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A finite difference Davidson procedure to sidestep full *ab initio* hessian calculation: Application to characterization of stationary points and transition state searches

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The cost of calculating nuclear hessians, either analytically or by finite difference methods, during the course of quantum chemical analyses can be prohibitive for systems containing hundreds of atoms. In many applications, though, only a few eigenvalues and eigenvectors, and not the full hessian, are required. For instance, the lowest one or two eigenvalues of the full hessian are sufficient to characterize a stationary point as a minimum or a transition state (TS), respectively. We describe here a method that can eliminate the need for hessian calculations for both the characterization of stationary points as well as searches for saddle points. A finite differences implementation of the Davidson method that uses only first derivatives of the energy to calculate the lowest eigenvalues and eigenvectors of the hessian is discussed. This method can be implemented in conjunction with geometry optimization methods such as partitioned-rational function optimization (P-RFO) to characterize stationary points on the potential energy surface. With equal ease, it can be combined with interpolation methods that determine TS guess structures, such as the freezing string method, to generate approximate hessian matrices in lieu of full hessians as input to P-RFO for TS optimization. This approach is shown to achieve significant cost savings relative to exact hessian calculation when applied to both stationary point characterization as well as TS optimization. The basic reason is that the present approach scales one power of system size lower since the rate of convergence is approximately independent of the size of the system. Therefore, the finite-difference Davidson method is a viable alternative to full hessian calculation for stationary point characterization and TS search particularly when analytical hessians are not available or require substantial computational effort.
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I. INTRODUCTION

The feasibility of applying quantum chemical tools to reaction kinetics studies is severely limited by the size of the system under examination. In particular, the cost of calculating analytical second derivatives, or the nuclear hessian, scales about one power of system size greater than the energy or gradient.[1,2] In situations where analytical second derivatives are not available, one is forced to use finite differences to evaluate the hessian, which is even more expensive.[1,2] Although its calculation is costly, the hessian matrix is essential for several reasons. From an analysis of the hessian one can determine whether a stationary point on a potential energy surface corresponds to a minimum or saddle point. Some eigenvector-following optimization techniques, such as the partitioned-rational function optimization (P-RFO) method[3–5] also rely on an initial hessian input for robust performance and faster convergence. Reaction path searches initiated at the transition state (TS) also require an exact hessian input.[6–11]

In most applications, however, it is not the full hessian but only a few eigenvalues or eigenvectors that are neces-

sary. When characterizing stationary points, if the exact hessian matrix has all non-negative eigenvalues, the geometry is classified as a minimum on the potential energy surface. If the hessian has exactly one negative eigenvalue, the geometry corresponds to a TS, with the negative mode representative of the reaction coordinate. In order to verify whether a given geometry corresponds to a minimum or a TS, one only needs to calculate the lowest one or two eigenvalues, respectively. The same principle can be applied to TS search methods that require an initial hessian input. The P-RFO, for example, is more reliable if the hessian input has exactly one negative eigenvalue that resembles the reaction coordinate.[12] Instead of calculating the full hessian, therefore, the lowest eigenvalue and eigenvector are sufficient to generate a matrix input with the correct eigenvalue structure.

Some efforts have been made in this direction, particularly to generate approximate hessians for initiating geometry optimization. Lindh *et al.*[13] have developed a method in which a model hessian, constructed as a function of force constant parameters, improved the efficiency of geometry optimization via the quasi-Newton-Raphson method. However, the efficiency was tested for only a small basis set and at the Hartree-Fock level of theory, and the model hessian was limited to systems involving atoms in the first three rows of the periodic

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table. A variational method implemented by Kumeda *et al.*[14] minimizes the finite-difference formulation of the Rayleigh-Ritz ratio using conjugate gradients. The crudely converged eigenvalue and eigenvector corresponding to the reaction coordinate are then used to initiate eigenvector following methods for TS search. More recently, an eigenvector following method that uses the eigensolutions of a finite-difference based Davidson approach has been proposed.[15] The approach uses all the eigensolutions generated by the Davidson method, even if they have not fully converged. As a consequence, the reliability of the saddle-point search based on this approximate hessian remains questionable. The Davidson approach has also been used in a hybrid quantum mechanics/molecular mechanics (QM/MM) approach along with RFO, since it can determine the desired eigenvalues without requiring the storage or calculation of the full hessian.[16] Olsen *et al.* have also reported the use of a Lanczos scheme for iteratively determining the lowest hessian mode for saddle point search.[17] We have previously reported a method that constructs the approximate hessian based on an interpolated curvature obtained from the freezing string method (FSM).[18,19] The technique shows promising results when the approximate hessian input is used with P-RFO. However, since the curvature is not optimized, the accuracy of the interpolated curvature and hence the efficiency of optimization relies heavily on the quality of the reaction path generated by FSM, which is not desirable.

The goal of our research is to develop a low-cost alternative to exact or finite difference hessians for applications where only the lowest eigenvalues are required. This paper describes an approach that employs a finite differences form of the Davidson method[20] in conjunction with the P-RFO, which can be applied to both stationary point characterizations as well as TS searches. The Davidson method calculates one or more lowest eigenvalues of a matrix without diagonalizing the full matrix. It does so by diagonalizing a matrix constructed using an orthonormal subspace of size smaller than that of the original matrix, and subsequently minimizing the error between the true and subspace eigensolutions. Any other iterative diagonalization method can also be used instead of the Davidson method for calculating the lowest eigenvalues.[21–23]

The P-RFO approach uses quasi-Newton hessian update methods in order to revise the (exact or approximate) hessian input at every step. For stationary point characterization, therefore, the lowest eigenvectors of this matrix at the end of geometry optimization constitute the initial subspace for the Davidson method. Depending on whether the optimization is searching for a minimum or TS, this approach determines the lowest one or two hessian eigenvalues and eigenvectors, respectively, without calculating the exact hessian itself. The Davidson approach is also extended to TS search, for which it uses reaction coordinate information generated by the FSM to calculate the lowest eigenvalue and eigenvector of the hessian at the TS guess. This information is then incorporated into a guess matrix that is employed as input to P-RFO in lieu of the exact hessian for the TS search. The performance of this method is examined for stationary point characterization and TS search in terms of accuracy, the cost savings it achieves relative to the full hessian calculation, and its scaling with respect to system size. Extensive testing shows that

this method requires significantly less computational effort when compared with calculation of the full hessian, and is also nearly independent of system size, making it a very valuable tool for studying large systems.

II. METHOD

A. Characterization of minima and transition states

The Davidson method has been employed traditionally in situations where the cost of full matrix diagonalization is prohibitive, such as configurational interaction (CI) calculations.[24] However, the original Davidson procedure requires the full matrix in order to determine its eigenvalues. The method, therefore, needs to be modified in order to apply to calculation of nuclear hessian eigenvalues. It can be made hessian-free by recognizing the fact that the action of the hessian matrix on the subspace vector is desired rather than the matrix itself. This can be determined approximately using finite differences:[15]

$$H_{ex}b_1 = y_1 \approx \frac{\nabla E\left(X_0 + \xi b_1\right) - \nabla E\left(X_0 - \xi b_1\right)}{2\xi}, \quad (1)$$

where X_0 is the converged geometry, b_1 is the first component of the orthonormal subspace, H_{ex} is the exact hessian, ξ is the finite difference stepsize taken to be 0.01 a_0,[25] and ∇E represents gradient of the energy.

The vectors comprising the initial orthonormal subspace, $\{b_i\}$, typically span the dominant components of the desired eigenvalue(s). Depending on whether P-RFO is searching for a minimum or a TS, the subspace can be constructed using the lowest one or two eigenvectors of the updated hessian at convergence, respectively. This choice may not be reliable when the system possesses symmetry, since the initial subspace may be orthogonal to the corresponding lowest eigenvector(s). For systems with symmetry, therefore, we choose the initial guess as a linear combination of the lowest few eigenvectors of the updated hessian at convergence, with randomly determined scalar coefficients. The action of the hessian on the subspace vector(s) is determined from Eq. (1).

For characterization of minima, the first eigenvalue is given by

$$\lambda_1^{(1)} = y_1^T b_1, \quad (2)$$

where the superscript corresponds to the current iteration. The residual for the first iteration, therefore, is

$$q_i^{(1)} = y_{i,1} - \lambda_1^{(1)} b_{i,1}, \quad i = 1, \ldots, 3N, \quad (3)$$

where N is the number of atoms. Subsequent iterations can be carried out using the standard Davidson procedure.[19] The diagonal elements of the P-RFO updated matrix, H, are used in the preconditioner in order to accelerate convergence towards the desired eigenvalue:

$$w_i^{(M+1)} = \left(\lambda_1^{(M)} - H_{i,i}\right)^{-1} q_i^{(M)}, \quad i = 1, \ldots, 3N. \quad (4)$$

The vector, $w^{(M+1)}$, is then orthonormalized against previous vectors in the subspace to generate the new subspace vector, b_{M+1}, in the Mth cycle. If P-RFO has found the minimum correctly, the Davidson approach should converge to an

TABLE I. Summary of the finite difference Davidson procedure for characterization of stationary points, for systems with and without symmetry. The lowest eigenvalue is calculated for characterizing minima, and the lowest two eigenvalues are for TSs.

Stationary point	Initial subspace $\{b_i\}$ from P-RFO updated hessian, H	Convergence conditions (Equation (5))
Minimum (no symmetry)	Lowest eigenvector	(i) or (ii)
Minimum (symmetry)	Linear combination of lowest eigenvectors	$\|q_k\| \leq \xi^2$
Transition state	1st eigenvalue – lowest eigenvector	(i) and (ii)
	2nd eigenvalue – second eigenvector	(i) or (ii)

eigenvalue that is greater than or equal to zero. The iterations terminate when one of the following convergence criteria is satisfied:

$$\text{(i)} \quad \left(\lambda_k^{(M)} - \lambda_k^{(M-1)}\right)/\lambda_k^{(M-1)} \leq \xi \quad \text{or}$$

$$\text{(ii)} \quad |q_k| \leq \xi, \tag{5}$$

where superscript denotes the iteration, λ_k corresponds to the eigenvalue ($k = 1$ for minima), and q_k is the residual corresponding to the kth eigenvalue. When the system has symmetry, only condition (ii) is imposed, with tighter tolerance, ξ^2, in order to ensure that the procedure that begins with a random guess locates the correct eigenvalue.

A subspace consisting initially of two orthonormal vectors is used to characterize TSs. The finite difference expression in Eq. (1) is used to determine the action of the hessian on both b_1 and b_2. The two sets of vectors, (b_1, b_2) and (y_1, y_2), are used to construct the smaller matrix that is then diagonalized. The original Davidson procedure is followed subsequently to obtain the lowest eigenvalue. The search for the second eigenvalue begins with the augmented subspace obtained upon convergence of the first eigenvalue. Convergence of the second eigenvalue is assumed when one of the two conditions in Eq. (5) are satisfied. A more rigorous condition is imposed on the first eigenvalue, requiring both criteria in Eq. (5) to be satisfied for convergence. This is found to be essential, particularly in cases where the P-RFO begins in the absence of any hessian information and as a result, the updated matrix is not a good approximation to the exact hessian. If the optimizer finds the TS correctly, then the lowest eigenvalue determined by the Davidson procedure is negative. The second eigenvalue is zero, since the six eigenvalues following the lowest mode correspond to translations and rotations in cartesian coordinates.[26] A summary of the procedure for characterization of minima and transition states is given in Table I.

B. Transition state search

The speed and reliability of P-RFO for TS search is vastly enhanced when a hessian input with the correct eigenvalue structure is employed as opposed to a unit-matrix or diagonal-matrix input. Although the best input is the exact hessian at the TS guess, it is not always computationally viable. In such cases, an approximate one can be calculated either from force fields or by using a lower level of theory.[12]

An approximate hessian with exactly one negative eigenvalue can also be constructed using the finite difference Davidson approach. Any double-ended interpolation method that calculates the TS guess structure from reactant and prod-

uct geometries also generates an approximate reaction coordinate at the guess. In this case, the reaction coordinate generated by FSM is taken as b_1. The remaining steps are similar to the finite-difference Davidson approach for calculation of the lowest eigenvalue. The criteria for convergence are given by Eq. (5).

The converged eigenvalue and eigenvector must then be incorporated into a guess matrix. There are several possible choices for this guess, the simplest being a unit matrix. However, a better initial guess is the one that contains chemical information such as bond stretches, bends, etc. Therefore, a diagonal matrix in primitive internal coordinates, H_{prim}, is transformed to delocalized internal coordinates,[31] and subsequently, cartesian coordinates:

$$H_{int} = U^T H_{prim} U, \tag{6}$$

$$H_{cart} = B^T H_{prim} B. \tag{7}$$

H_{cart} is then updated with the eigenvalue and eigenvector obtained from the Davidson method:

$$H = H_{cart} - 0.5 \sum_{j=1}^{3N} \left(e_j^T H_{cart} t_1\right)\left(t_1 e_j^T + e_j t_1^T\right) + \lambda_1 t_1 t_1^T, \tag{8}$$

where e_j's are the eigenvectors of H_{cart}, and t_1 and λ_1 are the converged eigenvector and corresponding eigenvalue, respectively. Equation (8) removes existing components of the guess matrix along the lowest eigenvector and replaces them with the correct components. The resulting matrix has exactly one negative eigenvalue by design, and serves as a substitute to the exact hessian input to P-RFO.

III. RESULTS

A. Characterization of transition states

The reliability, performance, and scaling of the Davidson method for stationary point characterization is examined with Test Set 1. This set consists of n-butyl lithium initiated butadiene oligomerization transition-state and product structures. The converged TS and product geometries for trimerization are shown in Figure 1. The TS guesses are generated from the monomer TS[27] by successively adding 1,3-butadiene to the growing chain. In this way, TS guesses for the formation of oligomers ranging from the trimer (44 atoms) to the undecamer (124 atoms) are generated. The guess geometries are then refined to true TS structures with the P-RFO method using exact hessian inputs. The Davidson procedure is applied when the optimization converges. In order to examine the benefit of coupling P-RFO optimization with Davidson
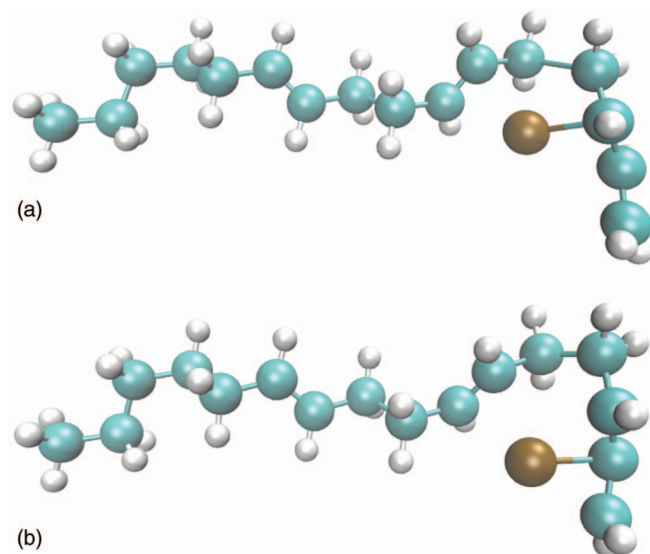
FIG. 1. Representative optimized structures for characterization of stationary points in Test set 1 comprising butadiene oligomers via alkyl lithium initiation. Brown atoms correspond to lithium, cyan represent carbon, and white represent hydrogen atoms. The TS and product structures correspond to 1-carbon attack by 1,3-butadiene of the allyl end of the chain.[27] The chain grows linearly as a result, and all the structures in this test set correspond to trans isomers. (a) Transition state for trimerization of *n*-butyl lithium. (b) Product of trimerization of *n*-butyl lithium.
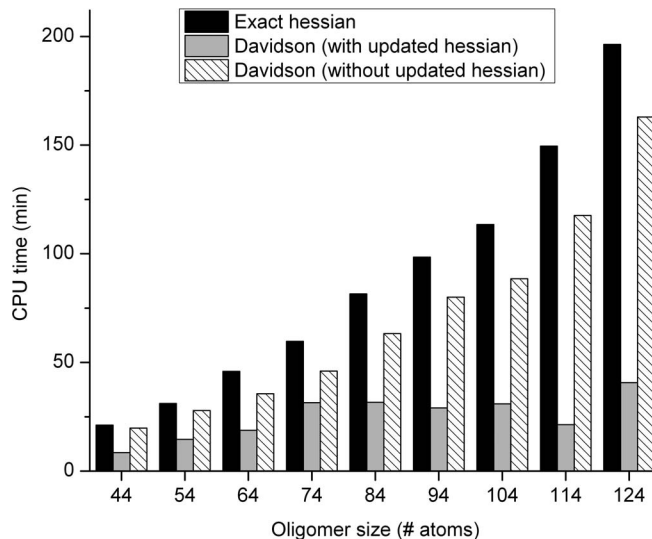

FIG. 2. Cost comparison between Davidson method and exact hessian calculation for characterization of TSs for Test Set 1. Oligomer sizes are plotted on the horizontal axis. The vertical axis represents the computational time (min) associated with either full hessian calculation or Davidson method for finding the two lowest eigenvalues. In all cases, P-RFO is initiated with an exact hessian input. Data labeled "with updated hessian" corresponds to the case when Davidson iterations begin with the P-RFO updated hessian. The "without updated hessian" label represents the cost of using the Davidson method with no hessian information. Full hessian calculation becomes intractable as system size increases. The Davidson approach with the updated hessian is largely independent of system size and can be up to 5 times less expensive relative to exact hessian calculation. In the absence of a P-RFO updated hessian, the approach is slower to converge. Therefore, it is recommended that the Davidson procedure be used in conjunction with a quasi-Newton optimizer for rapid TS characterization.

characterization, the method is also implemented without using any information from the updated hessian.

All calculations are carried out using a developmental version of Q-Chem 4.1,[28] and are run in parallel using 8 cores, each containing 4 GB RAM. Structures in Test Set 1 are treated at the B3LYP/6-31G level of theory.[29,30] P-RFO searches are carried out in delocalized internal coordinates[31] with an upper limit on step-size per iteration of 0.1 a_0. The cost and accuracy of the Davidson method for calculating the lowest two eigenvalues and thereby characterizing converged TS geometries is compared with the cost of calculating the full hessian.

The CPU time required to calculate the lowest eigenvalues with the Davidson method is determined by multiplying the number of force calculations in the finite-difference steps with the average time to calculate the gradient. This is then compared with the CPU time required for full analytical hessian calculation. For TS characterization, the eigenvalue and eigenvector corresponding to the reaction coordinate are also compared with eigensolutions of the exact hessian in order to verify convergence of the Davidson procedure.

Figure 2 compares the cost of full hessian calculation with the Davidson approach for characterizing oligomerization TSs. In all cases, the Davidson approach converges to the lowest eigenvalue within 2% error. The lowest eigenvector is also fully converged as verified by calculating its scalar product with the corresponding eigenvector of the exact hessian. When the Davidson approach begins with an updated hessian, the initial guess vector is a good approximation to the true reaction coordinate. In addition, preconditioning with the diagonal elements of the approximate hessian facilitates rapid convergence. The method is largely independent of system size, whereas the full hessian scales approximately cubi-

cally. For smaller systems, therefore, the Davidson approach is twice as fast as calculating the full hessian, and nearly 5 times faster for the largest system in the test set. On the other hand, if applied independent of the optimizer with no updated hessian information, the Davidson method is much slower to converge. Although computational effort is still lower than full hessian calculation, it is clear that the method is practical only when approximate hessian information, such as the P-RFO update, is available.

Based on these observations, a compromise can be considered that not only guarantees convergence of the P-RFO but also lowers costs associated with hessian calculations, particularly for large molecules. The full hessian can be quickly calculated using a very small basis set prior to TS search. The lowest eigenvalue and eigenvector can then be incorporated into a guess matrix as discussed earlier. The resulting approximate hessian is used for optimization using the P-RFO. This will ensure convergence of the P-RFO to the right saddle point and improve the performance of the Davidson method for characterization by providing a better initial guess of the subspace vector.

In order to ensure that this approach does not incorrectly characterize a higher-order saddle point as a TS, P-RFO optimization is carried out on a decanol molecule with a linear C-O-H bond. The optimization is carried out in the absence of a hessian input, and the system is treated at the B3LYP/6-31G level of theory. The converged structure corresponds to a second-order saddle point, and the hessian consists of two
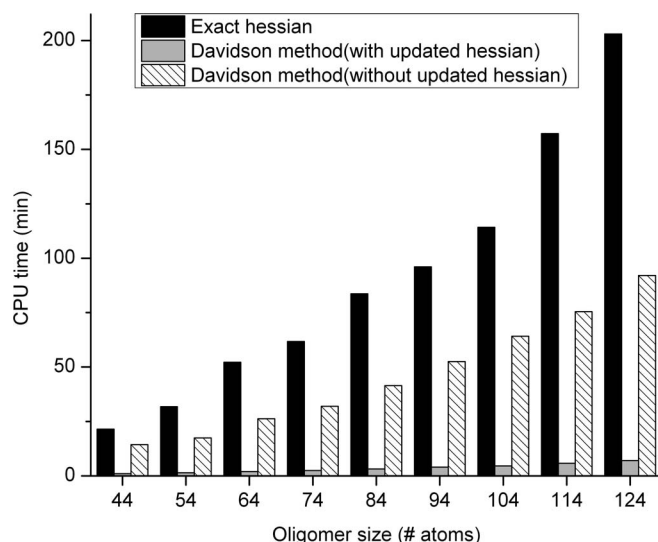
FIG. 3. Cost comparison between Davidson method and exact hessian calculation for characterization of minima for Test Set 1. In all cases, P-RFO is initiated without a hessian input, and the optimization begins with a diagonal matrix as a guess hessian. The Davidson method with the P-RFO updated hessian input characterizes the stationary point at significantly lower cost compared to full hessian calculation, with savings that increase approximately linearly with system size. Moving from left to right, the Davidson approach with the P-RFO updated hessian requires as much as 29 times less computational effort compared to the full hessian. Although the approach is more expensive in the absence of the P-RFO input, it is still more economical than full hessians for large systems.

degenerate negative eigenvalues, both of which are correctly calculated by the Davidson method. In addition, this approach is about 1.6 times faster than full hessian calculation. Higher-order saddle points are, therefore, accurately detected by this procedure.

B. Characterization of minima

The connectivities of the converged oligomerization TS structures in Test Set 1 are manually modified to resemble the product oligomers. These geometries are then refined to the correct product structure using the P-RFO method. Unlike TS search, all product optimizations are carried out in the absence of exact hessian inputs. The optimization, therefore, begins with a diagonal matrix as the hessian guess. The optimization parameters are identical to those for oligomer TS search.

For a minimum on a potential energy surface in cartesian coordinates, the lowest six modes typically correspond to external degrees of freedom. Consequently, the eigenvalues corresponding to these modes are zero. In Figure 3, the CPU time for full hessian calculation is compared with the time taken by the Davidson approach to converge to one of these modes. For the largest system consisting of 124 atoms, the cost of calculating the hessian is nearly 60 times the cost of the gradient. On the other hand, when the Davidson approach begins with the P-RFO updated hessian, the residual converges in the first finite-difference step itself, incurring a cost equal to only 2 gradients. As a result, the Davidson method with the P-RFO input is between 20 and 29 times faster than the full hessian calculation for this test set. The method is slower to converge without the P-RFO input, similar to what is observed in TS

characterization, but still twice as fast as the full hessian for the largest system in this test set.

The efficiency of applying the Davidson procedure is also tested in situations where the analytical hessian is not available. Since finite difference hessians are more expensive than analytical hessians, calculating second derivatives for even small molecules requires significant computational effort. The Davidson approach is tested in one such instance. Geometry optimization of fluoromethane (CH_3F), in the absence of a hessian input, is carried out using MP2/6-311G(d,p) level of theory with P-RFO parameters identical to those used in the oligomer optimizations. The time required to characterize the stationary point using the Davidson method is then contrasted with that for full finite difference hessian calculation. Calculation of the finite difference hessian requires 54.49 s of CPU time. The Davidson procedure can characterize the minimum in 5 iterations with a total CPU time of 7.29 s – nearly 7.5 times faster than the finite difference hessian, a gain that will only increase with system size. This approach is, therefore, not only useful for large molecules for which analytical hessians can become intractable but also systems that are treated with theory for which analytical hessians are unavailable.

A triflate anion in its eclipsed conformation is a molecule with C_s symmetry. Geometry optimization is carried out in parallel (8 cores) at BP86/6-311+G* level of theory. Although the P-RFO searches for a minimum, it converges to a first-order saddle point with the negative eigenvalue characteristic of a soft mode ($54i$ cm^{-1}). If the Davidson approach begins with a subspace consisting of the lowest eigenvector of the P-RFO updated hessian, it rapidly converges to an eigenvector that is orthonormal to the soft mode. When the subspace guess is a linear combination of the lowest eigenvectors, it converges correctly to within 3% of the lowest eigenvalue. Although the Davidson approach is more expensive, requiring 39 min (40 gradients), while the full hessian calculation needs only 24 min, the former is expected to scale more favorably with system size. The linear combination-based subspace guess can also be used for systems without symmetry in place of the single eigenvector in order to calculate the lowest and second eigenvalues for minima and TSs, respectively. For the minima in Test Set 1 with more than 50 atoms, replacing the lowest eigenvector with a linear combination increases the cost of characterization by only 2 gradients. This is still 15 times faster than full hessian calculation for the largest system in the test set.

C. Transition state search

A diverse set of reactions is chosen to evaluate the cost and performance of the P-RFO with the Davidson-based approximate hessian input relative to that with the full hessian. The reactions comprising Test Set 2, shown in Table II, are largely similar to those used in our previous work.[19] The TS guess structures are generated using FSM with a maximum of three perpendicular steps per iteration and roughly 20 nodes on the string. They are then refined to the correct TSs using P-RFO with both exact hessian as well as Davidson-based approximate hessian inputs. The two approaches are compared in terms of both hessian as well as optimization costs.

TABLE II. Test Set 2 for comparing the costs associated with exact and Davidson-based approximate hessian inputs, as well as cost of TS optimization with these inputs using the P-RFO method. The TS guesses are generated using FSM-BFGS with *ngrads* = 3 and *nnodes* = 20.[19]

Reaction	Description	Number of Atoms	Basis set	Theory
Formaldehyde decomposition	$H_2CO \leftrightarrow H_2 + CO$	4	6-31G	B3LYP
Silane formation	$SiH_2 + H_2 \leftrightarrow SiH_4$	5	6-31G	B3LYP
Ethanal rearrangement	$CH_3CHO \leftrightarrow CH_2CHOH$	7	STO-3G	HF
Ethane dehydrogenation	$CH_3CH_3 \leftrightarrow CH_2CH_2 + H_2$	8	6-31G**	B3LYP
Bicyclobutane ring opening	Bicyclobutane $\leftrightarrow CH_2CHCHCH_2$	10	STO-3G	HF
Hexadiene ring formation	*Cis,cis*-2,4-hexadiene $\leftrightarrow$ 3,4-dimethylcyclobutene	16	STO-3G	HF
Diels Alder reaction	$CH_2CHCHCH_2 + CH_2CH_2 \leftrightarrow$ cyclohexene	16	6-31G	B3LYP
Alanine dipeptide rearrangement	$C_5 \leftrightarrow C_{7AX}$	22	6-31G	B3LYP
Ireland Claisen rearrangement[35]	Silyl ketene acetal $\leftrightarrow$ silyl ester	56	6-31G	B3LYP
Cellotriose dehydration[36]	1,2 dehydration	66	6-31G	B3LYP

All calculations are carried out using a developmental version of Q-Chem 4.1 on single cores. For ease of visualization, both the hessian and optimization times are divided by the time required to calculate one energy and gradient. The resulting hessian cost is compared to the number of finite-difference steps required in the Davidson procedure. The number of P-RFO cycles required to converge to the correct TS is compared for the exact and approximate hessian inputs to determine whether the use of an approximation adversely affects the performance of P-RFO. TS searches for Test Set 2 are also carried out in delocalized internal coordinates with an upper limit on step-size per iteration of 0.1 a_0. Figure 4 shows the total cost of TS search with exact and approximate hessian
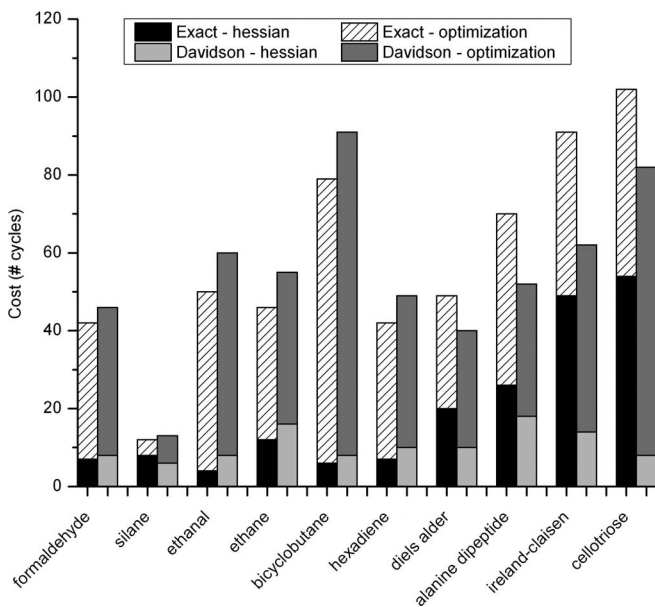

FIG. 4. Comparison of total costs between TS searches with exact and approximate hessian inputs using Test Set 2. The vertical axis represents the computational cost reported in terms of number of equivalent gradient calculations (cycles) by dividing computational time by the time required to calculate one energy and gradient. The total cost is broken down into its two components – firstly the cost of generating the exact or Davidson-based hessian as inputs to optimization, and secondly cost of optimization using P-RFO with this hessian input. With increasing size, the cost of calculating the exact hessian input constitutes a significant fraction of total cost. This can be avoided with the low cost, size-independent Davidson-based hessian. The penalty paid for using an approximate input is small compared to total cost savings achieved relative to TS search with the exact hessian.

inputs. The total cost is broken down into two components – the cost of calculating the exact/approximate hessian input, and the number of optimization steps required with this input. The results are shown in increasing order of system size.

Analytical hessians are relatively inexpensive for small systems consisting of fewer than 10 atoms. Therefore, the cost of hessian calculation is only a small fraction of total TS search cost. In such cases, the Davidson method does not offer any significant cost advantage. Although there is little benefit to using the Davidson-based hessian, it is interesting to note that the convergence of the optimizer is not adversely affected when an approximation replaces the exact hessian input, as long as it has the correct eigenvalue structure.

As the size of the system increases, the relative contribution of the hessian calculation to the total computational effort also rises. The cost of the hessian calculation is in fact higher than the optimization cost for the largest system in the test set, the dehydration of cellotriose. It can be inferred that further increase in the system size will result in domination of the hessian cost in the total cost of TS search. Significant reduction in computational effort can, therefore, be achieved by using an approximate hessian that scales more favorably with system size.

In Test Set 2, the cost of approximate hessian construction with the Davidson method does not exceed 9 finite-difference steps, or 18 gradients. Significant savings are achieved for the largest systems, Ireland-Claisen rearrangement and cellotriose dehydration, for which this method is 3.5 and 7 times less expensive than full hessian calculation, respectively. Again, the cost penalty associated with using an approximate input for optimization in place of an exact hessian is small. For cellotriose dehydration, although P-RFO requires 26 more steps to converge with the approximate hessian input relative to the exact hessian, the total cost of the TS search is still less with the approximate input.

The combined performance of the Davidson approach in TS search and optimization is shown in Table III. In addition to the costs associated with hessian construction (labeled "Hessian") and subsequent optimization (labeled "Opt.") presented in Figure 4, the cost of characterization (labeled "Charac.") with the Davidson method is also shown. The column labeled "Total" also includes, in parentheses, the total cost if the full hessian is used in place of the Davidson method.

TABLE III. Costs involved in TS search and characterization starting with the guess structure, using P-RFO with an exact hessian input and a Davidson-based hessian input. Costs are reported in terms of number of cycles obtained by dividing computational time by the time required to calculate one energy and gradient. Costs for calculation of an exact/approximate hessian prior to optimization, P-RFO optimization, and characterization using the Davidson method are labeled "Hessian," "Opt.," and "Charac," respectively. "Total" indicates the sum of all three components, with the values in parentheses corresponding to the total cost if characterization is carried out with a full hessian instead of the Davidson method. Davidson-based hessian construction and characterization can lead to significant overall cost reduction for large systems, as demonstrated by Ireland Claisen rearrangement and cellotriose dehydration reactions.

Costs (#cycles)	Exact hessian input				Davidson-based hessian input			
	Hessian	Opt.	Charac.	Total	Hessian	Opt.	Charac.	Total
Formaldehyde decomposition	7	35	12	54 (49)	8	38	14	60
Silane formation	8	4	6	18 (20)	6	7	6	19
Ethanal rearrangement	4	46	20	70 (54)	8	52	20	80
Ethane dehydrogenation	12	34	16	62 (58)	16	39	18	73
Bicyclobutane ring opening	6	73	30	109 (85)	8	83	26	117
Hexadiene ring formation	7	35	22	64 (49)	10	39	20	69
Diels Alder reaction	20	29	12	61 (69)	10	30	18	58
Alanine dipeptide rearrangement	26	44	34	104 (96)	18	34	34	86
Ireland Claisen rearrangement	49	42	24	115 (140)	14	48	24	86
Cellotriose dehydration	54	50	22	126 (158)	8	75	16	99

It is interesting to note that characterization costs are relatively insensitive to whether the P-RFO begins with an exact or an approximate hessian. Therefore, as long as the hessian input to P-RFO has the correct eigenstructure and reaction coordinate information, the Davidson approach is both speedy and reliable. For smaller molecules, as observed with approximate hessian construction, the cost of characterization with the Davidson method is typically higher than that of the full hessian. For the largest systems, however, using the Davidson approach for both hessian construction and TS characterization can result in nearly 40% cost reduction relative to using exact hessians.

The finite difference Davidson approach for search and characterization, therefore, promises significant cost reduction for saddle point searches in systems of very high dimensionality. There is an additional benefit to using a combination of FSM, Davidson-based hessian construction, P-RFO, and subsequent characterization with the Davidson method. The process of finding a TS from reactant and product structures can be fully automated with minimal user intervention, as described in our previous work.[19] However, it must be noted that in situations where the reaction coordinate is strongly coupled to other modes, construction of an approximate hessian with a single accurate eigenvalue may not be sufficient. In such cases, one may have to calculate the full hessian from force fields or by using a lower level of theory.[12]

D. Applications: Catalysis

DFT calculations for studying reactions involving an organometallic complex can be very expensive owing to the presence of one or more metal atoms. In such cases, the cost of calculating the full hessian can be prohibitive. Diaryldithiolene complexes of Co with different aryl substituents have been examined as potential electrocatalysts for proton reduction in the hydrogen evolution reaction (HER), for the conversion of solar energy to fuels.[32] The transition states for the H_2 evolution step in the catalytic cycle with two such complexes

are chosen in order to examine the cost reduction achieved using the Davidson approach for TS characterization.

TS optimizations are carried out in parallel (12 cores) using TS guess structures and exact hessian inputs for protonated bromo- and methoxy- derivatives of Co-diaryldithiolene. The system is treated at unrestricted BP86/6-31++G** level of theory with the exception of the Co atom, for which the Wachters+f basis set[33] is used. The structure of the optimized bromo-derivative TS is shown in Figure 5. The cost of calculating the full hessian is equivalent to 43 and 160 gradients, corresponding to about 4 and 5.4 days of computational time for the bromo- and methoxy-TS, respectively. On the other hand, the Davidson method converges within 3 iterations (6 gradients) in both cases. It is, therefore, 7 times faster than the full hessian calculation for the bromo-TS and nearly 27 times faster for the methoxy-TS, demonstrating substantial cost reduction in stationary point characterizations for systems containing metal atoms. It can be argued that since P-RFO begins with an exact hessian, the updated hessian input to Davidson is close to the true hessian, thereby
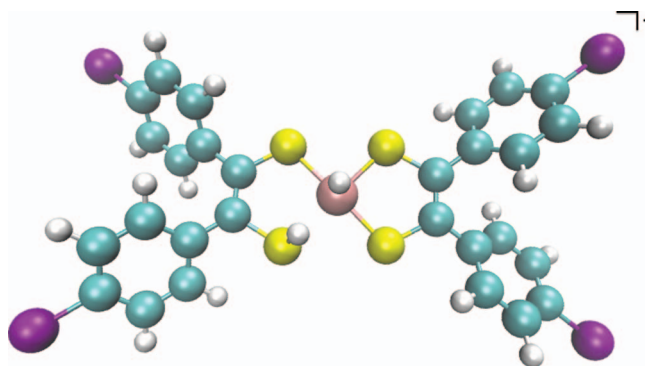

FIG. 5. Anionic transition state for H_2 evolution from the bromo-derivative of cobalt-diaryldithioline. Cobalt is in the center surrounded by sulfur atoms (yellow), and the aryl groups are para-substituted with bromo groups (violet). The Davidson approach for characterization is 7 and 27 times faster than full hessian calculation for the bromo- and methoxy-based TSs, respectively, thereby leading to substantial reduction in computational effort.

leading to rapid convergence. However, one can also construct an approximate hessian input to P-RFO, using the methods described earlier, without adversely affecting the performance of the Davidson approach, as demonstrated by the results in Table III.

Studying reaction kinetics in the pores of Brønsted acid catalysts such as zeolites can be computationally expensive since the role of the extended framework cannot be neglected.[34] The representation of the catalyst must include the non-reactive pore framework in addition to the active site containing the acidic proton. As a result, TS determination for propane dehydrogenation in H-MFI with even a small 23 tetrahedral (T) atom cluster model involves calculations on a system containing 100 atoms. The T5 region containing the active site and the adsorbate are allowed to relax. Input structures to the FSM consist of reactant and product geometries for the dehydrogenation of propane to propene and hydrogen – adsorbed propane and adsorbed propene plus H_2, respectively. The FSM parameters are identical to those used in Test Set 2. The P-RFO step size is 0.05 a_0 and search is carried out in cartesian coordinates. The system is treated at B3LYP/6-31G level of theory and optimizations are run in parallel (12 cores). The optimized TS for propane dehydrogenation in MFI is shown in Figure 6.
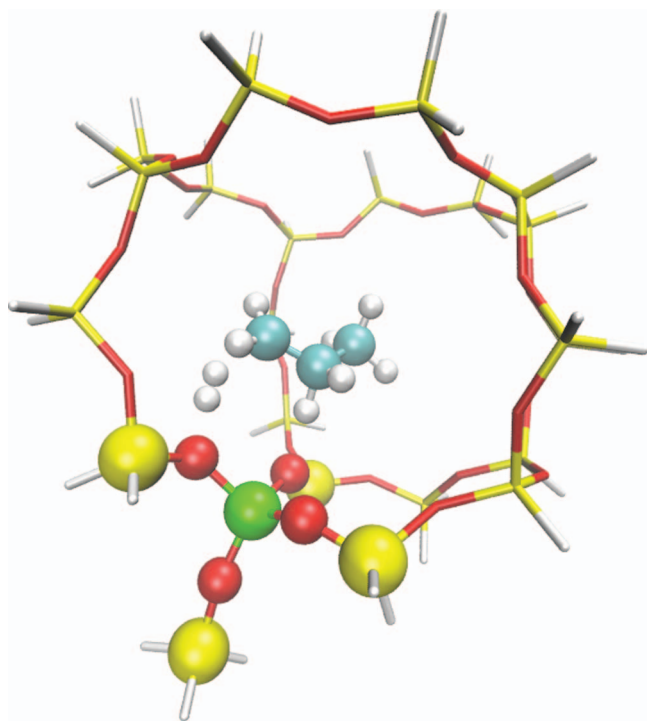

FIG. 6. Transition state for propane dehydrogenation in a T23 cluster of H-MFI (B3LYP/6-31G). The yellow atoms correspond to Si linked by O atoms in red, and the cluster is terminated with H atoms. The Al atom, shown in green, is representative of the active site where a neighboring O contains an acidic proton. The ball-and-stick representation is used for the active site and substrate, which are allowed to relax during optimization. Dehydrogenation is characterized by a late TS, where the H_2 molecule is nearly formed and re-generation of the acid site by proton migration from the substrate is initiated. For this system, the cost of calculating an approximate hessian for TS optimization is 6 times less than full hessian calculation. The penalty associated with using an approximate hessian input to the optimizer is also very low.

The cost of calculating the full hessian is equivalent to about 62 gradients, with an optimization cost of 263 gradients. The cost of constructing an approximate hessian, on the other hand, is only 10 gradients, and the optimizer performance is similar to that with the exact hessian input, costing 271 gradients. Therefore, even for complex reactions the Davidson method for approximate hessian construction is a viable alternative to full hessian input for the P-RFO, which cannot only cut costs associated with hessian computation but also not degrade the performance of the P-RFO.

IV. CONCLUSIONS

The finite-difference implementation of the Davidson method utilizes updated hessian information generated by P-RFO for stationary point characterization to find the lowest eigenvalues of the exact hessian matrix without actually calculating the matrix itself. This approach performs remarkably well, with significant cost savings relative to full hessian calculation for both minima and saddle point characterization. In addition, the rate of convergence is independent of system size, making this method ideally suited for large molecules. The cost of characterization of the largest test case, the butyl lithium undecamer TS (124 atoms) with the Davidson method is 5 times faster than the full hessian cost, and that of the undecamer product is 29 times faster. The efficiency of this approach is also demonstrated for a small molecule with theory for which analytical hessians are not available and finite-difference hessians are possibly more expensive. A similar procedure is used to construct low-cost approximate hessian inputs for TS optimization with P-RFO. For larger systems where hessian calculation constitutes a large fraction of the total TS search cost, the Davidson approach can significantly lower the hessian component of cost without adversely affecting the convergence of the optimizer. Therefore, the finite-difference Davidson method is a useful tool for both stationary point characterizations as well TS searches, particularly when the system contains a large number of atoms, or when analytical hessians are not available.

ACKNOWLEDGMENTS

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