | 0.999 | 0.065 | 0.070 | 1.000 |

[a] Constraint procedure used when far from convergence. Of course, in the local region no constraints are in use.
[b] Stationary point with two negative eigenvalues in **A**−**B** and 1 in **A**+**B** (see text).

Table 14
Occupied orbital overlaps for the converged $2\,^1\Sigma^+$ stationary points determined using the mode-controlled and the Fletcher procedures

| Occupied $2\,^1\Sigma^+$ orbitals (Fletcher) | Occupied $2\,^1\Sigma^+$ orbitals (mode controlled) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $1\sigma$ | $2\sigma$ | $3\sigma$ | $4\sigma$ | $5\sigma$ | $1\pi_x$ | $2\pi_x$ | $1\pi_y$ | $2\pi_y$ |
| $1\sigma$ | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $2\sigma$ | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $3\sigma$ | 0.000 | 0.000 | 1.000 | 0.006 | −0.001 | 0.000 | 0.000 | 0.000 | 0.000 |
| $4\sigma$ | 0.000 | 0.000 | −0.005 | 0.802 | −0.597 | 0.000 | 0.000 | 0.000 | 0.000 |
| $5\sigma$ | 0.000 | 0.000 | −0.003 | 0.597 | 0.802 | 0.000 | 0.000 | 0.000 | 0.000 |
| $1\pi_x$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.996 | −0.090 | 0.000 | 0.000 |
| $2\pi_x$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.090 | 0.991 | 0.000 | 0.000 |
| $1\pi_y$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.996 | −0.090 |
| $2\pi_y$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.090 | 0.991 |

may explain why there can be two (or more) near-lying stationary points with overlap approximately unity with considerably different $4\sigma$ and $5\sigma$ orbitals and considerably different $c_1$ and $c_2$ coefficients.

It is difficult, based on these characteristics of the state, to choose one of these stationary points over the other for being a better representation of the $2\,^1\Sigma^+$ state. It appears that either stationary point is a fairly good representation of the state, since both stationary points have both our primary characteristics of the first excited state. But, because of the upper-bound criterion the stationary point obtained via the mode-controlled procedure would probably be chosen as slightly more optimal. The possibility of several MC SCF stationary points being approximate representations of the same state has apparently not been previously recognized in general. Since all of our discussed criteria have not been monitored in previously reported MC SCF calculations [1] we also expect that many of these calculations have converged to stationary points which are not adequate representations of the state of interest. We point out that the characteristics, order in the MC SCF configuration and orbital CI, number of MC TDHF/MC RPA instabilities and negative excitation energies, and index of $(\mathbf{A}+\mathbf{B})$ are not controlled by either constraint procedure (Fletcher or mode control) or any other constraint procedure currently advocated or in use. At a slightly different starting point the Fletcher procedure may converge to the state obtained with the

Table 15
Summary of the characteristics of converged $^1\Sigma^+$ states of BeO

| State | Total energy (au) | Negative eigenvalues | | Root number in MC SCF CI | MC TDHF ($^1\Sigma^+$) instabilities | Negative excitation energies in MC TDHF ($^1\Sigma^+$) |
|---|---|---|---|---|---|---|
| | | $(\mathbf{A}-\mathbf{B})$ | $(\mathbf{A}+\mathbf{B})$ | | | |
| $X\,^1\Sigma^+$ | −89.5071645303 | 0 | 0 | 1 | 0 | 0 |
| Bauschlicher et al. [a] $X\,^1\Sigma^+$ | −89.507164 | | | 1 | | |
| Fletcher $2\,^1\Sigma^+$ | −89.4000631808 | 1 | 1 | 1 | 0 | 1 |
| mode control $2\,^1\Sigma^+$ | −89.3986311591 | 1 | 1 | 2 | 0 | 1 |
| Bauschlicher et al. [a] $2\,^1\Sigma^+$ | −89.398552 | | | 2 | | |
| Fletcher $3\,^1\Sigma^+$ | −89.1901344802 | 2 | 2 | 2 | 4 | 0 |
| mode control $3\,^1\Sigma^+$ | −89.1929801201 | 2 | 2 | 2 | 4 | 0 |
| Bauschlicher et al. [a,b] $3\,^1\Sigma^+$ | −89.188404 | | | 3 | | |
| $^1\Sigma^+$ [c] | −89.3984649748 | 2 | 1 | 2 | 1 | 1 |

[a] This state was determined by Bauschlicher and Yarkony in ref. [24].
[b] This state is not converged since no orbital operators involving the $5\sigma$ orbital were included on optimization [24].
[c] A stationary point with two negative eigenvalues in $\mathbf{A}-\mathbf{B}$ and one in $\mathbf{A}+\mathbf{B}$ (see text).

mode-controlled technique (and, of course, vice versa). A procedure based only on always choosing the MC SCF configuration CI second root to optimize in each iteration will frequently result in very slow convergence, convergence to the wrong stationary point (with many wrong characteristics), or even divergence, and that procedure should definitely not be used.

We strongly suspect that in many other previously reported calculations a more thorough searching of the energy hypersurfaces would have revealed several near-lying stationary points with many (or all) of the same characteristics. This is, of course, due to limited MC SCF configurational and orbital expansions. As the number of configuration state functions increases in an MC SCF calculation more orbital optimization operators become redundant and are removed from a calculation. In the limiting case of a full state expansion, all orbital operators are redundant. In the limit of a complete basis-set expansion of the orbitals, the calculation will give the exact energies and each stationary point will be an exact state of the system. Unfortunately, for the usual sized MC SCF configuration expansion there appears to be no way a priori to predict if a stationary point on the energy hypersurface is the *only* one which meets a reasonable number of criteria for representing a state.

Another interesting case involves the $3\,^1\Sigma^+$ state. Again the mode controlled and the Fletcher procedures converge to different stationary points on the energy hypersurface with slightly different energies (see table 15). Overlap (table 13) between these two states is large (0.999) and overlap with $X\,^1\Sigma^+$ and $2\,^1\Sigma^+$ states is small (less than 0.07). Both stationary points when used in an MC TDHF/MC RPA have four instabilities and no negative excitation energies. Although the proper number of negative eigenvalues in $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ is present, the MC TDHF/MC RPA does not give the correct number of negative excitation energies. Hence primary characteristic (2) is not completely fulfilled. There is also root-flipping since the converged state is the second (and not the third) in energy of a CI with the MC SCF configurations and orbitals. We regard this last point as the least important of the criteria which should be fulfilled.

The overlap between the two states representing the $3\,^1\Sigma^+$ state is found to be 0.999 and the overlaps between these two states and the two $2\,^1\Sigma^+$ state and the $X\,^1\Sigma^-$ state are small (less than 0.07). This really confirms that our $^1\Sigma^+$ state assignments are correct. The calculations on the $3\,^1\Sigma^-$ state illustrate also that it may be very dangerous to use just an upper-bound criterion for characterizing an MC SCF state. Both the $3\,^1\Sigma^+$ states have root-flipping and would therefore have been characterized as $2\,^1\Sigma^-$ if an upper-bound criterion had been exclusively used to characterize those states. The overlaps between these two root-flipped $3\,^1\Sigma^+$ states and the $2\,^1\Sigma^+$ states being smaller than 0.1 clearly demonstrates the danger in using an upper-bound criterion for characterizing states. Our stationary points for the $3\,^1\Sigma^-$ state thus meet some [$(\mathbf{A}-\mathbf{B})$ and $(\mathbf{A}+\mathbf{B})$ have the proper number of negative eigenvalues] but not all of the criteria for being a good representation of the $3\,^1\Sigma^+$ state. However, in certain situations this may be adequate, but, of course, not ideal.

Bauschlicher and Yarkony [24] report that a super-CI MC SCF calculation with the same configuration state functions and basis set as is reported here would converge to the $3\,^1\Sigma^-$ state only if excitations from the $5\sigma$ orbital were excluded from the super-CI procedure. Their "stationary point" is not correct since the inclusion of the excitations from the $5\sigma$ orbital at their "stationary point" will cause their calculation to move to another place on the energy hypersurface.

We also tried to converge to the $3\,^1\Sigma^+$ state using as the initial guess for CI coefficients of the state (iteration point 0) the second (not the third) root of the initial CI using the MC SCF configuration state functions. Both the Fletcher procedure and the mode-controlling procedure converged to the same stationary point, the characteristics of which are given in tables 12, 13 and 15. This stationary point has two negative eigenvalues of $(\mathbf{A}-\mathbf{B})$ and one negative eigenvalue of $\mathbf{A}+\mathbf{B}$. The MC TDHF/MC RPA has one negative excitation energy and one instability. Hence, this stationary point fulfills fewer of the conditions for a good representation than our previously discussed stationary points derived with mode control and with the Fletcher procedure. However, without examination of the eigenvalues of $(\mathbf{A}+\mathbf{B})$ (note that $(\mathbf{A}-\mathbf{B})$ is the hessian for real variations) and the MC TDHF/MC RPA excitation energies it could

easily be assumed that this stationary point is a good representation for the $3^1\Sigma^+$ state. From table 13 the overlap of this state with the $2^1\Sigma^+$ states is large ($> 0.99$) and it is small with the $3^1\Sigma^+$ states. Hence it appears that this stationary point is much closer to our previously discussed $2^1\Sigma^+$ stationary points rather than the $3^1\Sigma^+$ stationary points. However, this stationary point should be rejected as a representation of either the $2^1\Sigma^+$ or $3^1\Sigma^+$ states since other stationary points better fulfill our criteria.

These BeO calculations as summarized in table 15 as well as previously reported calculations [2] demonstrate that thorough examination of a stationary point (i.e. its eigenvalues of $(\mathbf{A}-\mathbf{B})$ and $(\mathbf{A}+\mathbf{B})$ and MC TDHF/MC RPA excitation energies and instabilities) is *required* in order to determine if the point is a good representation of a state. Examination of only the ordering in the MC SCF configuration CI is not adequate. However, even if a stationary point has several (or all) of the characteristics of a proper representation of an exact state, there may still be other (in energy) stationary points on the energy hypersurface which meet the same criteria. This is a difficulty present in *many* MC SCF calculations and not just in these BeO calculations.

When several stationary points have been found to be fairly good approximate representations of the same state these different stationary points when used to evaluate molecular properties (dipole moments, polarizabilities, etc.) may give very different numerical values and it is not a priori straightforward to decide which calculation to prefer. Also when the MC SCF orbitals of these different states are used in a multi-reference CI calculation the length of the configuration list that is required to obtain the same accuracy in energy may be very different. For example, the configuration list of a multi-reference CI calculation on the $2^1\Sigma^+$ state of BeO based on either the orbitals of the Fletcher $2^1\Sigma^+$ state or the orbitals of the mode-controlled $2^1\Sigma^+$ state may be very different and of very different length as the configuration amplitudes $c_1$–$c_4$ are so very different (see table 12). In the multiconfiguration CI calculation based on the orbitals of the mode-controlled state the $c_1$ configuration (amplitude $-0.09$) may not be included among the multireference configurations whereas in the corresponding calculations based on the orbitals of the Fletcher obtained state this configuration (amplitude $-0.63$) is the one that has the dominant amplitude. The problem of uniquely being able to characterize an MC SCF state is thus equally important whether the MC SCF state is used directly to evaluate molecular properties or the orbitals of the MC SCF calculation are used as basis for multireference CI or multireference many-body calculations.

A detailed examination of other additional characteristics of stationary points on the hypersurface may possibly be necessary to obtain such a unique identification (if a unique identification is possible!) and may first be obtained only when an even more thorough examination of the structure of the MC SCF energy hypersurface is carried out. We are currently working on these difficult problems in our laboratories [25].

## 6. Summary

We have demonstrated the necessity of carefully examining the characteristics of an MC SCF stationary point before assigning the stationary point as an approximate representation of an exact state. We have discussed criteria that may be used for assigning an MC SCF state as an approximate representation of the $N$th exact state. In particular we have examined the condition of having stability and $N-1$ negative excitation energies in a linear-response calculation for the $N$th MC SCF state. We have shown that this condition only can be fulfilled if the sum of the number of negative eigenvalues of the hessian matrix $(\mathbf{A}-\mathbf{B})$ and the $(\mathbf{A}+\mathbf{B})$ matrix is $2N-2$. For the lowest two states of a certain symmetry, each of the hessian and the $(\mathbf{A}+\mathbf{B})$ matrices will have $N-1$ negative eigenvalues if the linear-response calculation is stable and has $N-1$ negative excitation energies. As an additional constraint each of $(\mathbf{A}+\mathbf{B})$ and $(\mathbf{A}-\mathbf{B})$ should have index $N-1$. Previous calculations have, in general, not investigated these conditions and may have, in fact, converged to a poor or incorrect representation of a state.

Based on the idea of a trust region of the second-order Taylor series expansion, we have designed an

iterative algorithm that imposes directly as a constraint that the hessian matrix must have $N-1$ negative eigenvalues. Numerical calculations have indicated that the algorithm converges rapidly and reliably to a stationary point with hessian index $N-1$.

Our numerical calculations also indicate that often several stationary points may be found that satisfy some (or even all) of the objectives that may be expected for an MC SCF stationary point to be a representation of the $N$th exact state. The problem of not being able to always obtain a unique approximation to the $N$th state is a very severe problem of MC SCF theory which we feel needs to be given much more attention in future MC SCF theory and applications.

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