

Comparison of the convergence characteristics of some iterative wave function optimization methods

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The convergence properties of several iterative methods for the optimization of orbitals and configuration mixing coefficients in multiconfigurational electronic wave functions are compared. All of the iterative methods considered here are derived from corresponding approximate energy expressions. These energy expressions are discussed within the context of their suitability for the calculation of noninfinitesimal wave function corrections. A method based on the partitioned orbital Hessian matrix and which uses an approximate super-CI secular equation for the wave function corrections is shown to possess second-order convergence and to have the largest radius of convergence of the methods analyzed in detail in this work for several molecular examples. Particular attention is given to convergence properties for excited states, where the differences between these methods are most significant.

I. INTRODUCTION

The convergence properties of several iterative methods for the optimization of orbitals and configuration mixing coefficients in multiconfigurational electronic wave functions are compared. An examination of the iterative procedures reveals that each may be derived from some approximate energy expression which is correct in the sense that it is valid within some neighborhood of the trial wave function. These approximate energy expressions and the corresponding iterative procedures are examined both at a formal level, to determine various types of failures that may occur, and at an empirical level to determine the symptoms of these failures. Particular attention is given to the excited state wave function optimization problem, for which it is shown that some approximate energy expressions are more appropriate than others in determining noninfinitesimal wave function corrections. A detailed characterization of valid excited state wave function solutions leads to conditions that may be imposed during the iterative wave function optimization process in order to avoid convergence to undesired solutions.

Section II contains a discussion of the methods which are compared in this work. The exponential operator notation is employed to derive the second-order matrix expressions appropriate for Newton-Raphson iterative methods. The failures of these Newton-Raphson methods are examined and the level shifting methods and approximate super-CI methods are discussed as ways of overcoming these failures. Section III presents the application of these methods to several molecular systems, including $\text{PO}(\Sigma^+)$, $\text{CH}_2(1^1A_1, 2^1A_1)$, and $\text{BeO}(1-4^1\Sigma^+, 1^1\Delta)$.

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II. DISCUSSION OF METHODS

A. General

We begin the discussion of the convergence characteristics of these wave function optimization methods with a formal comparison of the equations used in the different iterative procedures. We use the exponential operator method of Dalgaard and Jørgensen¹ and of Yeager and Jørgensen² and we will follow the derivation of Shepard and Simons³ using the unitary group approach for configuration and density matrix specification.

Given a molecular orbital basis and a configuration space spanned by $\{|m\rangle\}$, an improved trial multiconfiguration wave function $|mc'\rangle$ is written in terms of a current trial wave function

$$|mc\rangle = \sum_m C_m |m\rangle \quad (1a)$$

as

$$|mc'\rangle = e^{i\hat{\Lambda}} e^{i\hat{S}} |mc\rangle. \quad (1b)$$

The unitary operators $e^{i\hat{\Lambda}}$ and $e^{i\hat{S}}$ are expressed in terms of the Hermitian operators $\hat{\Lambda}$ and \hat{S} :

$$\hat{\Lambda} = \sum_{rs} k_{(rs)} i(E_{rs} - E_{sr}) \equiv \sum_{(rs)} k_{(rs)} \hat{T}_{(rs)}, \quad (2a)$$

$$\hat{S} = \sum_{n \neq mc} p_n i(|n\rangle\langle mc| - |mc\rangle\langle n|) \equiv \sum_n p_n \hat{P}_n, \quad (2b)$$

where E_{rs} is a generator of the unitary group⁴ and the states $\{|n\rangle\}$ span the orthogonal complement of the state $|mc\rangle$ within the configuration space. The $e^{i\hat{S}}$ operator effects mixing coefficient variations, while the $e^{i\hat{\Lambda}}$ operator effects orbital variations equivalent to the orbital transformation

$$\phi' = \phi(e^{-\mathbf{K}}), \quad (3)$$

where the components of the matrix \mathbf{K} and the vector \mathbf{k}

[with (rs) treated as a single index] are related accordingly to

$$K_{rs} = -K_{sr} = k_{(rs)} \quad (r > s) .$$

With the electronic Hamiltonian operator⁴

$$\hat{H} = \sum_{ij} h_{ij} E_{ij} + \frac{1}{2} \sum_{ijkl} (ij|kl) e_{ijkl}$$

defined in terms of the one- and two-electron integrals h_{ij} and $(ij|kl)$ in the molecular orbital (MO) basis and $e_{ijkl} = E_{ij} E_{kl} - \delta_{jk} E_{il}$, the trial energy $E(\mathbf{k}, \mathbf{p}) = \langle m' | \hat{H} | m' \rangle$ is required to be minimized with respect to the parameters $\{k_{(rs)}, p_n\}$ while subject to any variational constraints from interacting lower energy states. The commutator expansion may be used to collect terms of E of various orders in the parameters $\{k, p\}$

$$E(\mathbf{k}, \mathbf{p}) = \langle m | [\hat{H} + [\hat{H}, i\hat{\Lambda}] + \frac{1}{2}[[\hat{H}, i\hat{\Lambda}], i\hat{\Lambda}] + [\hat{H}, i\hat{S}] + \frac{1}{2}[[\hat{H}, i\hat{S}], i\hat{S}] + [[\hat{H}, i\hat{\Lambda}], i\hat{S}] + \dots | m \rangle . \quad (4)$$

We impose the condition on the wave function that the energy is stable to first order with respect to the parameters $\{k, p\}$

$$\left. \frac{\partial E}{\partial k_{(rs)}} \right|_{\mathbf{k}=\mathbf{0}, \mathbf{p}=\mathbf{0}} = \langle m | [\hat{H}, i\hat{T}_{(rs)}] | m \rangle = 0 \quad \text{for all } (rs) , \quad (5a)$$

$$\left. \frac{\partial E}{\partial p_n} \right|_{\mathbf{k}=\mathbf{0}, \mathbf{p}=\mathbf{0}} = \langle m | [\hat{H}, i\hat{P}_n] | m \rangle = 0 \quad \text{for all } n . \quad (5b)$$

The first of these conditions [Eq. (5a)] is referred to as the generalized Brillouin theorem⁵ and the second condition [Eq. (5b)] implies that the mixing coefficients are an eigenvector of the Hamiltonian matrix $H(m)$ constructed in the configuration basis. For a sufficiently complete configuration space, the minimum energy solution satisfies Eqs. (5a) and (5b). For excited states with an insufficiently flexible configuration space, the minimum energy solution may not satisfy Eq. (5a), because of root switching with lower states (sometimes referred to as "variational collapse"). We assume hereafter that Eqs. (5a) and (5b) are satisfied for the desired minimum energy solution. Equations (4) and (5) cannot be solved in closed form for the optimum parameters $\{k, p\}$, and iterative schemes must be devised to reach the desired solution which satisfies Eqs. (5a) and (5b) and which minimizes the energy.

B. Second-order Newton-Raphson methods

In the second-order Newton-Raphson methods for iteratively solving Eqs. (5a) and (5b), Eq. (4) is truncated after the second-order terms in the parameters $\{k, p\}$ and rewritten in a symmetric matrix form as

$$E^{(2)}(\mathbf{k}, \mathbf{p}) = E(m) + (\mathbf{k}^\dagger \mathbf{p}^\dagger) \begin{pmatrix} \mathbf{w} \\ \mathbf{v} \end{pmatrix} + \frac{1}{2} (\mathbf{k}^\dagger \mathbf{p}^\dagger) \begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix} , \quad (6)$$

where

$$w_{(rs)} = \langle m | [\hat{H}, i\hat{T}_{(rs)}] | m \rangle , \quad (7a)$$

$$v_n = \langle m | [\hat{H}, i\hat{P}_n] | m \rangle , \quad (7b)$$

$$B_{(pq)(rs)} = \frac{1}{2} \langle m | [[\hat{H}, i\hat{T}_{(pq)}], i\hat{T}_{(rs)}] + [[\hat{H}, i\hat{T}_{(rs)}], i\hat{T}_{(pq)}] | m \rangle , \quad (7c)$$

$$C_{(rs),n} = C_{n,(rs)}^\dagger = \langle m | [[\hat{H}, i\hat{T}_{(rs)}], i\hat{P}_n] | m \rangle , \quad (7d)$$

$$M_{nn'} = \frac{1}{2} \langle m | [[\hat{H}, i\hat{P}_n], i\hat{P}_{n'}] + [[\hat{H}, i\hat{P}_{n'}], i\hat{P}_n] | m \rangle . \quad (7e)$$

The $\begin{pmatrix} \mathbf{w} \\ \mathbf{v} \end{pmatrix}$ vector is the *wave function gradient vector*, and is composed of the *orbital gradient vector* \mathbf{w} , the elements of which are the generalized Brillouin theorem terms, and the *state gradient vector* \mathbf{v} . The

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix}$$

matrix is the *wave function Hessian matrix*, and is composed of the *orbital Hessian matrix* \mathbf{B} , the *state Hessian matrix* \mathbf{M} , and the *coupling matrix* \mathbf{C} . If the mixing coefficients are optimum for the current set of orbitals, the state gradient \mathbf{v} has zero elements. Applying the necessary stability conditions to the above second-order energy expression gives

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix} + \begin{pmatrix} \mathbf{w} \\ \mathbf{v} \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ \mathbf{0} \end{pmatrix} . \quad (8)$$

If this set of linear Newton-Raphson equations is solved for the parameters $\{k, p\}$ and if these parameters are used to modify the mixing coefficients and to transform the orbital coefficients, then in the neighborhood of a solution the magnitudes of the elements of the wave function gradient vector decrease as the square of the elements of the gradient vector of the previous iteration.^{1-3,6} This kind of convergence characterizes a second-order iterative procedure.

If alternatively we choose the current mixing coefficients to be optimum so that $\mathbf{v} = \mathbf{0}$ at all times, Eq. (8) may be solved for \mathbf{p} in terms of \mathbf{k} . The resulting expression may then be used to eliminate \mathbf{p} from Eq. (6) and give

$$E^{(2)}(\mathbf{k}) = E(m) + \mathbf{k}^\dagger \mathbf{w} + \frac{1}{2} \mathbf{k}^\dagger (\mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger) \mathbf{k} . \quad (9)$$

The matrix $(\mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger)$ is the *partitioned orbital Hessian matrix*. While \mathbf{B} is the Hessian matrix for fixed or frozen mixing coefficients, the partitioned orbital Hessian is the matrix of second partial derivatives with respect to orbital variations when the mixing coefficients relax optimally along with the orbital changes. The Newton-Raphson equations resulting from Eq. (9) take the form

$$(\mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger) \mathbf{k} + \mathbf{w} = \mathbf{0} . \quad (10)$$

C. Characterization of wave function solutions

We begin the examination of these two Newton-Raphson procedures, Eqs. (8) and (10), with an analysis of converged wave function solutions. Once a solution, $\mathbf{w} = \mathbf{0}$ and $\mathbf{v} = \mathbf{0}$, is found for the necessary conditions, it must be analyzed to determine if it is a solution which minimizes the energy or only represents an energy saddle point or maximum. For this purpose the energy expression of Eq. (6) is written, since the gradient terms are equal to zero at convergence, as

$$E^{(2)}(\mathbf{k}, \mathbf{p}) = E(mc) + \frac{1}{2}(\mathbf{k}^\dagger \mathbf{p}^\dagger) \begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix} \quad (11)$$

For the lowest energy state of a given symmetry, it is clear from this expression that, for a small arbitrary wave function change given by some $\begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix}$ vector, $E(\mathbf{k}, \mathbf{p}) \geq E(mc)$ if and only if the wave function Hessian matrix possesses no negative eigenvalues. For higher energy states of a given symmetry the situation requires further discussion.

Within the configuration space we require that the energy is minimized with respect to mixing coefficient changes, but that it remains a rigorous upper bound to the exact excited state energy (i.e., the appropriate root of the full CI problem). It is well known⁷ that the successively higher eigenvalues of the $H(mc)$ matrix satisfy these conditions for the corresponding excited states. This is equivalent to the requirement that for the N th excited state ($N=0$ is the lowest energy state, $N=1$ the first excited state, etc.) the \mathbf{M} matrix must possess exactly N negative eigenvalues. We further require this trial energy, the appropriate eigenvalue of the $H(mc)$ matrix, to be minimized with respect to an arbitrary orbital variation. For $\mathbf{w}=0$, the energy expression of Eq. (9) gives

$$E^{(2)}(\mathbf{k}) = E(mc) + \frac{1}{2} \mathbf{k}^\dagger (\mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger) \mathbf{k} \quad (12)$$

It is again clear that, for both the lowest energy state and for higher energy states, $E(\mathbf{k}) \geq E(mc)$ if and only if the partitioned orbital Hessian matrix possesses no negative eigenvalues.

Therefore, to characterize the lowest energy state, solutions satisfying the necessary conditions [Eqs. (5a) and (5b)] are further required either; (1) to possess a wave function Hessian which is positive semidefinite, or else (2) to possess mixing coefficients which correspond to the lowest eigenvalue of the $H(mc)$ matrix and simultaneously to possess a partitioned orbital Hessian matrix that is positive semidefinite. For higher energy states of a given symmetry, the requirements are that the mixing coefficients correspond to the appropriate eigenvector of the $H(mc)$ matrix and that the partitioned orbital Hessian is positive semidefinite. We show in Appendix A that for the N th excited state, the last condition is equivalent to the requirement that the wave function Hessian matrix must possess exactly N negative eigenvalues while the state Hessian matrix \mathbf{M} also possesses N negative eigenvalues.

It can of course happen, particularly with relatively limited configuration spaces or near avoided crossings, that the best approximation to the N th excited state wave function within the given configuration space does not correspond to the $(N+1)$ st eigenvalue of $H(mc)$, and thus does not satisfy the conditions outlined above. But such a solution, which has fewer than N negative eigenvalues of the state Hessian \mathbf{M} , is difficult to identify confidently as the appropriate solution, and does not provide a rigorous upper bound for the desired energy. As previously noted (Sec. II A), this situation (which can, in principle, be avoided by enlarging the configuration space) is not considered in the present treatment. In-

stead, we are concerned with the process of locating the solution when it does satisfy the stated conditions.

Because the iterative procedure requires the one- and two-electron integrals to be transformed to the current molecular orbital basis in each iteration,³ it is important to minimize the total number of iterations required to reach the desired solution. In general, it is not possible to search large volumes of orbital and state space, converge the Newton-Raphson equations to the nearest energy stationary points, characterize the solutions according to the above criteria, and finally select from the possible solutions which satisfy these criteria the one with the lowest energy. A more reasonable approach to follow is to avoid undesired solutions as much as possible during the iterative procedure. When this is done, large volumes of wave function space will not have to be searched for possible solutions. Also, if adequate starting orbitals can be acquired (e.g., from a nearby geometry on a potential energy surface, SCF or modified SCF orbitals, approximate natural orbitals, etc.), then only one or a few solutions may have to be examined for the final wave function selection.

A comment concerning the number of solutions may be in order. Although in the general multiconfiguration case an analysis has not been performed, in the special case of a two-electron closed-shell single configuration Stanton⁸ has shown that the number of possible solutions grows exponentially as $(3^n - 1)/2$ with the number n of orbital basis functions. In the general multiconfiguration cases, the number of possible solutions could be even larger, since there are more orbital degrees of freedom. As more configurations are added, a saturation point will be reached where the number of orbital degrees of freedom begins to decrease due to the introduction of redundant operators. Finally, in the limit when all possible configurations have been included, all orbital transformation operators are redundant and the solution is determined completely within the configuration space. In contrast to the orbital space, the configuration space cannot possess multiple energy minima satisfying the same conditions. In many cases it is advantageous, therefore, to eliminate orbital degrees of freedom in favor of configuration degrees of freedom by modifying the configuration space. A familiar example of redundant orbital transformation operators is given by the configuration space consisting of all single excitations from a single reference configuration into a set of "external" orbitals unoccupied in the reference configuration. In this case the energy is invariant with respect to transformations within this external orbital space, provided the mixing coefficients are allowed to adjust. Trivial redundant operators also occur between orbitals that are doubly occupied in all configurations and between orbitals that are unoccupied in all configurations because, in these cases, the corresponding gradient terms are zero regardless of the mixing coefficients set. From the large number of possible solutions with $\mathbf{w}=0$, $\mathbf{v}=0$, most will correspond to the wrong eigenvector of the $H(mc)$ matrix or, for the correct eigenvector, some will correspond to saddle point or maximal solutions with respect to orbital variations, and the remaining (one or more) solutions represent minima.

Of these minima, we are of course interested in the lowest (global) minimum.

During the iterative wave function optimization procedure a large number of undesired solutions may be avoided simply by ensuring that the current set of mixing coefficients correspond to the appropriate eigenvector of the $H(mc)$ matrix. Using the unitary group approach,^{3,4,9,10} this CI step has been made so efficient as to be comparable in effort to the integral transformation step even for configuration spaces of dimension much larger than can conveniently be employed in a full wave function optimization procedure. When the mixing coefficients correspond to the appropriate CI eigenvector, other undesired stationary point solutions are characterized by partitioned orbital Hessian matrices that have negative eigenvalues. Thus, if there are several negative eigenvalues of the partitioned Hessian, no further iterations within that region of orbital space may be required. If there is reason to believe that the current orbitals are reasonable, then information from the gradient vector and Hessian matrix may still be used to determine some improvement to the current orbitals, even though the Newton-Raphson procedures fail under these conditions. Two approaches to the problem will be discussed; a level shifting approach and a super-CI approach. We examine these two approaches and develop hybrid methods that have some of the advantages of both approaches.

D. Level shifting methods

The level shifting or mode damping approaches (e.g., Ref. 1) are based on considerations that may be appreciated by examining an example in which the energy depends on only one variable. The Newton-Raphson procedure for energy minimization may be written as

$$k_1 = k_0 - w(k_0)/B(k_0),$$

where k_0 is the initial guess, k_1 the improved estimate, $w(k_0)$ the gradient evaluated at k_0 , and $B(k_0)$ the Hessian evaluated at k_0 . In general, the energy function has several minima characterized by zero gradients and positive Hessian values, several maxima characterized by zero gradients and negative Hessian values, and inflection points characterized by zero Hessian values. At least one inflection point exists between each minimum and maximum. One of these minima, for our purposes the one with the lowest energy, is the desired solution. When the initial guess is close to this desired solution and the second order energy expansion includes the dominant features of the function, then the Newton-Raphson procedure will display second-order convergence to that solution. However, if higher order terms are important, the Newton-Raphson procedure may converge slowly, oscillate about the solution, or even diverge away from the neighborhood of the energy minimum. As the initial guess approaches an inflection point, the small denominator in the Newton-Raphson expression causes an overestimation of the step size. The radius of convergence of the Newton-Raphson procedure to the desired energy minimum is thus somewhat less than the distance to this inflection point. Instead of using the Newton-Raphson procedure, the modified procedure

can be used in an attempt to increase the radius of convergence. If δ is some level shift parameter that forces the denominator to be positive, then the steps would be in the correct direction, along the negative gradient, but probably not of the correct length to ensure rapid convergence. This modification increases the radius of convergence past the inflection point and toward the energy maximum. Thus the level shifted procedure, in general, is not a second-order iterative procedure but has a larger radius of convergence than the Newton-Raphson procedure. In Appendix B we give an explicit example of these considerations for a one-dimensional model problem.

$$k_1 = k_0 - w(k_0)/(B(k_0) + \delta)$$

When the energy depends on several degrees of freedom, the usual approach is to transform the variables to a basis which diagonalizes the Hessian and to attempt to treat each of the new directions, or normal modes, independently of each other as separate one-dimensional problems. The above one-dimensional analysis may then be applied to each of these individual normal modes. Yeager *et al.*¹¹ use the magnitude and sign of the eigenvalues of the wave function Hessian matrix and other information to determine if level shifting parameters δ_i are to be used. These modes are treated as if they are independent of each other, and different parameters are used to shift along different modes. The complete diagonalization of the Hessian may be avoided with the equivalent procedure

$$\begin{pmatrix} B & C \\ C^\dagger & M \end{pmatrix}_{\text{shifted}} = \begin{pmatrix} B & C \\ C^\dagger & M \end{pmatrix} + \sum_i \delta_i \mathbf{u}_i \mathbf{u}_i^\dagger, \quad (13)$$

where the vectors \mathbf{u}_i are the eigenvectors corresponding only to the shifted eigenvalues. When some modes require level shifting, then the remaining modes may also require modification, particularly if the step sizes are fairly large, since the decoupling provided by the diagonalization of the Hessian is only approximate. In regions of wave function space that are not represented well with a second-order energy expansion, this decoupling may not be qualitatively accurate, and simultaneous shifting of all modes would be required to achieve convergence. A difficulty with this approach is that there is no apparent way to determine optimum shift parameters δ_i . If they are chosen too large then convergence may be slow; if they are not large enough the procedure may fail to locate some minima or even diverge. There is also no reason to expect a satisfactory set of δ_i for one iteration or geometry to be satisfactory for another. Another serious problem occurs for excited state calculations. If the elements of the coupling matrix C are small, then the normal modes will correspond either predominantly to orbital directions or predominantly to state directions, and the only negative eigenvalues that should occur are those which are predominantly in the state space. If the coupling between the orbital and state directions is large, however, this separation does not occur and the modes will contain mixtures of both orbital and state directions. If there are too many or too few negative eigenvalues of the wave

unction Hessian, then it is difficult to tell which ones should be shifted in order to move toward a valid solution. Since a valid solution is characterized by a positive semidefinite partitioned orbital Hessian, an alternative approach is then to apply level shifting based on the eigenvalues of the partitioned orbital Hessian matrix.¹ The above analysis is then applied to the second-order energy expression [Eq. (9)] and the Newton-Raphson procedure of Eq. (10). This method has the advantage of not requiring a decision as to which negative eigenvalue modes to keep or reject, but still no prescription is apparent for the determination of the optimum shift parameters.

E. Super-CI methods

There are several variations of the super-CI based iterative schemes.¹²⁻¹⁴ We present the iterative schemes most closely related to the second-order energy expression of the previous section. The super-CI procedure of Grein^{12,13} involves constructing a single-excitation configuration basis from the current multiconfiguration wave function:

$$\{|mc\rangle, (E_{pq} - E_{qp})|mc\rangle; p > q\}.$$

The matrix representation of the Hamiltonian is constructed and diagonalized in this basis according to

$$\begin{pmatrix} H(sci) & \mathbf{w} \\ \mathbf{w}^\dagger & E(mc) \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix} = E(sci) \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0}^\dagger & 1 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix}, \quad (14)$$

$$H(sci)_{(pq)(rs)} = \langle mc | (E_{qp} - E_{pq}) \hat{H} (E_{rs} - E_{sr}) | mc \rangle, \quad (14)$$

$$S_{(pq)(rs)} = \langle mc | (E_{qp} - E_{pq})(E_{rs} - E_{sr}) | mc \rangle.$$

The orbitals are then transformed according to Eq. (3) or some approximation to it. If the super-CI eigenvector corresponds to the lowest eigenvalue, then $E(sci)$ represents a rigorous upper bound to the lowest state of the particular symmetry and is bounded from above by the current approximate energy $E(mc)$ because of the bracketing theorem.¹⁵ In the neighborhood of an energy minimum, the orbital transformation lowers the energy such that $E(mc') \approx E(sci)$. Since both the approximate energy $E(mc)$ and the orbital corrections are calculated to lower the energy in each iteration, the super-CI method has the favorable aspect that it converges only to local minima and avoids saddle point and maximal solutions. However, as has been demonstrated,^{13,16} second-order terms of the double excitation form

$$\langle mc | \hat{H} E_{pq} E_{rs} | mc \rangle$$

are neglected in the calculation of the orbital corrections and no coupling between the orbital changes and mixing coefficient changes is accounted for, so the method does not demonstrate true second-order convergence.

Additionally, for excited state calculations using this super-CI method, no constraints are incorporated in the calculation of the orbital corrections to prevent the root switching problems associated with the "variational collapse" of the wave function. If the $E(mc)$ term is shifted¹⁷ so that the current wave function dominates the super-CI eigenvector (i.e., $|\mathbf{k}| \ll 1$), then convergence may be obtained for excited states with some sacrifice

in the convergence rate. We show in Appendix A that without this shift parameter to approximate the effect of the lower energy states, this super-CI method may not converge to certain types of valid excited state solutions.

An alternative procedure is to include explicitly the complement states of the configuration space in the single excitation basis

$$\{|mc\rangle, |n\rangle, (E_{pq} - E_{qp})|mc\rangle\}.$$

If the appropriate eigenvector of the configuration space is chosen to construct the single excitation space, and if the appropriate super-CI eigenvector is chosen to transform the orbitals, then again both $E(mc)$ and $E(sci)$ represent variational upper bounds to the excited state energy and $E(sci)$ is bounded from above by $E(mc)$. Coupling between the orbital changes and mixing coefficient changes is included via the matrix elements

$$H(sci)_{n,(pq)} = \langle n | \hat{H} (E_{pq} - E_{qp}) | mc \rangle,$$

so that the variational collapse and root switching problems are avoided in some cases.

The $H(sci)$ matrix may be modified to include some of the second-order terms usually neglected in the super-CI schemes,¹³ but the resulting $E(sci)$ is no longer a variational upper bound of the state of interest. The eigenvector solution of the super-CI equation still attempts to minimize $E(mc')$ instead of only stabilizing it to first order, so a major advantage of the super-CI approach is still retained. Chang and Schwarz¹⁸ have reported on the convergence properties for some excited states using this nonvariational approach with the orbital-state coupling included.

F. Approximate super-CI methods

A major disadvantage of the super-CI methods discussed above is that the construction of the Hamiltonian and overlap matrices in the single excitation basis becomes very time consuming as the number of configurations increases. In contrast, the Hessian matrix construction requires only the reduced one- and two-particle density matrices calculated from the configuration basis and mixing coefficients.^{1,3} We wish to use the form of the super-CI equations as a guide in the derivation of iterative procedures that have the energy minimization advantages of the super-CI procedures, but are expressed in terms of the Hessian and gradient matrix elements, which are relatively easy to calculate. To this end, we rewrite the second order-energy expression [Eq. (6)] as

$$E^{(2)}(\mathbf{k}, \mathbf{p}) - E(mc) = \Delta E = \frac{1}{2} (\mathbf{k}^\dagger \mathbf{p}^\dagger 1) \begin{pmatrix} \mathbf{B} & \mathbf{C} & \mathbf{w} \\ \mathbf{C}^\dagger & \mathbf{M} & \mathbf{v} \\ \mathbf{w}^\dagger & \mathbf{v}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix}. \quad (15)$$

Of course, requiring ΔE to be stationary results in the usual Newton-Raphson iterative procedure of Eq. (8). We now introduce an error of order $|\mathbf{k}^\dagger \mathbf{p}^\dagger|^2$ into this expression to bring it closer to the expectation value form of the super-CI energy expression

$$(\mathbf{k}^\dagger \mathbf{p}^\dagger 1) \mathbf{S} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix} \Delta E = \frac{1}{2} (\mathbf{k}^\dagger \mathbf{p}^\dagger 1) \begin{pmatrix} \mathbf{B} & \mathbf{C} & \mathbf{w} \\ \mathbf{C}^\dagger & \mathbf{M} & \mathbf{v} \\ \mathbf{w}^\dagger & \mathbf{v}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix},$$

where the \mathbf{S} matrix is some overlap matrix of the appropriate dimension. Stabilization of ΔE in this modified equation results in the secular equation

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} & \mathbf{w} \\ \mathbf{C}^\dagger & \mathbf{M} & \mathbf{v} \\ \mathbf{w}^\dagger & \mathbf{v}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix} = 2\Delta E \mathbf{S} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix}. \quad (16)$$

If the \mathbf{S} matrix is chosen to be the Chang and Schwarz overlap matrix,¹⁸ then this set of equations is equivalent to their super-CI secular equation. If the \mathbf{M} and \mathbf{C} matrices and the \mathbf{v} and \mathbf{p} vectors are neglected, this secular equation becomes equivalent to the Banerjee and Grein super-CI equations with the double-excitation terms discussed in the previous sections included in the $\mathbf{H}(\text{sci})$ matrix elements.^{13,19} Since the approximate super-CI energy $E(\text{mc}) + \Delta E$ is no longer a variational upper bound for the state energy, and since the contribution of the \mathbf{S} matrix involves the second-order error introduced into the second-order energy equation, it might be expected that various approximations to the matrix elements of \mathbf{S} would have little effect on the convergence rate. Shepard²⁰ and Lengsfeld²¹ have reported satisfactory convergence by approximating the \mathbf{S} matrix with a unit matrix for both ground and excited state calculations. Convergence has even been obtained in cases where the initial orbital guess was poor and Newton-Raphson iterative procedures failed to converge. This approximate super-CI secular equation

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} & \mathbf{w} \\ \mathbf{C}^\dagger & \mathbf{M} & \mathbf{v} \\ \mathbf{w}^\dagger & \mathbf{v}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix} = 2\Delta E \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix} \quad (17)$$

is derived from the correct second-order energy expression with the introduction of a second-order error and is equivalent to minimization of the energy subject to the same "normalization" constraint that is implicit in the derivation of all the super-CI iterative procedures. This constraint guarantees the existence of a solution to the minimization problem even when the Hessian possesses negative eigenvalues and the second-order energy expression [Eq. (6)] would therefore not possess a minimum. We apply this approximate super-CI iterative scheme to a one-dimensional model problem in Appendix B, and compare its convergence properties to those of the Newton-Raphson procedure. Herein, we refer to methods that require the calculation of a large Hamiltonian matrix (in terms of individual single-excitation configuration state functions) and its subsequent contraction to the smaller $\mathbf{H}(\text{sci})$ matrix as super-CI methods. This includes the methods of Banerjee and Grein and of Chang and Schwarz. Methods that do not require this contraction, but attempt to take advantage of an analogous secular equation [e.g., Eq. (17)] will be called approximate super-CI methods. Although in other contexts a different classification might be more appropriate, for our purposes in this work the most significant ad-

vantage of the approximate super-CI methods over the traditional super-CI methods is the ability to exploit the commutator expressions for the required matrix elements. The formal commutator evaluation results in matrix element expressions which involve only the reduced one- and two-particle density matrices and molecular integrals.^{3,16,20} This results in more efficient matrix construction algorithms than can be achieved with the traditional super-CI methods.

When convergence is achieved with the approximate super-CI method of Eq. (17), the mixing coefficients must still correspond to the appropriate eigenvector of the $\mathbf{H}(\text{mc})$ matrix, and the partitioned orbital Hessian matrix should have no negative eigenvalues. We show in Appendix A that, for the N th excited state, this is equivalent to requiring the \mathbf{M} matrix to have N negative eigenvalues and requiring the $(N+1)$ st lowest root of the approximate super-CI secular problem to be zero. The problem with using Eq. (17) directly, however, is that there appears to be no obvious procedure, during the iterative process, to move away from regions of wave function space that possess negative eigenvalues of the partitioned Hessian.

To gain further insight into the relation between orbital corrections obtained from the approximate super-CI iterative procedure and iterative procedures based on the second-order energy expression of Eq. (6), Eq. (17) may be rewritten in a form resembling Eq. (8),

$$\begin{pmatrix} \mathbf{B} + \lambda & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} + \lambda \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix} + \begin{pmatrix} \mathbf{w} \\ \mathbf{v} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \quad (18)$$

where $-\lambda = 2\Delta E = \mathbf{k}^\dagger \mathbf{w} + \mathbf{p}^\dagger \mathbf{v}$. Since adding a constant to the diagonal elements of a matrix results in shifting all the eigenvalues of the matrix by this constant, it is clear that solving the approximate super-CI system [Eq. (17)] is equivalent to a special case of the wave function level shifting procedure with all of the shift parameters set equal to λ .^{20,22} The advantage of this procedure over the general level shifting procedure is that there is a well defined prescription for the calculation of the shift parameter λ . As the wave function converges, this prescription gives shift parameters that automatically decrease and will not tend to overdamp the orbital change, as constant shift parameters along certain modes might tend to do. When the current orbitals are far from correct, this procedure has the advantage that all the modes are shifted. Thus, much of the ambiguity of a general level shifting procedure is avoided with this approximate super-CI method.

To determine the convergence properties of this approximate super-CI method, we write the derivatives of the energy with respect to the $\{\mathbf{k}, \mathbf{p}\}$ parameters as

$$\begin{pmatrix} \partial E / \partial \mathbf{k} \\ \partial E / \partial \mathbf{p} \end{pmatrix} = \begin{pmatrix} \mathbf{w} \\ \mathbf{v} \end{pmatrix} + \begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix} + \mathcal{O}(\epsilon^2),$$

where we assume that near a solution

$$\mathcal{O}(\epsilon) = \mathcal{O}(\mathbf{v}) = \mathcal{O}(\mathbf{w}) = \mathcal{O}(\mathbf{k}) = \mathcal{O}(\mathbf{p}) \ll 1.$$

the $\begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix}$ vector which is determined from the approximate

per-CI equations [Eqs. (17) and (18)] may be written

$$\begin{pmatrix} \mathbf{k} \\ \mathbf{p} \end{pmatrix} = - \begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{w} \\ \mathbf{v} \end{pmatrix} + \mathcal{O}(\lambda\epsilon).$$

Substitution of this into the expression for the derivatives gives

$$\begin{pmatrix} \frac{\partial E}{\partial \mathbf{k}} \\ \frac{\partial E}{\partial \mathbf{p}} \end{pmatrix} = \mathcal{O}(\lambda\epsilon) + \mathcal{O}(\epsilon^2).$$

This shows that if the shift parameter satisfies $\mathcal{O}(\lambda) \lesssim \mathcal{O}(\epsilon)$ then the iterative procedure will display second-order convergence. For the approximate super-CI procedure described above,

$$\lambda = -2\Delta E = -\mathbf{k}^\dagger \mathbf{w} - \mathbf{p}^\dagger \mathbf{v} = \mathcal{O}(\epsilon^2).$$

Therefore, the approximate super-CI procedure of Eq. (17) is a true second-order iterative procedure, even though it has been referred to as an approximate second-order procedure.^{20,21}

If we apply the same approach to the partitioned orbital Hessian second-order energy expression [Eq. (9)] the resulting approximate super-CI equation is

$$\begin{pmatrix} \mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger & \mathbf{w} \\ \mathbf{w}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix} = 2\Delta E \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix}, \quad (19)$$

where we have again set $S(\text{sci})=1$ for convenience. The solution of this approximate super-CI eigenvalue problem is equivalent to the solution of the equation

$$(\mathbf{B} + \lambda - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger) \mathbf{k} + \mathbf{w} = 0, \quad (20)$$

where $\lambda = -2\Delta E = -\mathbf{k}^\dagger \mathbf{w}$. Thus, this super-CI iterative procedure is equivalent to a special case of a level shifted partitioned orbital Hessian iterative procedure. When the shift parameter λ is equal to the negative of the lowest approximate super-CI eigenvalue, it is necessarily large enough to ensure that the shifted Hessian matrix has non-negative eigenvalues because of the bracketing theorem. Since $\lambda = \mathcal{O}(\epsilon^2)$, this super-CI iterative procedure displays second-order convergence in the neighborhood of a local minimum.²³

If the eigenvector obtained from Eq. (17) or (19) is scaled by a factor α before it is used to define the wave function corrections, then the resulting iterative procedure is still second order, provided $(1-\alpha) = \mathcal{O}(\epsilon^2)$. This condition is satisfied when the eigenvector is scaled to unit norm [e.g., $\alpha = (1 + \mathbf{k}^\dagger \mathbf{k})^{-1/2}$ in Eq. (19)]. This conventional super-CI normalization may therefore be viewed as resulting in a damped iterative procedure whenever \mathbf{k} is large.

When $\mathbf{v} = 0$, Eq. (20) may be compared with the partitioned form of Eq. (18)

$$[\mathbf{B} + \lambda - \mathbf{C}(\mathbf{M} + \lambda)^{-1} \mathbf{C}^\dagger] \mathbf{k} + \mathbf{w} = 0. \quad (21)$$

While Eq. (20) shows that the super-CI method based on the partitioned orbital Hessian results in an iterative procedure that moves away from undesired regions of wave function space, Eq. (21) shows that the same is not necessarily true for the super-CI method based on the

wave function Hessian. In particular, for excited states the value of λ may be large enough to shift away the negative eigenvalues of the state Hessian matrix \mathbf{M} that must exist for a valid wave function solution. This changes the nature of the $\mathbf{C} \mathbf{M}^{-1} \mathbf{C}^\dagger$ contributions, and thus has a large undesirable effect on the orbital corrections.

Another problem encountered with the wave function Hessian super-CI method [Eq. (17)] is that for poor orbitals there may not exist an eigenvector whose dominant component is the current $|mc\rangle$ state. The choices that are available for the orbital corrections for the N th excited state include: (1) the vector corresponding to the $(N+1)$ st eigenvalue, (2) the vector corresponding to a negative eigenvalue which has the most dominant $|mc\rangle$ contribution [i.e., the smallest $|\langle \mathbf{k}^\dagger \mathbf{p} \rangle|$], and (3) some combination of the vectors corresponding to the negative eigenvalues. We have used Eq. (21) along with a second-order perturbation theory approximation (i.e., $\lambda = \sum w_k^2 / B_{kk}$) to achieve the third option,²⁰ but have found this unsatisfactory in many cases. These problems with the wave function Hessian super-CI method are similar and related to the failure of the normal modes to decouple adequately the independent search directions in the wave function level shifting iterative procedure when the coupling elements are large.

We emphasize at this point that these failures of these iterative methods are not caused by the breakdown of the approximate energy expressions. In the neighborhood of the current wave function, these energy expressions are correct. The reason that some of these methods may fail where others succeed is that they use the energy expressions in different ways to calculate noninfinitesimal wave function changes. It therefore remains to be demonstrated which of these methods employs the approximate energy expressions in the most appropriate manner.

III. DISCUSSION OF RESULTS

We now examine the applications of the iterative methods discussed in the previous sections to some molecular examples. We have previously¹⁶ compared, in some detail, the fully variational super-CI formulation of Grein and co-workers^{12,13,17} with the Newton-Raphson methods. We restate the conclusions of that comparison before proceeding to the level shifted methods and approximate super-CI methods.

When the variational super-CI method of Grein is compared to the Newton-Raphson method with the coupling matrix \mathbf{C} neglected, both methods display first-order (i.e., geometric) convergence near the final solution. However, the radius of convergence of the super-CI method is much greater than that of this Newton-Raphson method. When the coupling matrix is included in the Newton-Raphson method, it displays true second-order convergence in the neighborhood of the final solution, as Eqs. (6) and (9) would indicate, but its radius of convergence may be even smaller than when the orbital-state coupling is neglected. We demonstrated that convergence to undesired saddle point solutions, even with fairly optimal configuration mixing coefficients, is a chronic failure of the second-order Newton-Raphson

method. This previous work,¹⁶ along with more recent experience,^{3,20,24} leads us to advocate the use of the second-order Newton-Raphson method only when the wave function is sufficiently refined so that convergence can be assured.

Before proceeding to the remaining comparisons, we present useful energy lowering prediction formulas that may be used to estimate convergence. The second-order energy expression of Eq. (6) or (when $v=0$) of Eq. (9) may be used to predict the energy which would be obtained as $E(mc)$ in the next iteration as a result of the currently determined wave function changes. For example, when \mathbf{k} satisfies Eq. (10), then $E^{(2)}(\mathbf{k}) - E(mc) = \frac{1}{2}\mathbf{k}^\dagger\mathbf{w}$. When an approximate super-CI method is used, either the true second-order energy expression or the modified second-order expression leading to the eigenvalue equation (16) or (19) may be used. We find that $\Delta E = -\lambda/2$ (where $-\lambda = \mathbf{k}^\dagger\mathbf{w}$ is the appropriate eigenvalue of the approximate super-CI secular equation) usually leads to an underestimation of the energy change. The use of the true second-order energy expression with \mathbf{k} determined from the super-CI secular problem results in

$$\begin{aligned} E^{(2)}(\mathbf{k}) - E(mc) &= \mathbf{k}^\dagger\mathbf{w} + \frac{1}{2}\mathbf{k}^\dagger(-\lambda\mathbf{k} - \mathbf{w}) \\ &= -\frac{1}{2}\lambda(1 + \mathbf{k}^\dagger\mathbf{k}) \\ &= -\frac{1}{2}\lambda/z_{mc}^2, \end{aligned}$$

where z_{mc} is the coefficient of the $|mc\rangle$ function in the normalized form

$$\mathbf{z} = (1 + \mathbf{k}^\dagger\mathbf{k})^{-1/2} \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix}$$

of the appropriate super-CI eigenvector. This scaling of the super-CI eigenvalue usually produces better predictions of the energy lowering than the unscaled quantity. These approximate energy lowering expressions require information from the current iteration only, and are therefore more suitable for use as convergence criteria than energy extrapolation procedures which require information from previous iterations.

In Table I we show the accuracy of these predicted energy lowerings for the $^2\Sigma^+$ state of PO with a minimal basis for the single configuration case using the approximate super-CI iterative procedure.²⁵ The prediction of the first iteration is only accurate to two significant figures, but on the third iteration it is seen to be accurate to five significant figures. Four iterations were required to obtain convergence to machine accuracy in the energy ($\approx 10^{-16}$ hartree), starting with orbitals from the $^1\Sigma^+$ closed-shell cation state. This convergence may be compared to that obtained by Banerjee and Grein,¹³ who used both a first-order SCF iterative procedure which failed to converge and a variational super-CI procedure which converged rapidly. It may also be compared to the convergence obtained by Grein²⁶ and by Kosugi²⁷ using modified SCF iterative procedures. In agreement with Grein and in contrast with Kosugi, we find that the $^2\Sigma^+$ state lies below the $^1\Sigma^+$ cation, and is therefore stable with respect to ionization at the listed bond length. For this calculation the difference between the approximate super-CI iterative procedure and the variational super-

TABLE I. Convergence of a single-configuration wave function for the $^2\Sigma^+$ state of PO with a minimal basis^a at $R=2.78$ a. u. Orbital corrections are obtained from the approximate super-CI secular equation. Initial orbitals are from the cation.

Iteration	ΔE	Predicted ΔE
1	(-414.816 597 607 8)	-1.675 546E-02
2	-1.633 922E-02	-2.981 959E-05
3	-2.984 003E-05	-3.857 819E-10
4	-3.857 835E-10	-5.104 739E-20
$E(^2\Sigma^+)$	-414.832 966 670 7	
$E(^1\Sigma^+)$ (cation)	-414.824 128 590 6	

^aThe P-atom basis is (6222,62) from A. D. McLean and G. S. Chandler, IBM Research Report RJ 2665 (34180), IBM Thomas J. Watson Research Center, Yorktown Heights, NY (1979). The O atom basis is STO-6G from W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).

CI procedure of Grein is that the latter method neglects some second-order terms, as discussed in the previous sections. This calculation was also performed with the Newton-Raphson method, and similar convergence and similar accuracy of the predicted energy lowerings were obtained. This example does not demonstrate the difference between the partitioned orbital Hessian super-CI (PSCI) and the wave function Hessian super-CI (WSCCI) methods, since there is only one configuration.

To determine the differences in the performance of these iterative methods, first under favorable conditions, we will now proceed to examine the convergence of the PSCI, WSCI, and the wave function Hessian level-shifted (WLS) iterative methods. For the latter method we follow the suggestion of Yeager *et al.*¹¹ and introduce a tolerance criterion of 0.1. For the N th excited state, all eigenvalues λ_i of the wave function Hessian that fall below this tolerance for $i > N$ are changed to $\lambda_i = 0.1$. Table II shows the convergence for the 2^1A_1 excited state of methylene at the 1^1A_1 geometry as described by the two most important closed-shell configurations. The PSCI method and the WSCI method show very similar convergence properties; both converge to machine precision after the sixth iteration. The first iteration of the WLS method shows that damping is probably required for more modes, although all the extra negative eigenvalues of the wave function Hessian are removed by the second iteration. The converged wave function Hessian possesses a small positive eigenvalue ($\lambda_2 = 0.0755$). The choice of 0.1 for the shift tolerance causes this eigenvalue to be modified in each iteration. This modification destroys the second-order convergence which would have been obtained otherwise, and illustrates a general weakness of the level shifting method. The choice of shifting parameters (or tolerances, as with the present method) is very critical to the convergence, and an appropriate set of parameters for one iteration may not be appropriate for another. Next we consider this same state of methylene under less favorable conditions.

Table III shows the convergence of the PSCI, WSCI, and WLS methods when the initial orbitals are a poor description for the final wave function. The initial orbitals for these calculations are obtained from the con-

TABLE II. Convergence of a two-configuration wave function for the 2^1A_1 state of CH_2 in a DZ basis^f at $R_{\text{CH}}=2.14$ a. u., $\angle\text{HCH}=105.1^\circ$. Starting orbitals are from the 1^1A_1 state.

Iteration	$E(\text{PSCI})^a$	$E(\text{WSCl})^b$	$E(\text{WLS})^c$	N^d
1	-38.296 802 4178	-38.296 802 4178	-38.296 802 4178	3
2	-38.655 560 9952	-38.654 915 3621	-38.627 025 5465	1
3	-38.703 335 8233	-38.703 377 8229	-38.700 915 5690	1
4	-38.703 780 0967	-38.703 781 0851	-38.703 776 9711	1
5	-38.703 782 5187	-38.703 782 5193	-38.703 782 3345	1
6	-38.703 782 5197	-38.703 782 5197	-38.703 782 5087*	1
7			-38.703 782 5190	1
8			-38.703 782 5196	1
9			-38.703 782 5197	1

^aPartitioned orbital Hessian super-CI method, Eq. (19).

^bWave function Hessian super-CI method, Eq. (17).

^cWave function Hessian level-shifted method (with a tolerance of 0.1).

^d N is the number of negative eigenvalues of the wave function Hessian of the corresponding iteration of the WLS method.

*The converged wave function Hessian has an eigenvalue of 0.0755. The tolerance of 0.1 results in the modification of this eigenvalue in each iteration, and thus destroys the second-order convergence.

^fL. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley, New York, 1972), pp. 20-25.

verged set for the 2^1A_1 state by mixing each of the occupied orbitals with a virtual orbital by a 15° rotation. This gives a relatively poor description of both the 1^1A_1 and 2^1A_1 states, as may be inferred from the energy of the first iteration. The PSCI method is seen to converge monotonically in the energy to machine precision after seven iterations. The second iteration of the WSCI method has no super-CI eigenvector in which the $|mc\rangle$ state is dominant. We chose the second lowest vector, which also was the vector with the largest $|mc\rangle$ component, but the energy diverged on the subsequent iterations. The WLS method also is not successful in converging to the desired solution. The number of negative

eigenvalues of the wave function Hessian is actually seen to increase on successive iterations. The last two columns show the result for the same starting orbitals but with rescaling applied to the \mathbf{k} vector. When the magnitudes of the elements of the \mathbf{k} vector are large, they correspond to rotations of the orbitals by many π radians. By scaling the \mathbf{k} vector we move in the direction determined by the approximate energy expression, but we also require the orbitals not to vary too drastically. For this example we rescaled when $(\mathbf{k}^\dagger\mathbf{k}) > 0.25$, which corresponds to a maximum allowed rotation of about $\pi/6$. The orbital rotations obtained by the PSCI method in the first column were always below this toler-

TABLE III. Convergence of a two-configuration wave function for the 2^1A_1 state of CH_2 . Starting orbitals were obtained by 15° rotations of occupied-virtual orbital pairs of the converged 2^1A_1 orbital set.

Iteration	$E(\text{PSCI})$	$E(\text{WSCl})$	$E(\text{WLS})$	N^a	$E(\text{WSCl})^b$	$E(\text{WLS})^b$	N^a
1	-33.607 808 6296	-33.607 808 6296	-33.607 808 6296	5	-33.607 808 6296	-33.607 808 6296	5
2	-38.167 102 3122	-34.332 369 2856 ^c	-27.833 992 0917	7	-31.407 908 1827	-34.733 350 1114	3
3	-38.371 075 1004	+51.734 293 7176	-27.202 801 6212	8	-30.971 158 2955	-35.943 063 8673	6
4	-38.693 632 2358	divergence	+195.407 416 4417	12	-32.565 684 3356	-37.318 354 4858	3
5	-38.703 754 9575		divergence		-34.690 134 1873	-38.274 071 2173	5
6	-38.703 782 4832				-37.264 288 0716	-14.454 353 8427	8
7	-38.703 782 5197				-37.666 352 5924	divergence	
18					-38.703 782 5197		

^a N is the number of negative eigenvalues of the wave function Hessian matrix in each iteration of the adjacent WLS column.

^bWith rescaling. When $\mathbf{k}^\dagger\mathbf{k} > 0.25$, \mathbf{k} is replaced by $[0.25/(\mathbf{k}^\dagger\mathbf{k})]^{1/2} \mathbf{k}$. This happens during the first ten iterations of the WSCI method and during all iterations of WLS.

^cThe lowest eigenvector of the wave function super-CI equation has $z_{mc}=0.62$, and the second lowest vector has $z_{mc}=0.62$. The second vector is used, with appropriate normalization, for the orbital transformation.

TABLE IV. Convergence of a symmetry restricted^a full valence space multiconfigurational wave function for the BeO $^1\Sigma^+$ ground state. The canonical SCF orbitals were used for the initial iteration. The basis set^b and bond length ($R=2.5$ bohr) are from Ref. 21.

Iteration	$E(\text{PSCI})^c$	$E(\text{WSCl-NR})^d$
1	-89.430 621 00	-89.430 621 49
2	-89.512 471 44	-89.469 211 73
3	-89.541 714 71	-89.502 796 62
4	-89.543 464 19	-89.524 620 69
5	-89.543 498 97	-89.535 773 03
6	-89.543 499 56	-89.540 775 84
7		-89.543 473 39
8		-89.543 499 07
9		-89.543 499 13

^aIncluding only $\sigma \rightarrow \sigma$, $\pi_x \rightarrow \pi_x$, $\pi_y \rightarrow \pi_y$ excitations relative to the Hartree-Fock configuration; see Ref. 21.

^bSee C. W. Bauschlicher Jr. and D. R. Yarkony, J. Chem. Phys. **72**, 1138 (1980).

^cPresent work, using the PSCI procedure. The \mathbf{k} vector was rescaled to unit magnitude in the first iteration, as explained in the text. $E(\text{SCF}) = -89.422\,816\,04$ hartree.

^dResults of Lengsfeld, Ref. 21. The WSCI method was used for the first six iterations [with the eigenvector of Eq. (17) scaled to unit magnitude], followed by the wave function Hessian Newton-Raphson method for the final iterations. $E(\text{SCF}) = -89.422\,815\,68$ hartree.

ance, although for some calculations we do find it necessary to apply this rescaling even with the PSCI method. The fourth column shows that the WSCI method converges to the correct solution, although not monotonically, after 18 iterations. The WLS method, still with a shift tolerance of 0.1, does not converge even with rescaling.

Werner and Meyer²⁸ have recently implemented a wave function optimization procedure that is not based on the minimization of a second-order energy expression of any of the types discussed in this paper. Instead, the stabilization of a different approximate energy expression leads to an analog of a Fock matrix, which is iteratively modified to include all the second-order and certain higher-order contributions from the wave function variations. The orbital modifications result from conditions that are formally analogous to those of the orthogonal gradient method of Hinze and co-workers.²⁹ One reported example²⁸ of the convergence of this method includes a comparison for the lowest $^1\Sigma^+$ state of BeO with a WSCI iterative procedure implemented by Lengsfeld.²¹ Tables IV and V respectively, compare the performance of the PSCI method with the WSCI results of Lengsfeld and with the second-order approach of Werner and Meyer, all with the same configuration space, basis set, bond length, and initial orbitals.^{21,28} The straightforward application of the PSCI procedure to this problem is shown in the first column of Table IV. The only deviation from the strict application of this procedure is a rescaling of the \mathbf{k} vector to a magnitude of 1.0 in the first iteration (initially $\mathbf{k}^T\mathbf{k} \approx 16.9$). This rescaling is

appropriate for comparison with the WSCI results in the second column, which are based on the normalization to unit magnitude of the entire eigenvector of the WSCI matrix [Eq. (17)] as discussed in Sec. II F. The difference of three iterations required to reach convergence between the PSCI and WSCI methods is not entirely typical for ground state calculations—the energy changes in corresponding iterations of the two methods are usually within an order of magnitude of each other for ground states. The reasons for the relatively slow WSCI convergence in this case, particularly during the initial iterations, are not investigated further in this work. The small differences between the listed energies for the two calculations at the SCF, starting iteration, and converged energy levels are presumably due to different integral accuracy and SCF convergence criteria in the corresponding calculations.

Table V compares the results of the PSCI method to those of the method of Werner and Meyer.²⁸ Although this method is not analyzed in the present paper, we include this comparison for completeness. Following the procedure of those authors (and unlike the calculations of Table IV), the 1σ and 2σ orbitals are frozen in their canonical SCF form. The iteration numbering begins with zero to be consistent with Ref. 28. The orbital-state coupling is neglected for one iteration with both methods, and no rescaling is applied to the PSCI method in any iteration. Under these conditions the PSCI method converges in one fewer iteration than in Table IV. Although the method of Werner and Meyer appears to be somewhat better behaved, any advantage is not significant enough to reduce the number of iterations required to achieve convergence in this example. The difference in the total energy lowerings between the two columns of Table V is presumably within integral accuracy and SCF convergence tolerances, although the two sets of results of Table IV are in closer agreement than those of Table V. The difference between the final energies of Tables IV and V shows the effect of the frozen orbital approximation for the 1σ and 2σ orbitals. An interesting

TABLE V. Convergence of a multiconfigurational wave function for the BeO ground state. The configuration space, basis set, bond length, and starting orbitals are the same as in Table IV, but the inner-shell 1σ and 2σ orbitals are frozen in their canonical SCF form.

Iteration	$\Delta E(\text{PSCI})^a$	$\Delta E(\text{WM})^b$
0	(-89.430 621 00)	
1	-0.101 211 93	-0.107 099 54
2	-0.011 172 51	-0.005 597 30
3	-0.000 418 65	-0.000 107 72
4	-0.000 006 17	-0.000 000 09
5	-0.000 000 00	-0.000 000 00
$\Delta E(1-5)$	-0.112 809 26	-0.112 804 65

^aThis work, using the PSCI procedure. The final energy is $-89.543\,430\,26$ hartree.

^bResults of Werner and Meyer, Ref. 28 (total energies not quoted).

TABLE VI. Convergence of the $2^1\Sigma^+$ state of BeO with a configuration space consisting of all single excitations from the valence orbitals.^a Starting orbitals are the converged $1^1\Sigma^+$ state orbitals.

Iteration	$E(\text{PSCI})$	$E(\text{WSCl})$	$E(\text{WLS})$	N^b
1	-89.278 374 9687	-89.278 374 9687	-89.278 374 9687	1
2	-89.364 374 4495	-89.364 898 3572 ^c	-89.362 867 8007	1
3	-89.365 381 1758	-89.361 057 2510	-89.365 327 8350 ^d	1
4	-89.365 383 1234	-89.304 839 0022	-89.365 355 1755	1
5	-89.365 383 1236	divergence	-89.365 367 9347	1
6			-89.365 373 9885	1
7			-89.365 376 9994	1
8			-89.365 378 6578	1

^aThe bond length is 2.569 bohr. The basis set is 6-31G for Be [J. D. Dill and J. A. Pople, J. Chem. Phys. **62**, 2921 (1975)] and 6-311G** for O [R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980)].

^b N indicates the number of negative eigenvalues of the wave function Hessian matrix in each iteration of the WLS method.

^cThe second lowest eigenvector had $z_{mc} = 0.906$, while the third lowest had $z_{mc} = 0.415$. The second lowest vector, with appropriate normalization, was used to define the orbital transformation.

^dThere are two small positive eigenvalues of the wave function Hessian matrix that are shifted in each iteration. Modification of these eigenvalues destroys the second-order convergence in the WLS method.

feature of all the calculations of Tables IV and V is that none of the methods display true second-order convergence except perhaps in the last one or two iterations. It has been our experience that this indicates the absence of some important configurations from the configuration space (possibly the excitations between the σ and π orbitals which have been omitted in this example²¹), but this is not explored further here. Finally, it should also be mentioned that methods based on stabilization, rather than minimization, of an approximate energy expression can converge to saddle points and not just to minimum points on a surface. The fact that some methods tend preferentially to converge to extremum points (local minima and local maxima) instead of saddle points is not formally well understood in all cases.³⁰ However experience with any of the iterative methods, when applied to a variety of both ground and excited states, must ultimately determine their ranges of applicability.

We next consider convergence for the first excited $^1\Sigma^+$ state of BeO. The symmetry restricted full valence configuration space used for the ground state leads to root switching during the excited state orbital optimization (again indicating the absence of important ground state configurations). Some of the most notoriously difficult wave function convergence is found for configuration spaces which contain many configurations which differ from each other by single excitations.^{12,31} However, it is the single excitations relative to the dominant configurations of the lower energy states that are most important in avoiding the root switching problem. Because we are concerned here with convergence characteristics and not with chemical interpretation or prediction based on our results, we have chosen to use a configuration space that consists of all single excitations from the occupied valence orbitals (3σ , 4σ , $1\pi_x$, and $1\pi_y$). Table VI

shows the convergence of the PSCI, WLS, and WSCI methods for the $2^1\Sigma^+$ state of BeO with this configuration space, starting with the $1^1\Sigma^+$ orbitals obtained with the same configuration space. The PSCI method converges to machine precision after the fifth iteration and displays second-order convergence throughout. On the second iteration of the WSCI method the energy is slightly lower than with the PSCI method, but the super-CI secular problem results in two vectors with large $|mc\rangle$ components. The second lowest vector has the largest $|mc\rangle$ component, and was used to define the orbital transformation, but the energy on the subsequent iterations is seen to increase. The WSCI method never produces a vector whose dominant component is the $|mc\rangle$ state after the second iteration. The WLS method would have displayed second-order convergence with a different choice of shift tolerance (again 0.1 was used). The converged Hessian possesses two small eigenvalues ($\lambda_2 = 0.0093$, $\lambda_3 = 0.0336$) which are modified in each iteration. Again this modification of the Hessian matrix destroys the second-order convergence.

We would like to emphasize at this point that the results of Table III and Table VI should not be interpreted as evidence that the WSCI and WLS methods cannot converge for these states. Indeed for the usual case, where adequate orbitals are available, and where the wave function Hessian matrix has only eigenvalues with large magnitudes, all these methods display very similar convergence. In this study we have chosen to compare these different methods under more difficult conditions. With this in mind, Tables III and VI should be interpreted simply as evidence that other constraints or modifications are required for the methods based on the wave function Hessian to obtain convergence in some cases for which the partitioned orbital Hessian method con-

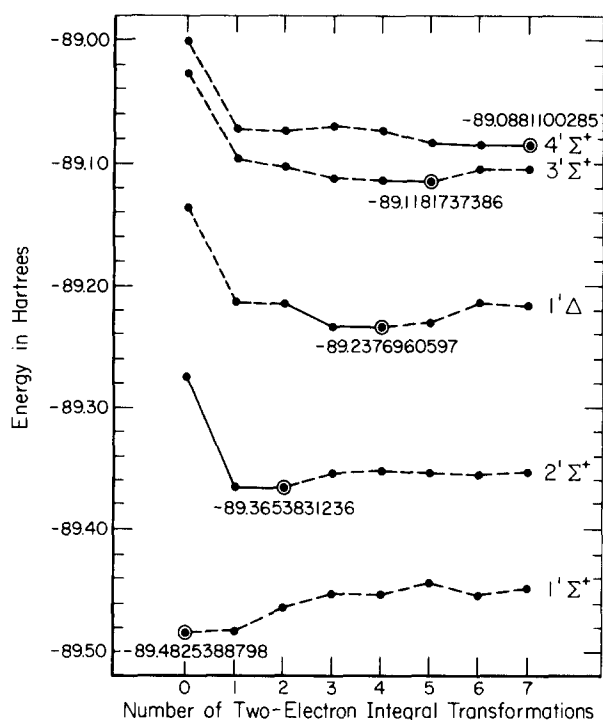


FIG. 1. Successive convergence of the lowest four excited $^1\Sigma^+$ and $^1\Delta$ states of BeO (all correspond to 1A_1 in the reduced C_{2v} symmetry in which the calculations were carried out) in an all-singles-excitations configuration space using the PSCI iterative method. The bond length and basis set are those specified in Table VI. Starting orbitals for each state are the converged orbitals of the next lower state. Only as many iterations as are needed for 10^{-5} hartree convergence in the energy (circled points) are shown for each state, but the iterations were continued in each case to at least 10^{-10} hartree convergence. The energies listed next to the circled points are the fully converged values. The dashed lines show the behavior of the other states as the orbitals are optimized for successively higher states (full lines).

verges without difficulty. We should also stress that for ground state wave function optimization these methods usually behave similarly. It is for excited state calculations, such as those of Tables III and VI, that the differences become most significant.

Finally, in Fig. 1 we show the PSCI method applied for some of the lowest electronic states of $^1\Sigma^+$ and $^1\Delta$ symmetry (both of these symmetries correlate to 1A_1 in the reduced C_{2v} symmetry in which these calculations were performed) with the all-singles configuration reference space. We have plotted the energy of these states as a function of iteration (i.e., the number of two-electron integral transformations) as the orbitals are successively optimized for the first excited state ($2^1\Sigma^+$), second excited state ($1^1\Delta$), and so on. Only the iterations required to achieve 10^{-5} hartree accuracy in the energy are plotted, but the iterations were actually continued until machine precision was obtained. Although the energies of these states are not quantitatively accurate, it is clear that all convergence problems caused by root switching have been circumvented by the choice of the all-singles configuration space. Second-order convergence is observed for all of these states beginning with the first iteration for each state. In fact the fifth

root of this series ($4^1\Sigma^+$) converges to machine precision in the wave function after only four integral transformations starting with the $1^1\Sigma^+$ orbitals. Systematic configuration selection^{17,24,32} could be applied to augment this reference space in order to bring the individual energies into quantitative agreement with more exact calculation. As long as the important single excitations are included for the lower energy states, the root switching problem should continue to be avoided, since there appear to be no pathological near degeneracies.

IV. SUMMARY AND CONCLUSIONS

The convergence characteristics of several wave function optimization methods which are based on valid approximate energy expressions have been compared. We have formally shown that the approximate super-CI methods compared in this paper are true second-order iterative methods and have demonstrated that they can display second-order convergence in practice. Of the methods analyzed in this report, the iterative method based on the partitioned orbital Hessian matrix and which uses the solution of an approximate super-CI secular equation displayed the best convergence properties. This method was shown to be a special case of a level shifted Newton-Raphson iterative scheme, with the advantage that empirical tolerance criteria and level shift parameters need not be specified. The types of failures that may occur with these methods have been analyzed, with particular attention being given to excited state calculations. Finally, we have also analyzed in detail the conditions satisfied by valid ground and excited state wave functions, and have shown how these conditions may be used during the iterative optimization procedures discussed in this paper to avoid convergence to undesired solutions.

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APPENDIX A: CHARACTERIZATION OF THE SOLUTIONS OF THE ITERATIVE PROCEDURES

A valid wave function solution for the N th excited state ($N=0$ is the lowest energy state, $N=1$ the first excited state, etc.) should provide a rigorous upper bound to the N th excited root of the full CI problem, and should correspond to an energy stationary point ($w=0, v=0$). This stationary point should be a minimum with respect to orbital variations, and therefore should possess a positive semidefinite partitioned orbital Hessian matrix ($B - CM^{-1}C^T$), while the state Hessian matrix M should possess exactly N negative eigenvalues. In this Appendix we will use these conditions and the partitioning

technique of Löwdin¹⁵ to demonstrate the necessary and sufficient conditions that are satisfied by valid solutions in the Newton-Raphson and super-CI iterative procedures discussed in this paper.

Newton-Raphson procedures

The Newton-Raphson procedure based on the partitioned orbital Hessian requires the straightforward application of the above conditions to characterize valid wave function solutions, and need not be analyzed further. For the Newton-Raphson procedure based on the wave function Hessian matrix, consider the eigenvalue problem of the wave function Hessian:

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix} = \lambda_i \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix},$$

where the order of the \mathbf{B} matrix is b , the order of the \mathbf{M} matrix is m , the eigenvalues of \mathbf{B} are $B_1 \leq B_2 \leq \dots \leq B_b$, and the eigenvalues of \mathbf{M} are $M_1 \leq M_2 \leq \dots \leq M_m$. For any λ_i for which the \mathbf{x}_i components of the eigenvector are nonvanishing, the above eigenvalue solutions are equivalent to the solutions of the partitioned equation

$$(\mathbf{B} - \mathbf{C}(\mathbf{M} - \lambda)^{-1}\mathbf{C}^\dagger)\mathbf{x} = \lambda\mathbf{x}.$$

If we define the multivalued function $L(\lambda)$ as the eigenvalues of the matrix $(\mathbf{B} - \mathbf{C}(\mathbf{M} - \lambda)^{-1}\mathbf{C}^\dagger)$, and the single valued function $R(\lambda) = \lambda$, then the eigenvalues of the wave function Hessian are given by the set of λ_i for which there exists an $L(\lambda_i) = R(\lambda_i)$. A graph of a typical $L(\lambda)$ is shown in Fig. 2. The horizontal asymptotes of $L(\lambda)$ are given as the eigenvalues B_i of the orbital Hessian matrix \mathbf{B} with

$$\lim_{\lambda \rightarrow \pm\infty} L(\lambda) = \{B_i : i = 1, 2, \dots, b\}.$$

The vertical asymptotes are located at λ values that correspond to the eigenvalues M_i of the state Hessian matrix. Each branch of $L(\lambda)$ is a nonincreasing function of λ and, except for rather unusual cases,¹⁵ satisfies a noncrossing rule with the other branches. As λ approaches a vertical asymptote M_p , only one branch of $L(\lambda)$ becomes singular, and has the principal part

$$L(\lambda)_p = -(M_p - \lambda)^{-1}(\mathbf{U}^\dagger \mathbf{C}^\dagger \mathbf{C} \mathbf{U})_{pp},$$

where \mathbf{U} is the unitary matrix which diagonalizes \mathbf{M} , while the corresponding eigenvector \mathbf{x}_p becomes proportional to the p th column of $(\mathbf{C} \mathbf{U})$.

For a valid wave function for the N th excited state, there must be N vertical asymptotes for negative values of λ , and the remaining $m - N$ vertical asymptotes must correspond to positive values of λ . At $\lambda = 0$ the branches of $L(\lambda)$ take the values of the eigenvalues of the partitioned orbital Hessian, and must therefore be non-negative for valid wave function solutions. We now examine the consequences of these conditions on the eigenvalues of the wave function Hessian matrix.

For each of the N negative asymptotes M_i ($i = 1, 2, \dots, N$) there is an associated branch of $L(\lambda)$ which intersects $R(\lambda)$ at some $\lambda < M_i < 0$, and thus we conclude that there are at least N negative eigenvalues of the wave function Hessian matrix. If there are more than N negative eigenvalues of the wave function Hessian, then there are

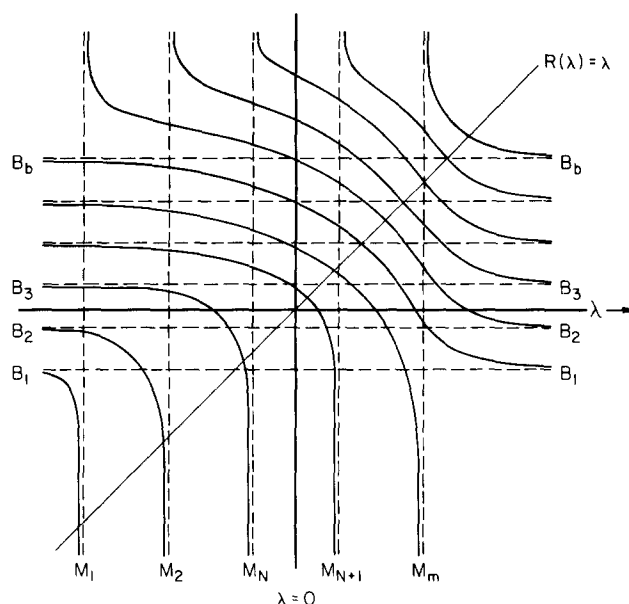


FIG. 2. Typical plot of the multivalued function $L(\lambda)$ (compare Ref. 15). The branches of this function represent the eigenvalues of the matrix $\mathbf{B} - \mathbf{C}(\mathbf{M} - \lambda)^{-1}\mathbf{C}^\dagger$, and the eigenvalues of the wave function Hessian matrix are represented by the intersections of these branches with the line $R(\lambda) = \lambda$. The intersections of the branches with the $\lambda = 0$ line are the eigenvalues of the partitioned orbital Hessian matrix and should be positive for valid wave function solutions. The vertical and horizontal asymptotes are the eigenvalues of the matrices \mathbf{M} and \mathbf{B} , respectively.

additional intersections of $L(\lambda)$ and $R(\lambda)$ for negative λ , and since the branches of $L(\lambda)$ are nonincreasing, the branches corresponding to these additional negative λ intersections must also cross the $\lambda = 0$ line with negative values. This is not allowed for valid wave functions, and therefore the wave function Hessian may not have more than N negative eigenvalues for valid solutions. A valid wave function for the N th excited state may therefore be characterized as possessing N negative eigenvalues of the \mathbf{M} matrix and exactly N negative eigenvalues of the wave function Hessian matrix. This type of characterization is useful for Newton-Raphson procedures based on the wave function Hessian matrix.

It is also clear from Fig. 2 that, for a valid wave function that corresponds to the N th excited state, there may be up to N negative eigenvalues of the orbital Hessian matrix \mathbf{B} . If \mathbf{B} possesses negative eigenvalues, then iterative procedures based on energy minimization (rather than stabilization) within the orbital space alone, without any coupling of the state space, cannot converge to these solutions, since they appear as saddle point solutions within that space. The ability to converge to such solutions, while avoiding undesired solutions, would be a critical test of the flexibility of an iterative wave function optimization method. In practice, the \mathbf{B} matrix has been found to be positive definite in all cases explicitly tested so far.

2. Approximate super-CI procedures

The approximate super-CI procedure based on the wave function Hessian uses the $(N + 1)$ st eigenvalue and

associated eigenvector of the equation

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} & \mathbf{w} \\ \mathbf{C}^\dagger & \mathbf{M} & \mathbf{v} \\ \mathbf{w}^\dagger & \mathbf{v}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix} = 2\Delta E \begin{pmatrix} \mathbf{k} \\ \mathbf{p} \\ 1 \end{pmatrix}$$

to define the wave function corrections in each iteration. At convergence ($\mathbf{w}=\mathbf{0}, \mathbf{v}=\mathbf{0}$), the eigenvalue spectrum of this super-CI matrix is identical to the spectrum of the wave function Hessian matrix, with an additional zero eigenvalue that may be associated with the vector

$$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

Valid wave functions may be characterized by solutions for which the \mathbf{M} matrix has N negative eigenvalues and the $(N+1)$ st lowest super-CI eigenvalue is equal to zero.

The super-CI procedure based on the partitioned orbital Hessian uses the lowest eigenvalue and associated eigenvector of the equation

$$\begin{pmatrix} \mathbf{B} - \mathbf{C}\mathbf{M}^{-1}\mathbf{C}^\dagger & \mathbf{w} \\ \mathbf{w}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix} = 2\Delta E \begin{pmatrix} \mathbf{k} \\ 1 \end{pmatrix}$$

to define the orbital corrections in each iteration. In each iteration the \mathbf{M} matrix possesses N negative eigenvalues as a consequence of solving the $H(mc)$ CI problem for the appropriate mixing coefficients. At convergence ($\mathbf{w}=\mathbf{0}$), the eigenvalue spectrum of this super-CI matrix is identical to that of the partitioned orbital Hessian matrix, with an additional zero eigenvalue associated with the vector $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Valid wave functions are characterized by solutions for which the \mathbf{M} matrix has N negative eigenvalues and the lowest eigenvalue of this super-CI matrix is equal to zero.

APPENDIX B: APPLICATION OF THE NEWTON-RAPHSON AND SUPER-CI ITERATIVE METHODS TO A ONE-DIMENSIONAL MODEL PROBLEM

In this appendix we discuss the application of the iterative procedures to the minimization of a simple one-dimensional model problem. Several of the difficulties with these procedures are not encountered with one-dimensional problems, particularly those related to excited state calculations, but valuable insight may still be obtained by consideration of this kind of model. We choose as our model the problem of locating the energy minimum of the function $E = -\cos k$ at $k=0$ using the iterative procedures discussed in this paper. For this energy function, the gradient and Hessian are given as

$$w(k_0) = \left. \frac{\partial E}{\partial k} \right|_{k_0} = \sin k_0,$$

$$B(k_0) = \left. \frac{\partial^2 E}{\partial k^2} \right|_{k_0} = \cos k_0,$$

and the second-order energy is

$$E^{(2)}(k) = -\cos k + \Delta k \sin k + \frac{1}{2}(\Delta k)^2 \cos k,$$

where $\Delta k = k - k_0$. The energy minimum at $k=0$ is characterized by a zero gradient and positive Hessian, the

inflection point at $|k| = \pi/2$ with a nonzero gradient but a zero Hessian, and the local maximum at $|k| = \pi$ with a zero gradient and a negative Hessian. The Newton-Raphson iterative procedure is given as

$$k_1 = k_0 - w(k_0)/B(k_0) = k_0 - \tan k_0.$$

Near the desired solution $k=0$ this procedure actually displays third-order convergence of the form

$$k_1 \approx -(1/3)k_0^3 \text{ for } k_0 \approx 0,$$

for this model problem instead of the usual second-order convergence, but this is unimportant to our present discussion.

As the initial guess for the Newton-Raphson procedure approaches the inflection point, the small denominator causes the corrections to become too large, and thus limits the values of k_0 for which the procedure converges. The radius of convergence is given by the solution close to $\pi/2$ of the equation $2k_r = \tan k_r$, or $k_r \approx 1.165561185$. For $|k_0| > k_r$ the Newton-Raphson procedure fails either because of divergence or because of convergence to the local maximum at $k = \pi$.

The level shifted procedure is given as

$$k_1 = k_0 - (\sin k_0)/(\cos k_0 + \delta),$$

where δ should be chosen to ensure a positive denominator so that the steps are along the negative gradient. If we choose $\delta > 1.0$, then the radius of convergence is extended beyond the $|k| = \pi/2$ inflection point and up to the $|k| = \pi$ maximum. Near the $|k| = \pi$ maximum the small gradient in the numerator causes only small steps to be taken, and thus slows the convergence rate. Near the $k=0$ minimum the convergence is only first order

$$k_1 \approx k_0 - k_0/(1 + \delta) = \frac{\delta}{1 + \delta} k_0, \text{ for } k_0 \approx 0,$$

when δ is kept fixed. An alternative form of level shifting is to adjust δ so that the denominator is always equal to a positive constant. This results in the local convergence of the form

$$k_1 = k_0 - (\sin k_0)/\Delta \approx k_0 - (k_0 - k_0^3/6)/\Delta$$

near $k_0 \approx 0$. The fortunate choice $\Delta = 1$ for the denominator results in good convergence, while other choices result in only first-order convergence. Such a fortunate choice cannot be made in general. Another alternative is to switch from the level shifted procedure back to the Newton-Raphson procedure when the denominator is large enough. For this model problem a choice which results in a Newton-Raphson iteration for $|k_0| > k_r$ will diverge. The convergence of the level shifting procedure is thus very dependent on the choice of several arbitrary parameters, including shift parameters and criteria for switching to the Newton-Raphson procedure.

The approximate super-CI iterative procedure applied to this problem results in the use of the lowest eigenvalue solution of the equation

$$\begin{pmatrix} \cos k_0 & \sin k_0 \\ \sin k_0 & 0 \end{pmatrix} \begin{pmatrix} \Delta k \\ 1 \end{pmatrix} = 2\Delta E \begin{pmatrix} \Delta k \\ 1 \end{pmatrix},$$

or equivalently

$$k_1 = k_0 - (\sin k_0)/(\cos k_0 + \lambda),$$

here

$$\lambda = -2\Delta E = \frac{1}{2}[-\cos k_0 + (\cos^2 k_0 + 4 \sin^2 k_0)^{1/2}].$$

near the solution then $k_1 \approx (2/3)k_0^3$, so that the super-CI iterative procedure, like the Newton-Raphson procedure for this model, displays third-order convergence. The denominator is non-negative in the super-CI procedure, and thus the radius of convergence extends past the $|k| = \pi/2$ inflection point. It is only when the initial guess is very close to the maximum $|k| = \pi$ that the small denominator begins to cause a fatal overestimation of the step size. The radius of convergence of this procedure is the solution near π of the equation

$$k_r = \sin k_r / [\cos k_r + (\cos^2 k_r + 4 \sin^2 k_r)^{1/2}],$$

or $k_r \approx 2.970\,03735$.

Thus the radius of convergence is increased by more than a factor of 2.5 over that of the Newton-Raphson method, with no sacrifice of the convergence rate near the final solution. To ensure convergence for $|k_0| > \pi$, third and fourth derivatives would be required, accompanied by a solution of the resulting second- or third-order equation for the lowest energy minimum. This nonlinear problem is not considered in this paper.

¹E. Dalgaard and P. Jørgensen, *J. Chem. Phys.* **69**, 3833 (1978); E. Dalgaard, *Chem. Phys. Lett.* **65**, 559 (1979).

²D. L. Yeager and P. Jørgensen, *J. Chem. Phys.* **71**, 755 (1979).

³R. Shepard and J. Simons, *Int. J. Quantum Chem. Symp.* **14**, 211 (1980).

⁴(a) J. Paldus, in *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring and D. J. Henderson (Academic, New York, 1976), Vol. 2, p. 131; (b) I. Shavitt, *Int. J. Quantum Chem. Symp.* **11**, 131 (1977); **12**, 5 (1978); (c) J. Paldus, in *The Unitary Group for the Evaluation of Electronic Energy Matrix Elements* (Lecture Notes in Chemistry), edited by J. Hinze (Springer, Berlin, 1981), Vol. 22, p. 1; (d) I. Shavitt, *ibid.*, p. 51.

⁵B. Levy and G. Berthier, *Int. J. Quantum Chem.* **2**, 307 (1968).

⁶C. C. J. Roothaan, J. Detrich, and D. G. Hopper, *Int. J. Quantum Chem. Symp.* **13**, 93 (1979).

⁷I. Shavitt, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 189.

⁸R. E. Stanton, *J. Chem. Phys.* **48**, 257 (1968).

⁹(a) B. R. Brooks and H. F. Schaefer III, *J. Chem. Phys.* **70**, 5092 (1979); (b) B. R. Brooks, W. D. Laidig, P. Saxe, N. C. Handy, and H. F. Schaefer III, *Phys. Scr.* **21**, 312 (1980); (c) F. E. M. Siegbahn, *J. Chem. Phys.* **70**, 5391 (1979); **72**, 1647 (1980).

¹⁰H. Lischka, R. Shepard, F. B. Brown, and I. Shavitt, *Int. J. Quantum Chem. Symp.* **15** (in press, 1981).

¹¹D. L. Yeager, P. Albertsen, and P. Jørgensen, *J. Chem. Phys.* **73**, 2811 (1980).

¹²F. Grein and T. C. Chang, *Chem. Phys. Lett.* **12**, 44 (1971);

T. C. Chang and F. Grein, *J. Chem. Phys.* **57**, 5270 (1972).

¹³A. Banerjee and F. Grein, *Int. J. Quantum Chem.* **10**, 123 (1976).

¹⁴K. Ruedenberg, L. M. Cheung, and S. T. Elbert, *Int. J. Quantum Chem.* **16**, 1069 (1979).

¹⁵P.-O. Löwdin, in *Perturbation Theory and Its Application in Quantum Mechanics*, edited by C. H. Wilcox (Wiley, New York, 1966), p. 255.

¹⁶R. Shepard, Ph.D. dissertation, Department of Chemistry, University of Utah, 1980.

¹⁷F. Grein and A. Banerjee, *Int. J. Quantum Chem. Symp.* **9**, 147 (1975); *Chem. Phys. Lett.* **31**, 281 (1975).

¹⁸T. C. Chang and W. H. E. Schwarz, *Theor. Chim. Acta* **44**, 45 (1977).

¹⁹F. W. Bobrowicz and W. A. Goddard III, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 79.

²⁰R. Shepard, in "Recent Developments and Applications of multiconfigurational Hartree-Fock Methods" (NRCC Proceedings No. 10), Report LBL-12157, Lawrence Berkeley Laboratory, University of California, Berkeley (1981), p. 117; R. Shepard and J. Simons, *ibid.*, p. 121.

²¹B. H. Lengsfeld III, *J. Chem. Phys.* **73**, 382 (1980).

²²D. R. Yarkony, *Chem. Phys. Lett.* **77**, 634 (1981).

²³In Refs. 2 and 11, an approximate iterative procedure is employed and is referred to as a "super-CI" procedure. The approximation involves the use of only the excitation terms (E_{pq} for $p \geq q$) instead of both excitation and deexcitation terms ($E_{pq} - E_{qp}$) in the construction of the Hessian matrix. Because of the importance of including both types of terms, particularly when the orbitals p and q are both partially occupied, this approximation cannot generally reproduce the convergence characteristics of either the super-CI or approximate super-CI procedures advocated here, even though it includes some terms not present in the usual super-CI method. In the single configuration limit the procedure of Refs. 2 and 11 corresponds to an approximate Newton-Raphson solution of Eq. (8), rather than a secular equation approximation for the solution of Eq. (14) or (16). It is therefore inaccurate to claim, as is done in Ref. 11, that this approximate method has the same convergence properties as the super-CI method of Grein.

²⁴R. Shepard, A. Banerjee, and J. Simons, *J. Am. Chem. Soc.* **101**, 6174 (1979); R. Shepard and J. Simons, *Int. J. Quantum Chem. Symp.* **14**, 349 (1980).

²⁵All the calculations reported here used the symmetry adapted gaussian integrals program of R. M. Pitzer and H. F. Schaefer III (private communication) based on the "equal contributions" principle [R. M. Pitzer, *J. Chem. Phys.* **58**, 3111 (1973)] and utilizing HONDO subroutines [M. Dupuis, J. Rys, and H. F. King, *J. Chem. Phys.* **65**, 111 (1976)] for primitive integrals evaluation.

²⁶T. J. Tseng and F. Grein, *J. Chem. Phys.* **59**, 6563 (1973); J. E. Grabenstetter and F. Grein, *Mol. Phys.* **31**, 1469 (1976).

²⁷N. Kosugi and H. Kuroda, *Chem. Phys. Lett.* **74**, 490 (1980).

²⁸H.-J. Werner and W. Meyer, *J. Chem. Phys.* **73**, 2342 (1980); **74**, 5794 (1981).

²⁹J. Hinze and E. Yurtsever, *J. Chem. Phys.* **70**, 3188 (1979); A. Golebiewski, J. Hinze, and E. Yurtsever, *ibid.* **70**, 1101 (1979).

³⁰For a discussion of this aspect of several optimization methods see, for example, E. Polak, *Computational Methods in Optimization* (Academic, New York, 1971).

³¹F. Grein and A. Banerjee, *Chem. Phys. Lett.* **25**, 255 (1974).

³²A. Banerjee and F. Grein, *J. Chem. Phys.* **66**, 1054 (1977); A. C. Wahl and G. Das, *Adv. Quantum Chem.* **5**, 261 (1970); G. Das, A. C. Wahl, and W. J. Stevens, *J. Chem. Phys.* **61**, 433 (1974); W. J. Stevens, G. Das, A. C. Wahl, M. Krauss, and D. Neumann, *ibid.* **61**, 3686 (1974).