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Accelerating and stabilizing the convergence of vibrational self-consistent field calculations via the direct inversion of the iterative subspace (vDIIS) algorithm **FREE**


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
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ABSTRACT

The vibrational self-consistent field (VSCF) method yields anharmonic states and spectra for molecular vibrations, and it serves as the starting point for more sophisticated correlated-vibration methods. Convergence of the iterative, non-linear optimization in VSCF calculations can be erratic or altogether unsuccessful, particularly for chemical systems involving low-frequency motions. In this work, a vibrational formulation of the Direct Inversion of the Iterative Subspace method of Pulay is presented and investigated. This formulation accounts for distinct attributes of the vibrational and electronic cases, including the expansion of each single-mode vibrational wavefunction in its own basis set. The resulting Direct Inversion of the Iterative Subspace method is shown to substantially accelerate VSCF convergence in all convergent cases as well as rectify many cases where Roothaan-based methods fail. Performance across systems ranging from small, rigid molecules to weakly bound molecular clusters is investigated in this analysis.

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I. INTRODUCTION

Infrared spectroscopy^{1–3} and its many variants^{4–11} provide unique and detailed information regarding the structure and chemical behavior of molecules, aggregates, and materials. Recent developments in cold-ion sources and tandem mass spectrometry-based spectroscopies, in particular, have generated unprecedented insights into the nature of fundamental ion–molecule interactions.^{12–20} They have also engendered a need for improved, generally applicable computational simulation techniques that can be used to assist in the prediction and interpretation of these experiments.

The vibrational self-consistent-field (VSCF) method^{21–32} is the counterpart of molecular orbital theory for molecular vibrations. The vibrational Schrödinger equation for single vibrational motions, in this method, is solved using an effective potential that is comprised of the mean field of the coupling to the remaining

$3N_{atoms} - 7$ motions. This method generates single-particle wavefunctions (“modals”) and their properties, along with multi-mode total energies, transition energies, and intensities. Correlated methods that go beyond this mean-field treatment, such as perturbation theories,^{31,33} configuration interaction,^{34–39} and coupled-cluster theory^{34,40–42} methods are also now available. This suite of theories provides the potential for general “model chemistries”⁴³ for the anharmonic vibrational problem, much in the same vein as the existence of a canon of methods for electronic structure theory.

For systems beyond small, rigid, isolated molecules, however, convergence of the non-linear, self-consistent optimization of the modals can sometimes fail in the absence of further approximations. A naïve implementation of the Roothaan-repeated-diagonalization method (hereafter “Roothaan”), wherein one optimization cycle’s wavefunction is recycled as the initial guess for the next cycle’s solution, leads to relatively slow convergence in the best-case sce-

nario or—more frequently for molecules of even modest size—a lack of convergence at all. The qualitative pathologies of the Roothaan method are well-known for quantum chemistry methods,⁴⁴ and one of the key motivations for the present Communication was to provide reliable (and, ideally, efficient) convergence in the latter case. Furthermore, as improvements in anharmonic and analytic-potential methods provide access to substantially larger chemical systems, the cost of the VSCF calculation itself, perhaps surprisingly, can become cost-prohibitive without further approximations.

Solutions to this convergence problem have been known in the electronic realm for more than four decades.^{44–46} Among many options,^{47–50} the Direct Inversion of the Iterative Subspace (DIIS) approach has proven efficient and reliable for most cases, and it (or a variant thereof) is the default convergence algorithm in many existing quantum chemistry software packages. The DIIS algorithm generates a new set of SCF coefficients by minimizing the predicted error—here defined as the orbital gradient—of a combination of m previous steps' effective Hamiltonians or density matrices. This approach both accelerates convergence for cases where Roothaan is slow and, in many cases, achieves convergence when Roothaan wanders far into unphysical regions of coefficient space.

Extension of the DIIS method toward vibrational problems—namely, in solving the VSCF equations—has, to our knowledge, not appeared in the literature, and a survey of existing VSCF software packages suggests that it is not currently in use. Given the aforementioned problems encountered when solving VSCF solutions, this omission is perhaps surprising. However, it may also stem from the fact that extension of DIIS to the VSCF problem is not as straightforward as it may superficially appear. In particular, although the electronic SCF method typically represents the molecular orbitals—and, therefore, their single-particle effective Hamiltonians—in a common basis set, this situation is rarely, if ever, true for the vibrational problem. In the latter, each modal is expanded in its own, unique set of basis functions (often, but not always, a set of harmonic oscillators with widths matched to the harmonic frequencies of each mode) or a related discrete variable representation, which leads to nuanced differences for a vibrational implementation of DIIS.

In the present Communication, we demonstrate that DIIS is indeed feasible for VSCF methods (vDIIS), and it corrects many of the “difficult” cases that otherwise have led to convergence failures for the Roothaan method. This convergence is achieved *without* invoking the common practice of omitting low-frequency modes or artificially rescaling vibrational couplings. We briefly present the theory governing this method, with a particular focus on the aspects of the formulation that are unique to the VSCF application. Thereafter, we demonstrate the performance of vDIIS for a handful of representative molecules and illustrate the scenarios where it corrects—and does not correct—VSCF convergence.

II. THEORY AND TEST CASES

For a system of N atoms, the $(3N - 6)$ -mode wavefunction Ψ of state ν is represented as a direct product of modals ψ_n in the VSCF formalism:³¹

$$\Psi^{(\nu)}(q_1, q_2, \dots, q_{3N-6}) \approx \prod_I \psi_{n_I}^{(\nu)}(q_I). \quad (1)$$

Unlike in the electronic problem, no antisymmetry of the wavefunction is generally required; i.e., the wavefunction is typically represented as a Hartree product, rather than a Slater determinant. Each modal can be expanded in a suitably chosen basis set ϕ of N_{basis} functions, based on the desired vibrational coordinates and quadrature scheme,

$$\psi_{n_I}^{(\nu)}(q_I) = \sum_{\mu}^{N_{basis}} C_{\mu n_I}^{(\nu)} \phi_{\mu}(q_I), \quad (2)$$

where the basis functions ϕ_{μ} are potentially specific to each mode q_I . These expansion coefficients C are self-consistently and variationally optimized to minimize the VSCF energy of each targeted total state ν separately (here written for rotational state $J = 0$ and neglecting both vibration-rotation coupling and the Watson term, although these omissions should have little impact on SCF convergence),

$$E_{\nu} = \sum_I^{3N-6} \varepsilon_{n_I}^{(\nu)} - (3N - 7) \left\langle \prod_I \psi_{n_I}^{(\nu)} | V(q_1, q_2, \dots, q_{3N-6}) | \prod_I \psi_{n_I}^{(\nu)} \right\rangle. \quad (3)$$

The single-particle energies ε are the eigenvalues of the modal Schrödinger equations involving the effective potential \bar{V} (with $\mu = \hbar = 1$):

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial q_I^2} + \bar{V}_{n_I}^{(\nu)}(q_I) \right] \psi_{n_I}^{(\nu)}(q_I) = \varepsilon_{n_I}^{(\nu)} \psi_{n_I}^{(\nu)}(q_I). \quad (4)$$

In analogy to the electronic SCF method, the states and effective Hamiltonians can be cast as density matrices P and Fock matrices F , respectively, in the chosen basis set for each mode:

$$P_{\lambda\sigma, I}^{(\nu)} = C_{\lambda n_I}^{(\nu)T} C_{\sigma n_I}^{(\nu)}, \quad (5)$$

$$F_{\lambda\sigma, I}^{(\nu)} = \langle \lambda | \left[-\frac{1}{2} \frac{\partial^2}{\partial q_I^2} + \bar{V}_{n_I}^{(\nu)}(q_I) \right] | \sigma \rangle \quad (6)$$

Note that the density matrix does not require a factor of two (unlike restricted Hartree–Fock for electrons), and the outer product of the expansion coefficients required to construct a mode-specific P only involves a single state's vector for vibrations. The vibrational Fock matrix for a single mode i in the two-mode representation (2-MR)^{23,25,51} of the potential, for example, may be equivalently represented as

$$F_{\lambda\sigma, I}^{(\nu)} = \left\langle \lambda \left| -\frac{1}{2} \frac{\partial^2}{\partial q_I^2} + V^{\{1\}}(q_I) \right| \sigma \right\rangle + \sum_{j \neq i}^{3N-6} \sum_{\mu\nu}^{N_{basis}} \langle \lambda \mu | \Delta V^{\{2\}}(q_I, q_j) | \sigma \nu \rangle P_{\mu\nu, j}^{(\nu)}. \quad (7)$$

In this expression, $V^{\{1\}}$ and $\Delta V^{\{2\}}$ represent the one-dimensional potential and two-mode differential coupling potential, respectively. Analogous expressions for 3-MR and higher (written in terms of their accordant P matrices) are also possible.

The DIIS method is based on an optimal extrapolation of previous information, which can ostensibly include densities or effective Hamiltonians. The density is employed in this work, although either version should, in principle, suffice. The density matrix for iteration $m + 1$ is based on the previous m densities, with vDIIS extrapolation coefficients d ,

$$P_{\lambda\sigma,I}^{(v)[m+1]} = \sum_{j=1}^m d^{[j]} P_{\lambda\sigma,I}^{(v)[j]}. \quad (8)$$

The vDIIS coefficients, which are constrained to $\sum_j d^{[j]} = 1$, are chosen to minimize the vDIIS error, and this component is where the vibrational version requires some subtle, yet critical, deviation from the electronic version. An “error vector” and its associated inner product must be employed in order to optimally determine the vDIIS coefficients.^{45,46} The derivative of the VSCF energy with respect to modal rotations, $[F, P]$, is selected in the present work (as is often used for electronic DIIS), but this commutator is necessarily represented in each mode’s own, often unique, basis set. These matrices (or their commutator) cannot, therefore, be summed for a total error matrix, as is easily performed for electrons. Instead, the commutators are retained in their modals’ basis set and represented as a $(3N - 6)$ -dimensional vector of small, $N_{basis} \times N_{basis}$ matrices. An inner product between iterations’ vectors is then defined as the inner tensor product of these commutators needed for DIIS B matrices,

$$B_{ij} = \left([F_1, P_1] \quad [F_2, P_2] \quad \cdots \quad [F_{3N-6}, P_{3N-6}] \right)^{[i]} \cdot \begin{pmatrix} [F_1, P_1] \\ [F_2, P_2] \\ \vdots \\ [F_{3N-6}, P_{3N-6}] \end{pmatrix}^{[j]}, \quad (9)$$

$$= \sum_K^{3N-6} [F_K, P_K]^{[i]} \cdot [F_K, P_K]^{[j]}, \quad (10)$$

where the commutators are represented in the basis corresponding to each modal $[\phi(q_k)]$. The optimal coefficients d can then be determined by solving the corresponding Euler–Lagrange equations that represent minimization of the total error:

$$\begin{pmatrix} B_{11} & B_{12} & \cdots & B_{1m} & -1 \\ B_{21} & B_{22} & & B_{2m} & -1 \\ \vdots & & \ddots & \vdots & -1 \\ B_{m1} & B_{m2} & \cdots & B_{mm} & -1 \\ -1 & -1 & -1 & -1 & 0 \end{pmatrix} \begin{pmatrix} d^{[1]} \\ d^{[2]} \\ \vdots \\ d^{[m]} \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ -1 \end{pmatrix}. \quad (11)$$

For clarity, the commutator in the present implementation is composed of the Fock matrix, from which the current (extrapolated) density matrix is constructed, and the same density matrix.⁴⁴ The underlying concept for vDIIS is, therefore, as follows. The $[F, P]$

commutators for each mode are computed, and they remain represented in their own, internal basis set. A *total* error across the set of modals is computed, and the density (or Fock) matrices are represented as expansions of m historical matrices using coefficients that minimize this total error. Importantly, the same coefficients are applied to matrices of every mode. This restriction is not necessarily required—and its relaxation could potentially be pursued in future investigations—but it nonetheless yields improved SCF performance in the test cases presented herein.

This method was tested on a variety of demonstrative chemical systems, as detailed below. In all cases, the modals were expanded in an orthogonal basis set of ten harmonic oscillator functions, with widths chosen to match their harmonic solutions and centered at equilibrium. Integration of the effective potentials was performed via Gauss–Hermite quadrature, using 11 quadrature points per mode. The potentials were generated with a variety of quantum chemistry and analytic-potential methods, but they were all truncated within the now-standard n -Mode Representation (n -MR).^{23,25,51} In this approach, 1-MR corresponds to single-mode cuts along vibrational motions through the full-dimensional potential. Although such one-dimensional cuts likely form the mental picture of anharmonicity in vibrational motions for many chemists, the resulting frequencies are insufficient for any spectroscopic application and in many cases yield the wrong sign of the anharmonicity. Therefore, the 2-MR includes requisite pairwise coupling surfaces, and 3- and higher-MR include higher-order mode-coupling effects.

In the present analysis, the ethylene molecule (using an HF/cc-pVTZ 2-MR potential), C_2H_4 , was examined as an “easy” comparison case for both the Roothaan and vDIIS methods. For this first case, convergence in both normal- and local-mode^{52–58} (500 cm^{-1} localization window⁵⁹) coordinates was performed in order to compare convergence behavior. The second test case involved the methanol molecule, CH_3OH (using a HF/6-31G potential and both 2- and 3-MR forms). The low-frequency, hindered-rotor motion of the alcohol, relative to the methyl group, is typically the type of motion that is considered challenging for VSCF methods in recitilinear, Cartesian coordinate systems. Indeed, a proper treatment of such a motion would include both basis functions and quadrature schemes designed to represent the three-fold symmetry of this embedded-rotor motion. However, as will be shown below, a stable VSCF solution can nonetheless be obtained in the current harmonic-oscillator basis set and normal-mode coordinates without omitting or scaling this mode’s vibrational couplings. Finally, two water clusters—the trimer, $(H_2O)_3$, and tetramer, $(H_2O)_4$ —were also investigated as particularly challenging test cases. The density of low-frequency, librational motions in such clusters renders the Roothaan method particularly slow or ineffective in these cases. Both 3- and 4-MR potentials were employed for these water-cluster cases, using the analytic MB-pol potential,^{60–64} because the 2-MR VSCF did not converge with either method (for reasons that are independent of the convergence algorithm and are presented in a separate analysis⁶⁵). Importantly, no low-frequency modes or their couplings were artificially removed or scaled in any of these calculations. All VSCF calculations that implement the equations above were performed with in-house codes; all quantum chemistry calculations were performed with a development version of the Q-Chem⁶⁶ quantum chemistry package.

In all cases, the efficiency and stability of the VSCF convergence are used as metrics for comparison. (The solution of the DIIS equations is a trivial additional computational cost for these systems, and efficiency is tacitly measured only in the number of VSCF iterations.) In order to make direct comparisons, the VSCF procedure was converged to a tolerance of 10^{-8} a.u. in the maximum value of the DIIS error (among all modes) in both methods and was considered non-convergent if this tolerance was not achieved in 500 SCF cycles. A vDIIS subspace size of six previous matrices was used except where noted. The initial guess for all calculations reported herein was the set of modals obtained from a 1-MR (coupling-free) calculation, with roots chosen according to the targeted state. Alternative guesses, such as using the converged ground-state modals for excited-state calculations, were also examined. The convergence behavior of this alternative guess was similar to the data reported here, and the relative differences between Roothaan and vDIIS algorithms were also observed to be similar. This outcome could potentially change for very large systems, and improved refinement of initial guesses is encouraged. The reported transitions in subsequent tables are ordered according to the harmonic frequencies.

III. RESULTS

The zero-point energy, transition frequencies, and requisite VSCF iterations for ethylene are displayed in Table I. Apart from one inconsequential round-off error, the state energies obtained from Roothaan and vDIIS are identical at the precision shown. In normal-mode coordinates, the acceleration due to vDIIS is modest, improving Roothaan's 8–12 cycles to a uniform 6 cycles in vDIIS. Local modes show somewhat more difficult convergence behavior—presumably due to the stronger two-mode coupling in these coordinates—and vDIIS provides a 7- to 9-cycle acceleration

in these coordinates (The degeneracy of states in the latter coordinates is a known artifact of VSCF, which neglects the effects of bilinear coupling terms for symmetric potentials in local-mode coordinates and can easily be corrected with vibrational correlation methods.^{58,59,67,68}).

More distinct convergence behavior was observed for methanol, as shown in Table II. With the 2-MR potential, the $\nu = 1$ state of the hindered-rotor mode did not converge with the Roothaan method, whereas the same state converged (albeit in 73 cycles) with vDIIS. This outcome suggests that the lack of convergence of this mode is not necessarily intrinsic to 2-MR or rectilinear coordinates; instead, it is at least partly an artifact of the convergence algorithm. All other modes in the 2-MR potential exhibited a roughly factor-of-two reduction in SCF cycles with vDIIS. All states of the 3-MR potential converged with both convergence algorithms, and the vDIIS method most notably reduced the number of cycles from 46 to 10 in the hindered-rotor mode. All other behavior was found to be similar to the behavior observed for ethylene.

All states of the water trimer are non-convergent under a 2-MR potential with Roothaan, and only the ground state and three fundamentals converge to meaningful values with vDIIS (data not shown).⁶⁵ For 3- and 4-MR, however, all states converge to equivalent, meaningful values with both methods, as shown in Table III. The vDIIS algorithm reduces the number of SCF cycles from 54–165 to 11–13 at 3-MR and from 70–443 to 11–14 at 4-MR. Therefore, the advantage of DIIS acceleration appears to be more significant for larger and more strongly coupled chemical systems, possibly due to the increased density of low-frequency states.

Finally, the water tetramer (Table IV) highlights a case in which Roothaan and vDIIS exhibit qualitatively different behavior. In this cluster, neither the ground state nor any fundamental excited VSCF state converges to physically meaningful energy with the Roothaan

TABLE I. State energies (cm^{-1}) and VSCF cycles for ethylene, in both normal- and local-mode coordinates, using a HF/cc-pVTZ 2-MR potential.

State	Normal modes				Local modes			
	Roothaan		vDIIS		Roothaan		vDIIS	
	Energy	Cycles	Energy	Cycles	Energy	Cycles	Energy	Cycles
ZPE	11 770.3	10	11 770.3	6	11 808.5	16	11 808.5	7
1	903.8	9	903.8	6	1 076.1	16	1 076.1	10
2	1 076.3	8	1 076.3	6	1 076.2	16	1 076.2	10
3	1 092.3	8	1 092.3	6	1 152.6	16	1 152.6	9
4	1 126.3	8	1 126.3	6	1 360.3	17	1 360.2	10
5	1 328.3	9	1 328.3	6	1 360.2	17	1 360.2	10
6	1 458.8	9	1 458.8	6	1 361.0	17	1 361.0	10
7	1 563.0	9	1 563.0	6	1 361.0	17	1 361.0	10
8	1 793.4	9	1 793.4	6	1 659.8	16	1 659.8	7
9	3 163.5	12	3 163.5	6	3 157.0	17	3 157.0	10
10	3 205.1	10	3 205.1	6	3 157.4	17	3 157.4	10
11	3 220.2	12	3 220.2	6	3 157.0	17	3 157.0	10
12	3 250.9	12	3 250.9	6	3 157.4	17	3 157.4	10

TABLE II. State energies (cm^{-1}) and VSCF cycles for methanol in normal-mode coordinates, using HF/6-31G 2- and 3-MR potentials.

State	2-MR				3-MR			
	Roothaan		vDIIS		Roothaan		vDIIS	
	Energy	Cycles	Energy	Cycles	Energy	Cycles	Energy	Cycles
ZPE	11 965.2	16	11 965.2	8	11 984.3	14	11 984.3	8
1	(673.5) ^a	(500) ^a	347.1	73	442.1	46	442.1	10
2	1 078.8	18	1 078.8	8	1 088.0	14	1 088.0	8
3	1 129.2	20	1 129.2	8	1 151.2	14	1 151.2	8
4	1 246.4	16	1 246.4	8	1 249.7	14	1 249.7	8
5	1 412.6	22	1 412.6	8	1 435.0	15	1 435.0	8
6	1 600.3	16	1 600.3	8	1 604.3	14	1 604.3	8
7	1 622.7	16	1 622.7	8	1 626.5	14	1 626.5	8
8	1 626.7	16	1 626.7	8	1 629.4	14	1 629.4	8
9	3 086.8	16	3 086.8	8	3 089.3	14	3 089.3	8
10	3 067.7	16	3 067.7	8	3 101.9	14	3 101.9	8
11	3 155.6	18	3 155.6	8	3 163.4	14	3 163.4	8
12	3 769.0	24	3 769.0	9	3 782.2	18	3 782.1	8

^aState did not converge. Displayed energy is taken from the last SCF step only to provide a relative measure of its vicinity to the converged value.

TABLE III. State energies (cm^{-1}) and VSCF cycles for the water trimer in local-mode coordinates, using MB-pol 3- and 4-MR potentials.

State	3-MR				4-MR			
	Roothaan		vDIIS		Roothaan		vDIIS	
	Energy	Cycles	Energy	Cycles	Energy	Cycles	Energy	Cycles
ZPE	16 479.3	104	16 479.3	11	16 472.4	180	16 472.4	11
1	382.5	75	382.5	11	378.2	128	378.2	11
2	383.8	96	383.8	11	379.5	167	379.5	12
3	200.0	94	200.0	11	198.4	174	198.4	12
4	204.7	95	204.7	11	203.0	168	203.0	12
5	204.9	68	204.9	11	203.2	172	203.2	11
6	444.0	64	444.0	12	439.7	143	439.7	13
7	510.2	54	510.2	12	501.6	90	501.6	13
8	495.6	62	495.6	13	487.3	70	487.3	13
9	501.6	58	501.6	13	493.4	86	493.4	13
10	667.4	69	667.4	13	661.6	73	661.6	14
11	703.3	64	703.3	13	696.8	95	696.8	13
12	692.7	94	692.7	12	686.4	85	686.4	13
13	1 627.9	91	1 627.9	11	1 624.4	165	1 624.4	11
14	1 628.9	91	1 628.9	11	1 625.5	154	1 625.5	12
15	1 629.8	164	1 629.8	11	1 626.4	158	1 626.4	11
16	3 427.8	165	3 427.8	12	3 428.1	443	3 428.1	12
17	3 425.1	160	3 425.1	11	3 425.4	432	3 425.4	11
18	3 440.3	113	3 440.3	11	3 440.5	412	3 440.5	12
19	3 620.3	104	3 620.3	12	3 618.9	233	3 618.9	13
20	3 625.1	112	3 625.1	12	3 623.6	201	3 623.6	13
21	3 625.1	75	3 625.1	12	3 623.8	225	3 623.8	13

TABLE IV. State energies (cm^{-1}) and VSCF cycles for the water tetramer in local-mode coordinates, using an MB-pol 3-MR potential.

State	3-MR			
	Roothaan		vDIIS	
	Energy	Cycles	Energy	Cycles
ZPE	(21 834.1) ^a	(500)	22 253.4	18
1	(722.4)	(500)	459.0	17
2	(222.2)	(500)	221.1	18
3	(516.2)	(500)	433.3	17
4	(123.0)	(500)	108.8	18
5	(549.6)	(500)	461.9	18
6	(481.1)	(500)	459.5	17
7	(221.0)	(500)	193.3	17
8	(126.2)	(500)	258.0	18
9	(212.4)	(500)	227.1	18
10	(225.6)	(500)	278.8	18
11	(786.4)	(500)	533.6	18
12	(793.6)	(500)	531.8	18
13	(596.5)	(500)	535.0	18
14	(619.2)	(500)	523.6	17
15	-2 20 830.7	177	(794.7)	(500)
16	(685.4)	(500)	778.0	19
17	(834.9)	(500)	788.1	18
18	(1 177.8)	(500)	788.3	20
19	(1 775.1)	(500)	1 636.4	18
20	(1 701.7)	(500)	1 636.8	18
21	(1 625.9)	(500)	1 636.8	17
22	(1 631.7)	(500)	1 636.6	18
23	(3 282.7)	(500)	3 307.2	18
24	(3 143.0)	(500)	3 305.6	18
25	(3 719.6)	(500)	3 300.8	18
26	(3 116.1)	(500)	3 303.5	17
27	(3 657.0)	(500)	3 625.1	18
28	(3 630.9)	(500)	3 625.2	18
29	(3 566.0)	(500)	3 625.2	18
30	(3 625.3)	(500)	3 625.2	18

^aStates in parentheses did not converge. Displayed energy is taken from the last SCF step only to provide a relative measure of its vicinity to the converged value.

method (one excited state does converge to an unphysical, negative energy⁶⁵), and several lead to oscillatory behavior. On the other hand, the ground state and 29 of the 30 fundamentals converge with vDIIS, typically in about 20 SCF cycles. Although the lone non-convergent excited state reached an energy that appeared reasonable, adjustment of the vDIIS subspace size did not yield convergence. A significant fraction of negative quadruples (composed of 3-MR triples) were found to involve this mode, hence its lack of convergence likely stems from issues related to the truncated n -MR,⁶⁵ rather than SCF convergence itself.

IV. SUMMARY

Convergence of the iterative self-consistent field method for molecular vibrations is often erratic or unsuccessful with naïve

algorithms. Through an extension of the well-established DIIS method toward vibrational problems—including an accounting of the fact that each modal is expanded in its own and often unique basis set, here termed vDIIS—this convergence difficulty can be alleviated in much the same manner as molecular orbital calculations with DIIS. Across four representative test systems, ranging from small, rigid molecules to flexible molecular clusters, this vDIIS method was demonstrated to be at least a substantial efficiency improvement over the naïve Roothaan method and, in many cases, yields convergence where the Roothaan method fails.

The issue of VSCF convergence is sometimes more nuanced than in its electronic analog. The choice of coordinates, the number and functional form of vibrational basis functions, and even the order of truncation of the n -Mode Representation can all affect convergence behavior.⁶⁵ However, as the examples in the present investigation have demonstrated, a significant fraction of these cases can be rectified by the vDIIS method. Of course, occasional non-convergent cases can be encountered with vDIIS, as well, and other variants of DIIS or other convergence algorithms are likely to prove useful in the vibrational realm. This approach, when combined with a paired analysis of truncated n -MR potentials and their corrections,⁶⁵ generally provides newfound robustness to VSCF convergence and allows for the avoidance of removing or scaling mode-coupling potentials.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Emily L. Yang: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (supporting). **Ryan J. Spencer:** Data curation (supporting); Investigation (supporting); Validation (supporting); Writing – review & editing (supporting). **Asylbek A. Zhanserkeev:** Data curation (supporting); Investigation (supporting); Validation (supporting); Writing – review & editing (supporting). **Justin J. Talbot:** Conceptualization (equal); Software (supporting); Visualization (supporting); Writing – review & editing (supporting). **Ryan P. Steele:** Conceptualization (equal); Data curation (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal);

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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