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A DISCUSSION OF SOME ASPECTS OF THE MCSCF METHOD

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INTRODUCTION

After a brief overview of the MCSCF (MultiConfiguration Self-Consistent-Field) method, a more detailed examination of the underlying model is undertaken. The problem of "multiple solutions" is examined with reference to the "symmetry-breaking" problem and with emphasis on single-state cases. It is argued that the most appropriate resolution of such problems is usually case-specific, and depends on the details of how the MCSCF wave function is being used to model the chemical system rather than on features characteristic of the MCSCF wave function itself. Finally, a recently introduced MCSCF wave function optimization method based on multidimensional trigonometric interpolation is briefly discussed.

THE MCSCF METHOD

There are several aspects of the MCSCF method that determine its usefulness, validity, and accuracy¹. Firstly, the MCSCF wave function is based on the Born-Oppenheimer approximation. This approximation is the basis of the "potential energy surface (PES)" concept. Secondly, it makes use of finite orbital basis sets, although it would be possible to imagine an ideal MCSCF method involving a finite number of molecular orbitals that are arbitrarily flexible (i.e. as if they were constructed from an infinite, complete, orbital basis set). A conceptual and computational advantage of the former approach is that the MCSCF wave function may be compared to the full-CI wave function in the same finite orbital basis, and in this sense it may be regarded as an approximation to this full-CI wave function.

The MCSCF wave function is usually written as a linear superposition of configuration state functions (CSFs) $\{|\tilde{n}\rangle : n = 1 \dots N_{CSF}\}$

$$|mc\rangle = \sum_{n=1}^{N_{CSF}} c_n |\tilde{n}\rangle \quad (1)$$

although several nonlinear expansion forms have been employed also¹. In a nonlinear expansion, the expansion coefficients c_n depend in some (nonlinear) manner on a usually much smaller number of underlying variational parameters. This discussion will focus primarily on the linear expansion as given above. It is not uncommon for the MCSCF wave function to be expanded in terms of primitive Slater determinants. Such expansions are usually larger than the equivalent CSF expansion, due to the fact that the determinants span the space of several spin states, but it is sometimes argued that the simplicity of this approach compensates for this disadvantage. The MCSCF wave function approximates the full-CI wave function by including only a small subset of the possible expansion terms in Eq. (1). If all expansion terms were included, there would be no approximation, and in this sense the full-CI wave function is a special case of an MCSCF wave function. If the summation in Eq. (1) is limited to a single expansion term, this leads to the other limiting case of the MCSCF expansion, namely, the (single configuration) SCF wave function. The remaining flexibility of the MCSCF wave function arises from the variation of the shape of the orbitals from which the expansion CSFs are constructed. The MCSCF wave function attempts to approximate the full-CI wave function, which in this discussion will hereafter be regarded as the "exact" wave function, by the simultaneous variation of the CSF mixing coefficients and of the orbitals from which the CSFs are constructed.

The MCSCF energy is generally taken to be the expectation value of the hamiltonian operator

$$E(mc) = \frac{\langle mc | H | mc \rangle}{\langle mc | mc \rangle} \quad (2)$$

for a particular choice of expansion coefficients and orbitals. This energy expression immediately introduces ambiguity in the definition of the wave function because the energy is independent of overall scaling of the CSF expansion coefficients in Eq. (1). This ambiguity is handled formally by imposing a normalization constraint on the expansion coefficients in the following way. A reference wave function, denoted as $|0\rangle$ and with expansion coefficients c^0 , is chosen which satisfies the normalization $\langle 0 | 0 \rangle = \langle c^0 | c^0 \rangle = 1$. For a given set of orbitals, variations of the trial wave function are then defined in terms of some arbitrary set of orthogonal expansion states $|n\rangle$ where $\langle n | 0 \rangle = 0$ and $\langle n | m \rangle = \delta_{nm}$ are satisfied. (Note that an expansion state $|n\rangle$ as used here is itself a linear expansion of CSFs $|\tilde{n}\rangle$.) It is convenient to use the operator^{3,4}

$$P = \sum_{n \neq 0} p_n (|n\rangle\langle 0| - |0\rangle\langle n|) \quad (3)$$

to define these variations. Note that $P|0\rangle$ is an arbitrary vector, with arbitrary normalization, within the orthogonal complement space, and that this vector is parameterized with $(N_{CSF}-1)$ parameters p_n . The trial wave function may then be written as

$$|mc\rangle = \exp(P)|0\rangle \quad (4)$$

where $\exp(P)$ is a unitary (or, for real transformations, orthogonal) operator. This parameterization results in the identity $\langle mc | mc \rangle = \langle 0 | \exp(-P) \exp(P) | 0 \rangle = \langle 0 | 0 \rangle = 1$, simplifying greatly the formal manipulations involving Eq. (2) by eliminating from further consideration the dependence of the denominator on the variational parameters.

It is possible to find also a similarly useful parameterization of the orbital variations. For real orbital transformations, let

$$\phi = \phi^0 U \quad (5)$$

where the row vector ϕ^0 is some orthonormal set of reference orbitals, and U is an orthogonal transformation matrix. The reference orbitals may be written in terms of a

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nonorthogonal atomic basis χ as $\phi^0 = \chi C^0$, giving implicitly $\phi = \chi C^0 U = \chi C$ where $C = C^0 U$. If the elements of the matrix C are used directly to describe the orbital variations, then complications arise due to the nonorthogonal nature of the basis χ and orbitals ϕ . One approach to address this issue is to introduce a large number, $\frac{1}{2}N_{\text{orb}}(N_{\text{orb}} + 1)$, of Lagrange multipliers, and to replace Eq. (2) accordingly with a more general Lagrange functional in terms of these nonorthogonal orbitals. This approach is generally considered to be too restrictive for a general MCSCF procedure. Instead, it has been found quite practical to formulate the orbital variations using the following approach¹⁻⁷.

The matrix U may be parameterized as $U = \exp(K)$ where the matrix K is skew-symmetric ($K^T = -K$, or in terms of matrix elements $K_{rs} = -K_{sr}$). An arbitrary subset of the $\frac{1}{2}N_{\text{orb}}(N_{\text{orb}} - 1)$ distinct matrix elements may be chosen to define K . For convenience of notation, we hereafter assume that these are chosen as the strictly lower triangle matrix elements, K_{rs} for $r > s$. For subsequent purposes, it will be convenient to define the vector κ to be the appropriate collection of these distinct parameters. This parameterization achieves a reduction in the number of energy-dependent orbital parameters, from $N_{\text{orb}}^2 + \frac{1}{2}N_{\text{orb}}(N_{\text{orb}} + 1)$, the number of elements of the matrix C plus the number of Lagrange multipliers, to only $\frac{1}{2}N_{\text{orb}}(N_{\text{orb}} - 1)$, the number of distinct elements of the matrix K (or of the vector κ). (For brevity, the additional reductions of the number of variational parameters for some wave function expansions due to redundant orbital rotations¹ will be ignored in this discussion.) Since the elements of K are completely free to vary, and the resulting orbitals ϕ are always orthonormal, the formulation of energy variations is greatly simplified. In order to proceed further, the one-electron operator⁵ K is defined as

$$K = \sum_{r,s} K_{rs} E_{rs} = \sum_{(rs)} \kappa_{rs} (E_{rs} - E_{sr}) \quad (6)$$

with $E_{rs} = a_{rs}^\dagger a_{rs} + a_{rs}^\dagger a_{sr}$ being the spin-symmetry-adapted combination of products of spin-orbital creation and annihilation operators¹. It is now relatively straightforward to show that an arbitrary trial wave function in terms of the orbital basis ϕ is exactly equivalent to

$$|mc; \phi\rangle = \exp(K) |mc; \phi^0\rangle \quad (7)$$

It is important to emphasize that this expression is not an approximation, and that it is valid for arbitrary values of the parameters K . Using the P operator parameterization for the MCSCF trial function finally gives

$$|mc; \phi\rangle = \exp(K) \exp(P) |0; \phi^0\rangle \quad (8)$$

where the wave function $|0; \phi^0\rangle$ is the reference wave function consisting of the reference CSF coefficients c^0 and of CSF expansion terms constructed from the reference orbital coefficients C^0 .

With these concepts in mind, we can now describe in more detail MCSCF wave functions and energy expressions. In terms of normalized CSF expansion coefficients, the trial energy may be written as

$$E^{\text{trial}} = c^T H(K) c \quad (9)$$

$$= \sum_{\alpha} c_{\alpha} \langle \tilde{m}; \phi | H | \tilde{n}; \phi \rangle c_{\alpha} \quad (10)$$

$$= \sum_{\alpha} c_{\alpha} \langle \tilde{m}; \phi^0 | \exp(-K) H \exp(K) | \tilde{n}; \phi^0 \rangle c_{\alpha} \quad (11)$$

In Eq. (10), the K dependence is implicit in the hamiltonian matrix elements, whereas in Eq. (11) it is given explicitly in the orbital transformation operator $\exp(K)$. Again, it should be stressed that Eqs. (10) and (11) are exactly equivalent; no approximations have yet been

introduced. If the usual second-quantized expression for the hamiltonian operator is used in these equations,

$$H = \sum_{r,s} h_{rs} E_{rs} + \frac{1}{2} \sum_{r,s,t,u} g_{rstu} e_{rstu} \quad (12)$$

with $e_{rstu} = E_{rs}E_{tu} - \delta_{rs}\delta_{tu}$, then these differences become more clear. Namely, all integrals, h_{rs} and g_{rstu} , are defined in Eq. (10) with respect to the trial orbital basis ϕ , whereas they are defined in Eq. (11) with respect to the reference orbital basis ϕ^0 . (The operators E_{rs} and e_{rstu} are called, respectively¹, the unitary group generators and normal order generator products.) Because this is the only essential difference between Eqs. (10) and (11), it is customary to associate this orbital dependence with the operator instead of with the CSF expansion basis. For example, the above energy expressions are written

$$E^{\text{trial}} = \sum_{\alpha} c_{\alpha} \langle \tilde{m} | H | \tilde{n} \rangle c_{\alpha} \quad (13)$$

$$= \sum_{\alpha} c_{\alpha} \langle \tilde{m} | \exp(-K) H | \phi^0 \rangle \exp(K) | \tilde{n} \rangle c_{\alpha} \quad (14)$$

where the orbital dependence is denoted with square brackets. In this sense, the primitive expansion kets contain only the occupation and spin-coupling information. Eqs. (13) and (14) lead to the operator identity

$$H|\phi\rangle = \exp(-K) H|\phi^0\rangle \exp(K) \quad (15)$$

which proves useful when considering orbital variations. If this expression is expanded by orders in the matrix elements of K

$$H|\phi\rangle = H^0 + [H^0, K] + \frac{1}{2}[[H^0, K], K] + \dots \quad (16)$$

then a series of approximations may be developed for the K -dependent hamiltonian matrix elements of Eqs. (10-14). Here, H^0 is used as a shorthand notation for $H|\phi^0\rangle$, the hamiltonian operator in terms of the reference orbitals. For each of these approximations to $H|\phi\rangle$, there is a corresponding approximation to the E^{trial} expression of Eq. (13) that determines an approximate dependence of the trial energy on the orbital variations. These approximate hamiltonian operators may be written in the usual form of Eq. (12) where the effective integrals, which are the coefficients of the generators and generator products, may be obtained numerically using successive one-index transformations^{1,8}.

When combined with the $\exp(P)$ parameterization of the CSF coefficient changes, the trial energy may be written as

$$E^{\text{trial}} = \langle 0 | \exp(-P) \exp(-K) H^0 \exp(K) \exp(P) | 0 \rangle \quad (17)$$

When expanded in the elements of the matrix K and vector p , Eq. (17) may be written as

$$E^{\text{trial}} = \langle 0 | H^0 + [H^0, K] + [H^0, P] + [[H^0, K], P] + \frac{1}{2}[[H^0, K], K] + \frac{1}{2}[[H^0, P], P] + \dots | 0 \rangle \quad (18)$$

In practice, the infinite expansion of Eq. (18) is often truncated to include the second-order terms, and written in matrix notation as

$$E^{(2)}(\kappa, p) = E(0) + (\kappa^T \quad p^T) \begin{pmatrix} w \\ v \end{pmatrix} + \frac{1}{2} (\kappa^T \quad p^T) \begin{pmatrix} B & C \\ C^T & M \end{pmatrix} \begin{pmatrix} \kappa \\ p \end{pmatrix} \quad (19)$$

This expansion is useful for considering variations of both the orbitals and the expansion coefficients, but it is accurate only for small values of the individual parameters of the κ and p vectors since it derives from a low-order truncation. In Eq. (19), w and v are the

orbital and CSF gradient vectors respectively, and the matrices **B**, **C**, and **M** are the corresponding blocks of the hessian matrix. (With this notation, the coupling hessian matrix block **C** and the orbital coefficient matrix **C** must be distinguished by context.)

If it is assumed that c^0 is an eigenvector of the matrix representation of H^0 , then the CSF gradient vector v vanishes from an expansion such as Eq. (19). This idea can be extended one step further⁷, by imposing the condition on $\mathbf{p}$ that the energy maintain this minimization condition for arbitrary $\mathbf{K}$. Conceptually for a ground state wave function, this is equivalent to requiring that c of Eq. (13) is always the lowest eigenvector of the matrix representation of $H|c\rangle$. This trial energy may be denoted as

$$E^{\text{trial}}(\kappa) = c_{\text{opt}}^T H|c\rangle c_{\text{opt}} = \langle 0 | \exp(-P_{\text{opt}}) \exp(-K) H^0 \exp(K) \exp(P_{\text{opt}}) | 0 \rangle \quad (20)$$

This condition establishes an implicit relationship of $\mathbf{p}$ on the matrix $\mathbf{K}$, denoted as $\mathbf{p}(\mathbf{K})$. As determined from the truncated Eq. (19), this relation is

$$\mathbf{p} = -\mathbf{M}^{-1} \mathbf{C}^T \kappa \quad (21)$$

Of course the exact condition would be associated with a nonlinear relation involving additionally higher-order terms in the elements of the vector κ . This relation can now be substituted into Eq. (19) to eliminate the explicit dependence of the trial energy on $\mathbf{p}$.

$$E^{(2)}(\kappa) = E(0) + \kappa^T \kappa + \frac{1}{2} \kappa^T (\mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^T) \kappa \quad (22)$$

The matrix $(\mathbf{B} - \mathbf{C} \mathbf{M}^{-1} \mathbf{C}^T)$ is called the partitioned orbital hessian matrix. Conceptually, it is the second derivative of the *eigenvalue* of the hamiltonian matrix with respect to pairs of orbital rotations. The matrix elements of **B**, by contrast, are the second derivatives of the *expectation value* of the hamiltonian matrix with respect to pairs of orbital rotations for the fixed reference CSF expansion vector c^0 . The approximate energy expression Eq. (22) may be regarded either as the exact representation of Eq. (19) within the orbital variation subspace, or as an approximation to Eq. (20) valid for small orbital variations.

Using Eq. (22) in an iterative manner, it is possible to minimize the trial energy with respect to both orbital variations and CSF coefficient variations. The MCSCF wave function is then determined by the features of this energy surface. This will be called the "minimum-energy" definition of the MCSCF wave function. A somewhat surprising result is that minimization of an arbitrary MCSCF hamiltonian eigenvalue with respect to orbital variations reduces also to Eq. (22). Using this local surface characterization, the minimum-energy definition may be extended in a natural way to the optimization of excited states^{1,7}.

Suppose, however, that for a given set of orbitals it is possible to compute some wave function that is judged to be more accurate than the truncated MCSCF expansion. In practice, this might be, for example, a large-scale multireference CI wave function based on the MCSCF expansion space; in principle, it could be the exact full-CI wave function. In this wave function, the individual CSF mixing coefficients will assume slightly different values from those of the lowest eigenvector of the MCSCF hamiltonian matrix. This could be regarded as a relaxation effect of the reference wave function vector. When expanded in the same orthonormal CSF expansion space, the overlap between these two vectors may be characterized using the quantity $\text{Cos}(\theta) = \frac{\langle c | c_{\text{full-CI}} \rangle}{\|c\| \|c_{\text{full-CI}}\|}$. This overlap with the exact wave function may also be used to characterize the MCSCF wave function. The "maximum-overlap" vector within the MCSCF expansion space, defined as $\text{Max}(\text{Cos}(\theta))$, is given by

$$c_j = c_{m_j}^{\text{full-CI}} \quad (23)$$

where the mapping vector $\mathbf{m}$ associates the MCSCF expansion CSFs with the full-CI expansion CSFs. For ground state calculations, the expectation value of this vector will be higher than the MCSCF-eigenvalue choice; for excited states, it may be either higher or lower since it is not necessarily orthogonal to any lower-energy MCSCF eigenvectors. In principal, it would be possible to maximize this overlap with respect to orbital variations for an eigenvector c . Note that although the exact wave function is independent of the choice of orbitals, the expansion coefficients of the exact wave function do in fact depend on the orbitals. Although this maximum-overlap concept has limited practical value, it defines an alternative to the energy-minimization definition of the MCSCF wave function. Other conditions could also be chosen to define the MCSCF vector c , including, for example, perturbative expansions or approximate solutions to various time-dependent formulations.

In summary, an essential feature of the MCSCF wave function is the simultaneous variations of the orbitals and expansion coefficients. In essentially all other electronic structure methods, the molecular orbitals are assumed to have been defined previously by some method. In practice, this is a (single configuration) SCF method, or, as is occurring more and more frequently, a more general MCSCF method. In this way, an understanding of the MCSCF method is essential to, and a basis for, the understanding of many other electronic structure methods.

THE MULTIPLE SOLUTION PROBLEM

In most cases the MCSCF optimization procedure based on energy minimization results in a well-defined energy and wave function at each molecular geometry. We now examine the behavior of the MCSCF energy and wave function where two distinct wave function solutions may be found. The cases examined here are characterized by a relatively abrupt change of the orbitals or of the CSF expansion coefficients with a small change in some external variable. This external variable is usually a continuous molecular geometry change, but generally this discussion applies also to changes in the strength of some applied field, or even a continuous change of some orbital basis function parameter (e.g. an orbital exponent or exponent scale factor). We herein assume that the external perturbation is a geometry change, since this is probably the most common occurrence of multiple solution problems. The multiple solution problem is usually discussed in the context of "root-flipping" problems for excited state optimization. The multiple solution problems associated with single-state, and in particular the ground state, cases will be emphasized primarily in this section. Consider the behavior of the MCSCF energy as a function of two coordinates, the external perturbation and one internal degree of freedom, characterized as

$$|\lambda; R\rangle = \exp(K(\lambda; R)) \exp(P(\lambda; R)) |0; R\rangle \quad (24)$$

By this notation it is implied that for each geometry R , there exists at least one value for λ which satisfies the MCSCF optimization conditions. At some values of R , there may exist more than one MCSCF solution, and each solution is associated with a distinct value of the parameter λ . These multiple solutions could correspond, for example, to distinct covalent and ionic descriptions of a polar molecule, or to two distinct, symmetry-related descriptions of an electronic state, or to two distinct correlated descriptions of a single electronic state. The contour plot of Fig. 1 shows a schematic representation of the behavior of the energy as a function of these two degrees of freedom.

Consider first the path marked A in Fig. 1. At small R , the energy minimum is unique and is located in the upper left of the graph, corresponding to large- λ values. The minimum energy path intersects the points at which the contour lines are exactly vertical.

As seen in the graph, there is no reason why individual contour lines must have such a vertical slope, and as the path A progresses towards larger R values, it is seen to end abruptly at point A_0 . The contour lines associated with larger R values in the neighborhood of point A_0 do not have a vertical slope. Consequently, the smooth path defined by this sequence of points of vertical energy contour slope vanishes in this neighborhood beyond this critical point. Similarly, path B is a distinct minimum-energy path that begins in the lower right of the graph and progresses to higher energy regions of this surface until it ends abruptly at point B_0 . It is clear from this graph that the two separate, smooth, minimum-energy paths A and B do not intersect.

Recall from the discussion in the previous section that the ground state MCSCF energy may be defined as that which minimizes the lowest hamiltonian eigenvalue with respect to orbital variations. For a given orbital set, the lowest energy solution, corresponding to c_{opt} of Eq. (20), may be determined distinctly and unambiguously as the lowest eigenvalue of

Fig. 1. Contour plot of $E(\lambda, R)$ where λ is an "internal" wave function variational parameter and R is an "external" parameter such as a molecular geometry change. The minimum energy paths of optimization are denoted as path-A and path-B.

the hamiltonian matrix. However, different orbital choices will lead to different hamiltonian matrices, and the minimum of the energy with respect to orbital variations is only a local characterization of $E(K)$. As a function of R , this local characterization of the MCSCF wave function is not guaranteed to be continuous everywhere. With a careful parameterization of $K(\lambda, R)$ and $P(\lambda, R)$, a situation similar to that depicted in Fig. 1 can be recognized.

Recall however, that the usual description of the Born-Oppenheimer PES does not involve λ -type coordinates (but rather geometrical coordinates only), and that at a fixed geometry the wave function optimization problem does not involve geometrical coordinates (but K and P coordinates only). It is instructive to consider the consequences of the general energy surface shown in Fig. 1 from these two, more familiar, points of view. Consider first the PES behavior for large values of R . The computed MCSCF energy corresponds to the energy along the path B in Fig. 1. If small steps are taken along the R coordinate, and if the initial MCSCF wave functions in the optimization process are chosen to be those of the nearby point, then smooth convergence behavior will be observed all the way to the neighborhood of the point B_0 . However, at point B_0 , the wave function will suddenly collapse to the lower energy point A_1 on path A of Fig. 1. This will be observed as a discontinuity of the energy curve $E(R)$ as shown in Fig. 2. Hopefully, the abrupt energy change will be large enough to draw attention, but there is no guarantee that this must occur since this depends on the quantitative details of the energy surface rather than the qualitative aspects discussed here. Having observed an abrupt energy change, further examination reveals the nature of the corresponding abrupt change of the wave function (*i.e.* in the orbitals and/or CSF coefficients). The stepping procedure could now be reversed, from small values of R to larger ones. This time another smooth curve is computed along path A from point A_1 to the neighborhood of point A_0 of Fig. 1. As before, the wave function optimization at each new geometry is assumed to start from the converged wave function of the nearest point on the path. Smooth and rapid convergence will usually be observed, past the intersection point I_{MCSCF} in Fig. 2, until, as before, the energy collapses suddenly at the critical point A_0 back to the B_1 point on the original path.

Fig. 2. Curves of $E(R)$ for the two distinct MCSCF solutions corresponding to path-A and path-B of Fig. 1. The "figure-8" loop corresponds to the projection of the hysteresis path of Fig. 1.

in Fig. 1. This procedure can be repeated indefinitely, and with arbitrarily small geometry steps, and as long as the wave function optimization procedure is directed toward local energy minimization, and as long as a sufficiently accurate trial wave function is chosen for the optimization step, this hysteresis behavior will be observed. When projected onto the $E(R)$ graph of Fig. 2, this appears to be a rather puzzling "figure-8" pattern.

Consider next the wave function optimization for specific values of R . For this purpose, several cuts $E(\lambda)$ are displayed for different values R in Fig. 3. The optimization process is the determination of λ for which $E(\lambda)$ is locally minimized. For the smallest value of R there is a single energy minimum at large λ . As R increases, a new high-energy minimum appears at small λ in addition to the global minimum at large λ . At intermediate values of R , both minima are seen to be comparable in energy value. At larger values of R , the small- λ minimum becomes the global minimum, and the large- λ minimum eventually becomes simply an inflection point (specifically a stationary point with zero second derivative) and then vanishes. These inflection points correspond to the critical points A_0 and B_0 of Fig. 1.

Note in passing that the overall symmetry displayed in Figs. 1-3 is consistent with two symmetry-broken descriptions of an electronic state, with $R=0$ being the point at which the atomic nuclei assume a symmetric position. The two equivalent minima in the $E(\lambda)$ curve for $R=0$ in Fig. 3 correspond to the two symmetry-related broken-symmetry solutions. Other cases, such as competing covalent and ionic descriptions of a molecular state mentioned previously, would not likely display the overall symmetry of Fig. 1. An attempt has been made to frame the present discussion in a general manner consistent with the description of any such multiple-solution situation. See Ref. 9 and references therein for

Fig. 3. Curves of $E(\lambda)$ for various values of R . The local minima of these curves correspond to points on the path A and path B curves of Figs. 1 and 2.

specific discussions of the symmetry-breaking problem for small hydrocarbon radicals.

Of course there are many other similar situations that could be observed. The question then arises as to when, and if, the definition of the wave function should change from one MCSCF minimum solution to the other. Consider first the situation depicted schematically in Fig. 4. This situation is analogous to that given previously in Fig. 2, but now three new energy curves are added: an exact (full-CI) curve, and two approximate curves, one with each of the possible sets of MCSCF orbitals. The full-CI curve is independent of the orbital choice, so this curve could in principle be computed with either choice of orbital sets. This curve is depicted schematically as a smooth curve, characteristic of an avoided crossing, but essentially any kind of behavior could arise, even the cusp behavior associated with allowed state crossings of polyatomic molecules. This exact energy curve is usually not available for examination, but must be inferred from the various approximate curves.

In order for the MCSCF curve to be continuous in R , it is clear from Fig. 4 that we must switch wave functions exactly at the point I_{MCSCF} . Any other switching point would result in a discontinuous MCSCF energy curve. Even at this switching point, we must accept the fact that the wave function itself is discontinuous. This implies that, in general, any property other than the energy will be discontinuous, as there are no choices left in the wave function once the energy continuity condition has been imposed.

It is typical however to use the MCSCF method simply for defining the orbitals of a more accurate wave function. In Fig. 4, an MRCI wave function is used as an example of such a wave function¹⁰. In general, any wave function which is deemed to be more accurate than the MCSCF wave function could be used for this illustration, including those determined using contracted CI methods¹¹⁻¹³, multireference ACPF methods¹⁴, multireference coupled-cluster methods¹⁵⁻¹⁷, or multireference perturbation theory methods¹⁸⁻²². All such methods have the characteristic that they depend on the orbital choice, and they all attempt to describe the exact energy and wave function. An important point to make in such a situation is that the intersection point of the two MCSCF energy

Fig. 4. $E(R)$ for various wave functions. The two distinct MCSCF wave function solutions define the orbitals used in the two MRCI curves. The full-CI curve is independent of the orbital choice.

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Fig. 6. EPR for two distinctly different cases: (a) the MCSF curves correspond to an avoided crossing in the full CI curve of the MCSF curve crossing is artificial, and the full CI curve corresponds most closely to only one of the distinct MCSF solutions.

THE METHOD OF TRIGONOMETRIC INTERPOLATION

The energy expressions $E^{[2]}(\kappa, \mathbf{p})$ and $E^{[2]}(\kappa)$ of Eqs. (19) and (22) have both been used in the MCSCF optimization process¹, the former being associated with those optimization methods based on the wave function hessian matrix and the latter being associated with those involving the partitioned orbital hessian matrix. In this section, a recently introduced wave function optimization method, called multidimensional trigonometric interpolation²⁵, is described briefly, and the relation of this method to the previous methods based on Eqs. (19) and (22) is discussed.

The basis of this interpolation method is understood most easily by considering the dependence of the MCSCF trial energy as a function of a single orbital rotation variable. In this special case, the energy depends on (the scalar) κ through the orbital transformation matrix $\mathbf{U}$. The appropriate 2×2 subblock of this matrix may be written as

$$\mathbf{U}(\kappa) = \exp(\mathbf{K}) = \begin{pmatrix} \cos(\kappa) & -\sin(\kappa) \\ \sin(\kappa) & \cos(\kappa) \end{pmatrix} \quad (25)$$

which is clearly periodic in κ with period 2π . For further analysis, either of the two types of energy expressions discussed previously might be used: trial energy expressions of the type Eqs. (10-14), which are appropriate for considering independent variations of the orbitals and CSF coefficients, or expressions such as Eq. (20), which are appropriate for considering orbital rotations as independent variables and the CSF coefficients as implicit dependent variables. The work to date using the trigonometric interpolation approach has concentrated on the latter choice due to the following simplification. Observe first that $\mathbf{U}(\kappa + \pi)$ is related to $\mathbf{U}(\kappa)$ according to the trigonometric addition relations

$$\mathbf{U}(\kappa + \pi) = \begin{pmatrix} \cos(\kappa + \pi) & -\sin(\kappa + \pi) \\ \sin(\kappa + \pi) & \cos(\kappa + \pi) \end{pmatrix} \quad (26)$$

$$= \begin{pmatrix} \cos(\kappa) & -\sin(\kappa) \\ \sin(\kappa) & \cos(\kappa) \end{pmatrix} \begin{pmatrix} \cos(\pi) & -\sin(\pi) \\ \sin(\pi) & \cos(\pi) \end{pmatrix} = \begin{pmatrix} \cos(\kappa) & -\sin(\kappa) \\ \sin(\kappa) & \cos(\kappa) \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \quad (27)$$

$$= -\mathbf{U}(\kappa) \quad (28)$$

In other words, the two orbitals simply change signs at $(\kappa + \pi)$ relative to their values at κ . The trial energy of Eq. (20) does not depend on orbital phases since the elements of $c_{opt}(\kappa + \pi)$ must compensate exactly for any sign changes relative to $c_{opt}(\kappa)$. The trial energy of Eq. (20) must therefore be periodic in κ with period π . Consequently, $E^{trial}(\kappa + \pi) = E^{trial}(\kappa)$ under this assumption of optimal CSF expansion coefficients. Clearly, truncated energy expressions such as $E^{[2]}(\kappa, \mathbf{p})$ and $E^{[2]}(\kappa)$ do not reproduce this periodic behavior, and therefore are valid only for small values of the parameters κ .

The next problem is how to use this insight into the periodic nature of the trial energy expression of Eq. (20) in order to improve the behavior of an approximate energy expression. There are many ways that this could be done; the following approach builds upon some of the previous experience in using truncated energy expressions such as $E^{[2]}(\kappa)$ of Eq. (22). Again taking a one-dimensional case as a model, the truncated energy expression has the form

$$E^{[2]}(\kappa) = E(0) + w\kappa + \frac{1}{2}B\kappa^2 \quad (29)$$

where it is assumed that the energy, gradient, and hessian are known at the reference point, $\kappa = 0$. We now wish to use this information not only at $\kappa = 0$, but also at $\kappa = \pi$, $\kappa = 2\pi, \dots$. The general idea is that by imposing this periodic condition on the trial energy function, it will more closely mimic the true trial energy function and will be useful for a larger domain of κ values. In a sense, we are interpolating the unknown trial energy function between the

infinite number of points $\kappa = (0, \pi, 2\pi, \dots)$ at which certain information is known. The strategy used is to replace the independent variable κ with a periodic function $f(\kappa)$. This automatically results in a periodic interpolating function having the form

$$E^{TIF}(\kappa) = E(0) + wf + \frac{1}{2}Bf^2 \quad (30)$$

Differentiating this expression with respect to κ gives

$$E^{TIF}(\kappa)' = wf' + Bff' \quad (31)$$

$$E^{TIF}(\kappa)'' = wf'' + Bff'' + B(f')^2 \quad (32)$$

where the derivatives are denoted with primes. In order for $E^{TIF}(0) = E(0)$ to be satisfied for arbitrary w and B , it follows that $f(0) = 0$ must be satisfied. Similarly, for $E^{TIF}(0)' = w$, it follows that $f(0)' = 1$. Finally, for $E^{TIF}(0)'' = B$, it follows that $f(0)'' = 0$. Some reflection on this problem reveals that functions of the form $f(\kappa) = \frac{1}{2\pi} \sin(2\pi\kappa)$ (or linear combinations thereof) satisfy all of these conditions and also display the correct periodicity. The simplest of these is the function consisting of the single term $f(\kappa) = \frac{1}{2} \sin(2\kappa)$. In the one-dimensional case, this results in the interpolating function

$$E^{TIF}(\kappa) = E(0) + \frac{1}{2}w \sin(2\kappa) + \frac{1}{8}B \sin^2(2\kappa) \quad (33)$$

$$= E(0) + \frac{1}{2}w \sin(2\kappa) + \frac{1}{16}B(1 - \cos(4\kappa)) \quad (34)$$

The second form shows clearly that the gradient contributes to a component of the interpolating function that possesses sinusoidal behavior of period π , whereas the hessian term contributes a component with period $\pi/2$.

In the general multidimensional case, the functional form for the coordinate transformation is taken to be

$$\mathbf{F}(\mathbf{K}) = \frac{1}{4} (\exp(2\mathbf{K}) - \exp(-2\mathbf{K})) = \frac{1}{2} \sinh(2\mathbf{K}) \quad (35)$$

The matrix $\sinh()$ function appears instead of the $\sin()$ function because the skew-symmetric matrix $\mathbf{K}$ has purely imaginary eigenvalues. The vector $\mathbf{f}$ is now defined to be the unique elements of the skew-symmetric matrix $\mathbf{F}(\mathbf{K})$ (in the same way that κ is related to $\mathbf{K}$). The multidimensional interpolating function is then written explicitly as

$$E^{TIF}(\kappa) = E(0) + w^T \mathbf{f} + \frac{1}{2} \mathbf{f}^T (\mathbf{B} - \mathbf{C}\mathbf{M}^{-1}\mathbf{C}^T) \mathbf{f} \quad (36)$$

Conceptually, MCSCF wave function optimization using this approach consists first of determining the energy, gradient, and hessian (*i.e.* $E(0)$, $\mathbf{w}$, $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{M}$) using the current trial wave function. Then using these matrices, the corresponding $E^{TIF}(\kappa)$ is optimized with respect to the orbital rotation parameters $\mathbf{K}$. New orbitals are defined using the transformation $\exp(\mathbf{K})$, and new CSF expansion coefficients are determined from the MCSCF hamiltonian eigenvalue equation. This process is repeated until convergence is obtained²⁵. For practical reasons, it is useful to consider optimization procedures that do not require the explicit computation and storage of the hessian matrix blocks $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{M}$. With this goal in mind, it is possible to design procedures that optimize $E^{TIF}(\kappa)$ while requiring only the computation of matrix-vector products of the form $\mathbf{B}\mathbf{x}$, $\mathbf{C}^T\mathbf{x}$, $\mathbf{C}\mathbf{y}$, and $\mathbf{M}\mathbf{y}$ for subspace expansion vectors $\mathbf{x}$ and $\mathbf{y}$. Such matrix-vector products may be computed in several ways, depending on the relative costs of hessian matrix construction, partial integral transformations, hamiltonian matrix-vector products, and transition density matrix construction^{1,6,12,26}. Since these operations are required already in most second-order

MCSCF optimization schemes¹, the trigonometric interpolation approach may be added to most existing programs as an option with only relatively minor modifications.

The global behavior of the $E^{TIF}(\kappa)$ interpolating function may be seen in Fig. 7. These energy curves are one-dimensional slices from the multidimensional energy surface. This line is determined by a constant direction matrix Δ and the scalar parameter t as $\mathbf{K} = t\Delta$ (see Reference 25 for further details). Two other approximate energy curves are also displayed in Fig. 7 for comparison purposes. These are the truncated $E^{[2]}(\kappa)$ curves corresponding to Eq. (22) and the corresponding rational approximation $E^{PSCI}(\kappa)$. The $E^{PSCI}(\kappa)$ function has been used successfully for accelerating the convergence of MCSCF wave function optimization. Observe that $E^{trial}(\kappa)$ is periodic with period π as discussed above. When the expansion point t_0 is close to the energy minimum, as in Fig. 7a, then all three approximating curves predict accurately the location of the actual minimum. In fact, all three curves are correct through second order and lead to the same asymptotic convergence behavior.

As seen in Fig. 7b, as the reference point is moved further away from the minimum, the truncated expansion $E^{[2]}(\kappa)$ fails to predict the location of the energy minimum. The periodic $E^{TIF}(\kappa)$ function and the rational function approximation $E^{PSCI}(\kappa)$ both still approximate the minimum position reasonably well. As the reference point is moved even further away from the minimum as in Fig. 7c, the periodic $E^{TIF}(\kappa)$ is the only approximate function that predicts the position of the minimum. Since this region of the curve has negative curvature, the truncated $E^{[2]}(\kappa)$ curve has no minimum. The high-energy local minimum of the trial energy curve is also predicted by the $E^{TIF}(\kappa)$. Finally in Fig. 7d, the reference point is moved to a neighborhood of a maximum. Again, only the $E^{TIF}(\kappa)$

function approximates the position of the energy minimum. Due to the small gradient at the expansion point, the interpolating curve is dominated by the period $\pi/2$ contributions from the hessian as discussed above. These figures demonstrate that the $E^{TIF}(\kappa)$ interpolating function is capable of approximating the features of the true trial energy function even when the reference wave function is not in the region of the optimal solution. These figures also show that $E^{TIF}(\kappa)$ may be useful in locating multiple minima.

In addition to displaying the correct periodic behavior for individual orbital rotations, the interpolating function $E^{TIF}(\kappa)$ also displays qualitatively correct behavior in several other instances²⁵. These include orbital variations consisting of sets of mutually-commuting orbital rotation operators, and along certain lines in the multidimensional variational space called "direction patterns" which are related to the eigenvectors of the matrix $\mathbf{K}$ corresponding to specific eigenvalues. Qualitatively correct behavior is also displayed for redundant orbital rotations; namely, both $E^{TIF}(\kappa)$ and $E^{trial}(\kappa)$ are independent of such orbital transformations.

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Fig. 7 Comparison of the κ -dependence for the trial energy and three approximating functions for various expansion points — $E^{trial}(\kappa)$, --- $E^{TIF}(\kappa)$, ... $E^{[2]}(\kappa)$, and -.- $E^{PSCI}(\kappa)$. The expansion points (●) are 0.0, -0.5, -0.625, and -0.84 for figures a-d respectively along a line in the multidimensional orbital variational space

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