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The Representation and Parametrization of Orthogonal Matrices

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ABSTRACT: Four representations and parametrizations of orthogonal matrices $\mathbf{Q} \in \mathbb{R}^{m\times n}$ in terms of the minimal number of essential parameters $\{\boldsymbol{\varphi}\}$ are discussed: the exponential representation, the Householder reflector representation, the Givens rotation representation, and the rational Cayley transform representation. Both square $n = m$ and rectangular $n < m$ situations are considered. Two separate kinds of parametrizations are considered: one in which the individual columns of $\mathbf{Q}$ are distinct, the Stiefel manifold, and the other in which only span($\mathbf{Q}$) is significant, the Grassmann manifold. The practical issues of numerical stability, continuity, and uniqueness are discussed. The computation of $\mathbf{Q}$ in terms of the essential parameters $\{\boldsymbol{\varphi}\}$, and also the extraction of $\{\boldsymbol{\varphi}\}$ for a given $\mathbf{Q}$ are considered for all of the parametrizations. The transformation of gradient arrays between the $\mathbf{Q}$ and $\{\boldsymbol{\varphi}\}$ variables is discussed for all representations. It is our hope that developers of new methods will benefit from this comparative presentation of an important but rarely analyzed subject.

$$E(\boldsymbol{\varphi}) \equiv E(\mathbf{Q}(\boldsymbol{\varphi}))$$

1. INTRODUCTION

Orthogonal matrices occur commonly in many aspects of physics and chemistry. The manifolds of continuous Lie groups and the symmetry operations in point group theory can be represented by such matrices with the irreducible representations being fundamental.[1−4] The applications of group theoretic techniques are manifold in spectroscopy[5,6] and solid state physics.[7,8] A myriad of uses of rotation matrices include performing rotational steps in Brownian dynamics simulations[9] and Monte Carlo simulations,[10−13] specifying orientations of ligands in molecular docking,[14−16] representing orientational distribution functions in macromolecular science,[17] transforming substructures in three-dimensional structural alignment algorithms,[18−24] and computing atomic positions in molecular visualization programs.[25,26] In quantum chemistry, orthogonal matrices are important in the expansion of vibrational and electronic wave functions in terms of orthonormal bases.[27,28] In particular, through self-consistent field (SCF) methods, they arise in Hartree−Fock (HF) theory,[29] Kohn−Sham density-functional theory[30] (KS-DFT), and most semiempirical[31] approaches. Finally, we mention in passing that a unitary matrix, the analogue of an orthogonal matrix in the complex numbers, also occurs within electronic structure theory,[32,33] quantum dynamics,[34] and constrained optimization problems.[35]

This work considers the common situation in which some scalar function to be optimized $E(\mathbf{Q})$ depends on the elements of an orthogonal matrix $\mathbf{Q}$, the orthogonal matrix $\mathbf{Q}$ depends on some smaller number of parameters $\{\boldsymbol{\varphi}\}$, $\mathbf{Q} \equiv \mathbf{Q}(\boldsymbol{\varphi})$, and it is desirable to formulate the optimization problem directly in terms of these parameters as $E(\boldsymbol{\varphi}) \equiv E(\mathbf{Q}(\boldsymbol{\varphi}))$. It is typical for E to depend on only a subset of columns of the full square matrix $\mathbf{Q}$. This raises the question of how the variations of the elements of the rectangular matrix $\mathbf{Q} \in \mathbb{R}^{m\times n}$ for $n \le m$ can be parametrized during the optimization procedure. In general, there are (mn) elements of $\mathbf{Q}$. The columns of $\mathbf{Q}$ are normalized, which corresponds to n constraints on these elements, and the columns are mutually orthogonal, which corresponds to an additional $n(n-1)/2$ constraints. There are two situations involving the matrix element variations that are discussed in this paper. The first is the one in which the individual columns of $\mathbf{Q}$ play distinct roles in the optimization. In this case, $\mathbf{Q}$ belongs to the Stiefel manifold,[36] and the orthonormalization constraints result in $N_e = mn - n(n+1)/2$ degrees of freedom in the matrix $\mathbf{Q}$, where N_e is the number of *essential variables*. The second situation is when E is invariant to an arbitrary orthogonal transformation of the columns of $\mathbf{Q}$; that is, $E(\mathbf{QZ}) = E(\mathbf{Q})$ for any arbitrary orthogonal matrix $\mathbf{Z} \in \mathbb{R}^{n\times n}$. One familiar example of this situation[37−39] is the closed-shell SCF energy E, which depends only on the orbital coefficients of the m (orthogonal) basis functions of the n occupied orbitals $(n \le m)$ and in which the energy is invariant to transformations within the occupied orbital space. This invariance condition results in an additional $n(n-1)/2$ redundant variations in the problem, resulting in $N_e = (m-n)n$ essential variables. In both of the rectangular cases, the essential variables will be denoted $\{\boldsymbol{\varphi}\} \equiv \{\varphi_\mu: \mu = 1, ..., N_e\}$. In this second situation, E depends only on span($\mathbf{Q}$), and not on the particular choice of $\mathbf{Z}$, and $\mathbf{Q}$ belongs to the Grassmann manifold.[36] Another common situation in which the

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Grassmann manifold parametrization occurs is when the underlying problem involves an initial contraction step, with $\mathbf{Q} \in \mathbb{R}^{m\times n'}$ to define a subspace, and then the final result depends on the subsequent determination of the smaller matrix $\mathbf{Z} \in \mathbb{R}^{n'\times n}$ through a matrix diagonalization or other canonicalization step within that subspace. That is, the Stiefel manifold itself is parametrized in two steps as the product $\mathbf{QZ}$. Examples of this situation are the determination of one or more adiabatic electronic states within a diabatic basis,[40,41] "perturb-then-diagonalize" formulations of wave functions,[28,42,43] and other similar separations that occur when slowly varying "weaker" correlations are separated from more abrupt, or even discontinuous, "stronger" correlations.

Given the scalar function $E(\boldsymbol{\varphi}) \equiv E(\mathbf{Q}(\boldsymbol{\varphi}))$, a commonly required operation is the chain-rule transformation of gradients

$$\frac{\partial E}{\partial \varphi_\mu} = \sum_{pq} \frac{\partial E}{\partial Q_{pq}} \frac{\partial Q_{pq}}{\partial \varphi_\mu} \tag{1}$$

from the variables $\mathbf{Q}$ to the essential variables $\{\boldsymbol{\varphi}\}$. If computed in a straightforward way, this would require up to $O(N_e m^2)$ or $O(m^4)$ effort to compute and store the full set of transformation elements $\partial Q_{pq}/\partial \varphi_\mu$. More efficient computational approaches for this gradient transformation are presented for all of the parametrizations.

Four different ways to parametrize $\mathbf{Q}$ in terms of the essential variables $\{\boldsymbol{\varphi}\}$ will be examined and discussed: the exponential representation, the Householder reflector representation, the Givens rotation representation, and the rational Cayley transform representation. The construction of $\mathbf{Q}$ in terms of $\{\boldsymbol{\varphi}\}$, denoted $\mathbf{Q}(\boldsymbol{\varphi})$, and the extraction of $\{\boldsymbol{\varphi}\}$ for a given $\mathbf{Q}$, denoted $\boldsymbol{\varphi}(\mathbf{Q})$, will be examined for all of the parametrizations.

This topic has been discussed recently in the specific context of representation of wave functions within the graphically contracted function (GCF) electronic structure method[44] using Householder reflectors. In the present work, this discussion is expanded in a general context to also include the exponential, Givens rotation, and rational Cayley transform parametrizations of orthogonal matrices. Once a parametrization of $\mathbf{Q}$ has been chosen, all of the methods discussed in this work allow for the interpolation and extrapolation in terms of those parameters. For example, given a $\mathbf{Q}_0(\boldsymbol{\varphi}_0)$ and a $\mathbf{Q}_1(\boldsymbol{\varphi}_1)$, a smooth representation for intermediate orthogonal matrices may be defined as $\mathbf{Q}(t) \equiv \mathbf{Q}(\boldsymbol{\varphi}(t))$ with $\boldsymbol{\varphi}(t=0) = \boldsymbol{\varphi}_0$ and $\boldsymbol{\varphi}(t=1) = \boldsymbol{\varphi}_1$. Two such interpolation forms are $\boldsymbol{\varphi}(t) = t\boldsymbol{\varphi}_1 + (1-t)\boldsymbol{\varphi}_0$ or $\boldsymbol{\varphi}(t) = \sin(t\pi/2)\boldsymbol{\varphi}_1 + \cos(t\pi/2)\boldsymbol{\varphi}_0$. These kinds of one-dimensional interpolations may be used for line searches within various optimization procedures.[45] Other functional forms may be chosen as appropriate to model any known cyclic and/or asymptotic behaviors, and the interpolations may be extended in a straightforward way to multiple dimensions. One particularly important application of multidimensional interpolation is the DIIS method[39,46−49] used for convergence acceleration and to damp oscillatory behavior of iterative procedures; once the orthogonal matrix is parametrized using any of the four parametrizations discussed in this work, DIIS may be applied within that framework, and the interpolated result will automatically satisfy the orthonormality conditions. This parametrized orthogonal interpolation can be contrasted to the simple interpolation of the matrix elements, e.g. $\mathbf{Q}(t) = t\mathbf{Q}_1 + (1-t)\mathbf{Q}_0$, for which the intermediate matrices $\mathbf{Q}(t)$ are not orthogonal, and a subsequent orthonormalization step would be required. Other applications of interpolation within quantum chemistry include the smooth graphical representation of wave functions, densities, molecular structures, and other molecular properties and the smooth propagation of wave functions along chemical reaction paths based on sets of discrete points.[25,50] Smooth interpolations are used in the study of avoided crossings and cusps of potential energy surfaces; a change of sign while following the adiabatic electronic wave function around a closed loop demonstrates the existence of a cusp within that loop.[51,52] Interpolated or extrapolated wave functions are also used to generate initial guesses for iterative optimization procedures, and in exceptional situations they may substitute for wave functions at particular geometries for which the underlying iterative optimization procedure fails.[53]

2. DISCUSSION

2.1. General Background. Before discussing the specific parametrizations of orthogonal matrices, some common background and notations are introduced. First, note that the product of two real square ($n = m$) orthogonal matrices is itself an orthogonal matrix: if $\mathbf{Q}_3 = \mathbf{Q}_1\mathbf{Q}_2$, then $\mathbf{Q}_3^{\mathrm{T}}\mathbf{Q}_3 = \mathbf{Q}_2^{\mathrm{T}}\mathbf{Q}_1^{\mathrm{T}}\mathbf{Q}_1\mathbf{Q}_2 = \mathbf{1}$. The set of all such matrices thereby forms a group under matrix multiplication, and that group is the orthogonal group of order n, denoted $\mathrm{O}(n)$. The relation $1 = \det(\mathbf{Q}^{\mathrm{T}}\mathbf{Q}) = \det(\mathbf{Q})^2$ shows that $\det(\mathbf{Q}) = \pm 1$. The subset of matrices with $\det(\mathbf{Q}) = +1$ is closed under multiplication, so these matrices form a subgroup of $\mathrm{O}(n)$ called the special orthogonal group or the rotation group, denoted $\mathrm{SO}(n)$. The subset of matrices with $\det(\mathbf{Q}) = -1$ is not closed under multiplication; these matrices are called reflectors, improper rotations, or rotary reflections. There is no continuous transformation of underlying parameters that results in a smooth transition within $\mathrm{O}(n)$ between the rotation matrices with $\det(\mathbf{Q}) = +1$ and the reflection matrices with $\det(\mathbf{Q}) = -1$. The parametrizations discussed in this work are then effectively restricted to either one or the other of these subsets of matrices at any one time. In two dimensions, examples of these matrices may be written as

$$\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \in \mathrm{SO}(2) \subset \mathrm{O}(2) \tag{2}$$

and

$$\begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \in \mathrm{O}(2) \tag{3}$$

Note that there is no angle θ for which these two matrices are equal. Matrices of the SO(2) form in eq 2 are called plane rotations, and they will occur frequently in the following discussions. It may be verified that the matrix rotates a point $\binom{x}{y}$ clockwise about the origin by the angle θ. Every possible plane rotation matrix can be written in the form of eq 2 with the essential variable θ, but due to the cyclic nature of the trigonometric functions, there is a many-to-one mapping from θ onto the set of rotation matrices. In the general case, a plane rotation can be defined within a larger dimension; such a plane rotation matrix is denoted $\mathbf{G}(i, j, \theta) \in \mathbb{R}^{m\times m}$ for $m \geq i > j > 0$ and is defined with the nonzero matrix elements

$$\begin{aligned} G(i,j,\theta)_{ii} &= G(i,j,\theta)_{jj} = \cos\theta \\ G(i,j,\theta)_{ji} &= -G(i,j,\theta)_{ij} = \sin\theta \quad \text{for } i > j \\ G(i,j,\theta)_{kk} &= 1 \quad \text{for } k \notin \{i,j\} \end{aligned} \tag{4}$$

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Note that $\mathbf{G}(i,j,\theta)^{-1} = \mathbf{G}(i,j,-\theta) = \mathbf{G}(i,j,\theta)^{\mathrm{T}}$ and that $\mathbf{G}(i,j,\theta_1)\mathbf{G}(i,j,\theta_2) = \mathbf{G}(i,j,\theta_1+\theta_2)$. A useful practical feature of plane rotations is that a matrix-vector product $\mathbf{x} \leftarrow \mathbf{G}(i,j,\theta)\mathbf{x}$ may be computed in-place with only 6 floating point operations (FLOPs), and a more general matrix−matrix product $\mathbf{A} \leftarrow \mathbf{G}(i,j,\theta)\mathbf{A}$ with $\mathbf{A} \in \mathbb{R}^{m\times n}$ may be computed in-place with only $6n$ FLOPs, independent of the dimension m; in both cases, only the rows i and j are accessed and modified by the operation. The matrix $\mathbf{G}'(i,j,\theta) \equiv d\mathbf{G}(i,j,\theta)/d\theta$ has only four nonzero elements, given by

$$G'(i,j,\theta)_{ii} = G'(i,j,\theta)_{jj} = -\sin\theta$$
$$G'(i,j,\theta)_{ji} = -G'(i,j,\theta)_{ij} = \cos\theta \quad \text{for } i > j \tag{5}$$

Skew-symmetric matrices satisfy $\mathbf{X} = -\mathbf{X}^{\mathrm{T}}$ with $\mathbf{X} \in \mathbb{R}^{m\times m}$. The matrix $\mathbf{E}^{jk}$ for $j > k$ is defined as a skew-symmetric matrix that has only two nonzero elements

$$E^{jk}_{pq} = \delta_{pj}\delta_{qk} - \delta_{pk}\delta_{qj} \tag{6}$$

These matrices form a basis in which an arbitrary skew-symmetric matrix $\mathbf{X}$ may be expanded

$$\mathbf{X} = \sum_{j>k} X_{jk}\mathbf{E}^{jk} \tag{7}$$

in terms of its unique matrix elements. This expansion results in the relation

$$\frac{\partial \mathbf{X}}{\partial X_{jk}} = \mathbf{E}^{jk} \tag{8}$$

From eqs 4, 5, and 6, it may be verified that

$$\mathbf{G}(i,j,\theta)\mathbf{G}'(i,j,\theta)^{\mathrm{T}} = \mathbf{E}^{ij} \tag{9}$$

It is sometimes useful to consider a rectangular target matrix $n < m$ to be the product of a square orthogonal matrix and a rectangular matrix of the form

$$\mathbf{Q}^{m\times n} = \tilde{\mathbf{Q}}^{m\times m}\mathbf{1}^{m\times n} \tag{10}$$

in which the rectangular matrix $\mathbf{1}^{m\times n} = (\mathbf{e}_1\mathbf{e}_2...\mathbf{e}_n)$ is composed of the first n columns of the unit matrix. Such a matrix satisfies $\mathbf{Q}^{\mathrm{T}}\mathbf{Q} = \mathbf{1}^{n\times n}$, but $\mathbf{Q}\mathbf{Q}^{\mathrm{T}} \neq \mathbf{1}^{m\times m}$. In fact, the product $\mathbf{P} = \mathbf{Q}\mathbf{Q}^{\mathrm{T}} \in \mathbb{R}^{m\times m}$ is a projection matrix of rank n; $\mathbf{P}^2 = \mathbf{Q}\mathbf{Q}^{\mathrm{T}}\mathbf{Q}\mathbf{Q}^{\mathrm{T}} = \mathbf{P}$, and $\mathbf{P}$ has n unity eigenvalues corresponding to span($\mathbf{Q}$) and $(m - n)$ null eigenvalues corresponding to the orthogonal complement.

2.2. Exponential Parametrization. Matrix exponentials have been studied extensively, formally and numerically, within many application areas.[37−39,54−56] (See section 2.2.4 of ref 57 for a brief summary of the computation of the matrix exponential in the context of orbital coefficients.) In this section, a square or rectangular orthogonal matrix $\mathbf{Q} \in \mathbb{R}^{m\times n}$ for $n \leq m$ may be parametrized in terms of the elements of the skew-symmetric matrix $\mathbf{X} \in \mathbb{R}^{m\times m}$.

$$\mathbf{Q} = \exp(\mathbf{X})\mathbf{1}^{m\times n} \tag{11}$$

In the square case, $n = m$, the orthogonality follows from $\exp(\mathbf{X})^{\mathrm{T}} = \exp(\mathbf{X}^{\mathrm{T}}) = \exp(-\mathbf{X}) = \exp(\mathbf{X})^{-1}$. The matrices $\mathbf{Q}$ and $\mathbf{X}$ are normal, each commutes with its transpose, so they may be diagonalized with a complex unitary matrix $\mathbf{U}$. Consider an eigenvector $\mathbf{u}_j$ of the matrix $\mathbf{X}$:

$$\mathbf{X}\mathbf{u}_j = \mathbf{u}_j\lambda_j \tag{12}$$

Taking the complex conjugate of this equation gives

$$\mathbf{X}\mathbf{u}_j^* = \mathbf{u}_j^*\lambda_j^* \tag{13}$$

showing that $\mathbf{u}_j^*$ is also an eigenvector of $\mathbf{X}$. The nonzero eigenvalues must thereby occur in complex conjugate pairs, and the eigenvectors associated with zero eigenvalues may be chosen to be real. The matrix $i\mathbf{X}$ is Hermitian with real eigenvalues, so the nonzero eigenvalues of $\mathbf{X}$ must be purely imaginary, $\lambda_j = -\lambda_j^*$. The full set of eigenvalues may then be written as $\{\boldsymbol{\lambda}\} = \{\pm i\theta_1, \pm i\theta_2, ..., \pm i\theta_k, 0_{2k+1}, ..., 0_m\}$ with real θ_j. When m is odd, there is at least one zero eigenvalue. The series expansion

$$\mathbf{Q} = \exp(\mathbf{X}) = \mathbf{1} + \mathbf{X} + \frac{1}{2}\mathbf{X}^2 + \frac{1}{3!}\mathbf{X}^3 + ... \tag{14}$$
$$= \mathbf{1} + \mathbf{U}\boldsymbol{\lambda}\mathbf{U}^\dagger + \frac{1}{2}(\mathbf{U}\boldsymbol{\lambda}\mathbf{U}^\dagger)^2 + \frac{1}{3!}(\mathbf{U}\boldsymbol{\lambda}\mathbf{U}^\dagger)^3 + ... \tag{15}$$
$$= \mathbf{U}\left(\mathbf{1} + \boldsymbol{\lambda} + \frac{1}{2}\boldsymbol{\lambda}^2 + \frac{1}{3!}\boldsymbol{\lambda}^3 + ...\right)\mathbf{U}^\dagger = \mathbf{U}\exp(\boldsymbol{\lambda})\mathbf{U}^\dagger \tag{16}$$

shows that an eigenvector $\mathbf{u}_j$ corresponds to an eigenvalue $\lambda_j = i\theta_j$ of $\mathbf{X}$ and to an eigenvalue $\omega_j = \exp(i\theta_j) = \cos\theta_j + i\sin\theta_j$ of the matrix $\mathbf{Q}$. The determinant of $\mathbf{Q}$ is given by

$$\det(\mathbf{Q}) = \prod_j \exp(\lambda_j) = \exp(\sum_j \lambda_j) = \exp(\mathrm{tr}(\mathbf{X}))$$
$$= \exp(0) = +1 \tag{17}$$

Thus, the square matrices $\mathbf{Q}$ that are defined by eq 14 belong to SO(n). For square $\mathbf{Q}$, the essential parameters $\{\boldsymbol{\varphi}\}$ correspond to the $m(m-1)/2$ unique (e.g., lower-triangular) elements of the matrix $\mathbf{X}$. For the rectangular case, $n < m$, the parameters in the Grassmann manifold $N_e = (m-n)n$ correspond to the block off-diagonal (BOD) elements $\{\boldsymbol{\varphi}\} = \{X_{ij}: j = 1, ..., n; i = n+1, ..., m\}$, and the parameters in the Stiefel manifold $N_e = mn - n(n+1)/2$ correspond to the strictly lower-trapezoidal elements $\{\boldsymbol{\varphi}\} = \{X_{ij}: j = 1, ..., n; i = j+1, ..., m\}$.

Consider the spectral resolution of the matrix $\mathbf{X}$

$$\mathbf{X} = \mathbf{U}\lambda\mathbf{U}^\dagger = \sum_j \lambda_j\mathbf{u}_j\mathbf{u}_j^\dagger \tag{18}$$

with the pairwise unitary transformations

$$(\mathbf{u}_j, \mathbf{u}_j^*) = (\mathbf{x}_j, \mathbf{y}_j)\begin{pmatrix}1 & 1\\ i & -i\end{pmatrix}\frac{1}{\sqrt{2}} \tag{19}$$

for $\mathbf{x}_j, \mathbf{y}_j \in \mathbb{R}^m$. The contribution in eq 18 of each pair of complex conjugate eigenvalues can then be written as

$$(\mathbf{u}_j, \mathbf{u}_j^*)\begin{pmatrix}i\theta_j & 0\\ 0 & -i\theta_j\end{pmatrix}\begin{pmatrix}\mathbf{u}_j^\dagger\\ \mathbf{u}_j^{*\dagger}\end{pmatrix} = (\mathbf{x}_j, \mathbf{y}_j)\begin{pmatrix}0 & \theta_j\\ -\theta_j & 0\end{pmatrix}\begin{pmatrix}\mathbf{x}_j^{\mathrm{T}}\\ \mathbf{y}_j^{\mathrm{T}}\end{pmatrix} \tag{20}$$

This shows that the matrix $\mathbf{X}$ can be factored as $\mathbf{X} = \mathbf{V}\mathbf{D}\mathbf{V}^{\mathrm{T}}$ with $\mathbf{V}$ orthogonal and where the real skew-symmetric matrix $\mathbf{D}$ is block diagonal with skew-symmetric 2×2 subblocks of the form in eq 20, or 1×1 subblocks with zero entries. This is called a *quasidiagonal orthogonal factorization* of the matrix $\mathbf{X}$. The exponential matrix $\mathbf{Q}$ may be computed as $\exp(\mathbf{X}) = \mathbf{V}\exp(\mathbf{D})\mathbf{V}^{\mathrm{T}}$. The exponential of a 1×1 subblock is

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simply $\exp(0) = 1$, and the exponential of a 2×2 subblock is given by

$$\exp\begin{pmatrix} 0 & \theta_j \\ -\theta_j & 0 \end{pmatrix} = \begin{pmatrix} \cos\theta_j & \sin\theta_j \\ -\sin\theta_j & \cos\theta_j \end{pmatrix} \tag{21}$$

which is a plane rotation as in eq 2. Note that the exponential operator is a many-to-one mapping because all of the angles $\theta_j + 2\pi k$ for integer k result in the same plane rotation matrix in eq 21. The practical advantage of this representation is that only real arithmetic is required for the computation of the matrix exponential. The real quasidiagonal factorization of the skew-symmetric matrix $\mathbf{X}$ is described by Ward and Gray[58] in ACM TOMS algorithm 530. This algorithm consists of three steps: the first step brings $\mathbf{X}$ to skew-symmetric tridiagonal form and requires about $4m^3/3$ FLOPs effort; the second step is iterative and brings the tridiagonal matrix to block diagonal form $\mathbf{D}$ and requires about $7m^3/2$ FLOPs, although the 1×1 blocks can reduce this effort; the final step computes the real vectors $\mathbf{V}$ and requires about $4m^3/3$ effort. The total quasidiagonal factorization effort is about $6m^3$ FLOPs. The computation of the matrix exponential from these factors then requires an additional $2m^3$ FLOPs, for a total of about $8m^3$ FLOPs effort.

Given a square orthogonal $\mathbf{Q} \in \mathbb{R}^{m\times m}$ with $\det(\mathbf{Q}) = +1$, the above procedure may be reversed in order to compute $\mathbf{X}$. This is a special case of the matrix logarithm. The initial factorization is accomplished with the LAPACK routines[59,60] xGEES (x = S or D for single and double precision respectively). This routine generally factors an arbitrary real matrix into the real Schur form $\mathbf{Q} = \mathbf{V}\mathbf{T}\mathbf{V}^{\mathrm{T}}$, where $\mathbf{V}$ is orthogonal and where the matrix $\mathbf{T}$ is real block upper-triangular with diagonal 2×2 subblocks that correspond to pairs of complex conjugate eigenvalues, and with diagonal 1×1 subblocks that correspond to real eigenvalues. However, in this situation, $\mathbf{T}$ must be orthogonal because it is equivalent to the product of the orthogonal matrices $\mathbf{T} = \mathbf{V}^{\mathrm{T}}\mathbf{Q}\mathbf{V}$, and it follows from the relations $\mathbf{T}\mathbf{T}^{\mathrm{T}} = \mathbf{T}^{\mathrm{T}}\mathbf{T} = \mathbf{1}$ that the off-diagonal subblocks must be zero. The matrix $\mathbf{T}$ is thereby a real quasidiagonal orthogonal matrix with $\det(\mathbf{T}) = +1$. The skew-symmetric matrix $\mathbf{X}$ is then computed as $\mathbf{X} = \log(\mathbf{Q}) = \mathbf{V}\log(\mathbf{T})\mathbf{V}^{\mathrm{T}}$. The 1×1 diagonal subblocks with positive eigenvalues are computed as $\log(+1) = 0$, and the corresponding vectors do not contribute to $\mathbf{X}$. The 2×2 diagonal subblocks are computed according to

$$\log\begin{pmatrix} \cos\theta_j & \sin\theta_j \\ -\sin\theta_j & \cos\theta_j \end{pmatrix} = \begin{pmatrix} 0 & \theta_j \\ -\theta_j & 0 \end{pmatrix} \tag{22}$$

which is the inverse operation of eq 21. The phases of the Schur vectors $\mathbf{v}_j$ are arbitrary, so the computed θ_j may lie in any of the four quadrants. Because $\det(\mathbf{T}) = +1$, the 1×1 diagonal subblocks with eigenvalues of −1 must occur in pairs. Consequently, pairs of these subblocks with negative eigenvalues may be taken together to form a 2×2 subblock, and the logarithm may be computed as in eq 22 with $\theta_j = (\pm\pi, \pm 3\pi, \ldots)$. Thus, in all cases, the principal values may be taken in the range $-\pi < \theta_j \leq \pi$ and the corresponding matrix logarithm contribution is real skew-symmetric. When eigenvalues are repeated, the computed $\mathbf{X}$ satisfies $\mathbf{Q} = \exp(\mathbf{X})$, but the associated Schur vectors $\mathbf{v}_j$ are not unique. When repeated eigenvalues result in nonzero θ_j, as occurs for example with multiple 2×2 $\theta_j = \pi$ subblocks, then the resulting contributions to $\mathbf{X}$ are not unique, but are defined only to within a similarity transformation within the degenerate subspace. The Schur decomposition of $\mathbf{Q}$ requires about $25m^3$ FLOPs effort, and the matrix logarithm requires an additional $2m^3$ FLOPs, for about $27m^3$ FLOPs total effort for the computation of $\mathbf{X}(\mathbf{Q})$. This is significantly more than the $\mathbf{Q}(\mathbf{X})$ computational effort discussed above.

With this discussion of the Schur decomposition in mind, consider again the factorization of the skew-symmetric matrix, $\mathbf{X} = \mathbf{V}\mathbf{T}\mathbf{V}^{\mathrm{T}}$, where $\mathbf{T}$ is block upper-triangular, and the Schur vectors $\mathbf{V}$ are orthogonal. From the expression $\mathbf{T} = \mathbf{V}^{\mathrm{T}}\mathbf{X}\mathbf{V}$, it follows that $\mathbf{T} = -\mathbf{T}^{\mathrm{T}}$, and $\mathbf{T}$ must be block-diagonal and skew-symmetric. Therefore, the LAPACK subroutine xGEES could also be used to compute the matrix exponential as $\exp(\mathbf{X}) = \mathbf{V}\exp(\mathbf{T})\mathbf{V}^{\mathrm{T}}$. The result is equivalent to the Ward and Gray factorization[58] discussed above, except possibly for the order of the individual vectors, the vector phases, and the signs of the elements of the quasidiagonal $\mathbf{T}$, none of which affect the final result $\exp(\mathbf{X})$. However, in contrast to the general Schur decomposition algorithm, the Ward and Gray algorithm fully exploits the skew-symmetric nature of the intermediate results.

Consider next the important special case of the matrix exponential $\exp(\mathbf{X})$ with BOD $\mathbf{X}$ of the form

$$\mathbf{X} = \begin{pmatrix} \mathbf{0} & -\mathbf{A}^{\mathrm{T}} \\ \mathbf{A} & \mathbf{0} \end{pmatrix} \tag{23}$$

where $\mathbf{A} \in \mathbb{R}^{p\times n}$ with $p = (m - n)$. This form arises in many situations.[37−39] The importance is associated with the representation of general orthogonal matrices in the factored form

$$\mathbf{Q} = \exp(\mathbf{X})\exp(\mathbf{Y}) = \exp\begin{pmatrix} \mathbf{0} & -\mathbf{A}^{\mathrm{T}} \\ \mathbf{A} & \mathbf{0} \end{pmatrix}\exp\begin{pmatrix} \mathbf{Y}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{Y}_2 \end{pmatrix} \tag{24}$$

with the skew-symmetric matrices $\mathbf{Y}_1 \in \mathbb{R}^{n\times n}$ and $\mathbf{Y}_2 \in \mathbb{R}^{p\times p}$. This allows the $m(m-1)/2$ degrees of freedom in the matrix $\mathbf{Q}$ to be separated into the $N_e = pn$ *essential* variables in $\mathbf{A}$ and the $n(n-1)/2 + p(p-1)/2$ *redundant* variables in the $\mathbf{Y}_1$ and $\mathbf{Y}_2$ matrices. One example of this separation is the representation of molecular orbitals in electronic structure calculations; for certain expansion forms, the wave function does not depend on the redundant rotations among the first n orbitals, associated with the $\mathbf{Y}_1$ parameters, or on the redundant rotations among the remaining p orbitals, associated with the $\mathbf{Y}_2$ parameters, but it does depend on the essential rotations between these two orbital spaces that are associated with the $\mathbf{X}$ parameters. The CISD and CCSD expansions are two common examples of wave functions that display this kind of orbital invariance.

Consider first the computation of the orthogonal matrix $\tilde{\mathbf{Q}} \in \mathbb{R}^{m\times m}$

$$\tilde{\mathbf{Q}} = \exp(\mathbf{X}) = \exp\begin{pmatrix} \mathbf{0} & -\mathbf{A}^{\mathrm{T}} \\ \mathbf{A} & \mathbf{0} \end{pmatrix} \tag{25}$$

This may of course be computed using the general decomposition approach discussed above by simply ignoring the BOD form of $\mathbf{X}$, but this may be inefficient, for example, when $n \ll m$ or when $n \approx m$. In order to exploit the sparsity in $\mathbf{X}$, the singular value decomposition (SVD) of the matrix $\mathbf{A}$ is computed

$$\mathbf{A} = \mathbf{V}\boldsymbol{\theta}\mathbf{W}^{\mathrm{T}} \tag{26}$$

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The SVD of a general real matrix may be computed with the LAPACK subroutines xGESVD. There are two separate decompositions in this form that are considered. The first is when $\mathbf{V} \in \mathbb{R}^{p\times n}$ satisfies $\mathbf{V}^{\mathrm{T}}\mathbf{V} = \mathbf{1}$, $\boldsymbol{\theta} \in \mathbb{R}^{n\times n}$ is diagonal, and $\mathbf{W}^{\mathrm{T}} \in \mathbb{R}^{n\times n}$ is orthogonal; in this case, the SVD in eq 26 requires about $6pn^2 + 20n^3$ FLOPs effort.[73] The second is when $\mathbf{V} \in \mathbb{R}^{p\times p}$ is orthogonal, $\boldsymbol{\theta} \in \mathbb{R}^{p\times p}$ is diagonal, and $\mathbf{W}^{\mathrm{T}} \in \mathbb{R}^{p\times n}$ satisfies $\mathbf{W}^{\mathrm{T}}\mathbf{W} = \mathbf{1}$; in this case, the SVD in eq 26 requires about $6p^2n + 20p^3$ FLOPs effort. In both cases the singular values are nonnegative, $0 \le \theta_j$. There are at most $\min(n,p)$ nonzero singular values of $\mathbf{A}$. Consequently, the first decomposition form is more compact when $n < p$, and the second is more compact when $n > p$. With this SVD, the expansion of the exponential results in

$$\exp(\mathbf{X}) = \tilde{\mathbf{Q}} = \begin{pmatrix} \mathbf{1}^{n\times n} + \mathbf{W}(\cos(\boldsymbol{\theta}) - \mathbf{1})\mathbf{W}^{\mathrm{T}} & -\mathbf{W}\sin(\boldsymbol{\theta})\mathbf{V}^{\mathrm{T}} \\ \mathbf{V}\sin(\boldsymbol{\theta})\mathbf{W}^{\mathrm{T}} & \mathbf{1}^{p\times p} + \mathbf{V}(\cos(\boldsymbol{\theta}) - \mathbf{1})\mathbf{V}^{\mathrm{T}} \end{pmatrix} \tag{27}$$

Note that each of the diagonal subblocks of this matrix is symmetric, and that the off-diagonal subblocks together satisfy $\tilde{\mathbf{Q}}_{12} = -\tilde{\mathbf{Q}}_{21}^{\mathrm{T}}$.

When $\mathbf{W}$ is square orthogonal, then the first diagonal subblock of eq 27 may be computed in the simpler form $\mathbf{W}\cos(\boldsymbol{\theta})\mathbf{W}^{\mathrm{T}}$, and similarly when $\mathbf{V}$ is square, then the second diagonal subblock may be computed as $\mathbf{V}\cos(\boldsymbol{\theta})\mathbf{V}^{\mathrm{T}}$. Consider the special case when $n = p = m/2$, and both of these simplifications can be applied. In this case, the matrix $\tilde{\mathbf{Q}}$ takes the simple form

$$\tilde{\mathbf{Q}} = \begin{pmatrix} \mathbf{W} & \mathbf{0} \\ \mathbf{0} & \mathbf{V} \end{pmatrix} \begin{pmatrix} \cos(\boldsymbol{\theta}) & -\sin(\boldsymbol{\theta}) \\ \sin(\boldsymbol{\theta}) & \cos(\boldsymbol{\theta}) \end{pmatrix} \begin{pmatrix} \mathbf{W}^{\mathrm{T}} & \mathbf{0} \\ \mathbf{0} & \mathbf{V}^{\mathrm{T}} \end{pmatrix} \tag{28}$$

This matrix factorization may be brought to the quasidiagonal form discussed above with a "perfect shuffle permutation," $\{k \to 2k-1 : k \le n\}$ and $\{k \to 2(k-n) : k > n\}$, of the columns of the first matrix, the rows and columns of the middle matrix, and the rows of the last matrix.

Given the arrays $\mathbf{Y}_1$ and $\mathbf{Y}_2$ in eq 24, the computation of the redundant factor $\exp(\mathbf{Y})$ is achieved with the general Ward and Gray factorization algorithm applied to each of the diagonal subblocks individually.

$$\exp(\mathbf{Y}) = \exp\begin{pmatrix} \mathbf{Y}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{Y}_2 \end{pmatrix} = \begin{pmatrix} \exp(\mathbf{Y}_1) & \mathbf{0} \\ \mathbf{0} & \exp(\mathbf{Y}_2) \end{pmatrix} = \begin{pmatrix} \mathbf{Z}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{Z}_2 \end{pmatrix} = \mathbf{Z} \tag{29}$$

with block-diagonal (BD) $\mathbf{Z}$. This allows the target matrix $\mathbf{Q}$ to be computed as the product $\mathbf{Q} = \tilde{\mathbf{Q}}\mathbf{Z}$.

$$\mathbf{Q} = \begin{pmatrix} \tilde{\mathbf{Q}}_{11} & \tilde{\mathbf{Q}}_{12} \\ \tilde{\mathbf{Q}}_{21} & \tilde{\mathbf{Q}}_{22} \end{pmatrix} \begin{pmatrix} \mathbf{Z}_1 & \mathbf{0} \\ \mathbf{0} & \mathbf{Z}_2 \end{pmatrix} = \begin{pmatrix} \tilde{\mathbf{Q}}_{11}\mathbf{Z}_1 & \tilde{\mathbf{Q}}_{12}\mathbf{Z}_2 \\ \tilde{\mathbf{Q}}_{21}\mathbf{Z}_1 & \tilde{\mathbf{Q}}_{22}\mathbf{Z}_2 \end{pmatrix} \tag{30}$$

This factorization form, which results from the combination of eqs 27 and 29, is related to the cosine−sine decomposition[61,62] (CSD) of an orthogonal matrix, a feature that is used below.

There are two cases to consider when only the first n columns of $\mathbf{Q}$ are required. In the first rectangular case, $n < m$, the matrix $\mathbf{Q}$ belongs to the Stiefel manifold with $N_e = mn - n(n+1)/2$ degrees of freedom. An example of this is an arbitrary electronic wave function that depends only on the first n active orbitals, and the remaining p orbitals are unoccupied; in this case, $\mathbf{Q}$ defines the expansion of the n active orbitals in terms of the underlying orthogonal orbital basis of dimension m. The second case is when the underlying mathematical problem depends only on span($\mathbf{Q}$), in which case this Grassmann manifold is characterized by $N_e = pn$ degrees of freedom. An example of this is the closed-shell HF wave function that depends only on the space spanned by the orbital coefficients of the first n occupied orbitals and that does not depend on the remaining p unoccupied orbitals. With the exponential parametrization, the BOD form for $\mathbf{X}$ thereby contains exactly the correct number of essential variables to characterize the Grassmann manifold. The factorization is written as

$$\mathbf{Q} = \exp(\mathbf{X})\begin{pmatrix} \mathbf{Z} \\ \mathbf{0} \end{pmatrix} = \exp(\mathbf{X})\mathbf{1}^{m\times n}\mathbf{Z} = \tilde{\mathbf{Q}}\mathbf{Z} \tag{31}$$

where $\mathbf{Z} \in \mathbb{R}^{n\times n}$ is an orthogonal matrix. With this BOD $\mathbf{X}$, the matrix $\exp(\mathbf{X})\mathbf{1}^{m\times n}$ parametrizes the Grassmann manifold and is represented by the specific matrix $\tilde{\mathbf{Q}} \in \mathbb{R}^{m\times n}$. The redundant transformation $\mathbf{Z}$ may be parametrized with $n(n-1)/2$ parameters, and this accounts exactly for the difference in the number of degrees of freedom in the orthogonal matrices $\tilde{\mathbf{Q}}$ and $\mathbf{Q}$. It is straightforward to compute the matrices $\mathbf{Q} \in \mathbb{R}^{m\times n}$, $\tilde{\mathbf{Q}} \in \mathbb{R}^{m\times n}$, and $\mathbf{Z} \in \mathbb{R}^{n\times n}$ from the appropriate $\mathbf{Q}_{11}$ and $\mathbf{Q}_{21}$ subblocks of eqs 27 and 29 with no extraneous effort associated with the unrequired $\mathbf{Q}_{12}$ and $\mathbf{Q}_{22}$ subblocks. The computation of $\tilde{\mathbf{Q}} \in \mathbb{R}^{m\times n}$ for the Grassmann manifold requires about $8mn^2 + 22n^3$ FLOPs effort, and the computation of $\mathbf{Q} \in \mathbb{R}^{m\times n}$ for the Stiefel manifold in this factored form requires about $8mn^2 + 30n^3$ FLOPs effort.

Given an orthogonal $\mathbf{Q} \in \mathbb{R}^{m\times n}$ for $n < m$, this procedure can be reversed in order to compute the matrices $\mathbf{X}$ and $\mathbf{Z}$. First consider the partitioning $\mathbf{Q} = \begin{pmatrix} \mathbf{Q}_1 \\ \mathbf{Q}_2 \end{pmatrix}$. The orthonormality condition results in $\mathbf{1}^{n\times n} = \mathbf{Q}^{\mathrm{T}}\mathbf{Q} = \mathbf{Q}_1^{\mathrm{T}}\mathbf{Q}_1 + \mathbf{Q}_2^{\mathrm{T}}\mathbf{Q}_2$. The matrix $(\mathbf{Q}_1^{\mathrm{T}}\mathbf{Q}_1)$ is real symmetric, and it can be diagonalized by an orthogonal matrix $\mathbf{Y}^{\mathrm{T}}(\mathbf{Q}_1^{\mathrm{T}}\mathbf{Q}_1)\mathbf{Y} = \boldsymbol{\lambda}$ with $0 \le \lambda_j \le 1$. It follows that

$$\mathbf{Y}^{\mathrm{T}}(\mathbf{Q}_2^{\mathrm{T}}\mathbf{Q}_2)\mathbf{Y} = \mathbf{1} - \boldsymbol{\lambda} \tag{32}$$

Thus, both matrices are diagonalized by the same matrix $\mathbf{Y}$, and the corresponding eigenvalues of the two matrices are complementary. The eigenvectors $\mathbf{Y}$ are also the right singular vectors of the matrices $\mathbf{Q}_1$ and $\mathbf{Q}_2$. The matrix $\mathbf{Q}$ can then be written as

$$\mathbf{Q} = \begin{pmatrix} \mathbf{Q}_1 \\ \mathbf{Q}_2 \end{pmatrix} = \begin{pmatrix} \mathbf{W}\cos(\theta)\mathbf{Y}^{\mathrm{T}} \\ \mathbf{V}\sin(\theta)\mathbf{Y}^{\mathrm{T}} \end{pmatrix} \tag{33}$$

with $\cos^2(\theta_j) = \lambda_j$. This factorization form is the CSD[61,62] of the rectangular matrix $\mathbf{Q}$ and it allows the matrices $\mathbf{X}$ and $\mathbf{Z}$ to be computed as follows. First, the SVD is applied to the upper $n\times n$ subblock of $\mathbf{Q}$.

$$\mathbf{Q}_1 = \mathbf{W}\sigma\mathbf{Y}^{\mathrm{T}} = (\mathbf{W}\sigma\mathbf{W}^{\mathrm{T}})(\mathbf{W}\mathbf{Y}^{\mathrm{T}}) \tag{34}$$

This last expression is one way to compute the left polar decomposition[63,64] of the matrix $\mathbf{Q}_1$. The first factor is symmetric and the second factor is orthogonal. This factorization always exists, and it is unique when $\mathbf{Q}_1$ has nonzero singular values (i.e., when $\mathbf{Q}_1$ is invertible). The polar decomposition is

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closely related to the symmetric orthogonalization method of Löwdin.[65] This decomposition allows $\boldsymbol{\theta}$ to be computed as $\boldsymbol{\theta} = \arccos(\boldsymbol{\sigma})$ and $\mathbf{Z} = \mathbf{W}\mathbf{Y}^{\mathrm{T}}$. In exact arithmetic, $\sigma_j \leq 1$ should be satisfied from the SVD. However, floating point errors can result in small violations of this condition, and the computed values of σ_j should be clipped as necessary when computing θ_j. The angles θ_j in this computation are always in the first quadrant, but this places no limitations on the validity of the factorization; the phases of the columns of $\mathbf{W}$ and $\mathbf{Y}$ are adjusted to account for this condition as they are computed. The matrix $\mathbf{V}$ may be determined from the expression $\mathbf{V} = \mathbf{Q}_2\mathbf{Y}(\sin(\boldsymbol{\theta}))^{-1}$, and substitution into eq 26 gives

$$\mathbf{A} = \mathbf{Q}_2\mathbf{Y}(\sin(\boldsymbol{\theta}))^{-1}\boldsymbol{\theta}\mathbf{W}^{\mathrm{T}} \tag{35}$$

which then determines the BOD $\mathbf{X}$ in eq 25. The $\theta_j = 0$ situation is handled by taking the limiting value, $\lim_{\theta\to 0}\theta/\sin\theta = 1$. There are no other singularities in the first quadrant $0 \leq \theta_j \leq \pi/2$ that require special treatment in eq 35. It may be noted that with exact arithmetic there is an equivalent algebraic expression $\theta/\sin\theta = \theta/(1-\sigma^2)^{1/2}$; however, this alternative expression suffers from cancellations in floating point arithmetic when a singular value is near unity, $\sigma_j \approx 1$. This $\mathbf{X}(\mathbf{Q})$ computation requires $2(m + 13n)n^2$ FLOPs effort for the Grassmann parametrization, and $2(m + 14n)n^2$ FLOPs for the Stiefel parametrization in factored form. Recent versions of LAPACK, 3.5 and later,[60] include the routines xORCSD and xORCSD2BY1 for computing the full CSD and the 1-column block CSD, respectively. These routines can also be used to compute the $\mathbf{A}$ and $\mathbf{Z}$ matrices, and the computation of $\mathbf{X}(\mathbf{Q})$ would require about $8mn^2 + 18n^3$ FLOPs effort with this approach.

Another common factorization problem is the computation of the skew-symmetric matrix $\mathbf{X}$ and the orthogonal $\mathbf{Z} \in \mathbb{R}^{n\times n}$ that solves

$$\mathbf{U} = \exp(\mathbf{X})\mathbf{Q}\mathbf{Z} \tag{36}$$

given the matrices $\mathbf{U} \in \mathbb{R}^{m\times n}$ and $\mathbf{Q} \in \mathbb{R}^{m\times n}$. An orthogonal $\mathbf{V} \in \mathbb{R}^{m\times m}$ may be defined by appending p orthogonal columns to the matrix $\mathbf{Q}$.

$$\mathbf{V} = (\mathbf{Q}, \mathbf{Q}_\perp) \tag{37}$$

Equation 36 can then be transformed as

$$\tilde{\mathbf{U}} = \mathbf{V}^{\mathrm{T}}\mathbf{U} = \mathbf{V}^{\mathrm{T}}\exp(\mathbf{X})\mathbf{V}(\mathbf{V}^{\mathrm{T}}\mathbf{Q})\mathbf{Z} = \exp(\mathbf{V}^{\mathrm{T}}\mathbf{X}\mathbf{V})\mathbf{1}^{m\times n}\mathbf{Z} = \exp(\tilde{\mathbf{X}})\mathbf{1}^{m\times n}\mathbf{Z} \tag{38}$$

This transformed equation has the same form as eq 31 in which $\tilde{\mathbf{X}}$ has BOD form, and the desired $\mathbf{X}$ is thereby given by $\mathbf{X} = \mathbf{V}\tilde{\mathbf{X}}\mathbf{V}^{\mathrm{T}}$.

The chain-rule transformation of gradients eq 1 for $E(\mathbf{X}) \equiv E(\mathbf{Q}(\mathbf{X}))$ consists of

$$\frac{\partial E}{\partial X_{jk}} = \sum_{pq}\frac{\partial E}{\partial Q_{pq}}\frac{\partial Q_{pq}}{\partial X_{jk}} = \mathrm{tr}\left(\frac{\partial E}{\partial \mathbf{Q}}^{\mathrm{T}}\frac{\partial \mathbf{Q}}{\partial X_{jk}}\right) \tag{39}$$

from the variables $\mathbf{Q}$ to the essential variables $\mathbf{X}$ for $j > k$. If computed in a straightforward way, this would require up to $O(m^4)$ effort to compute and store the full set of transformation elements $\partial Q_{pq}/\partial X_{jk}$. These elements are defined as

$$\frac{\partial \mathbf{Q}}{\partial X_{jk}} = \lim_{h\to 0}\frac{1}{h}(\exp(\mathbf{X} + h\mathbf{E}^{jk}) - \exp(\mathbf{X})) \tag{40}$$

with $\mathbf{E}^{jk}$ given in eq 6. This derivative may be represented in various ways,[66,67] one of which is

$$\frac{\partial \mathbf{Q}}{\partial X_{jk}} = \int_0^1 \exp((1-t)\mathbf{X})\mathbf{E}^{jk}\exp(t\mathbf{X})\,\mathrm{d}t \tag{41}$$

Substitution into eq 39 then gives

$$\frac{\partial E}{\partial X_{jk}} = \mathrm{tr}\left(\mathbf{g}^{\mathrm{T}}\int_0^1 \exp((1-t)\mathbf{X})\mathbf{E}^{jk}\exp(t\mathbf{X})\,\mathrm{d}t\right) \tag{42}$$

$$= \mathrm{tr}\left(\mathbf{E}^{jk}\int_0^1 \exp(t\mathbf{X})\mathbf{g}^{\mathrm{T}}\exp((1-t)\mathbf{X})\,\mathrm{d}t\right) \tag{43}$$

$$= F_{kj} - F_{jk} \tag{44}$$

with $g_{pq} = \partial E/\partial Q_{pq}$ and

$$\mathbf{F} = \int_0^1 \exp((t\mathbf{X})\mathbf{g}^{\mathrm{T}}\exp((1-t)\mathbf{X})\,\mathrm{d}t \tag{45}$$

Equation 43 follows from application of the identity $\mathrm{tr}(\mathbf{AB}) = \mathrm{tr}(\mathbf{BA})$. Note that a single evaluation of the matrix $\mathbf{F}$ is sufficient to compute the entire gradient $\partial E/\partial \mathbf{X}$. Since only the lower triangle of the skew-symmetric component of $\mathbf{F}$ is required, the integral may be evaluated as

$$\mathbf{F}^{(-)} \equiv \mathbf{F}^{\mathrm{T}} - \mathbf{F} = \int_0^1 \exp(t\mathbf{X})\mathbf{g}^{(-)}\exp(-t\mathbf{X})\,\mathrm{d}t \tag{46}$$

with the skew-symmetric matrix $\mathbf{g}^{(-)} = (\mathbf{Q}^{\mathrm{T}}\mathbf{g} - \mathbf{g}^{\mathrm{T}}\mathbf{Q})$. The quasidiagonal factorization of the skew-symmetric $\mathbf{X}$ allows the matrix $\mathbf{F}^{(-)}$ to be written as

$$\mathbf{F}^{(-)} = \mathbf{V}\int_0^1 \exp(t\mathbf{D})(\mathbf{V}^{\mathrm{T}}\mathbf{g}^{(-)}\mathbf{V})\exp(-t\mathbf{D})\,\mathrm{d}t\,\mathbf{V}^{\mathrm{T}} = \mathbf{V}\tilde{\mathbf{F}}\mathbf{V}^{\mathrm{T}} \tag{47}$$

with the skew-symmetric

$$\tilde{\mathbf{F}} = \int_0^1 \exp(t\mathbf{D})\tilde{\mathbf{g}}\exp(-t\mathbf{D})\,\mathrm{d}t \tag{48}$$

and the skew-symmetric $\tilde{\mathbf{g}} = (\mathbf{V}^{\mathrm{T}}\mathbf{g}^{(-)}\mathbf{V})$. This may be evaluated according to the 1×1 and 2×2 subblocks of the quasidiagonal matrix $\mathbf{D}$. A pair of 1×1 subblocks, for which $D_p = D_q = 0$, result in

$$\tilde{F}^{pq} = \tilde{g}^{pq} \tag{49}$$

A 1×1 and a 2×2 subblock pair result in a contribution of the form

$$\tilde{\mathbf{F}}^{pq} = (\tilde{g}_1^{pq}, \tilde{g}_2^{pq})\int_0^1 \begin{pmatrix}\cos(t\theta_q) & -\sin(t\theta_q)\\ \sin(t\theta_q) & \cos(t\theta_q)\end{pmatrix}\mathrm{d}t \tag{50}$$

$$= (\tilde{g}_1^{pq}, \tilde{g}_2^{pq})\begin{pmatrix}\mathrm{sinc}\,\theta_q & -\mathrm{cosc}\,\theta_q\\ \mathrm{cosc}\,\theta_q & \mathrm{sinc}\,\theta_q\end{pmatrix} \tag{51}$$

with $\mathrm{sinc}(\theta) \equiv \sin\theta/\theta$ and $\mathrm{cosc}(\theta) \equiv (1-\cos\theta)/\theta$. In this equation and below, the identity $1 - \cos\theta = 2\sin^2(\theta/2)$ may be used to avoid floating point cancellation errors, e.g., for $\theta \approx 0, \pm 2\pi, \ldots$, in the evaluation of $\mathrm{cosc}(\theta)$. It follows that $\lim_{\theta_q\to 0}\tilde{\mathbf{F}}^{pq} = \tilde{\mathbf{g}}^{pq}$. A 2×2 and a 1×1 subblock pair

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result in

$$\tilde{\mathbf{F}}^{pq} = \int_0^1 \begin{pmatrix} \cos(t\theta_p) & \sin(t\theta_p) \\ -\sin(t\theta_p) & \cos(t\theta_p) \end{pmatrix} \mathrm{d}t \begin{pmatrix} \tilde{g}_1^{\,pq} \\ \tilde{g}_2^{\,pq} \end{pmatrix} \tag{52}$$

$$= \begin{pmatrix} \operatorname{sinc}\theta_p & \operatorname{cosc}\theta_p \\ -\operatorname{cosc}\theta_p & \operatorname{sinc}\theta_p \end{pmatrix} \begin{pmatrix} \tilde{g}_1^{\,pq} \\ \tilde{g}_2^{\,pq} \end{pmatrix} \tag{53}$$

It follows that $\lim_{\theta_p \to 0} \tilde{\mathbf{F}}^{pq} = \tilde{\mathbf{g}}^{pq}$. A pair of 2×2 subblocks result in

$$\tilde{\mathbf{F}}^{pq} = \int_0^1 \begin{pmatrix} \cos(t\theta_p) & \sin(t\theta_p) \\ -\sin(t\theta_p) & \cos(t\theta_p) \end{pmatrix} \begin{pmatrix} \tilde{g}_{11}^{\,pq} & \tilde{g}_{12}^{\,pq} \\ \tilde{g}_{21}^{\,pq} & \tilde{g}_{22}^{\,pq} \end{pmatrix} \begin{pmatrix} \cos(t\theta_q) & -\sin(t\theta_q) \\ \sin(t\theta_q) & \cos(t\theta_q) \end{pmatrix} \mathrm{d}t \tag{54}$$

The matrix elements are

$$\tilde{F}_{11}^{pq} = \tilde{g}_{11}^{\,pq} s_+^{pq} + \tilde{g}_{21} c_+^{pq} + \tilde{g}_{12} c_-^{pq} - \tilde{g}_{22}^{\,pq} s_-^{pq} \tag{55}$$

$$\tilde{F}_{21}^{pq} = -\tilde{g}_{11}^{\,pq} c_+^{pq} + \tilde{g}_{21} s_+^{pq} + \tilde{g}_{12} s_-^{pq} + \tilde{g}_{22}^{\,pq} c_-^{pq} \tag{56}$$

$$\tilde{F}_{12}^{pq} = -\tilde{g}_{11}^{\,pq} c_-^{pq} + \tilde{g}_{21} s_-^{pq} + \tilde{g}_{12} s_+^{pq} + \tilde{g}_{22}^{\,pq} c_+^{pq} \tag{57}$$

$$\tilde{F}_{22}^{pq} = -\tilde{g}_{11}^{\,pq} s_-^{pq} - \tilde{g}_{21} c_-^{pq} - \tilde{g}_{12} c_+^{pq} + \tilde{g}_{22}^{\,pq} s_+^{pq} \tag{58}$$

with

$$\theta_+ = \theta_p + \theta_q \tag{59}$$

$$\theta_- = \theta_p - \theta_q \tag{60}$$

$$s_+^{pq} = (\operatorname{sinc}\theta_+ + \operatorname{sinc}\theta_-)/2 \tag{61}$$

$$s_-^{pq} = (\operatorname{sinc}\theta_+ - \operatorname{sinc}\theta_-)/2 \tag{62}$$

$$c_+^{pq} = (\operatorname{cosc}\theta_+ + \operatorname{cosc}\theta_-)/2 \tag{63}$$

$$c_-^{pq} = (\operatorname{cosc}\theta_+ - \operatorname{cosc}\theta_-)/2 \tag{64}$$

It follows that $\lim_{\theta_p,\theta_q \to 0} \tilde{\mathbf{F}}^{pq} = \tilde{\mathbf{g}}^{pq}$.

From these expressions, it is seen that the computation of $\tilde{\mathbf{g}}$ requires about $3m^3$ FLOPs effort, the matrix $\tilde{\mathbf{F}}$ requires an additional $6m^2$ FLOPs, and the matrix $\mathbf{F}^{(-)} = \mathbf{V}\tilde{\mathbf{F}}\mathbf{V}^{\mathrm{T}}$ requires an additional $3m^3$ FLOPs. Only the unique (e.g., lower-triangular) elements need to be computed explicitly for all of these skew-symmetric matrices. Assuming $\mathbf{Q}$ and the quasidiagonal factorization are available, the total gradient transformation with the above algorithm requires about $6(m+1)m^2$ FLOPs effort.

2.3. Householder Parametrization. The Householder reflector[45,68−74] parametrization of the orthogonal matrix $\mathbf{Q} \in \mathbb{R}^{m\times n}$ has been discussed in detail in ref 44. The important features are summarized here. A Householder reflector $\mathbf{H}^{(p)} \in \mathbb{R}^{m\times m}$ is written as

$$\mathbf{H}^{(p)} = \mathbf{1} - 2\mathbf{u}^{(p)}\mathbf{u}^{(p)\mathrm{T}} \tag{65}$$

$$= \mathbf{1} - \tau^{(p)} \begin{pmatrix} 0 \\ 1 \\ \mathbf{v}^{(p)} \end{pmatrix} \begin{pmatrix} 0 & 1 & \mathbf{v}^{(p)\mathrm{T}} \end{pmatrix} \tag{66}$$

In eq 65, the vector $\mathbf{u}^{(p)} \in \mathbb{R}^m$ is normalized as $\mathbf{u}^{(p)\mathrm{T}}\mathbf{u}^{(p)} = \|\mathbf{u}^{(p)}\|^2 = 1$, and with this property it is straightforward to verify that $\mathbf{H}^{(p)}$ is symmetric $\mathbf{H}^{(p)\mathrm{T}} = \mathbf{H}^{(p)}$, orthogonal $\mathbf{H}^{(p)\mathrm{T}}\mathbf{H}^{(p)} = \mathbf{1}$, and self-inverse $\mathbf{H}^{(p)}\mathbf{H}^{(p)} = \mathbf{1}$ (also termed *involutory*). $\mathbf{H}^{(p)}\mathbf{u}^{(p)} = -\mathbf{u}^{(p)}$, and $\mathbf{H}^{(p)}\mathbf{u}^{\perp} = +\mathbf{u}^{\perp}$, where $\mathbf{u}^{\perp}$ is an arbitrary vector satisfying $\mathbf{u}^{(p)\mathrm{T}}\mathbf{u}^{\perp} = 0$. These eigenvalue equations show that $\mathbf{H}^{(p)}$ has a single eigenvalue of -1 and the remaining $(m-1)$ eigenvalues are $+1$; consequently, $\det(\mathbf{H}^{(p)}) = \prod_j \lambda_j = -1$ and $\mathbf{H}^{(p)}$ is a reflector. Equation 66 shows the equivalent representation of the reflectors used in ref 44. (this is also the LAPACK convention[59,72]). Specifically, the first $(p-1)$ elements are zero, the pth element has a value of $+1$, and the remaining $(m-p)$ elements are associated with the essential variables $\{\boldsymbol{\varphi}\}$. The scale factor $\tau^{(p)} = 2/(1 + \|\mathbf{v}^{(p)}\|^2)$ ensures the equivalence between the two representations, eqs 65 and 66. Given the $\tau^{(p)}$ and $\mathbf{v}^{(p)}$ that define the Householder reflector in eq 66, an arbitrary matrix−vector product $\mathbf{x} \leftarrow \mathbf{H}^{(p)}\mathbf{x}$ may be computed in-place with only $4(m-p)+3$ FLOPs, and a more general matrix−matrix product $\mathbf{A} \leftarrow \mathbf{H}^{(p)}\mathbf{A}$ with $\mathbf{A} \in \mathbb{R}^{m\times n}$ may be computed in-place with only $(4(m-p)+3)(m-p+1)$ FLOPs; in both cases only the lower $p{:}m$ rows are accessed and modified.

Householder reflectors are useful in the elimination of vector elements during reduction and factorization procedures. In particular, the elements $\mathbf{v}^{(p)}$ may be chosen to satisfy

$$\mathbf{H}^{(p)} \begin{pmatrix} \alpha \\ \mathbf{x} \end{pmatrix} = \begin{pmatrix} \beta \\ \mathbf{0} \end{pmatrix} \tag{67}$$

As discussed in detail in ref 44, for a given vector $(\alpha,\mathbf{x}^{\mathrm{T}})^{\mathrm{T}}$, there are generally two choices for β and $\mathbf{v}^{(p)}$ that satisfy eq 67, given by $\beta = \pm(\alpha^2 + \|\mathbf{x}\|^2)^{1/2}$ and $\mathbf{v}^{(p)} = \mathbf{x}(\alpha-\beta)^{-1}$. α and β have opposite signs in the numerically stable solution, and α and β have the same sign in the possibly unstable solution; this instability is associated with vectors $\mathbf{v}^{(p)}$ that have large norm. In most quantum chemical applications, the phases of the columns of $\mathbf{Q}$ may be chosen to be consistent with the stable solution, or at least limited to parameter vectors $\mathbf{v}^{(p)}$ with modest norm.

Householder reflectors may be used in the factorization $\mathbf{A} = \mathbf{QR}$ of an arbitrary matrix $\mathbf{A} \in \mathbb{R}^{m\times n}$ as the product of an orthogonal matrix $\mathbf{Q} \in \mathbb{R}^{m\times n}$ and an upper-triangular matrix $\mathbf{R} \in \mathbb{R}^{n\times n}$. This factorization is achieved by rearranging this equation into the form $\mathbf{R} = \mathbf{Q}^{\mathrm{T}}\mathbf{A}$, and the $\mathbf{Q}^{\mathrm{T}}$ matrix is determined with a stepwise (noniterative) procedure that transforms $\mathbf{A}$ to the upper-triangular $\mathbf{R}$. With Householder reflectors, this factorization may be achieved as follows. First $\mathbf{H}^{(1)}$ is chosen to eliminate elements $2{:}m$ in the first column of $\mathbf{A}$, giving the intermediate $\mathbf{A}^{(1)} = \mathbf{H}^{(1)}\mathbf{A}$. Next, $\mathbf{H}^{(2)}$ is chosen to eliminate elements $3{:}m$ in the second column of $\mathbf{A}^{(1)}$, giving the intermediate $\mathbf{A}^{(2)} = \mathbf{H}^{(2)}\mathbf{A}^{(1)}$. This second transformation does not result in any fill-in of the previously eliminated elements in the first column, and the strictly lower-trapezoidal elements of the first two columns of $\mathbf{A}^{(2)}$ are eliminated. The elimination of the lower-trapezoidal elements within each column is continued, giving eventually after n steps

$$\begin{pmatrix} \mathbf{R} \\ \mathbf{0} \end{pmatrix} = \mathbf{H}^{(n)} \cdots \mathbf{H}^{(2)}\mathbf{H}^{(1)}\mathbf{A} = \mathbf{Q}^{\mathrm{T}}\mathbf{A} \tag{68}$$

The desired $\mathbf{Q}$ is then given by the reverse sequence of factors

$$\mathbf{Q} = \mathbf{H}^{(1)}\mathbf{H}^{(2)}\mathbf{H}^{(3)} \cdots \mathbf{H}^{(n)}\mathbf{I}^{m\times n} = \tilde{\mathbf{Q}}^{m\times m}\mathbf{I}^{m\times n} \tag{69}$$

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The individual reflectors generally do not commute, so $\mathbf{Q}$ is given as the *ordered* product of the factors as shown in eq 69. Because each $\mathbf{H}^{(p)}$ factor is a reflector, $\det(\tilde{\mathbf{Q}}^{m\times m}) = -1^n$. Thus, for even n, the square transformation $\tilde{\mathbf{Q}}^{m\times m} \in \mathrm{SO}(m)$, whereas for odd n, $\tilde{\mathbf{Q}}^{m\times m} \in \mathrm{O}(m)$. A consequence of this is that given two square matrices $\tilde{\mathbf{Q}}_1$ and $\tilde{\mathbf{Q}}_2$ that are each parametrized with an odd number of reflectors, the product $\tilde{\mathbf{Q}}_3 = \tilde{\mathbf{Q}}_1\tilde{\mathbf{Q}}_2$ cannot then be represented with an odd number of reflectors. In situations in which closure with respect to matrix multiplication is important, the number of reflectors must be chosen appropriately.

When $\mathbf{A}$ is orthogonal, this procedure results in an $\mathbf{R}$ that is a diagonal sign matrix, $R_{jk} = \pm\delta_{jk}$. That is, the columns of $\mathbf{A}$ and $\mathbf{Q}$ differ by at most a sign factor. As discussed above, there are generally two choices for each vector of reflector parameters $\mathbf{v}^{(p)}$, and these two choices correspond to the two possible signs for the diagonal element R_{pp}. In order to represent the input $\mathbf{A}$ in terms of essential parameters $\{\boldsymbol{\varphi}\}$, the sign choice must be made that results in $R_{pp} > 0$ (i.e., $R_{pp} = +1$ for orthogonal $\mathbf{A}$). When the $R_{pp} > 0$ factorization is desired, some care must be taken to monitor the instabilities so that numerical errors are not propagated. This sign choice also results in smooth and continuous changes of $\mathbf{Q}$ with respect to small changes in the input $\mathbf{A}$. Thus, depending on the specific needs at any time, it is sometimes beneficial to switch between the stable QR factorization mode, for which α and β have opposite signs, and the continuous QR factorization mode, associated with $\beta > 0$.

The essential parameters $\{\boldsymbol{\varphi}\}$ are associated with the reflector parameters in eq 69. The $\boldsymbol{\varphi}(\mathbf{Q})$ mapping is therefore achieved by subjecting the matrix $\mathbf{Q}$ to the QR decomposition procedure. For the Stiefel parametrization, $N_e = mn - n(n+1)/2$, these parameters may be stored in the strictly lower-trapezoidal array $\mathbf{V} = (\mathbf{v}^{(1)}, \mathbf{v}^{(2)}, ..., \mathbf{v}^{(n)})$, $\{\boldsymbol{\varphi}\} = \{V_{ij}: j = 1, ..., n; i = j+1, ..., m\}$. This QR factorization requires $2(m - n/3)n^2$ FLOPs, and the computation of $\mathbf{Q}$ according to eq 69 also requires $2(m - n/3)n^2$ FLOPs. For the Grassmann parametrization, consider the following sequence of transformations:

$$\mathbf{A} = \begin{pmatrix}\mathbf{A}_1\\ \mathbf{A}_2\end{pmatrix} = \begin{pmatrix}\mathbf{R}_1\mathbf{Q}_1\\ \mathbf{A}_2\end{pmatrix} = \begin{pmatrix}\mathbf{R}_1\\ \mathbf{A}_2\mathbf{Q}_1^T\end{pmatrix}\mathbf{Q}_1 = \mathbf{B}\mathbf{Q}_1 = \tilde{\mathbf{Q}}\mathbf{R}\mathbf{Q}_1 = \tilde{\mathbf{Q}}\mathbf{Z} \tag{70}$$

where $\mathbf{A}_1 \in \mathbb{R}^{n\times n}$ and $\mathbf{R}_1$ is upper-triangular. When $\mathbf{A}$ is orthogonal, then $\mathbf{Z} = \mathbf{R}\mathbf{Q}_1$ is also orthogonal. The QR factorization of the matrix $\mathbf{B}$ in which the leading subblock is upper-triangular results in $n(n-1)/2$ associated zero reflector elements that need not be stored. Thus, the Grassmann manifold $\tilde{\mathbf{Q}}$ may be represented with the remaining $N_e = (m-n)n$ essential parameters that are associated with the rectangular array elements $\{\boldsymbol{\varphi}\} = \{V_{ij}: j = 1, ..., n; i = n+1, ..., m\}$. The factorization sequence in eq 70 always exists, and it is unique when $\mathbf{A}_1$ is nonsingular and when $\mathbf{B}$ is factored with the continuous QR convention.[44]

The Grassmann $\mathbf{Q}(\boldsymbol{\varphi})$ computation according to eq 69 with just the nonzero rectangular array elements requires $2(m-n)n^2$ FLOPs. If $\mathbf{A}_1$ is upper-triangular, then $\boldsymbol{\varphi}(\mathbf{Q})$ requires $2(m-n)n^2$ FLOPs if the sparsity is exploited during the QR factorization. Otherwise, the sequence of operations in eq 70 requires about $(4m - 2n/3)n^2$ FLOPs.

The chain-rule transformation of gradients eq 1 consists of application of the relation

$$\frac{\partial\mathbf{Q}}{\partial V_{kp}} = \left(\prod_{q=1}^{p-1}\mathbf{H}^{(q)}\right)\frac{\partial\mathbf{H}^{(p)}}{\partial V_{kp}}\left(\prod_{r=p+1}^{n}\mathbf{H}^{(r)}\right)\mathbf{I}^{m\times n} \tag{71}$$

This follows from eq 69 and the fact that the Householder reflector parameters V_{kp} occur only within the reflector $\mathbf{H}^{(p)}$. Substitution into eq 1 then gives

$$\frac{\partial E}{\partial V_{kp}} = \sum_{st}\frac{\partial E}{\partial Q_{st}}\left(\left(\prod_{q=1}^{p-1}\mathbf{H}^{(q)}\right)\frac{\partial\mathbf{H}^{(p)}}{\partial V_{kp}}\left(\prod_{r=p+1}^{n}\mathbf{H}^{(r)}\right)\mathbf{I}^{m\times n}\right)_{st} \tag{72}$$

$$= \mathrm{tr}\left(\boldsymbol{\Lambda}^{(p)T}\frac{\partial\mathbf{H}^{(p)}}{\partial V_{kp}}\boldsymbol{\Omega}^{(p)}\right) \tag{73}$$

with

$$\boldsymbol{\Lambda}^{(p)} = \left(\prod_{q=1}^{p-1}\mathbf{H}^{(q)}\right)^{\mathrm{T}}\frac{\partial E}{\partial\mathbf{Q}} \tag{74}$$

$$\boldsymbol{\Omega}^{(p)} = \left(\prod_{r=p+1}^{n}\mathbf{H}^{(r)}\right)\mathbf{I}^{m\times n} \tag{75}$$

These rectangular $\mathbb{R}^{m\times n}$ matrices may be computed recursively as

$$\boldsymbol{\Lambda}^{(1)} = \frac{\partial E}{\partial\mathbf{Q}}; \quad \boldsymbol{\Lambda}^{(p+1)} = \mathbf{H}^{(p)}\boldsymbol{\Lambda}^{(p)} \qquad p = 1, ..., (n-1) \tag{76}$$

$$\boldsymbol{\Omega}^{(1)} = \mathbf{H}^{(1)}\mathbf{Q}; \quad \boldsymbol{\Omega}^{(p+1)} = \mathbf{H}^{(p+1)}\boldsymbol{\Omega}^{(p)} \qquad p = 1, ..., (n-1) \tag{77}$$

The matrix $\partial\mathbf{H}^{(p)}/\partial V_{kp}$ consists of three computationally efficient rank-1 terms.[44] The entire gradient computation procedure requires only about $(6m - 2n - 3)n^2$ FLOPs for the trapezoidal Stiefel parametrization and about $(6m - 6n - 2)n^2$ FLOPs for the rectangular Grassmann parametrization.[44]

2.4. Givens Rotation Parametrization. A plane rotation may be chosen to eliminate a selected element of a vector. In two dimensions, a rotation that satisfies

$$\begin{pmatrix}\cos\theta & \sin\theta\\ -\sin\theta & \cos\theta\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix} = \begin{pmatrix}r\\ 0\end{pmatrix} \tag{78}$$

is called a Givens rotation.[73−77] For a nonzero vector $(x,y)^{\mathrm{T}}$, there are two distinct matrices, which differ by an overall sign, that satisfy this relation, one corresponding to $r > 0$ and one to $r<0$. In terms of the two principal angles, these two matrices correspond to $|\theta_1 - \theta_2| = \pi$. Unlike the Householder transformation choice discussed in Section 2.3, both rotation angles yield the same numerical error. There are several conventions that are used to choose between these two possible solutions that are discussed in detail in refs 76 and 77. In the present work, the matrix is chosen for which $r > 0$ because this choice results in smooth and continuous values for $\cos\theta$ and $\sin\theta$ with respect to perturbations in $(x,y)^{\mathrm{T}}$ everywhere except in the neighborhood of the origin, $(x,y)^{\mathrm{T}} = (0,0)^{\mathrm{T}}$. See in particular algorithm 4 of ref 77 and the associated discussion. The pair of $\cos\theta$ and $\sin\theta$ values that solve eq 78 are computed algebraically in the typical mathematical library with about 5 FLOPs.

In addition to the wide range of applications within linear algebra, products of plane rotations have been used by Raffenetti and Ruedenberg,[78] Hoffmann et al.,[79] and Raffenetti et al.[80] in the parametrization of molecular orbital

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coefficients. In general, an orthogonal matrix $\mathbf{Q} \in \mathbb{R}^{m\times n}$ may be written as

$$\mathbf{Q} = \mathbf{G}(i_1, j_1, \theta_1)^{\mathrm{T}}\mathbf{G}(i_2, j_2, \theta_2)^{\mathrm{T}}...\mathbf{G}(i_{N_e}, j_{N_e}, \theta_{N_e})^{\mathrm{T}}\mathbf{I}^{m\times n}$$
$$= \tilde{\mathbf{Q}}^{m\times m}\mathbf{I}^{m\times n} \quad (79)$$

$$= \mathbf{G}^{(1)\mathrm{T}}\mathbf{G}^{(2)\mathrm{T}}...\mathbf{G}^{(N_e)\mathrm{T}}\mathbf{I}^{m\times n} \quad (80)$$

with $\theta_\mu \equiv \theta_{i_\mu j_\mu}$ and where each plane rotation has the sparse form of eq 4. $\mathrm{Det}(\tilde{\mathbf{Q}}^{m\times m}) = \prod_{p=1}^{N_e}\mathrm{det}(\mathbf{G}^{(p)}) = +1$, and consequently all matrices represented in eq 79 satisfy $\tilde{\mathbf{Q}}^{m\times m} \in \mathrm{SO}(m)$. With the above parametrization, $\mathbf{Q}$ depends both on the sequence of row and column indices $\{i_1j_1, i_2j_2, ...\}$ and on the associated rotation angle parameters $\{\theta_1, \theta_2, ...\}$. The specific sequence order is important because the individual plane rotations do not always commute. However, there is a wide range of possible row and column index sequences that may be used to represent a given $\mathbf{Q}$, including sequences in which particular ij pairs are repeated (see, e.g., Section 5.2.3 and Problem P5.2.3 of ref 73). In the present work, a sequence is chosen that corresponds closely to the QR factorization using Householder reflectors discussed in Section 2.3. This allows much of the general discussion of that section to be applied to the current situation. The sequence order that accomplishes this task is given by the following QR decomposition algorithm:

DO $j = 1, ..., n$
DO $i = m, ..., (j + 1)$
Determine θ_{ij} from A_{jj} and A_{ij} that eliminates A_{ij}; save θ_{ij}.
Compute $\mathbf{A} \leftarrow \mathbf{G}(i,j,\theta_{ij})\mathbf{A}$ in-place.
ENDDO
ENDDO

The columns are processed in the same order as the Householder QR algorithm in Section 2.3. The result of this sequence order is that once the strictly lower-trapezoidal elements within $\mathbf{A}$ have been eliminated through column j, the operations on subsequent columns do not result in any fill-in. The choice of the rotation angle θ_{ij} discussed above results in a nonnegative updated A_{jj} after the first rotation in that column, and then the A_{jj} value remains nonnegative and increases monotonically in value for all of the subsequent rotations within that column. After accounting for this sparsity, this QR factorization requires $3(m - n/3)n^2$ FLOPs for the Stiefel manifold parametrization and about $3(m - n)n^2$ FLOPs for the Grassmann manifold parametrization. If $\mathbf{A}_1$ in eq 70 is not upper-triangular, then the total effort is about $(5m - 11n/3)n^2$ FLOPs for the Grassmann manifold. These operation counts are about 3/2 times larger than those for the equivalent Householder algorithm. At the end of this procedure, a general matrix $\mathbf{A}$ is reduced to upper-triangular form,

$$\begin{pmatrix}\mathbf{R}\\ \mathbf{0}\end{pmatrix} = \mathbf{G}(i_{N_e}, j_{N_e}, \theta_{N_e})...\mathbf{G}(i_2, j_2, \theta_2)\mathbf{G}(i_1, j_1, \theta_1)\mathbf{A} = \mathbf{Q}^{\mathrm{T}}\mathbf{A} \quad (81)$$

and the matrix $\mathbf{Q}$ is given in eq 79. When the original $\mathbf{A}$ is orthogonal, then $\mathbf{A}$ is reduced to a unit matrix, $\mathbf{R} = \mathbf{1}$. The rotation angles θ_{ij} are saved, and $\mathbf{Q}$ may be computed according to eq 79 if necessary, or matrix product operations such as $\mathbf{QB}$ and $\mathbf{Q}^{\mathrm{T}}\mathbf{B}$ may be computed directly from the saved rotation angles. The computation of $\mathbf{Q}$ requires about $3(m - n/3)n^2$ FLOPs for the Stiefel manifold parametrization and about $3(m - n)n^2$ FLOPs for the Grassmann manifold parametrization. Note that within a column, the elements are eliminated in reverse order. This allows the same decomposition process to be used for both the Stiefel and Grassmann cases using the operation sequence in eq 81 simply by skipping the operations associated with plane rotations for which $\theta_{ij} = 0$. Similar to the Householder parametrization, the mapping $\boldsymbol{\theta}(\mathbf{Q})$ is achieved by subjecting the orthogonal matrix $\mathbf{Q}$ to the QR decomposition algorithm.

Consider a situation during the above QR decomposition in which both A_{jj} and A_{ij} are zero. Any angle θ_{ij} may be chosen at that point, and the new A_{jj} and A_{ij} elements will remain zero. In this case, the orthogonal matrix $\mathbf{A}$ does not depend on that degree of freedom. However, the choice of θ_{ij} at that point may affect the value of subsequent rotation angles. This shows that some orthogonal matrices have multiple rotation angle representations (in addition to the cyclic trigonometric ambiguities previously mentioned), and the associated plane rotation angles are redundant. In three dimensions SO(3), this condition is called "gimbal lock" (see ref 16 for a discussion in the context of molecular modeling), and alternative rotation parametrizations such as quaternions[21] are often used to avoid this condition. An example of this ambiguity is the set of matrices

$$\begin{pmatrix}0 & \cos\alpha & \sin\alpha\\ -1 & 0 & 0\\ 0 & -\sin\alpha & \cos\alpha\end{pmatrix} = \mathbf{G}(3, 1, -\theta)\mathbf{G}(2, 1, \pi/2)\mathbf{G}(3, 2, \theta + \alpha) \quad (82)$$

It may be verified that the matrix product on the right is independent of the angle θ, and there are an infinite number of ways a matrix on the left may be factored into the three plane rotations. This condition is detected during the first step of the QR decomposition of the matrix by noting that $A_{1,1}$ and $A_{3,1}$ are both zero, resulting in an undetermined angle in the Givens rotation $\mathbf{G}(3,1,\theta)$. The next step of the QR decomposition determines $\mathbf{G}(2,1,-\pi/2)$, which is independent in this example of both θ and α. The final step determines the rotation $\mathbf{G}(3,2,-\theta - \alpha)$. The original matrix is then the product of the inverse of these three matrices as given in eq 82. The arbitrary angle θ in the first step affects the final angle, but the end result is that the product of the three factors is independent of θ. This same ambiguity can exist, for multiple angles, in more general SO(m) matrices. When this occurs, taking arbitrarily $\theta_{ij} = 0$ is a practical choice because it eliminates the effort associated with the subsequent rotation steps involving that angle. The rotation angle parametrization is generally discontinuous in this situation; small perturbations to the original orthogonal matrix that result in small nonzero values for A_{jj} and/or A_{ij} can result in widely varying $\boldsymbol{\theta}$, not just for that particular θ_{ij} but also for other rotation angles associated with the redundancy. This is an unavoidable situation with the Givens parametrization of orthogonal matrices.

For the square $n = m$ case, the computation of $\mathbf{Q}$ according to eq 79 is similar to that implemented by Raffenetti and Ruedenberg (RR) in ref 78. The main difference with respect to the present formulation is that the sequence of plane rotations of RR was chosen in order to compute recursively the orthogonal leading subblocks of $\mathbf{Q}$. In contrast, the evaluation of eq 79 results in a recursive computation of orthogonal trailing subblocks of $\mathbf{Q}$. There are no practical differences in the two sequences, both are numerically stable and both have the same operation counts. However, there are significant differences in the decomposition of $\mathbf{Q}$ into its primitive plane rotations. In the present work, the $\boldsymbol{\theta}(\mathbf{Q})$ mapping is achieved

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by performing the QR factorization on the orthogonal matrix $\mathbf{Q}$. In contrast, RR proposed using an iterative nonlinear minimization of the least-squares error $f(\boldsymbol{\theta}) = \sum_{i,j}(U_{ij} - Q(\boldsymbol{\theta})_{ij})^2$. This algorithm was subsequently replaced[79] with one based on closed-form expressions for the intermediate matrix elements of the leading orthogonal subblocks. However, with the hindsight afforded by the current formulation, it may be seen that the RR rotation angles may be determined by reversing the plane rotation sequence order and noting simply which elements of the intermediate matrices are eliminated by each plane rotation. When this is done, it is observed that the RR rotation angles may be determined by the QL decomposition of the original orthogonal matrix. That is, for a general matrix, the $\mathbf{L}$ factor would be lower-triangular rather than the upper-triangular factor $\mathbf{R}$ that is used in the present work. While the QR decomposition corresponds to a sequential orthogonalization of the columns of the input matrix in natural order, the QL decomposition corresponds to a sequential orthogonalization of the columns in reverse order. The QL decomposition has the same numerical properties and operation counts as the QR decomposition, and it is thereby possible to determine the RR plane rotation angles with a stable noniterative procedure based on Givens rotations that requires $2m^3$ FLOPs. One other difference is that all but the last rotation angle within each column in the RR algorithm are restricted to the range $-\pi/2 \le \theta_{ij} \le \pi/2$. This is equivalent to the common convention that cos $\theta_{ij} \ge 0$ within the plane rotation matrices. However, as discussed in ref 77, this introduces discontinuities in both the plane rotation matrices and in the angle parametrization at the boundaries.

It may be noted in passing that the rotation angles θ_{ij} are not computed or stored typically in standard linear algebra libraries that work with Givens rotations. Instead, an alternative parametrization is chosen that avoids any computation of trigonometric or inverse trigonometric functions. Typically, the parameter z is chosen to be proportional to either sin θ or $1/\cos\theta$, depending on the relative magnitudes of the two values (see ref 74). However, this convention necessarily introduces discontinuities into the parametrization. For many typical linear algebra applications, these discontinuities have no practical consequences (see ref 77 for some counter examples). However, for the parametrization of manifolds for which smooth and continuous mappings $\mathbf{Q}(\boldsymbol{\varphi})$ and $\boldsymbol{\varphi}(\mathbf{Q})$ are desired, the natural parametrization in terms of the rotation angles is advantageous. In the present work, this is accomplished with the Fortran two-argument arctangent function; given the cos θ and sin θ parameters that have been computed algebraically, the angle is given by θ = ATAN2(y = sin θ, x = cos θ).

The chain-rule transformation of gradients eq 1 consists of application of the relation

$$\frac{\partial \mathbf{Q}}{\partial \theta_p} = (\mathbf{G}^{(1)\mathrm{T}} \cdots \mathbf{G}^{(p-1)\mathrm{T}}) \frac{\partial \mathbf{G}^{(p)\mathrm{T}}}{\partial \theta_p} (\mathbf{G}^{(p+1)\mathrm{T}} \cdots \mathbf{G}^{(N_e)\mathrm{T}}) \mathbf{I}^{m\times n} \tag{83}$$

This follows from eq 79 and the fact that the rotation parameter θ_p occurs only within the single plane rotation $\mathbf{G}^{(p)}$. Substitution into eq 1 using eqs 4, 5, 6, and 9 then gives

$$\frac{\partial E}{\partial \theta_p} = \mathrm{tr}\left(\frac{\partial E}{\partial \mathbf{Q}}^{\mathrm{T}} (\mathbf{G}^{(1)\mathrm{T}} \cdots \mathbf{G}^{(p)\mathrm{T}})(\mathbf{G}^{(p)} \mathbf{G}'^{(p)\mathrm{T}})(\mathbf{G}^{(p+1)\mathrm{T}} \cdots \mathbf{G}^{(N_e)\mathrm{T}}) \mathbf{I}^{m\times n}\right) \tag{84}$$

$$= \mathrm{tr}(\boldsymbol{\Lambda}^{(p)\mathrm{T}} \mathbf{E}^{i_p j_p} \boldsymbol{\Omega}^{(p)}) \tag{85}$$

$$= \sum_{k=j_p}^{n} \Lambda_{i_p k}^{(p)} \Omega_{j_p k}^{(p)} - \sum_{k=j_p+1}^{n} \Lambda_{j_p k}^{(p)} \Omega_{i_p k}^{(p)} \tag{86}$$

The arrays $\boldsymbol{\Lambda}^{(p)} \in \mathbb{R}^{m\times n}$ and $\boldsymbol{\Omega}^{(p)} \in \mathbb{R}^{m\times n}$ may be computed recursively in-place as

$$\boldsymbol{\Lambda}^{(0)} = \frac{\partial E}{\partial \mathbf{Q}}; \quad \boldsymbol{\Lambda}^{(p)} = \mathbf{G}^{(p)} \boldsymbol{\Lambda}^{(p-1)}$$

$$\boldsymbol{\Omega}^{(0)} = \mathbf{Q}; \quad \boldsymbol{\Omega}^{(p)} = \mathbf{G}^{(p)} \boldsymbol{\Omega}^{(p-1)} \quad \text{for } p = 1, \ldots, N_e \tag{87}$$

At step p, the array element $\Omega_{i_p j_p}$ is eliminated. This results in the restricted summations in eq 86, which in turn implies that only the $(j_p{:}m, j_p{:}n)$ subblocks of the $\boldsymbol{\Lambda}$ and $\boldsymbol{\Omega}$ arrays need to be updated in eq 87. Consequently, each step of the recursive procedure of eqs 86 and 87 requires about $16(n - j_p + 1)$ FLOPs, and the total effort for the full chain-rule transformation of the gradient is about $(8m - (n+2)/3)(n^2 + n)$ FLOPs for the Stiefel parametrization and $8(m - n)(n^2 + n)$ FLOPs for the Grassmann parametrization.

2.5. Rational Cayley Transform Parametrization. The Cayley transform[73] of the skew-symmetric matrix $\mathbf{X} \in \mathbb{R}^{m\times m}$ is denoted

$$\mathrm{Cay}(\mathbf{X}) = (\mathbf{1} + \mathbf{X})(\mathbf{1} - \mathbf{X})^{-1} \tag{88}$$

$$= 2(\mathbf{1} - \mathbf{X})^{-1} - \mathbf{1} \tag{89}$$

The relation $\mathrm{Cay}(\mathbf{X})^{-1} = \mathrm{Cay}(-\mathbf{X}) = \mathrm{Cay}(\mathbf{X})^{\mathrm{T}}$ shows that $\mathbf{Q} = \mathrm{Cay}(\mathbf{X})$ is orthogonal and parametrized by the unique elements of $\mathbf{X}$. This is one of the first parametrizations of orthogonal matrices, introduced by Cayley early after matrices themselves were first studied mathematically.[81] For any matrix parametrized as $\mathbf{Q} = \mathrm{Cay}(\mathbf{X})$, it follows that $\mathrm{Det}(\mathbf{Q}) = \det(\mathbf{1} + \mathbf{X})/\det((\mathbf{1} + \mathbf{X})^{\mathrm{T}}) = +1$, so that $\mathbf{Q}^{m\times m} \in \mathrm{SO}(m)$. Given an orthogonal matrix $\mathbf{Q} \in \mathrm{SO}(m)$, the parameter matrix $\mathbf{X}$ is given by

$$\mathbf{X} = \mathrm{Cay}^{-1}(\mathbf{Q}) = (\mathbf{Q} - \mathbf{1})(\mathbf{Q} + \mathbf{1})^{-1} \tag{90}$$

$$= \mathbf{1} - 2(\mathbf{Q} + \mathbf{1})^{-1} \tag{91}$$

These expressions for $\mathbf{X}$ require that the matrix $(\mathbf{Q} + \mathbf{1})$ is invertible, which means that $\mathbf{Q}$ must not have an eigenvalue $\omega_j = -1$. This eliminates all matrices with $\det(\mathbf{Q}) = -1$ and also all $\mathrm{SO}(m)$ matrices with an even number of $\omega_j = -1$ eigenvalues from being represented with the Cayley transform. Substitution of $\mathbf{Q}^{\mathrm{T}}\mathbf{Q} = \mathbf{1}$ into eq 90 shows that the computed $\mathbf{X}$ is indeed skew-symmetric, and these expressions give a unique $\mathbf{X}$ when $(\mathbf{Q} + \mathbf{1})$ is invertible. Given the quasidiagonal factorization $\mathbf{X} = \mathbf{V}\mathbf{D}\mathbf{V}^{\mathrm{T}}$ from eq 20, the Cayley transform may be written as $\mathrm{Cay}(\mathbf{X}) = \mathbf{V}\mathrm{Cay}(\mathbf{D})\mathbf{V}^{\mathrm{T}}$, in which the 1×1 diagonal subblocks of $\mathrm{Cay}(\mathbf{D})$ are given by $\mathrm{Cay}(0) = 1$, and the 2×2 subblocks are given by

$$\mathrm{Cay}\begin{pmatrix} 0 & \theta_j \\ -\theta_j & 0 \end{pmatrix} = \begin{pmatrix} 1 & \theta_j \\ -\theta_j & 1 \end{pmatrix}\begin{pmatrix} 1 & -\theta_j \\ \theta_j & 1 \end{pmatrix}^{-1} = \frac{1}{1+\theta_j^2}\begin{pmatrix} 1-\theta_j^2 & 2\theta_j \\ -2\theta_j & 1-\theta_j^2 \end{pmatrix} \tag{92}$$

$$= \begin{pmatrix} \cos\alpha_j & \sin\alpha_j \\ -\sin\alpha_j & \cos\alpha_j \end{pmatrix} \tag{93}$$

with $\theta_j = \tan(\alpha_j/2)$, in which α_j is limited to the open interval $-\pi < \alpha_j < \pi$. The 1×1 subblocks of $\mathbf{D}$ never contribute a

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negative ω_j eigenvalue, and the plane rotations of the 2×2 subblocks contribute eigenvalues $\omega_j = \exp(\pm i\alpha_j)$, which only approach −1 asymptotically as $\theta_j \to \pm\infty$. Thus, the unique skew-symmetric matrix $\mathbf{X}$ of parameters may be extracted from any Cayley matrix defined by eqs 88 or 89 using either of eqs 90 or 91. Using the quasidiagonal factorization,

$$\det(\mathbf{1} - \mathbf{X}) = \det(\mathbf{1} - \mathbf{D}) = \prod_j \det(\mathbf{1}_j - \mathbf{D}_j)$$
$$= \prod_{j=1}^{k} (1 + \theta_j^2) \cdot \prod_{j=2k+1}^{m} (+1) > 1 \tag{94}$$

where the k 2×2 subblocks are in the first product factor and the $(m - 2k)$ 1×1 subblocks are in the second product factor. The determinant is never zero, $(\mathbf{1} - \mathbf{X})$ is invertible, and $\mathrm{Cay}(\mathbf{X})$ is well-defined for any $\mathbf{X}$.

Given two Cayley matrices, $\mathbf{Q}_1 = \mathrm{Cay}(\mathbf{X}_1)$ and $\mathbf{Q}_2 = \mathrm{Cay}(\mathbf{X}_2)$, the product $\mathbf{Q}_3 = \mathbf{Q}_1\mathbf{Q}_2 \in \mathrm{SO}(m)$, but this product is not necessarily a Cayley matrix for which $\mathbf{Q}_3 = \mathrm{Cay}(\mathbf{X}_3)$. A counter example is the matrix $\mathbf{Q}_1 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$, which corresponds to $\alpha = \pi/2$ in eq 93; the product $\mathbf{Q}_3 = \mathbf{Q}_1\mathbf{Q}_1 = -\mathbf{1}$ corresponds to the angle $\alpha = \pi$ and therefore cannot be represented with the Cayley parametrization. This obviously generalizes to any pair of matrices characterized by plane rotation angles of α and $(\pi - \alpha)$ in eq 93. The Cayley matrices defined by eqs 88 or 89 therefore span only a subset of the full $\mathrm{SO}(m)$ set of orthogonal matrices, and although the identity $\mathrm{Cay}(\mathbf{0}) = \mathbf{1}$ is contained in this subset, and the inverse of each matrix is contained in this subset, the subset does not form a subgroup because it is not closed under multiplication.

Further connections between the Cayley and the exponential parametrization follow from the fact that eq 88 is the rational [1/1] Padé approximant to the matrix exponential $\exp(2\mathbf{X})$. Expansion about $\mathbf{X} = \mathbf{0}$,

$$\mathrm{Cay}(\mathbf{X}) = \mathbf{1} + 2\mathbf{X} + 2\mathbf{X}^2 + 2\mathbf{X}^3 + \ldots \tag{95}$$

$$\exp(2\mathbf{X}) = \mathbf{1} + 2\mathbf{X} + 2\mathbf{X}^2 + \frac{4}{3}\mathbf{X}^3 + \ldots \tag{96}$$

shows that the low-order terms match through second order. For small $\mathbf{X}$, the parameters have the same qualitative meaning.

For the computation of $\mathbf{Q} \in \mathbb{R}^{m\times m}$, either of eqs 88 or 89 may be used. This requires approximately $2m^3/3$ FLOPs for the LU decomposition of $(\mathbf{1} - \mathbf{X})$, and approximately $2m^3$ FLOPs for the linear equation solution, for about $8m^3/3$ total effort. The factorization and the solution steps, including partial pivoting with row permutations, are performed by the LAPACK routines xGESV, xGETRF, and xGETRS. The computation of $\mathbf{X}(\mathbf{Q})$ from eqs 90 or 91 also requires $8m^3/3$ FLOPS using the same routines. For an arbitrary $\mathbf{Q}$, some care is required to monitor errors introduced by the potentially large condition number of the matrix $(\mathbf{Q} + \mathbf{1})$ during the linear equation solution and also to monitor the errors in the skew-symmetry in the resulting $\mathbf{X}$.

For the computation of $\mathbf{Q} \in \mathbb{R}^{m\times n}$, for the parametrization of the Stiefel and Grassmann manifolds, the matrix $\mathbf{X}$ is taken as

$$\mathbf{X} = \begin{pmatrix} \mathbf{B} & -\mathbf{A}^{\mathrm{T}} \\ \mathbf{A} & \mathbf{0} \end{pmatrix} \tag{97}$$

with skew-symmetric $\mathbf{B} \in \mathbb{R}^{n\times n}$ and where $\mathbf{A} \in \mathbb{R}^{p\times n}$ with $p = (m - n)$. The Grassmann manifold parametrization corresponds to $\mathbf{B} = \mathbf{0}$ and to a BOD $\mathbf{X}$. The matrix $\mathbf{Q}$ is given by

$$\mathbf{Q} = (\mathbf{1} + \mathbf{X})(\mathbf{1} - \mathbf{X})^{-1}\mathbf{1}^{m\times n} = \begin{pmatrix} \mathbf{1} + \mathbf{B} & -\mathbf{A}^{\mathrm{T}} \\ \mathbf{A} & \mathbf{1} \end{pmatrix}\begin{pmatrix} \mathbf{1} - \mathbf{B} & \mathbf{A}^{\mathrm{T}} \\ -\mathbf{A} & \mathbf{1} \end{pmatrix}^{-1}\begin{pmatrix} \mathbf{1}^{n\times n} \\ \mathbf{0}^{p\times n} \end{pmatrix} \tag{98}$$

$$= \begin{pmatrix} \mathbf{1} - \mathbf{A}^{\mathrm{T}}\mathbf{A} + \mathbf{B} \\ 2\mathbf{A} \end{pmatrix}(\mathbf{1} + \mathbf{A}^{\mathrm{T}}\mathbf{A} - \mathbf{B})^{-1} \tag{99}$$

$$= \begin{pmatrix} \mathbf{1} - \mathbf{F} \\ 2\mathbf{A} \end{pmatrix}(\mathbf{1} + \mathbf{F})^{-1} \tag{100}$$

with $\mathbf{F} = \mathbf{A}^{\mathrm{T}}\mathbf{A} - \mathbf{B}$. The computation of $\mathbf{F} \in \mathbb{R}^{n\times n}$ requires $2(m - n)n^2$ FLOPs, the LU factorization of $(\mathbf{1} + \mathbf{F})$ requires $2n^3/3$ FLOPs, the leading subblock $\mathbf{Q}_1$ requires $2n^3$ FLOPs, and the $\mathbf{Q}_2$ subblock requires $2(m - n)n^2$ FLOPs, for about $4(m - n/3)n^2$ FLOPs total effort. Note that when $\mathbf{B} = \mathbf{0}$, the matrix $(\mathbf{1} + \mathbf{F})$ is symmetric and positive definite and the leading $\mathbf{Q}_1$ subblock is symmetric. This allows the use of Cholesky factorization of $(\mathbf{1} + \mathbf{F})$, which requires only $n^3/3$ FLOPs, and reduces the $\mathbf{Q}_1$ effort by a factor of 2, for about $4(m - 2n/3)n^2$ FLOPs total effort. The Cholesky factorization and solution are performed with the LAPACK routines xPOSV, xPOTRF, and xPOTRS.

Given a $\mathbf{Q} \in \mathbb{R}^{m\times n}$, this process may be reversed to compute the parameter matrix $\mathbf{X}$ by the following sequence:

$$\mathbf{F} = (\mathbf{1} - \mathbf{Q}_1)(\mathbf{1} + \mathbf{Q}_1)^{-1} \tag{101}$$

$$\mathbf{B} = \frac{1}{2}(\mathbf{F}^{\mathrm{T}} - \mathbf{F}) \tag{102}$$

$$\mathbf{A} = \frac{1}{2}\mathbf{Q}_2(\mathbf{1} + \mathbf{F}) \tag{103}$$

The LU factorization of $(\mathbf{1} + \mathbf{Q}_1)$ requires $2n^3/3$ FLOPs, the computation of $\mathbf{F}$ then requires $2n^3$ FLOPs, extraction of $\mathbf{B}$ the skew-symmetric component of $\mathbf{F}$ requires $n(n - 1)$ FLOPs, and the matrix multiplication for $\mathbf{A}$ requires $2(m - n)n^2$ effort, for a total effort of about $2(m + n/3 + 1/2)n^2$ FLOPs. If the leading subblock $\mathbf{Q}_1$ is symmetric, then the Cholesky factorization of $(\mathbf{1} + \mathbf{Q}_1)$ requires $n^3/3$ FLOPs, the symmetric $\mathbf{F}$ requires n^3 FLOPs, and the computation of $\mathbf{A}$ requires $2(m - n)n^2$ effort, for a total effort of about $2(m - n/3)n^2$ FLOPs. In this case, $\mathbf{B} = \mathbf{0}$ and $\mathbf{X}$ is BOD in eq 97. If the parametrization of the Grassmann manifold is required and $\mathbf{Q}_1$ is not symmetric, then the left polar decomposition $\mathbf{Q}_1 = \tilde{\mathbf{Q}}_1\mathbf{Z}$ and the transformation $\tilde{\mathbf{Q}}_2 = \mathbf{Q}_2\mathbf{Z}^{\mathrm{T}}$ results in the factorization $\mathbf{Q} = \tilde{\mathbf{Q}}\mathbf{Z}$, with $\tilde{\mathbf{Q}} = \mathrm{Cay}(\mathbf{X})\mathbf{1}^{m\times n}$ representing the Grassmann manifold with BOD $\mathbf{X}$.

The chain-rule transformation of gradients eq 1 consists of application of the relation

$$\frac{\partial \mathbf{Q}}{\partial X_{jk}} = 2(\mathbf{1} - \mathbf{X})^{-1}\frac{\partial \mathbf{X}}{\partial X_{jk}}(\mathbf{1} - \mathbf{X})^{-1} \tag{104}$$

which follows from eq 89 and from the general matrix identity $\partial\mathbf{A}^{-1}/\partial t = \mathbf{A}^{-1}(\partial\mathbf{A}/\partial t)\mathbf{A}^{-1}$. Using eq 8, the gradient element $\partial E/\partial X_{jk}$ is given by

$$\frac{\partial E}{\partial X_{jk}} = \mathrm{tr}\left(\frac{\partial E}{\partial \mathbf{Q}}^{\mathrm{T}}(\mathbf{1} - \mathbf{X})^{-1}\frac{\partial \mathbf{X}}{\partial X_{jk}}(\mathbf{1} - \mathbf{X})^{-1}\mathbf{1}^{m\times n}\right) \tag{105}$$

$$= \mathrm{tr}(\mathbf{\Lambda}^{\mathrm{T}}\mathbf{E}^{jk}\mathbf{\Omega}) \tag{106}$$

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$$= \sum_{i=1}^{n} \Lambda_{ji}\Omega_{ki} - \Lambda_{ki}\Omega_{ji} \tag{107}$$

with

$$\mathbf{\Lambda} = (\mathbf{1} + \mathbf{X})^{-1}\mathbf{g} \tag{108}$$

$$\mathbf{\Omega} = 2(\mathbf{1} - \mathbf{X})^{-1}\mathbf{I}^{m\times n} = \mathbf{Q} + \mathbf{I}^{m\times n} \tag{109}$$

Because $(\mathbf{1} + \mathbf{X}) = (\mathbf{1} - \mathbf{X})^{\mathrm{T}}$, the same LU factors may be used for the computation of $\mathbf{\Lambda}$ and for $\mathbf{Q}$ or $\mathbf{\Omega}$. In the full $n = m$ case, the gradient transformation effort requires up to $2m^3/3$ FLOPS for the LU decomposition, $2m^3$ FLOPs for the computation of $\mathbf{\Lambda}$, and $4m$ FLOPS for each gradient element in eq 107, for a total of approximately $(14m/3 - 2)m^2$ FLOPs; if the LU decomposition step can be skipped, then the total effort is $(4m - 2)m^2$ FLOPs. For the $n < m$ case, the computation of the $\mathbf{\Lambda}$ matrix using the partitioning of eq 97 results in

$$\mathbf{\Lambda}_1 = (\mathbf{1} + \mathbf{F})^{-\mathrm{T}}(\mathbf{g}_1 + \mathbf{A}^{\mathrm{T}}\mathbf{g}_2) \tag{110}$$

$$\mathbf{\Lambda}_2 = \mathbf{g}_2 - \mathbf{A}\mathbf{\Lambda}_1 \tag{111}$$

Each gradient element requires $4n$ FLOPs in eq 107. Assuming that $\mathbf{Q}$ and the LU or Cholesky factorization of $(\mathbf{1} + \mathbf{F})$ have been previously computed, the gradient transformation requires about $8(m - n/2)n^2$ FLOPs for the Stiefel manifold and $(8m - 6n)n^2$ FLOPs for the Grassmann manifold.

2.6. Single-Vector Parametrizations. A common situation within quantum chemistry is the characterization of a single normalized vector $\|\mathbf{Q}\| = 1$, $\mathbf{Q} \in \mathbb{R}^m$. This corresponds to the parametrization of a single point on the surface of a unit hypersphere of dimension m (sometimes denoted topological dimension $m - 1$). Although there are no orthogonalization constraints associated with this situation, the vector may be parametrized using the four approaches discussed herein with the condition $n = 1$. The Grassmann and Stiefel parametrizations are equivalent for this situation, with $N_e = m - 1$ essential parameters $\{\boldsymbol{\varphi}\}$.

Using the BOD $\mathbf{X}$ of eq 25, the exponential parametrization results in the SVD, $\mathbf{A} = \mathbf{V}\theta$ with $\theta = \|\mathbf{A}\|$, and in

$$\mathbf{Q} = \begin{pmatrix} Q_1 \\ \mathbf{Q}_2 \end{pmatrix} = \exp(\mathbf{X})\mathbf{e}_1 = \begin{pmatrix} \cos\theta \\ \mathbf{V}\sin\theta \end{pmatrix} \tag{112}$$

Given the unit vector $\mathbf{Q}$, the parameter vector $\mathbf{A}$ may be determined from eq 35 as $\theta = \arccos(Q_1)$ and $\mathbf{A} = \mathbf{Q}_2(\theta/\sin\theta)$. This parametrization has the useful feature that individual vector elements A_k or Q_k may be computed or extracted without necessarily determining the full vectors. See refs 28 and 82 for examples of quantum chemistry applications that use this parametrization.

The Householder parametrization corresponds to eqs 66 and 69 with the single reflector $\mathbf{H}^{(1)}$

$$\mathbf{Q} = \mathbf{H}^{(1)}\mathbf{e}_1 = \begin{pmatrix} 1 - \tau \\ -\tau\mathbf{v}^{(1)} \end{pmatrix} \tag{113}$$

Given the unit vector $\mathbf{Q}$, the parameter vector $\mathbf{v}^{(1)}$ is given by a single determination of eq 67. For the continuous parametrization ($\beta = +1$ in eq 67), this results in $\tau = (1 - Q_1)$ and $\mathbf{v}^{(1)} = \mathbf{Q}_2(Q_1 - 1)^{-1}$. As with the previous exponential parametrization, the Householder parametrization allows the computation and extraction of individual Q_k and $v_k^{(1)}$ elements.

The Givens parametrization corresponds to eq 79 and yields

$$\mathbf{Q} = \mathbf{G}(m, 1, \theta_{m,1})^{\mathrm{T}}\ldots\mathbf{G}(2, 1, \theta_{2,1})^{\mathrm{T}}\mathbf{e}_1 = \begin{pmatrix} \cos\theta_{m,1}\cos\theta_{m-1,1}\ldots\cos\theta_{2,1} \\ \sin\theta_{2,1} \\ \sin\theta_{3,1}\cos\theta_{2,1} \\ \vdots \\ \sin\theta_{m,1}\cos\theta_{m-1,1}\ldots\cos\theta_{2,1} \end{pmatrix} \tag{114}$$

The elements of $\mathbf{Q}$ may be evaluated recursively from the sequence of Givens rotations. Given the unit vector $\mathbf{Q}$, the rotation angles are determined recursively with the QR factorization procedure limited to the single column. Thus, unlike the previous exponential and Householder parametrizations, individual Q_k and $\theta_{k,1}$ parameters cannot be computed without first determining at least some of the previous parameters within the recursions. It is interesting to also consider the following alternative sequence of Givens rotation angles:

$$\mathbf{Q} = \mathbf{G}(m, m-1, \theta_{m,m-1})^{\mathrm{T}}\ldots\mathbf{G}(3, 2, \theta_{3,2})^{\mathrm{T}}\mathbf{G}(2, 1, \theta_{2,1})^{\mathrm{T}}\mathbf{e}_1 = \begin{pmatrix} \cos\theta_{2,1} \\ \sin\theta_{2,1}\cos\theta_{3,2} \\ \vdots \\ \sin\theta_{2,1}\sin\theta_{3,2}\ldots\cos\theta_{m,m-1} \\ \sin\theta_{2,1}\sin\theta_{3,2}\ldots\sin\theta_{m,m-1} \end{pmatrix} \tag{115}$$

These rotation angles correspond to a codiagonal sequence of parameters rather than the angles within the first column. This parametrization corresponds to the familiar mapping between the hyperspherical coordinates and the Cartesian coordinates $\mathbf{Q}$. Given the unit vector $\mathbf{Q}$, it is then seen that the hyperspherical rotation parameters may be determined with a QR decomposition using the appropriately ordered sequence of rotation angles.

Finally the Cayley parametrization of eq 100 results in

$$\mathbf{Q} = \begin{pmatrix} 1 - F \\ 2\mathbf{A} \end{pmatrix}(1 + F)^{-\mathbf{1}} \tag{116}$$

with $F = \mathbf{A}^T\mathbf{A}$. Given the unit vector $\mathbf{Q}$, the parameters may be determined from $\mathbf{A} = \mathbf{Q}_2(1 + Q_1)^{-1}$. As with the previous exponential and Householder parametrizations, the Cayley parametrization allows the computation and extraction of individual Q_k and A_k elements. Comparing eqs 113 and 116 in terms of the corresponding parameters $\{\boldsymbol{\varphi}\}$, it is seen that $\tau = 2/(1 + F)$ and $(1 - \tau) = -(1 - F)/(1 + F)$; therefore the single-vector Householder and Cayley parametrizations of $\mathbf{Q}$ differ only by an overall sign.

3. SUMMARY AND CONCLUSIONS

Four representations and parametrizations of orthogonal matrices $\mathbf{Q} \in \mathbb{R}^{m\times n}$ in terms of the minimal number of essential parameters $\{\boldsymbol{\varphi}\}$ have been discussed: the exponential representation, the Householder reflector representation, the Givens rotation representation, and the rational Cayley transform representation. Given a set of parameters, approximate operation counts for the $\mathbf{Q}(\boldsymbol{\varphi})$ computation, the $\boldsymbol{\varphi}(\mathbf{Q})$

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Table 1. Operation Counts for $\mathbf{Q}(\boldsymbol{\varphi})$ Computation

parametrization	$n < m$ Grassmann	$n < m$ Stiefel	$n = m$
exponential	$(8m + 22n)n^2$	$(8m + 30n)n^2$	$8m^3$
Householder	$2(m - n)n^2$	$2(m - n/3)n^2$	$4m^3/3$
Givens	$3(m - n)n^2$	$3(m - n/3)n^2$	$2m^3$
Cayley	$4(m - 2n/3)n^2$	$4(m - n/3)n^2$	$8m^3/3$

Table 2. Operation Counts for $\boldsymbol{\varphi}(\mathbf{Q})$ Computation

parametrization	$n < m$ Grassmann[a]	$n < m$ Stiefel	$n = m$
exponential	$2(m + 13n)n^2$	$2(m + 14n)n^2$	$27m^3$
Householder	$2(m - n)n^2$	$2(m - n/3)n^2$	$4m^3/3$
Givens	$3(m - n)n^2$	$3(m - n/3)n^2$	$2m^3$
Cayley	$2(m - n/3)n^2$	$2(m + n/3)n^2$	$8m^3/3$

[a]It is assumed that the leading subblock of $\mathbf{Q}$ is symmetric for the exponential and Cayley parametrizations and is upper-triangular for the Householder and Givens parametrizations.

Table 3. Operation Counts for the Gradient Transformation[a]

parametrization	$n < m$ Grassmann	$n < m$ Stiefel	$n = m$
exponential[b]	-	-	$6m^3$
Householder	$6(m - n)n^2$	$(6m - 2n)n^2$	$4m^3$
Givens	$8(m - n)n^2$	$(8m - n/3)n^2$	$23m^3/3$
Cayley[c]	$(8m - 6n)n^2$	$8(m - n/2)n^2$	$4m^3$

[a]It is assumed that $\mathbf{Q}$ is available for all of the parametrizations. [b]It is assumed that the quasidiagonal factorization is available. [c]It is assumed that the LU factorization is available for $(\mathbf{1} + \mathbf{X})$ or $(\mathbf{1} + \mathbf{F})$.

computation, and the gradient transformation computation are summarized in Tables 1−3.

From these tables, it is clear that the exponential parametrization generally requires the most effort of the four methods. In the $\mathbf{Q}(\boldsymbol{\varphi})$ computation, for example, the leading terms for the rectangular $n < m$ parametrizations are $8mn^2$, which is 2 to 4 times larger than the leading terms of the other parametrizations. In the square $n = m$ case, the exponential parametrization requires 3 to 6 times more effort than the other parametrizations for the $\mathbf{Q}(\boldsymbol{\varphi})$ mapping, and up to about 20 times the effort for the $\boldsymbol{\varphi}(\mathbf{Q})$ mapping. The primary reason for this is that the exponential parametrization requires relatively expensive iterative quasidiagonal factorization, Schur decomposition, and SVD steps, while the other parametrizations require noniterative and less demanding computational kernels such as QR decomposition and LU factorization. The gradient transformation for the $n < m$ cases is also problematic for the exponential parametrization because it is formulated only using the square $n = m$ factorization, whereas the other methods can all take advantage of the partitioning of the $\mathbf{X}$ and $\mathbf{Q}$ matrices in order to reduce the computational effort. One conclusion of this work is that new algorithms for the exponential parametrization need to be explored in order to compete with the efficiency of the other parametrizations. There are other algorithms to compute the matrix exponential and matrix logarithm (see refs 54 and 55). For example, one popular approach[56] to compute the matrix exponential for general matrices is based on the identity $\exp(\mathbf{X}) = \exp(\mathbf{X}/p)^p$, where $p = 2^k$ for some integer k. The integer k is chosen to be sufficiently large so that $\exp(\mathbf{X}/p)$ may be computed accurately with a low-order Taylor expansion or a low-order Padé approximant (such as the Cayley transform discussed in Section 2.5). This intermediate matrix is then recursively squared k times to compute the final result. An analogous approach may be applied to the matrix logarithm. This approach requires typically at least $\sim 2m^3$ FLOPs to approximate $\exp(\mathbf{X}/p)$ (e.g., $\sim 8m^3/3$ for the Cayley transform), and the subsequent recursive squaring requires $2km^3$ FLOPs, for a minimum of about $2(k + 1)m^3$ effort. In order to compete favorably with the quasidiagonal factorization algorithms used herein, which require $8m^3$ effort, k would need to be 3 or smaller. This would only apply to matrices with small $\|\mathbf{X}\|$. In contrast, the quasidiagonal factorization approach requires approximately constant effort, regardless of $\|\mathbf{X}\|$.

The Householder and Givens parametrizations are both based on QR decomposition, so they share many common features. The main difference is that a single Householder transformation requires less effort than the equivalent sequence of Givens rotations, so the resulting operation counts all favor the Householder-based approach in Tables 1−3. However, the implementation of the Givens parametrization is overall simpler than that of the Householder parametrization; an example of this is the gradient transformation algorithm, which is considerably simpler for the Givens parametrization. Going beyond operation counts to determine the overall efficiency, another important factor is the fraction of those arithmetic operations that occur in scalar operations, vector operations (level-1 BLAS), matrix−vector operations (level-2 BLAS), and matrix−matrix operations (level-3 BLAS). In this respect, the Householder-based approach also has advantages over the Givens approach. In the Givens-based approach, almost all of the arithmetic operations occur within vector operations, whereas in the Householder-based approach, most of the operations occur within matrix−vector operations and even some within matrix−matrix operations.

The Cayley transform parametrization is comparable to the QR-based approaches in operation counts. Its main advantage is that a good fraction of the arithmetic operations occur within matrix−vector and matrix−matrix operations. The Cayley parametrization also results in a relatively simple gradient transformation algorithm. The main disadvantage is that not all $\mathrm{SO}(m)$ matrices can be represented with the Cayley parametrization, and even some matrices that can be represented have large condition numbers in the $\boldsymbol{\varphi}(\mathbf{Q})$ mapping, which can result in large numerical errors. This can be monitored and detected, but, depending on the application, it may be unclear how the array $\mathbf{Q}$ should be changed to eliminate this situation. However, for those matrices that can be represented with the Cayley transform, the mapping between $\mathbf{Q}$ and $\boldsymbol{\varphi}$ is one-to-one. This is in contrast to the exponential parametrization for which the $\mathbf{Q}(\boldsymbol{\varphi})$ mapping is many-to-one due to the cyclic nature of the plane rotation angles, to the Householder parametrization which has an ambiguity associated with each elementary reflector, and to the Givens parametrization which, in addition to the gimbal lock situations, also has a many-to-one mapping associated with each plane rotation angle.

Overall, the Householder parametrization is the most efficient for all three of the operations examined in this work. In the $\mathbf{Q}(\boldsymbol{\varphi})$ mapping in Table 1, it is seen to be more efficient for the rectangular Grassmann, rectangular Stiefel, and the square parametrizations by a significant amount. For the $\boldsymbol{\varphi}(\mathbf{Q})$ mapping in Table 2, it is still the most efficient, but by a smaller degree. For the rectangular gradient transformation in Table 3, it is 25% faster than the Givens and Cayley parametrizations, whereas for the square parametrization it is about 50% faster than the Givens transformation, 33% faster than the exponential

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parametrization, and comparable to the Cayley transformation. There are two caveats to the use of the Householder parametrization. The first is that the continuous choice of reflector parameters during the QR decomposition step can result in larger numerical errors; the importance of this depends on the specific application, and for the QR decomposition of orthogonal or near-orthogonal matrices for which the phases of the columns may be chosen arbitrarily, any errors are minimal and this is not a significant disadvantage. The second is that for square matrices, the sign of $\det(\mathbf{Q})$ depends on the number of reflectors that are used in the parametrization, and the number of reflectors must be carefully chosen in some applications that depend either on closure with respect to matrix multiplication or on the representation of only $\mathrm{SO}(m)$ matrices.

In the multifacet generalization of the GCF method,[44,82,83] the individual configuration state function (CSF) expansion coefficients within a contracted basis function are given by the ordered sequence of rectangular matrix products

$$x_k = \boldsymbol{\alpha}_{\mathrm{tail},j(1;k)}\boldsymbol{\alpha}_{j(1;k),j(2;k)}\boldsymbol{\alpha}_{j(2;k),j(3;k)}\cdots\boldsymbol{\alpha}_{j(N_{\mathrm{orb}}-1;k),\mathrm{head}} \tag{117}$$

This general representation form is associated with *matrix product state* (MPS) wave functions,[84,85] and the MFGCF wave function is then given as a linear combination of MPSs. The first matrix $\boldsymbol{\alpha}_{\mathrm{tail},j(1;k)}$ is a row vector, and the last matrix $\boldsymbol{\alpha}_{j(N_{\mathrm{orb}}-1;k),\mathrm{head}}$ is a column vector, so that the sequence of matrix products in eq 117 is a scalar quantity. The matrix $\boldsymbol{\alpha}_{j(q-1;k),j(q;k)}$ contains the arc factors associated with the Shavitt graph arc that connects node $j(q-1;k)$ at level $q-1$ and node $j(q;k)$ at level q for CSF k of the underlying graph. Each CSF k touches a unique subset of the arcs within the graph, allowing each CSF coefficient to assume a unique value. For full-CI Shavitt graphs with N_{orb} orbitals and N_{el} electrons, the number of CSFs increases exponentially as $O((N_{\mathrm{orb}})^{N_{\mathrm{el}}})$, whereas the number of arcs in the graph increases only polynomially as $O(N_{\mathrm{el}}^2 N_{\mathrm{orb}})$. The optimization of the wave function reduces to the optimization of the elements of the arc factor arrays $\boldsymbol{\alpha}_{j,j'}$. A common feature of MPS expansions is the redundancy associated with transformations of the form

$$\begin{aligned} x_k &= \boldsymbol{\alpha}_{\mathrm{tail},j(1;k)}(\boldsymbol{\alpha}_{j(1;k),j(2;k)}\mathbf{B}_{j(2;k)})(\mathbf{B}^{-1}_{j(2;k)}\boldsymbol{\alpha}_{j(2;k),j(3;k)})\cdots\boldsymbol{\alpha}_{j(N_{orb}-1;k),\mathrm{head}} \\ &= \boldsymbol{\alpha}_{\mathrm{tail},j(1;k)}\tilde{\boldsymbol{\alpha}}_{j(1;k),j(2;k)}\tilde{\boldsymbol{\alpha}}_{j(2;k),j(3;k)}\cdots\boldsymbol{\alpha}_{j(N_{\mathrm{orb}}-1;k),\mathrm{head}} \end{aligned} \tag{118}$$

where $\mathbf{B}_j$ is some arbitrary nonsingular square transformation matrix associated with node j, and $\tilde{\boldsymbol{\alpha}}_{j,j'}$ are the transformed arc factors. Because x_k is unchanged by this transformation of adjacent sets of arc factors, the representation in terms of the elements of the arc factor arrays is redundant (or overdetermined). Further analysis[83] shows that the number of degrees of freedom in this redundancy corresponds exactly to the Grassmann manifold, and this allows the arc factor arrays to be parametrized as subblocks of rectangular orthogonal matrices without loss of flexibility in the basis function. The original basis function parametrization[82] (called a single-facet GCF) allowed only for column dimensions $n = 1$, and an exponential parametrization of these matrix elements was used as discussed in Section 2.6. The subsequent multifacet generalization allows more general column dimensions, resulting in matrix dimensions $\mathbf{Q} \in \mathbb{R}^{m\times n}$ typically in the range of $n = 10$ to 20 and $m \approx 4n$. The arc factor arrays $\boldsymbol{\alpha}_{j,j'}$ are subblocks of the orthogonal array $\mathbf{Q}$. In principle, any of the four parametrizations discussed herein could have been chosen for this task. This particular application involves the repeated computation of both the $\mathbf{Q}(\boldsymbol{\varphi})$ and the $\boldsymbol{\varphi}(\mathbf{Q})$ mappings during the wave function optimization procedure, in contrast to some other electronic structure applications which rely predominantly or entirely on just the $\mathbf{Q}(\boldsymbol{\varphi})$ mapping.[38,57] This is because part of the optimization process occurs directly using the arc factor elements within one orbital level with the assumption that all other arc factors are held fixed; during this step, the redundancy associated with arc factor transformations at adjacent levels as shown in eq 118 does not apply. However, at other steps of the optimization, simultaneous arc factor variations at multiple levels are allowed, and it is appropriate to work within just the essential Grassmann manifold parametrization in order to avoid numerical singularities associated with the arc factor redundancies. Furthermore, it is sometimes appropriate to transform the columns of the $\boldsymbol{\alpha}_{j,j'}$ arrays to impose some temporary conditions, for example, in order to characterize the contribution of each individual column to the overall wave function or to some molecular property. This corresponds to the Stiefel manifold parametrization, which must subsequently be factored as the product of the essential Grassmann manifold and the transformation arrays $\mathbf{B}_j$ as in eq 118. Finally, the optimization gradient elements are computed initially in the arc factor representation, and these must be transformed each optimization iteration using the chain rule, eq 1. Thus, in this application, several aspects of the Grassmann and Stiefel manifold parametrizations that have been discussed come into play. The ultimate parametrization choice was based primarily on the overall efficiency advantage of the Householder representation, including, in particular, the efficient gradient transformation as shown in Table 3. The potential difficulties associated with the Householder representation are unimportant in this method, as might not be the case for other quantum chemical applications. In particular, the signs of the columns of the arc factor arrays may be chosen freely, thereby allowing the final wave function to be represented always using the stable parameter choice for the individual reflectors. The continuous parameter choice is imposed during the optimization procedure when continuity is important, and this is converted immediately if necessary to the stable parameter choice upon completion of that step. Further details of this quantum chemical application may be found in refs 44 and 83.

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Notes

The authors declare no competing financial interest.

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