I. INTRODUCTION

Proton and hydride transfer reactions play a vital role throughout chemistry and biochemistry. They occur in systems ranging in size from gas phase molecular reactions involving a small number of atoms to enzyme-catalyzed biochemical reactions involving tens of thousands of atoms. The importance of such hydrogen transfer reactions ensures their status as among the most widely studied class of chemical reactions. Experimental data and theoretical calculations indicate the importance of nuclear quantum effects such as zero point energy and hydrogen tunneling in hydrogen transfer reactions. These nuclear quantum effects, which are due to the light mass of the hydrogen nucleus, may significantly affect the reaction mechanisms of hydrogen transfer reactions.

Thus, the inclusion of hydrogen nuclear quantum effects in theoretical and computational studies of hydrogen transfer reactions is critical in order to gain a meaningful understanding of such processes. In systems of only a few degrees of freedom, all nuclei may be treated quantum mechanically, and fully quantum dynamical simulations may be carried out through wavepacket propagation. This approach is computationally intensive even for a few of degrees of freedom and is not feasible for large or even moderately sized systems. A more practical approach for these larger systems is to treat the transferring hydrogen nuclei (and possibly also any coupled hydrogen nuclei) quantum mechanically and the remainder of the nuclei classically. This mixed quantum/classical approach forms the basis for a variety of mixed quantum/classical methods, including the surface hopping molecular dynamics with quantum transitions (MDQT) method and the mean field methods.

Both exact quantum dynamics and mixed/quantum classical dynamics require multiple calculations of accurate nuclear wavefunctions. In surface hopping and mean field mixed quantum/classical methods, hydrogen vibrational wavefunctions are required at every molecular dynamics time step. This requirement represents a modest computational cost for one-dimensional systems (i.e., one nuclear quantum degree of freedom). Unfortunately, however, the cost of the calculation of these nuclear wavefunctions increases dramatically with the dimensionality of the quantum subsystem. Thus, although mixed quantum/classical methods reduce the intractable problem of a large number of nuclear quantum degrees of freedom to a problem of only a few important quantum modes, the considerable cost associated with the calculation of the multidimensional nuclear wavefunctions remains. This paper addresses the important issue of the efficient calculation of multidimensional nuclear wavefunctions, particularly for mixed quantum/classical molecular dynamics simulations.

In general, a method for calculating multidimensional hydrogen nuclear wavefunctions for use in mixed quantum/classical molecular dynamics simulations of hydrogen transfer reactions should satisfy three main requirements.
due to the dynamically changing environment of the transferring hydrogen atom during the reaction, the entire range of the hydrogen coordinates should be treated without bias. Second, due to the importance of excited vibrational states in hydrogen transfer reactions, this method should provide an orthogonal set of accurate ground and excited state wavefunctions. (Typically, no more than 5–10 excited hydrogen vibrational states are required for standard applications.) Third, since the hydrogen vibrational wavefunctions must be calculated at every molecular dynamics time step, this method should be extremely computationally efficient. (Note that typically the potential can be determined very rapidly for these types of simulations, rendering the calculation of the nuclear wavefunction the bottleneck of the calculation.)

Previously Hammes-Schiffer and Drukker\(^9\) developed a Multiconfigurational Self-Consistent-Field (MCSCF) approach for calculating multidimensional hydrogen vibrational wavefunctions. This MCSCF approach represents the vibrational wavefunctions as linear combinations of single configurations that are products of one-dimensional wavefunctions.\(^10\) The diagonalization of large matrices is avoided by including only a relatively small number of configurations. This approach has been used in conjunction with the mixed quantum/classical MDQST method to simulate proton transport along hydrogen-bonded water chains.\(^11\) This previous implementation utilized harmonic oscillator basis functions, which require costly numerical integration of the potential energy matrix elements and introduce bias due to the choice of the centers and frequencies of the basis functions. Moreover, in this previous implementation the energy of only a single vibrational adiabatic state was optimized, leading to inaccuracies in the other states. Thus, this previous implementation of the MCSCF approach does not adequately satisfy the three requirements listed above.

The limitations of the basis set used in this previous implementation may be avoided by representing the one-dimensional wavefunctions directly on a grid. A number of grid-based techniques have been developed for the calculation of nuclear wavefunctions in the context of fully quantum dynamics simulations. These techniques include the discrete variable representation (DVR) developed by Light and co-workers,\(^12,13\) the discrete Fourier transform (DFT) methods pioneered by Kosloff,\(^14\) and the Fourier grid Hamiltonian (FGH) method introduced by Balint-Kurti and Marston.\(^15,16\) All three methods avoid the cost and difficulties associated with the numerical calculation of potential energy integrals over basis functions. In the DFT and FGH methods, the kinetic energy integrals are efficiently calculated with Fourier transformations between coordinate and momentum representations. Thus, for one-dimensional systems all three methods facilitate the efficient construction of a Hamiltonian matrix representation of order \(N\), where \(N\) is the number of one-dimensional grid points. Diagonalization of the Hamiltonian matrix provides the nuclear wavefunction amplitudes directly on the grid, as well as the energies of the system. Typically the diagonalization step is fast for one-dimensional systems.

These grid-based methods are easily extended to multiple dimensions (i.e., multiple nuclear quantum degrees of freedom).\(^13,17\) Since they allow for the separation of the kinetic energy operator, construction of the multidimensional Hamiltonian matrix elements is often relatively inexpensive. The main difficulty is the rapid increase in the size of the Hamiltonian matrix, which scales as \(N^n\), where \(n\) is the number of dimensions. If conventional techniques are used, the diagonalization step scales as \(N^{3n}\). This represents an enormous increase in computational cost with the dimensionality of the system. For use with dynamical simulations, this effectively rules out systems with \(n > 2\) and severely limits the number of grid points per dimension (which can impact the accuracy). This serious limitation of conventional grid-based methods has been addressed by a number of research groups, resulting in the development of grid-based methods that avoid such scaling problems. These methods include a successive diagonalization and truncation multidimensional DVR method,\(^18,19\) as well as the application of Lanczos and Davidson diagonalization schemes to DVR\(^20–22\) and FGH.\(^23\) An alternative approach to calculating vibrational energies of many-mode systems is the variational self-consistent-field method.\(^24,25\)

In this paper we present a FGH implementation of the MCSCF method described above. This FGH-MCSCF method is more efficient, accurate, and robust than the previous implementation of the MCSCF method. The use of a grid-based method eliminates the need for costly numerical integration and treats the entire range of hydrogen coordinates without bias. Moreover, in the current implementation a state-averaged MCSCF approach is utilized to obtain an orthogonal set of accurate ground and excited state wavefunctions. This state-averaged approach is particularly important for mixed quantum/classical molecular dynamics simulations that incorporate vibrationally nonadiabatic effects. Furthermore, as will be shown below, the state-averaged FGH-MCSCF method is more efficient and scales better than the standard grid-based methods for the calculation of the hydrogen vibrational states in typical applications to hydrogen transfer reactions. Note that our previous implementations of the MCSCF approach were applied to systems in which the quantum mechanical subsystem contained two or three hydrogen nuclei, each moving in a single dimension. The current implementation is also applied to a single hydrogen nucleus moving in three dimensions. (A related method has been presented by Dutta and co-workers for two-dimensional systems.\(^26\))

The remainder of this paper presents the detailed derivation of the FGH-MCSCF method, as well as a series of test calculations comparing its performance with exact diagonalization (iterative and conventional) schemes.

II. THEORY

The Fourier Grid Hamiltonian Multiconfigurational Self-Consistent-Field (FGH-MCSCF) method is designed for the inexpensive but accurate calculation of multidimensional hydrogen nuclear wavefunctions on a grid. The theoretical formulation is organized into two sections. Section II A reviews the background required for development and discussion of the FGH-MCSCF method. Section II B presents the develop-
A. Background

This section reviews grid-based methods for calculation of one-dimensional and multidimensional nuclear wavefunctions. Consider a particle with mass \( m \) moving in a one-dimensional potential \( V(x) \). The nonrelativistic Hamiltonian operator, \( \hat{H} \), for this system can be written as a sum of the kinetic energy and potential energy operators \( \hat{T} \) and \( V(\hat{x}) \), respectively,

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\hat{x}) = \hat{T} + V(\hat{x}).
\]  

In general, analytical solutions to the Schrödinger equation for such a system will not exist. Approximate solutions are found by introducing an incomplete basis set leading to a truncated matrix representation \( \mathbf{H} \) of the Hamiltonian. For a basis set of \( N \) orthonormal functions, \( \{ \phi_\mu(x) \}_N \), the kinetic energy and potential energy matrix elements comprising the Hamiltonian matrix elements are

\[
T_{\mu\mu'} = \langle \phi_\mu(x) | \hat{T} | \phi_{\mu'}(x) \rangle,
\]

\[
V_{\mu\mu'} = \langle \phi_\mu(x) | V(\hat{x}) | \phi_{\mu'}(x) \rangle.
\]

The resulting eigenvalue problem can be written in matrix form as \( \mathbf{H}\text{c} = \text{ec} \) and is solved by diagonalization of \( \mathbf{H} \). The \( N \) eigenvalues correspond to one-dimensional wavefunction energies \( \epsilon_\mu \), and the eigenfunctions correspond to expansion coefficients \( c_{\mu i} \), where \( \psi_i(x) \approx \sum_\mu c_{\mu i} \phi_\mu(x) \).

This representation of wavefunctions and Hamiltonian matrix elements is often called the function basis representation (FBR) and will be referred to as such in this paper. Usually the kinetic energy integrals can be calculated analytically, but this is often not the case for the potential energy integrals required for the calculation of vibrational wavefunctions. Although the potential energy matrix elements can be approximated by numerical integration, this can introduce considerable error as well as computational expense. In the area of quantum dynamics a number of techniques have been developed to address this problem. These include the widely used discrete variable representation (DVR) method, pioneered by Light and co-workers,\(^{12,13}\) and the related Fourier grid Hamiltonian (FGH) method introduced by Balint-Kurti and co-workers.\(^{15,16}\) We now review both these treatments for the one-dimensional case in order to provide a clear basis for the development of grid-based multidimensional self-consistent-field methods.

In conventional DVR methods, the basis functions are chosen as classical orthogonal polynomials. The kinetic energy integrals can easily be calculated analytically for these functions. For the potential energy integrals a Gaussian quadrature appropriate to the basis can be found by diagonalizing the coordinate matrix \( \mathbf{X}^\text{FBR} \) in the function basis representation (FBR). The matrix elements of \( \mathbf{X}^\text{FBR} \) can always be determined analytically. The eigenvalues resulting from the diagonalization of \( \mathbf{X}^\text{FBR} \) give the sample points for the potential in the DVR basis, i.e., they define the DVR grid points. The eigenfunctions of \( \mathbf{X}^\text{FBR} \) represent a unitary transformation matrix \( \mathbf{U} \) between the FBR and the DVR bases,

\[
\mathbf{H}^\text{DVR} = \mathbf{U}^\dagger \mathbf{H}^\text{FBR} \mathbf{U} = \mathbf{U}^\dagger \mathbf{T}^\text{FBR} \mathbf{U} + \mathbf{V}^\text{DVR} = \mathbf{T}^\text{DVR} + \mathbf{V}^\text{DVR}. \tag{4}
\]

The central approximation in the DVR method is that the potential energy matrix, \( \mathbf{V}^\text{DVR} \), is diagonal. As a result only the value of the potential at the DVR points is needed, and the sometimes troublesome and expensive numerical integration over basis functions is avoided altogether. For classical orthogonal polynomials this is equivalent to determining the potential energy matrix in the FBR by means of an \( N \) point Gaussian quadrature. \( \mathbf{H}^\text{DVR} \) may be diagonalized to give wavefunctions directly on the grid. In addition the wavefunctions may be transformed into the FBR basis if so desired by use of the matrix \( \mathbf{U} \).

The Fourier grid Hamiltonian (FGH) method is closely related to the DVR approach. The FGH method is based on the fact that the kinetic energy matrix \( \mathbf{T} \) is most easily formed in the momentum representation, and the potential energy matrix \( \mathbf{V} \) is most easily formed in the coordinate representation. Fourier transforms provide a convenient method of transformation between the two representations. The definition of a grid in the coordinate representation and the momentum representation is required for the FGH method. If the uniform grid spacing in the coordinate representation is chosen as \( \Delta x \) the \( N \) grid points in coordinate space are

\[
x_\mu = (\mu - 1) \Delta x, \quad \text{where} \quad \mu = 1, \ldots, N, \tag{5}
\]

and the length, \( L \), of the grid sample range is \( L = N \Delta x \). The grid spacing in the momentum representation, \( \Delta k \), depends on \( \Delta x \),

\[
\Delta k = 2 \pi / N \Delta x = 2 \pi / L \tag{6}
\]

and is used to determine the grid points in momentum space, \( k_\sigma \),\(^{27}\)

\[
k_\sigma = \sigma \Delta k, \quad \text{where} \quad \sigma = -N/2, \ldots, N/2. \tag{7}
\]

In this discrete representation, the wavefunctions are expressed as linear combinations of the coordinate space basis functions \( |x_\mu\rangle \), which can loosely be viewed as discretized unit Dirac delta functions,\(^{15}\)

\[
|x_\mu\rangle = (0,0,...,1,...,0)^T, \tag{8}
\]

where the 1 is at the \( \mu \)th position and the superscript \( T \) indicates the transpose of the vector (i.e., a column vector). The analogous definition holds for the basis functions \( |k_\sigma\rangle \) in momentum space. Given these definitions, the matrix representations of the kinetic and potential energy operators are clear. The kinetic energy matrix \( \mathbf{T} \) is diagonal in momentum space,

\[
T_{\sigma\sigma'} = \langle k_\sigma | \hat{T} | k_{\sigma'} \rangle = \frac{\hbar^2}{2m} k_\sigma^2 \delta_{\sigma\sigma'} \tag{9}
\]

and is easily determined in this representation. The potential energy matrix \( \mathbf{V} \) is diagonal in coordinate space,

\[
V_{\mu\mu'} = \langle x_\mu | V(\hat{x}) | x_{\mu'} \rangle = V(x_\mu) \delta_{\mu\mu'}, \tag{10}
\]
and the value of the potential at each grid point is required for its formation. The expense of calculating numerical potential energy matrix integrals over basis functions is therefore avoided, as in DVR.

Through Fourier transforms, the kinetic energy matrix \( T \) can be transformed into coordinate space, where it is no longer diagonal, and added to the potential energy matrix to form the total FGH Hamiltonian matrix. Balint-Kurti and co-workers present two separate but equivalent methods by which this can be achieved\(^{15,16}\) (1) use of an explicit expression for the Hamiltonian matrix elements derived from Fourier transforms, and (2) use of the fast Fourier transform (FFT) technique\(^{27}\) where each basis function vector undergoes a FFT, the kinetic energy matrix is formed in the momentum representation, and an inverse FFT is carried out to form the kinetic energy matrix in the coordinate representation. The potential energy matrix is then added to form the total Hamiltonian matrix. The following summarizes this second procedure:

\[
H_{\mu\nu} = \langle \phi_\mu | F^{-1} \hat{T} F + V(\hat{\chi}) | \phi_\nu \rangle = T_{\mu\nu} + V_{\mu\nu},
\]

where \( F \) and \( F^{-1} \) represent a FFT and an inverse FFT, respectively. The Hamiltonian matrix \( H \) is diagonalized to give \( N \) eigenvectors corresponding to one-dimensional wavefunctions directly on the grid and \( N \) eigenvalues corresponding to one-dimensional wavefunction or state energies.

As discussed in the literature\(^{13,15}\) the FGH method is closely related to and, in fact, a special case of DVR with the matrix form of Eq. (11) identical to that found in DVR [Eq. (4)] except the transformation matrix is now a Fourier matrix. Furthermore, the FGH method and DVR method based on Chebyshev polynomials\(^{28}\) both utilize an evenly spaced grid and both thereby effectively employ a plane wave basis set. It has been suggested that a plane wave basis set is poorly suited for the description of vibrational wavefunctions since more grid points are required for a given accuracy than for other basis sets.\(^{21}\) However, for reactions such as proton or hydride transfer a plane wave basis set offers the advantage that no region of the grid is biased over any other and the whole reaction is described in an equivalent manner. Given our stated aims in the Introduction, we find the FGH plane wave basis highly suitable. On the other hand, the methodology to be outlined is also applicable for use with DVR and the wide range of basis sets it can employ.

The Hamiltonian operator presented in Eq. (1) may be extended to an \( n \)-dimensional system,

\[
\hat{H}(r) = -\frac{\hbar^2}{2m} \sum_{p} \nabla_{p}^{2} + V(\hat{\mathbf{r}}) = \sum_{p} \hat{T}_{p} + V(\hat{\mathbf{r}}),
\]

where the vector \( \hat{\mathbf{r}} \) represents \( n \) particles, \( \{ \hat{r}^{(1)}, \hat{r}^{(2)}, \ldots, \hat{r}^{(n)} \} \), \( n \) spatial dimensions, \( \{ \hat{x}, \hat{y}, \hat{z} \} \), or some other appropriate orthogonal coordinate system. In this paper we assume that the potential is not separable; however, in cases where there are separable potential terms these may simply be grouped with the one-dimensional kinetic energy terms.

The extension of the DVR and FGH methods from one-dimensional systems to the multiple dimensional systems described by Eq. (12) is straightforward. For DVR a transformation matrix may be found for each dimension. The multidimensional FBR-DVR transformation matrix is simply the direct product of these and may be used to form the multidimensional kinetic energy matrix. The multidimensional potential energy integrals are diagonal in the DVR, so the total multidimensional DVR Hamiltonian matrix may easily be formed.\(^{13}\) Diagonalization of this multidimensional Hamiltonian yields the exact multidimensional solutions for the DVR.

Similarly, the FGH method may be extended to multiple dimensions by use of multidimensional FFTs to form the multidimensional kinetic energy matrix.\(^{17,23}\) Due to the one-dimensional nature of the kinetic energy operator, \( \hat{T} \), the multidimensional kinetic energy matrix elements may also be formed from the separate \( n \) one-dimensional kinetic energy matrices calculated according to Eq. (11).

\[
T_{\mu_{1}\mu_{1}^\prime} \cdots \mu_{n}\mu_{n}^\prime} = \sum_{p} \left[ t_{\mu_{1}^\prime}^{(p)} , \prod_{q \neq p} \delta_{\mu_{q}, \mu_{q}^\prime} \right].
\]

Here the indices \( p \) and \( q \) each refer to a specific dimension and will do so throughout this paper. The multidimensional potential energy matrix is diagonal with its diagonal elements given simply by the value of the potential at the multidimensional grid points,

\[
V_{\mu_{1}\mu_{1}^\prime} \cdots \mu_{n}\mu_{n}^\prime} = \langle \rho^{(1)}(r^{(1)}), \ldots, \rho^{(n)}(r^{(n)}) | V(\hat{\mathbf{r}}) | \rho^{(1)}(r^{(1)}), \ldots, \rho^{(n)}(r^{(n)}) \rangle
\]

\[
\times \delta_{\mu_{1}^\prime}, \mu_{2}^\prime, \ldots, \delta_{\mu_{n}^\prime}, \mu_{n}^\prime}
\]

\[
= \rho^{(1)}(r^{(1)}), \ldots, \rho^{(n)}(r^{(n)}).
\]

[Here the \( r_{p}^{(n)} \) are discretized unit Delta functions as defined in Eq. (8).] The multidimensional FGH Hamiltonian is formed by addition of the multidimensional kinetic energy and potential energy matrices and is diagonalized to give the exact FGH solution for the number of grid points chosen.

The construction of the multidimensional Hamiltonian matrix elements for the DVR and FGH methods is relatively cheap. In fact, the main problem in multidimensional cases lies not with the construction of the multidimensional Hamiltonian but rather with its large size and the resulting cost of storage and conventional diagonalization. As discussed in the introduction, a successive diagonalization and truncation scheme\(^{18,19}\) and several iterative diagonalization schemes\(^{20–23}\) have been developed to address these difficulties.

B. Development of the FGH-MCSCF method

1. Fourier grid Hamiltonian single configuration self-consistent-field (FGH-SCSCF)

Before discussing the FGH-MCSCF method we will first consider the simpler single configurational analog FGH-SCSCF. This type of approach is a relatively simple and inexpensive method to generate multidimensional ground state nuclear wavefunctions.

Consider the \( n \)-dimensional wavefunction \( \Psi_{0}(\mathbf{r}) \), which is a single product of the orthonormal one-dimensional wavefunctions \( \psi_{\mu}^{(p)} \).

\[\Psi_{0}(\mathbf{r}) = \prod_{p} \psi_{\mu_{p}}^{(p)}(r_{p}).\]
\[ \Psi_0(\mathbf{r}) = \psi^{(1)}(r^{(1)}) \psi^{(2)}(r^{(2)}) \cdots \psi^{(n)}(r^{(n)}) = \prod_n \psi_p(r^{(p)}). \]  

(15)

(The subscript 0 signifies a zeroth order wavefunction analogous to the Hartree–Fock wavefunction in electronic structure.) Initial guess one-dimensional wavefunctions may be determined by extracting one-dimensional grid potentials from the fully \(n\)-dimensional grid potential and carrying out \(n\) one-dimensional FGH calculations or may be taken from a previous FGH-SCSCF calculation. Only the \(n\) ground state one-dimensional wavefunctions denoted \(\psi_p^{(p)}\) are needed in FGH-SCSCF.

The total ground state energy \(E_0\) may be expressed as the expectation value of \(\hat{H}(\mathbf{r})\),

\[ E_0 = \langle \Psi_0(\mathbf{r}) | \hat{H}(\mathbf{r}) | \Psi_0(\mathbf{r}) \rangle = \sum_n \langle \psi^{(p)} | \hat{T}_p | \psi^{(p)} \rangle + \sum_{q \neq p} \langle \psi^{(p)} | V(\mathbf{r}) | \psi^{(q)} \rangle \prod_{q \neq p} \psi^{(q)}(r_q), \]

(16)

where \(p\) in the potential term can be any dimension index from 1 to \(n\). We now apply the method of linear variation and Lagrange’s method of undetermined multipliers to minimize \(E_0\) with respect to \(\psi^{(p)}\) subject to normality constraints. One dimension is varied at a time, leading to the following eigenvalue equation:

\[ F_p^{(p)}(r^{(p)}) \psi^{(p)} = \epsilon_p^{(p)} \psi^{(p)}, \]

(17)

where we have defined a new one-dimensional operator,

\[ F_p^{(p)}(r^{(p)}) = \hat{T}_p + V_p^{(p)}(r^{(p)}) \]

and \(V_p^{(p)}(r^{(p)})\) represents a potential energy operator averaged over all dimensions except \(p\).

\[ V_p^{(p)}(r^{(p)}) = \prod_{q \neq p} \psi^{(q)} \bigg| V(\mathbf{r}) \bigg| \prod_{q \neq p} \psi^{(q)} \bigg), \]

(18)

There are \(n\) such eigenvalue equations, each of which is dependent on the eigenvectors of the remaining \(n - 1\); therefore, an iterative scheme is required and iterations between dimensions should be carried out to self-consistency within some chosen tolerance.

In FGH-SCSCF the eigenvalue equations represented by Eq. (18) are solved on a grid. We now determine their explicit form in terms of the FGH integrals seen in Sec. II A; these will be the working equations of FGH-SCSCF. In the FGH method the \(\psi^{(p)}\) are approximated as linear combinations of discretized eigenfunctions of the coordinate operator, i.e., unit delta-functions, \(\psi_m^{(p)}\), placed at evenly spaced grid points. If the number of grid points for dimension \(p\) is \(N_p^{(p)}\), the ground state one-dimensional wavefunction \(\psi^{(p)}\) may be expressed as

\[ \psi^{(p)} = \sum_{\mu} e_{\mu}^{(p)} | \psi_{\mu}^{(p)} \rangle \]

(19)

For ease of notation we assume that the number of grid points in each dimension is identical, \(N_{p-1,n} = N\). Substituting Eq. (21) into Eq. (18), multiplying by \(\langle r_{\mu}^{(p)} |\), and integrating yields the matrix equation

\[ F_p^{(p)} \psi_{\mu}^p = \epsilon_p^{(p)} \psi_{\mu}^p, \]

(20)

where \(F_p^{(p)}\) is a matrix with elements \(F_{\mu \mu}^{(p)}\) and \(\psi_{\mu}^p\) is a vector with elements \(c_{\mu}^{(p)}\). The matrix elements \(F_{\mu \mu}^{(p)}\) are sums of kinetic energy and potential energy matrix elements,

\[ F_{\mu \mu}^{(p)} = T_{\mu \mu}^{(p)} + V_{\mu \mu}^{(p)}. \]

(21)

The kinetic energy matrix elements \(T_{\mu \mu}^{(p)}\) are simply the FGH kinetic energy integrals found through the Fourier transform technique reviewed in Sec. II A,

\[ T_{\mu \mu}^{(p)} = \langle r_{\mu}^{(p)} | \hat{T}_p | r_{\mu}^{(p)} \rangle = \langle r_{\mu}^{(p)} | F^{-1} \hat{T}_p F | r_{\mu}^{(p)} \rangle. \]

(22)

The averaged potential energy operator matrix elements \(V_{\mu \mu}^{(p)}\) are only nonzero on the diagonal but their determination is somewhat complex,

\[ V_{\mu \mu}^{(p)} = \langle r_{\mu}^{(p)} | V_p^{(p)}(r^{(p)}) | r_{\mu}^{(p)} \rangle = \sum_{\mu_1}^{N} c_{\mu_1}^{(p)} \sum_{\mu_{p-1}}^{N} c_{\mu_{p-1}}^{(p-1)} \sum_{\mu_{p-2}}^{N} c_{\mu_{p-2}}^{(p-2)} \cdots \sum_{\mu_{n-1}}^{N} c_{\mu_{n-1}}^{(n-1)} \sum_{\mu_{n}}^{N} c_{\mu_{n}}^{(n)} \]

(23)

\[ \times V_{\mu_1 \mu_2 \cdots \mu_n} \delta_{\mu \mu_1 \mu_2 \cdots \mu_n}. \]

where \(\mu = \mu_p\) is implied and \(V_{\mu_1 \mu_2 \cdots \mu_n}\) are the \(n\)-dimensional FGH potential energy integrals defined in Eq. (14). The construction of \(V_{\mu \mu}^{(p)}\) amounts to a sequential partial transformation of the \(n\)-dimensional FGH potential energy integrals to a one-dimensional wavefunction basis. The total ground state energy may easily be found during and at the conclusion of the SCF procedure according to

\[ E_0 = \sum_{\mu} \sum_{\mu} N (c_{\mu}^{(p)} T_{\mu \mu}^{(p)}) + \sum_{\mu} N (c_{\mu}^{(p)} V_{\mu \mu}^{(p)}). \]

(24)

where again \(p\) in the potential term can be any dimension index from 1 to \(n\).

The FGH-SCSCF method can only be used to determine ground state energies and includes limited correlation between dimensions due to the averaged potential energy operator \(V_p^{(p)}\). The eigenvalue equation above [Eq. (22)] can easily be solved by full diagonalization of \(F_p^{(p)}\) to give \(N\) eigenvalues \(\epsilon_{\mu_1}^{(p)}\) and eigenvectors \(\psi_{\mu_1}^{(p)}\). In FGH-SCSCF only the ground states \(\psi^{(p)}\) are relevant. The remaining eigenvectors, however, can be useful as initial guess one-dimensional wavefunctions in the FGH-MCSCF method we will now describe.

2. Fourier grid Hamiltonian multiconfigurational self-consistent-field (FGH-MCSCF)

The single configuration method outlined above may be extended to multiple configurations, thereby including correlation between dimensions and allowing the determination of
excited state $n$-dimensional wavefunctions. Our approach to the presentation of FGH-MCSCF will consist of two steps. First we develop the exact multiconfigurational solution (exact within the underlying grid basis and equivalent to the $n$-dimensional FGH solution reviewed in Sec. II A) in a manner somewhat analogous to full configuration interaction (FCI) in electronic structure. Secondly, we introduce the approximations and modifications leading to FGH-MCSCF.

The FCI $s$th state $n$-dimensional wavefunction $\Phi_s(r)$ may be written as a linear combination of all possible configurations $\Psi_s(r)$,

$$
\Phi_s(r) = \sum_{I} C_s^I \Psi_s(r).
$$

(27)

The $C_s^I$ are CI coefficients which are to be determined variationally within the constraint of normality of the total CI wavefunction $\Phi_s(r)$. The configurations $\Psi_s(r)$ are products of one-dimensional wavefunctions $\psi_s^{(p)}$,

$$
\Psi_s(r) = \psi_s^{(1)} \psi_s^{(2)} \cdots \psi_s^{(n)} = \prod_p \psi_s^{(p)}.
$$

(28)

Initial guess wavefunctions $\psi_s^{(p)}$ may be obtained from uncoupled one-dimensional FGH calculations, from a FGH-SCSCF calculation (see above), or from a previous FGH-MCSCF calculation. The configuration index $I$ is defined by the combined indices of the one-dimensional wavefunctions $\psi_s^{(p)}$ comprising the configuration, $I = \{i_1, i_2, \ldots, i_n\}$, $i_p = 1, \ldots, N$, where again for ease of notation we shall assume equal numbers of grid points $N$ for each dimension. The total number of possible configurations for FCI is $N_{ci} = n^N$. For the remainder of this paper the indices $I$ and $J$ will refer to CI configurations. In addition, unless otherwise stated, we will consider only a single CI state in the following discussion and therefore drop the subscript $s(\Phi = \Phi_s)$). Furthermore, the set of subscripts $i, j, k, l, m, n$ will signify one-dimensional wavefunction indices and may carry their own subscripts to identify the dimension with which they are associated, as in Eq. (28).

The FCI energy can be expressed in terms of the CI coefficients $C_s$ and the FCI Hamiltonian matrix elements $H_{IJ}$ as

$$
E = \langle \Phi(r) | H | \Phi(r) \rangle = \sum_{IJ} C_I C_J H_{IJ},
$$

(29)

where the FCI $H_{IJ}$ contain kinetic and potential energy terms,

$$
H_{IJ} = \langle \Phi_J(r) | \sum_p \hat{T}_p | \Phi_J(r) \rangle + \langle \Phi_J(r) | V(r) | \Phi_J(r) \rangle.
$$

(30)

Recalling that the kinetic energy operator is separable, we can write the kinetic energy FCI matrix elements as

$$
\langle \Phi_J(r) | \sum_p \hat{T}_p | \Phi_J(r) \rangle = \sum_{p} \langle \psi_s^{(p)} | \hat{T}_p | \psi_s^{(p)} \rangle \prod_{q \neq p} \delta_{i_q j_q}.
$$

(31)

Before we express these matrix elements in terms of FGH integrals we introduce the quantities $\gamma_{IJIJ}^{(p)}$, which are one-dimensional coupling constants between configurations and one-dimensional wavefunctions. Their values are simply one or zero and are determined according to the Kronecker-deltas in Eq. (31),

$$
\gamma_{IJIJ}^{(p)} = \delta_{k_1 i_1} \delta_{l_1 j_1} \prod_{p \neq q} \delta_{i_q j_q}.
$$

(32)

In practice they are never formed and are introduced here for notational simplification in later developments. The kinetic energy FCI matrix elements in Eq. (31) can now be written as

$$
\begin{align*}
\sum_{p} \sum_{kl} \gamma_{IJIJ}^{(p)} (| \psi_s^{(p)} | \hat{T}_{kl} | \psi_s^{(p)} \rangle,
\end{align*}
$$

(33)

$$
\sum_{p} \sum_{kl} \gamma_{IJIJ}^{(p)} T_{kl}^{(p)} = \sum_{p} \sum_{kl} \gamma_{IJIJ}^{(p)} \left[ \sum_{\mu \mu'} \gamma_{IJIJ}^{(p)} \right],
$$

(34)

where $T_{\mu \mu'}^{(p)}$ are again the FGH kinetic energy matrix elements defined in Eq. (24).

In general the potential energy term is non-separable and is obtained from the $n$-dimensional FGH potential energy integrals [Eq. (14)] via a sequential multiple-index transformation from the grid basis to the one-dimensional wavefunction basis,

$$
V_{\alpha} = V_{i_1 j_1 i_2 j_2 \cdots i_n j_n},
$$

(35)

$$
\langle \Phi_J(r) | V(r) | \Phi_J(r) \rangle = \left( \prod_{p} \psi_s^{(p)} \right) \left( \prod_{p} \psi_s^{(p)} \right)
$$

(36)

where we have introduced the collective index $\alpha = \{i_1 j_1 i_2 j_2 \cdots i_n j_n\}$ (or equivalently $\alpha = \{k_1 l_1 k_2 l_2 \cdots k_n l_n\}$). We now also introduce the $n$-dimensional coupling constants $\Gamma_{\alpha \alpha}^{IJ}$, which act as Kronecker-delta functions and pick out the unique multiple index of the one-dimensional wavefunctions associated with a configuration pair,

$$
\Gamma_{\alpha \alpha}^{IJ} = \Gamma_{k_1 l_1 k_2 l_2 \cdots k_n l_n}^{i_1 j_1 i_2 j_2 \cdots i_n j_n} \delta_{i_1 i_1} \delta_{i_2 i_2} \cdots \delta_{i_n i_n} \delta_{k_1 k_1} \delta_{k_2 k_2} \cdots \delta_{k_n k_n}.
$$

(37)

In practice the $n$-dimensional coupling constant matrix is never formed and is introduced to simplify notation later. It is clear that $\sum_{\alpha} \Gamma_{\alpha \alpha}^{IJ} = \sum_{k_1 l_1 k_2 l_2 \cdots k_n l_n}^{i_1 j_1 i_2 j_2 \cdots i_n j_n}$ and we can now formally rewrite the potential energy term in Eq. (30) as

$$
\langle \Phi_J(r) | V(r) | \Phi_J(r) \rangle = \sum_{\alpha} \Gamma_{\alpha \alpha}^{IJ} V_{\alpha},
$$

(38)
where $V_{\alpha}$ is given by Eq. (34). The total FCI Hamiltonian matrix elements are then given by

$$H_{IJ} = \sum_{p} \sum_{kl} \gamma_{kl}^{(p)} T_{kl}^{(p)} + \sum_{a} \Gamma_{a} V_{\alpha}.$$  

(37)

This FCI Hamiltonian matrix may be used in conjunction with the linear variation method to give the standard CI eigenvalue equations,

$$\sum_{I} C_{I} (H_{II} - \delta_{II}) = 0.$$  

(38)

The FCI coefficients and energies may be determined by diagonalization of the FCI Hamiltonian matrix.

The exact solution to the $n$-dimensional problem presented above is less practicable than the standard $n$-dimensional FGH method reviewed in Sec. II A. The diagonalization problem is the same size, and there is additional expense due to the required potential energy integral transformation in Eq. (34). However, this FCI method leads to the central idea of the MCSCF approach; the size of the one-dimensional wavefunction space (active space) is truncated, thereby drastically reducing the size of the CI Hamiltonian matrix. In addition, in order to recover some of the lost wavefunction flexibility, the one-dimensional wavefunctions in the active space are minimized to total energy. We include all possible CI configurations within the truncated active space, making our approach analogous to FORS-MCSCF (Ref. 29) or equivalently CASSCF (Ref. 30) in electronic structure theory.

We now rewrite Eq. (27) with a summation over a drastically reduced number of CI configurations resulting from the truncated one-dimensional wavefunction active space,

$$\Phi(r) = \sum_{\text{mcscf}} \sum_{n} C_{I} \Psi_{I}(r).$$  

(39)

where $N_{\text{mcscf}} = (N_{\text{wt}})^{n} \leq N_{\text{FCI}}$ as $N_{\text{wt}} \leq N.$  

(40)

Here $N_{\text{wt}}$ is the number of one-dimensional wavefunctions included in the MCSCF active space per dimension. The CI matrix elements are given by

$$H_{IJ} = \sum_{p} \sum_{kl} \gamma_{kl}^{(p)} T_{kl}^{(p)} + \sum_{a} \Gamma_{a} V_{\alpha},$$  

(41)

where $T_{kl}^{(p)}$ and $V_{\alpha}$ are defined in Eqs. (33) and (34), respectively. In this case the CI Hamiltonian matrix is formed and diagonalized at small cost to yield the CI coefficients. One-dimensional and $n$-dimensional density matrices are formally defined as

$$\gamma_{kl}^{(p)} = \sum_{IJ} C_{I} C_{J} \gamma_{kl}^{(p)},$$  

(42)

$$\Gamma_{a} = \sum_{IJ} C_{I} C_{J} \Gamma_{a}^{IJ}.$$  

(43)

These density matrices lead to an efficient formulation of the MCSCF problem and are formed in practice. The CI energy may then be expressed as

$$E = \sum_{p} \sum_{kl} \gamma_{kl}^{(p)} T_{kl}^{(p)} + \sum_{a} \Gamma_{a} V_{\alpha}.$$  

(44)

We now construct a functional imposing orthonormality constraints,

$$L = \sum_{k} \epsilon_{kl}^{(p)} \langle \psi_{k}^{(p)} | \psi_{l}^{(p)} \rangle - \delta_{kl}.$$  

(45)

For notational convenience we define another collective index $\alpha = \{k_{1} \cdots k_{p-1} l_{p-1} \cdots k_{p+1} l_{p+1} \cdots n\}$, where the indices for the $p$th one-dimensional wavefunctions have been included but may be reintroduced to form the full collective index $\alpha = k_{1}^{p} \alpha_{p} = k l \alpha_{p}$. These definitions lead to the following relationship:

$$\sum_{a}^{N_{\text{mcscf}}} \Gamma_{a}^{(p)} V_{\alpha} = 0,$$

(46)

where the one-dimensional operator $F_{kl}^{(p)}$ is defined as

$$F_{kl}^{(p)} = \sum_{\alpha} \Gamma_{a}^{(p)} V_{\alpha} V_{\alpha}^{\dagger}.$$  

(47)

with the one-dimensional potential energy operator defined as

$$V_{\alpha}^{(p)} = \left( \prod_{q \neq p} \psi_{q}^{(p)} \right) V(r) \left( \prod_{q \neq p} \psi_{q}^{(p)} \right).$$  

(48)

Hinze has shown that Eq. (46) can be solved by enforcing the Hermiticity of the Lagrange matrix multiplier,$^{31}$

$$\epsilon_{kl}^{(p)} = \epsilon_{kl}^{(p)} *,$$  

(49)

where

$$\epsilon_{kl}^{(p)} = \sum_{m}^{N_{\text{mcscf}}} \langle \psi_{l}^{(p)} | F_{km}^{(p)} | \psi_{m}^{(p)} \rangle$$

$$= \sum_{m}^{N_{\text{mcscf}}} \gamma_{kl}^{(p)} \gamma_{lm}^{(p)} + \sum_{m}^{N_{\text{mcscf}}} \sum_{\alpha}^{N_{\text{mcscf}}} \sum_{\beta}^{N_{\text{mcscf}}} \Gamma_{k \alpha} V_{\beta \alpha} V_{\beta \alpha}^{\dagger}. $$  

(50)

Since the initial one-dimensional wavefunctions will not usually satisfy this condition, a unitary transformation to a set of one-dimensional wavefunctions that does satisfy this condition must be found. The unitary transformation used in this paper involves Jacobi rotations between one-dimensional wavefunctions belonging to the same dimension. The angles of rotation between pairs of one-dimensional wavefunctions required to satisfy Eq. (49) are determined to second order.$^{31}$

This results in cycles of rotations between pairs similar to that in a Jacobi diagonalization. Note that we are seeking a transformation spanning the full one-dimensional wavefunc-
tion space in order to find the optimum total wavefunction for the chosen CI active space. In other words, the virtual orbitals are mixed with the active orbitals to maximize the flexibility of the wavefunction. For this reason, the index \(l\) is extended to \(N\) during the Jacobi rotation procedure used to ensure the Hermicity condition given in Eq. (49).

For the Jacobi rotation procedure, calculation of the rotation angle for a specific one-dimensional wavefunction pair \(k\) and \(l\) requires the Lagrangian matrix elements \(\epsilon_{kl}^{(p)}\), \(\epsilon_{kl}^{(p)}\), \(\epsilon_{kl}^{(p)}\), and \(\epsilon_{kl}^{(p)}\), as well as a number of specific matrix elements of the type \(\langle \psi_k^{(p)} | F_{kl}^{(p)} | \psi_l^{(p)} \rangle\). We now consider their determination in the context of FGH integrals, i.e., integrals over the grid basis,

\[
\epsilon_{kl}^{(p)} = \sum_{m} \sum_{\mu \mu'} C_{p l}^{(p)} C_{p m}^{(p)} \mu_{\mu' k m}
\]

and

\[
\langle \psi_k^{(p)} | F_{kl}^{(p)} | \psi_l^{(p)} \rangle = \sum_{\mu \mu'} C_{p k}^{(p)} C_{p \mu'}^{(p)} F_{\mu \mu' k l}^{(p)},
\]

where

\[
F_{\mu \mu' k l}^{(p)} = \langle \psi_k^{(p)} | F_{kl}^{(p)} | \psi_l^{(p)} \rangle = \gamma_{kl}^{(p) \mu \mu'} + \sum_{\nu} \Gamma_{k l \mu \nu} V_{\nu \mu \mu' k l}^{(p)},
\]

and

\[
V_{\mu \mu' \mu'' \nu \mu'' \nu''}^{(p)} = \prod_{\mu = 1}^{N_{w f}} C_{\mu k}^{(p)} C_{\mu l}^{(p)} \cdots \prod_{\nu = 1}^{N_{w f}} C_{\nu k}^{(p)} C_{\nu l}^{(p)} \prod_{\mu = 1}^{N_{w f}} C_{\mu p_{\mu} \mu' p_{\mu'}}^{(p)} C_{\mu_{\mu'} p_{\mu'} \mu'_{\mu'} p_{\mu'}^{(p)}},
\]

Possible classes of the Jacobi rotations are active–active and active–virtual. As the density matrix indices are restricted to active (occupied in the CI) indices we can determine the nature of the Lagrangian symmetry conditions for the various classes of rotations. For \(k\) active and \(l\) active, the condition to be satisfied is

\[
\sum_{m} \langle \psi_l^{(p)} | F_{kl}^{(p)} | \psi_m^{(p)} \rangle = 0,
\]

and for \(k\) active and \(l\) virtual, the condition is

\[
\sum_{m} \langle \psi_l^{(p)} | F_{kl}^{(p)} | \psi_m^{(p)} \rangle = 0,
\]

as \(F_{lm}^{(p)} = 0\) when \(l\) is virtual. For active–virtual rotations the determination of the angle of rotation is also simplified in a similar manner. Note that if the index \(l\) in Eq. (49) only runs to \(N_{w f}\) (i.e., only active–active Jacobi rotations) and all possible CI configurations are included in the MCSCF active space, cyclic invariance of the total energy results as in FORS-MCSCF\(^{29}\) or CASSCF.\(^{30}\)

The MCSCF scheme we have implemented is an unfolded two step algorithm in that the CI coefficients and the one-dimensional wavefunction coefficients are each determined separately. Iterations to self-consistency between these steps is therefore required. In addition, during the determination of the one-dimensional wavefunctions microiterations between dimensions are required. We have found that for robust convergence to self-consistency during the determination of the one-dimensional wavefunction coefficients the matrix elements that are needed to determine the next rotation angle must be updated after each pair rotation. Storage of \(F_{\mu \mu' k l}^{(p)}\) in Eq. (53) allows this to be done in an efficient manner with only the terms affected by the newly rotated pair coefficients being recalculated and added to the remaining unchanged terms in Eqs. (51) and (52).

As in electronic structure theory, the one-dimensional wavefunctions in FGH-MCSCF may often be optimized for a particular state to give high quality energies for that state and somewhat lower quality energies for the other states obtained from the diagonalization of the CI Hamiltonian matrix. Except for cases of degenerate states, optimal one-dimensional wavefunctions can almost always be found for ground states. Optimal one-dimensional wavefunctions for excited states can be found in cases where coupling with nearby states is not significant. However, in cases where there are degenerate (or nearly degenerate states) or coupling with nearby excited states, state-averaged wavefunctions are required. In addition, state-averaging is needed if orthogonal total wavefunctions are desired. Entirely analogous to electronic structure MCSCF, state-averaged FGH-MCSCF simply requires the weighting of the CI coefficients corresponding to the states of concern,

\[
[C_f C_J] = \sum_{s} w_s C_f^s C_J^s,
\]

where \(N_{av}\) is the number of states being averaged over, \(w_s\) is the weight of state \(s\), and

\[
\sum_{s} w_s = 1.
\]
III. TEST APPLICATIONS

We now present a series of test cases to demonstrate the accuracy and efficiency of the FGH-MCSCF method. Timings and energies obtained from the FGH-MCSCF method, a Davidson iterative diagonalization scheme, and full diagonalization (where possible), are compared. The test cases include treatment of multiple protons as quantum degrees of freedom in water chains and treatment of a single proton with three spatial quantum degrees of freedom in H$_2$O$_2^+$ and in malonaldehyde. For the water systems, the Stillinger polarizable water potential is used; for malonaldehyde, the AM1 semiempirical method is used to generate the potential via an interface with the electronic structure code GAMESS.

Note that these potentials are intended only to provide a basis for testing of the FGH-MCSCF method. Due to the well-known limitations of these potentials, they are not expected to yield quantitatively accurate vibrational state energies suitable for comparison with experimental values. For all test cases presented the grids were centered between the donor and acceptor atoms and all grid lengths were chosen to be 2.4 Å with equal spacing. Unless otherwise stated four donor and acceptor atoms and all grid lengths were chosen to be 2.4 Å with equal spacing. Unless otherwise stated four.

Our implementation of the Davidson iterative diagonalization scheme follows that of Balint-Kurti and Pulay in that the kinetic energy matrix elements are formed on the fly according to Eq. (13). We approximate the inverse operator for each target state using the diagonal of the Hamiltonian matrix according to Davidson’s original electronic structure implementation.

The self-consistency convergence criterion for the FGH-MCSCF method was set at 6.0×10$^{-5}$ kcal/mol for the energy and a RMS of 1.0×10$^{-6}$ for the Lagrangian asymmetry [Eq. (49)]. For the Davidson method the convergence criterion was 1.0×10$^{-5}$ for the norm of the residue vector.

All calculations were carried out on an SGI Indigo 1000 workstation. The exact same initial guess wavefunctions were provided to the FGH-MCSCF and Davidson algorithms. These initial guess wavefunctions were generated by using the FGH-SCSCF method and took negligible time.

A. Water chains

The water chain test systems can be seen in Figs. 1 and 2. These structures were chosen to produce mixed single and double well test cases. In the first system (H$_2$O)(H$_2$O$^+$)(H$_2$O) the two O–O distances are 2.70 and 2.50 Å (see Fig. 1). In the (H$_2$O)(H$_2$O)(H$_2$O$^+$) system (see Fig. 2) the O–O distances are 2.70, 2.50, and 2.90 Å. Only the hydrogen bonding hydrogen nuclei are treated quantum mechanically (i.e., are represented as wavefunctions on a grid), as indicated in Figs. 1 and 2.

Table I contains the energies, timings, and required number of iterations for the 2 quantum proton water chain. The calculated vibrational energies show that for the chosen grid length at least 32 grid points per dimension are required for reasonable vibrational state energies. Convergence of the calculated energies to 10$^{-4}$ kcal/mol with respect to the number of grid points is achieved at 64 grid points per proton. The

TABLE I. Proton vibrational state energies, timings, and required number of iterations for the 2 quantum proton system shown in Fig. 1.

<table>
<thead>
<tr>
<th>State</th>
<th>16 Grid points/proton</th>
<th>32 Grid points/proton</th>
<th>64 Grid points/proton</th>
<th>128 Grid points/proton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCSCF</td>
<td>FCI</td>
<td>MCSCF</td>
<td>FCI</td>
</tr>
<tr>
<td></td>
<td>Opt$^a$</td>
<td>Avg$^b$</td>
<td>FCI</td>
<td>MCSCF</td>
</tr>
<tr>
<td></td>
<td>Dav$^c$</td>
<td>Full$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$</td>
<td>17.2448</td>
<td>17.2452</td>
<td>17.2448</td>
<td>17.2448</td>
</tr>
<tr>
<td>$E_2$</td>
<td>23.6314</td>
<td>23.6328</td>
<td>23.6314</td>
<td>23.6314</td>
</tr>
<tr>
<td>$E_3$</td>
<td>25.7585</td>
<td>25.7611</td>
<td>25.7585</td>
<td>25.7585</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>17.2661</td>
<td>17.2661</td>
<td>17.2660</td>
<td>17.2660</td>
<td>17.2661</td>
<td>17.2661</td>
<td>17.2661</td>
<td>17.2661</td>
<td>17.2661</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time$^f$</th>
<th>0.17</th>
<th>0.02</th>
<th>0.01</th>
<th>0.30</th>
<th>0.68</th>
<th>0.09</th>
<th>0.07</th>
<th>32.32</th>
<th>2.64</th>
<th>0.42</th>
<th>0.82</th>
<th>2318.29</th>
<th>17.73</th>
<th>2.82</th>
<th>25.51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iterations$^g$</td>
<td>12</td>
<td>2</td>
<td>11</td>
<td>13</td>
<td>2</td>
<td>16</td>
<td>13</td>
<td>2</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Each vibrational state wavefunction optimized separately (including 16 configurations).

$^b$State-averaged MCSCF calculation (including 16 configurations) with equal weighting to all 4 states.

$^c$Davidson diagonalization.

$^d$Full conventional diagonalization.

$^e$Proton vibrational state energies in kcal/mol relative to the lowest point on the 128 grid points/proton grid potential.

$^f$Total CPU time in seconds for calculation of all 4 states [for MCSCF includes time taken to calculate total wavefunctions according to Eq. (39)].

$^g$Total number of iterations required for calculation of all 4 states.
TABLE II. Proton vibrational state energies, timings, and required number of iterations for the 3 quantum proton system shown in Fig. 2.

<table>
<thead>
<tr>
<th></th>
<th>16 Grid points/proton</th>
<th>32 Grid points/proton</th>
<th>64 Grid points/proton</th>
<th>128 Grid points/proton</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MCSCF</td>
<td>FCI</td>
<td>MCSCF</td>
<td>FCI</td>
</tr>
<tr>
<td></td>
<td>Opt(^a) Avg(^b) Dav(^c) Full(^d)</td>
<td>Opt(^a) Avg(^b) Dav(^c)</td>
<td>Opt(^a) Avg(^b) Dav(^c)</td>
<td>Opt(^a) Avg(^b) Dav(^c)</td>
</tr>
<tr>
<td>Energy(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E_0)</td>
<td>13.8113</td>
<td>13.8113</td>
<td>13.8113</td>
<td>13.8113</td>
</tr>
<tr>
<td>(E_1)</td>
<td>20.3883</td>
<td>20.3883</td>
<td>20.3883</td>
<td>20.3883</td>
</tr>
<tr>
<td>(E_3)</td>
<td>32.3860</td>
<td>32.3860</td>
<td>32.3860</td>
<td>32.3860</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time(^f)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.04</td>
<td>0.28</td>
<td>0.40</td>
<td>2324.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.58</td>
<td>0.73</td>
<td>14.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>89.98</td>
<td>8.11</td>
<td>348.56</td>
<td>732.41</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>3</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>2</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iterations(^g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Each vibrational state wavefunction optimized separately (including 64 configurations).
\(^b\)State-averaged MCSCF calculation (including 64 configurations) with equal weighting to all 4 states.
\(^c\)Davidson diagonalization.
\(^d\)Full conventional diagonalization.
\(^e,\)Proton vibrational state energies in kcal/mol relative to the lowest point on the 128 grid points/proton grid potential.
\(^f\)Total CPU time in seconds for calculation of all 4 states [for MCSCF includes time taken to calculate total wavefunctions according to Eq. (39)].
\(^g\)Total number of iterations required for calculation of all 4 states.

The state-averaged FGH-MCSCF calculation is found to be the fastest for the 64 and 128 grid point calculations, while the Davidson method is most efficient for the 16 and 32 grid point cases. Moreover, the state-averaged FGH-MCSCF reproduces the eigenvalues to \(10^{-4}\) kcal/mol in most cases and always to \(10^{-3}\) kcal/mol. Optimizing for each state separately adds some expense to the FGH-MCSCF, and this approach is more expensive than the Davidson scheme until 128 grid points per proton are included. Note that full diagonalization for \(N=128\) is not computationally feasible.

Table II contains the energies, timings, and required number of iterations for the 3 quantum proton water chain. Again, at least 32 points per proton are required to obtain reasonable energies for the chosen grid length, and convergence is reached at 64 points per proton. The state-averaged FGH-MCSCF is fastest in all cases and reproduces the FCI energies due to the asymmetry of the geometry along the O–O axis. The O–O distance was chosen to be 2.80 Å to ensure an asymmetric double well potential. Table III shows timings and three-dimensional vibrational state energies for this system. Again for the chosen grid length 32 grid points per dimension are required to give reasonable proton vibrational energies. For 32 and 64 grid points per dimension the FGH-MCSCF methods (separate optimization and state-averaged) are considerably faster than the Davidson scheme. The proton vibrational state energies calculated by the MCSCF method reproduce those found with the Davidson method to at least an accuracy of 0.02 kcal/mol and better in most cases. Figure 4 shows three dimensional plots\(^35\) of the proton wavefunctions corresponding to the first 4 proton vibrational states calculated with \(N=32\). Note that for the geometry studied, the proton moves in an asymmetric double well potential with the donor well lower than the acceptor well. \(\Phi_0\) represents the lowest energy vibrational wavefunction localized in the donor well, and \(\Phi_2\) represents the lowest energy vibrational wavefunction localized in the acceptor well. Both of these vibrational wavefunctions are nodeless, and \(\Phi_2\) has a higher energy due to the asymmetry of the geometry along the O–O axis. \(\Phi_1\) and \(\Phi_3\) represent excited state vibrational wavefunctions localized in the donor well. These excited state wavefunctions each have a single node and have different energies due to the asymmetry of the geometry in the directions perpendicular to the O–O axis. Plots of the resulting wavefunctions for all methods presented in Table III are identical regarding visual inspection.

We expect the FGH-MCSCF method to produce reasonable energies for up to the first 10 vibrational states. Table IV presents the energies, timings, and required number of iterations for state-averaged FGH-MCSCF and Davidson
and then exceed that of the Davidson scheme. This increased coupling may also account for the slightly lower accuracy seen in the 

$\text{H}_2\text{O}_2$ case than in the water chains. Note that the energies produced by the FGH-MCSCF method can be systematically improved by the inclusion of more configurations. Of course, this will result in increased expense, which will at some point equal and then exceed that of the Davidson scheme.

### C. Malonaldehyde

The transition state for the intramolecular proton transfer in malonaldehyde was found using the AM1 semiempirical method (see Fig. 5). The structure was confirmed as a transition state at this level of theory by calculation of the Hessian and subsequent diagonalization to yield one imaginary frequency. This $C_{2v}$ structure represents a difficult test case due to its high symmetry. The potential felt by the proton in this structure is symmetric with regard to the donor and acceptor oxygens and will therefore result in near degenerate pairs of proton vibrational energy levels. Note that a number of high quality studies have been carried out to determine the nature of the reaction path and proton tunneling in malonaldehyde.\(^{5,36}\) Our interest in malonaldehyde here is simply that it offers a difficult test case for the FGH-MCSCF method.

Calculated proton vibrational energies and timings for malonaldehyde are given in Table V. We consider only the first two proton vibrational states. For these two states convergence is achieved at 32 grid points per dimension. The state-averaged FGH-MCSCF method is considerably faster than the Davidson method for $N=32$ and is even more so for $N=64$. However, the energy levels calculated with the Davidson method are reproduced by the state-averaged MCSCF only to within $\sim0.1$ kcal/mol in this case. Due to the near degeneracy the FGH-MCSCF wavefunction cannot be optimized for $E_1$.

The near degenerate proton vibrational energy levels $E_0$ and $E_1$ are associated with symmetric and antisymmetric wavefunctions normally associated with the tunnel splitting. This is clearly demonstrated by the wavefunctions in Fig. 6. This “tunnel splitting” is predicted to be 0.1525 kcal/mol
Again, we note that the FGH-MCSCF performance can be systematically improved by adding more configurations. If six one-dimensional wavefunctions are included per dimension, the state-averaged FGH-MCSCF reproduces the Davidson numbers to 0.02 kcal/mol and gives a tunnel splitting of 0.1534 kcal/mol.

However, the calculation time increases from 2.44 s (216 configurations) to 26.10 s (216 configurations). We emphasize that these tunnel splittings are not quantitatively accurate due to limitations of the AM1 potential. Here they are viewed only as an indication of the accuracy of the FGH-MCSCF method by comparison to the Davidson method. Moreover, this type of highly symmetrical environment of the proton is unlikely to occur for mixed quantum/classical molecular dynamics simulations of hydrogen transfer reactions in large systems.

### IV. CONCLUSIONS

This paper presented a FGH implementation of the MCSCF method for the calculation of hydrogen vibrational

---

**TABLE IV.** Proton vibrational state energies, timings, and required number of iterations with 32 grid points per quantum degree of freedom for the 3 quantum proton system shown in Fig. 2 and the three-dimensional quantum proton system shown in Fig. 3.

<table>
<thead>
<tr>
<th>State</th>
<th>MCSCF/Avg</th>
<th>FCI/Dav</th>
<th>MCSCF/Avg</th>
<th>FCI/Dav</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>15.7110</td>
<td>9.7411</td>
<td>15.7110</td>
<td>9.7406</td>
</tr>
<tr>
<td>$E_1$</td>
<td>22.7101</td>
<td>12.9112</td>
<td>22.7101</td>
<td>12.9087</td>
</tr>
<tr>
<td>$E_2$</td>
<td>27.4130</td>
<td>13.0152</td>
<td>27.4130</td>
<td>13.0147</td>
</tr>
<tr>
<td>$E_4$</td>
<td>34.2915</td>
<td>15.8784</td>
<td>34.2914</td>
<td>15.8596</td>
</tr>
<tr>
<td>$E_5$</td>
<td>35.3701</td>
<td>16.0436</td>
<td>35.3701</td>
<td>16.0407</td>
</tr>
<tr>
<td>$E_6$</td>
<td>36.3397</td>
<td>16.8976</td>
<td>36.3395</td>
<td>16.8893</td>
</tr>
<tr>
<td>$E_7$</td>
<td>38.0351</td>
<td>17.6860</td>
<td>38.0350</td>
<td>17.6734</td>
</tr>
<tr>
<td>$E_8$</td>
<td>39.1584</td>
<td>18.6867</td>
<td>39.1584</td>
<td>18.6828</td>
</tr>
</tbody>
</table>

*State-averaged MCSCF calculation (including 216 configurations) with equal weighting to all 10 states.*

*Davidson diagonalization.*

*Proton vibrational state energies in kcal/mol relative to the points defined in Tables II and III.*

*Total CPU time in seconds for calculation of all 10 states [for MCSCF includes time taken to calculate total wavefunctions according to Eq. (39)].*

*Total number of iterations required for calculation of all 10 states.*
wavefunctions in hydrogen transfer reactions. This FGH-MCSCF approach combines a MCSCF variational method, which describes the vibrational wavefunction as linear combinations of configurations that are products of one-dimensional wavefunctions, with a Fourier grid method that represents the one-dimensional wavefunctions directly on a grid. In this approach a FCI calculation is carried out in a truncated one-dimensional wavefunction space analogous to CASSCF in electronic structure theory. A state-averaged implementation may be used if orthogonal multidimensional vibrational wavefunctions are required. The advantages of this approach are that it eliminates the costly calculation of multidimensional integrals, treats the entire range of the hydrogen coordinates without bias, avoids the expensive diagonalization of large matrices, and accurately describes ground and excited state hydrogen vibrational wavefunctions. The test cases presented in this paper indicate that FGH-MCSCF produces the energies of the hydrogen vibrational states as accurately as and cheaper than the Davidson iterative diagonalization scheme in cases with 32 grid points or more per dimension for three-dimensional systems. (Note that the FGH-MCSCF method is most advantageous for situations in which less than about 10 vibrational states are required.) The FGH-MSCSCF approach will be particularly useful for the calculation of hydrogen vibrational wavefunctions in mixed quantum/classical molecular dynamics simulations of hydrogen transfer reactions.

The FGH-MCSCF method is very general and will be extended in a number of directions in the future. For example, this method may be used in conjunction with alternative coordinate systems. In addition, the density matrix formulation of the FGH-MCSCF method presented in this paper will allow us to easily implement powerful analysis tools, such as a natural orbital analysis, routinely used in electronic structure MCSCF. Another future direction is to extend FGH-MCSCF to allow the inclusion of thousands of configurations for a relatively large number of particles moving in a many-body potential. In this extension, all nonpairwise potential interactions will be treated in an average way within an iterative self-consistent-field scheme, and the CI Hamiltonian will be diagonalized with the Davidson method.

Furthermore, since the MCSCF approach discussed in this paper simply requires a diagonal grid potential and separable kinetic energy terms, any DVR method using orthogonal coordinate systems could be used in conjunction with this MCSCF method. Note that the Gaussian quadrature accuracy of conventional DVR is retained since the positions of the grid points are never varied (i.e., the grid remains constant as an underlying basis). Future work may include the development of DVR-MCSCF approaches utilizing DVR with different basis sets to generate the one-dimensional wavefunctions.

In addition to these methodological extensions, the FGH-MCSCF will be utilized in a variety of applications. FGH-MCSCF may be used in conjunction with fully quantum dynamical simulations of gas phase hydrogen transfer reactions, as well as with mixed quantum/classical molecular dynamics simulations of hydrogen transfer reactions in solution, solids, and proteins. Thus, the FGH-MCSCF approach presented in this paper will allow the simulation of a wide range of biologically and chemically important hydrogen transfer reactions.

![Three-dimensional plots of $\Phi_0$ and $\Phi_1$, the ground and first excited state proton vibrational wavefunctions of the malonaldehyde system (shown in Fig. 5) corresponding to $E_0$ and $E_1$ in Table V. The surface contour is 0.01 bohr$^{1/2}$.](image)
ACKNOWLEDGMENTS

We thank Professor Balint-Kurti and Professor Bowman for allowing us to incorporate a portion of their Davidson diagonalization code in our program. We are grateful for financial support from the NIH Grant No. GM56207 and the AFOSR Grant No. F49620-98-1-0209. S. H. S. is the recipient of an Alfred P. Sloan Foundation Research Fellowship and a Camille Dreyfus Teacher–Scholar Award.

2See, for example, A. Ramaswamy, H. Eklund, and B. V. Plapp, Biochemistry 33, 5230 (1994); X. Ren, C. Tu, P. J. Laipis, and D. N. Silverman, ibid. 34, 8492 (1995).