

Eigenspace Update for Molecular Geometry Optimization in Nonredundant Internal Coordinate

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Abstract: An eigenspace update method is introduced in this article for molecular geometry optimization. This approach is used to obtain the nonredundant internal coordinate space and diagonalize the Hessian matrix. A select set of large molecules is tested and compared with the conventional method of direct diagonalization in redundant space. While all methods considered herein take on similar optimization pathways for most molecules tested, the eigenspace update algorithm becomes much more computationally efficient with increasing size of the molecular system. A factor of 3 speed-up in overall computational cost is observed in geometry optimization of the 25-alanine chain molecule. The contributing factors to the computational savings are the reduction to the much smaller nonredundant coordinate space and the $O(N^2)$ scaling of the algorithm.

I. Introduction

Molecular geometry optimization underlies all computational chemistry investigations by providing characteristic stationary point structures on potential energy surfaces (PESs).^{1,2} The most widely used geometry optimization method is the so-called quasi-Newton approach, in which analytical first derivatives and approximate second derivatives are used to search for a lower energy point on the PES. In this method, a Newton–Raphson step, $\Delta\mathbf{x}$, is taken on a local quadratic PES:

$$\Delta\mathbf{x} = -\mathbf{H}^{-1}\mathbf{g} \quad (1)$$

where \mathbf{g} is the gradient (first derivative) and \mathbf{H} is the Hessian (second derivative). In practical implementations, the Newton–Raphson step is stabilized with a control technique such as the rational function optimization (RFO)^{3,4} and the trust radius model (TRM).^{5–8} In the quasi-Newton approach for geometry optimizations, computationally expensive ana-

lytical evaluations of the second derivatives are replaced with a numerical Hessian update scheme, such as BFGS,^{9–12} SR1,¹³ and PSB.^{14,15} To obtain an optimization step $\Delta\mathbf{x}$, eq 1 can be solved with a direct inversion of the Hessian or RFO/TRM in the eigenvector space of the Hessian. However, inversion or diagonalization of a Hessian matrix incurs an $O(N^3)$ scaling, where N is the number of nuclear degrees of freedom. Such a cubic scaling can become a substantial bottleneck in the optimization of large molecules with semiempirical or linear scaling electronic structure methods. Alternatively, an iterative $O(N^2)$ approach can be carried out to search for the RFO solution in the reciprocal space of the Hessian.¹⁶ However, iterative solutions are often associated with numerical instabilities and a large scaling prefactor. In addition, iterative solutions do not offer direct computation of eigenvectors and eigenvalues that are important in vibrational analysis and transition state optimizations.

On the other hand, the choice of coordinate system in which the geometry optimization is conducted is crucial for successful convergence of the geometry optimization algorithm. Generally, geometry optimization in an appropriate set of internal coordinates can converge significantly faster than in Cartesian coordinates.^{17–19} However, a practical internal coordinate system for molecular geometry optimiza-

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tions usually contains redundancy. For large-scale systems, coordinate redundancy can become the speed-limiting factor arising from operating on excessively large matrices. In principle, redundancy can be removed by transformation to the nonredundant internal coordinate, leading to a much smaller coordinate space and less computationally expensive matrix inversion. However, obtaining the redundant–nonredundant vectors is another $O(N^3)$ procedure where N is the number of nonredundant coordinates. This dilemma largely prevents a practical application of geometry optimization in nonredundant coordinate space.

In this paper, we present an eigenspace update scheme with an $O(N^2)$ scaling in the nonredundant internal coordinate space. Computational performance and efficiency are compared for a select set of large molecules with the standard full diagonalization-based Berny algorithm^{18,20} in the redundant internal coordinate with RFO.

II. Methodology

A. Eigenspace Update—An $O(N^2)$ Algorithm for Molecular Geometry Optimization. Assume eigenvectors, \mathbf{C}_i , and eigenvalues, λ_i , of the Hessian exist at step i :

$$\mathbf{H}_i = \mathbf{C}_i \cdot \lambda_i \cdot \mathbf{C}_i^\dagger \quad (2)$$

Then, a forward optimization step, $\Delta \mathbf{x}_i$, can be obtained by means of RFO or TRM, using eq 1, resulting in a new geometry, \mathbf{x}_{i+1} ; a new gradient, \mathbf{g}_{i+1} ; and a new and updated Hessian, \mathbf{H}_{i+1} . In the current implementation, we use a weighted combination of BFGS^{9–12} and SR1¹³ with the square root of the Bofill²¹ weighting factor (see refs 22 and 23 for details). The new Hessian \mathbf{H}_{i+1} can be projected into the previous eigenvector space \mathbf{C}_i as

$$\Delta_{i+1} = \mathbf{C}_i^\dagger \cdot \mathbf{H}_{i+1} \cdot \mathbf{C}_i \quad (3)$$

Equation 3 can be considered as an intermediate diagonalization step. In principle, one can obtain the eigenvalues, λ_{i+1} , and eigenvectors, \mathbf{C}_{i+1} , of the Hessian by diagonalizing Δ_{i+1} :

$$\lambda_{i+1} = \mathbf{A}_{i+1}^\dagger \cdot \Delta_{i+1} \cdot \mathbf{A}_{i+1} \quad (4)$$

$$\mathbf{C}_{i+1} = \mathbf{C}_i \cdot \mathbf{A}_{i+1} \quad (5)$$

However, eqs 4 and 5 do not initially seem advantageous over the traditional approach of direct diagonalization of \mathbf{H}_{i+1} . From the molecular vibration standpoint, nonzero off-diagonal elements in eq 3 are related to vibrational couplings and anharmonicities. For any given normal mode, there exists a vibration which gives rise to the strongest coupling, or the largest off-diagonal element in Δ_{i+1} . Usually, in a nearly quadratic potential energy surface, changes in the Hessian matrix are small. If we only consider changes of the Hessian from the strongest couplings, Δ_{i+1} in eqs 3 and 4 can be replaced with a tridiagonal form, $\Delta_{3,i+1}$, where the only nonzero off-diagonal elements are the first diagonal below/above the main diagonal. Diagonalization of a tridiagonal matrix in eq 4 formally scales as $O(N^2)$ when the *Divide and Conquer*²⁴ algorithm is employed. As a result, eqs 3–5

become an eigenvector and eigenvalue update scheme, which is much more efficient than direct diagonalization.

In the following tests, we use a LAPACK subroutine to obtain eigenvalues and eigenvectors of a tridiagonal matrix $\Delta_{3,i+1}$. The projected Hessian matrix Δ_{i+1} is reorganized by swapping rows/columns in every optimization step so that the largest off-diagonal element for any given mode is positioned in the first diagonal below/above the main diagonal. The reorganization starts from the first projection vector in \mathbf{C}_i . When the projected Hessian matrix is reorganized, the related projection eigenvectors \mathbf{C}_i are also rearranged consistently according to the rows/columns being swapped in Δ_{i+1} . Note that this reorganization does not change the map between eigenvectors \mathbf{C} and the geometric coordinates \mathbf{x} .

B. Transformation to Nonredundant Coordinate Space. Analytical gradients, \mathbf{g} , are usually computed in the Cartesian coordinate and require geometries, \mathbf{x} , represented in the same coordinate as well. The transformation from the Cartesian coordinate \mathbf{x} to the redundant internal coordinate \mathbf{q} can be done with a symmetric \mathbf{G} matrix built from the Wilson \mathbf{B} matrix:²⁵

$$\mathbf{B} = \frac{d\mathbf{q}}{d\mathbf{x}} \quad (6)$$

$$\mathbf{G} = \mathbf{B}\mathbf{B}^T \quad (7)$$

where $d\mathbf{q}$ and $d\mathbf{x}$ are infinitesimal displacements in internal and Cartesian coordinates, respectively. With the transformation matrices defined in eqs 6 and 7, the gradient and optimization step can be transformed between two representations (Cartesian and redundant internal):

$$\mathbf{f}_q = \mathbf{G}^{-1}\mathbf{B}\mathbf{f}_x \quad (8)$$

$$\Delta \mathbf{x} = \mathbf{B}^T \mathbf{G}^{-1} \Delta \mathbf{q} \quad (9)$$

where \mathbf{f}_x and \mathbf{f}_q are forces in the Cartesian and redundant internal coordinate, and the Newton–Raphson step, $\Delta \mathbf{q}$, in the redundant internal coordinate is

$$\Delta \mathbf{q} = \mathbf{H}^{-1}\mathbf{f} \quad (10)$$

Note, in the quasi-Newton approach, the Hessian matrix can be updated in redundant internal coordinates without transformation back to the Cartesian coordinate.

For optimizations of large-scale systems, a smaller nonredundant coordinate space is preferred. The redundancy condition can be determined by single value decomposition (SVD) of the matrix \mathbf{G} :¹⁹

$$\mathbf{G} = (\mathbf{K}\mathbf{L}) \begin{pmatrix} \Lambda & 0 \\ 0 & 0 \end{pmatrix} (\mathbf{K}\mathbf{L})^T, \Lambda \neq 0 \quad (11)$$

In eq 11, \mathbf{K} corresponds to the nonredundant coordinate space with nonzero eigenvalues Λ , and \mathbf{L} consists of redundant eigenvectors of \mathbf{G} . However, obtaining the eigenspace of the \mathbf{G} matrix is another $O(N^3)$ procedure and speed-limiting step, and large molecules often have a large number of redundant coordinates. The eigenspace update concept introduced in section II.A can be used here to reduce the

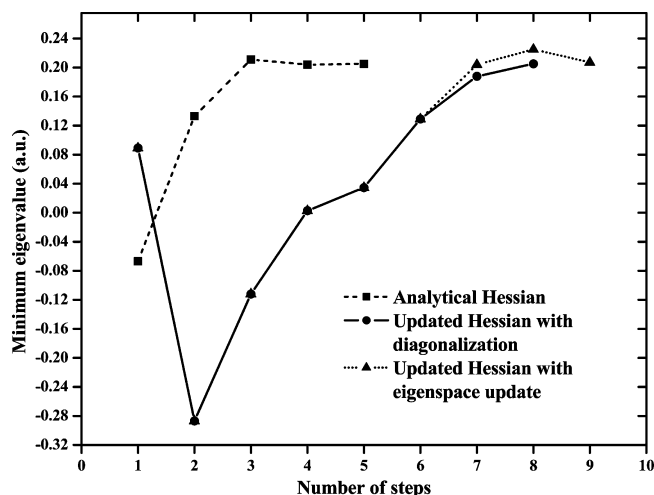


Figure 1. Comparison of minimum eigenvalues of the Hessian during optimization of a single water molecule, using analytical Hessian, updated Hessian with diagonalization, and Hessian eigenspace update approaches.

dimension of the \mathbf{G} matrix. Assuming the linear dependence in the internal coordinate space remains the same from step to step, the full \mathbf{G} matrix can then be reduced into the nonredundant coordinate space using the previous nonredundant vectors \mathbf{K} , followed by an SVD of the reduced and much smaller $\tilde{\mathbf{G}}$ matrix.

$$\tilde{\mathbf{G}} = \mathbf{K}_i^T \cdot \mathbf{G}_{i+1} \cdot \mathbf{K}_i \quad (12)$$

$$\tilde{\mathbf{G}} = \mathbf{U}_{i+1} \cdot \Lambda_{i+1} \cdot \mathbf{U}_{i+1}^T \quad (13)$$

The nonredundant coordinate space at the $i + 1$ step can be constructed accordingly:

$$\mathbf{K}_{i+1} = \mathbf{K}_i \cdot \mathbf{U}_{i+1} \quad (14)$$

The SVD of the full \mathbf{G} matrix in redundant internal space is performed only once in the first step. Subsequent geometry optimization steps will take advantage of this eigenspace update scheme (eqs 12–14) to obtain the nonredundant coordinate space \mathbf{K}_{i+1} . As the reduced $\tilde{\mathbf{G}}$ matrix is significantly smaller than the original \mathbf{G} matrix in redundant space, the SVD on $\tilde{\mathbf{G}}$ is no longer computationally dominant. As a result, obtaining the redundant–nonredundant transformation matrix \mathbf{K}_{i+1} becomes a pseudo- $O(N^2)$ approach.

Table 1. Comparison of Computational Costs for RFO Approach Using the Diagonalization in Redundant Space and Eigenspace Update Method^a

molecules (numbers of atoms)	energy (au)	diagonalization in redundant space			eigenspace update		
		geom ^b	SCF	steps ^c	geom ^b	SCF	steps ^c
hydrazobenzene (26)	0.129468	1.00	8.70	20	0.52	8.70	20
taxol (113)	−0.666862	1.00	0.68	63	0.45	0.71	66
for-(Ala) ₁₀ -NH ₂ (106)	−0.733344	1.00	0.82	100	0.66	0.97	115
for-(Ala) ₂₀ -NH ₂ (206)	−1.424445	1.00	0.63	206	0.52	0.70	238
for-(Ala) ₂₅ -NH ₂ (259)	−1.779332	1.00	0.48	82	0.38	0.50	87
crambin (642)	−4.167923	1.00	0.27	389			
crambin (642)	−4.169380				0.20	0.23	333

^a The computational cost is evaluated using the total CPU time of geometry steps using full diagonalization in redundant internal coordinate as the unit reference. ^b One geometry step includes forming the Wilson \mathbf{B} matrix; obtaining the nonredundant eigenspace, Hessian update, diagonalization, or eigenspace update; and solving the RFO equation. ^c Total number of geometry optimization steps.

With the eigenspace of the nonredundant internal coordinate, the Newton–Raphson step in eq 10 can be transformed into the nonredundant internal coordinate space with the following equation:

$$\mathbf{K}^{-1} \Delta \mathbf{q} = (\mathbf{K}^T \mathbf{H} \mathbf{K})^{-1} \mathbf{K}^T \mathbf{f} \quad (15)$$

If we define the Newton–Raphson step, Hessian, and force in the nonredundant internal coordinate as

$$\Delta \tilde{\mathbf{q}} = \mathbf{K}^{-1} \Delta \mathbf{q} \quad (16)$$

$$\tilde{\mathbf{H}} = \mathbf{K}^T \mathbf{H} \mathbf{K} \quad (17)$$

$$\tilde{\mathbf{f}} = \mathbf{K}^T \mathbf{f} \quad (18)$$

eq 15 becomes the familiar form of the Newton–Raphson step, but in the nonredundant internal coordinate space:

$$\Delta \tilde{\mathbf{q}} = \tilde{\mathbf{H}}^{-1} \tilde{\mathbf{f}} \quad (19)$$

The RFO correction can be applied to eq 19 with the Hessian eigenspace update scheme presented in the previous section. The displacement is then transformed back to redundant internal coordinate:

$$\Delta \mathbf{q} = \mathbf{K} \Delta \tilde{\mathbf{q}} \quad (20)$$

followed by another transformation to the Cartesian coordinate using the curvilinear eq 9 through an iterative approach.¹⁹

III. Benchmarks and Discussion

Optimizations are carried out using the AM1 Hamiltonian as implemented in the development version of the Gaussian program²⁶ with the addition of the geometry optimization algorithm using the eigenspace update (ESU) method in the nonredundant internal coordinate presented in sections II.A and B. For all test cases, the geometry optimization is considered converged when the maximum component of the force vector is less than 4.5×10^{-4} au, the root-mean-square (RMS) force is less than 3×10^{-4} au, the maximum component of the geometry displacement is less than 1.8×10^{-3} au, and the RMS geometry displacement is less than 1.2×10^{-3} au. To ensure a smooth convergence, the tridiagonal approximation of the reduced Hessian matrix is turned on when the regular RFO correction is smaller than one-tenth of the minimum

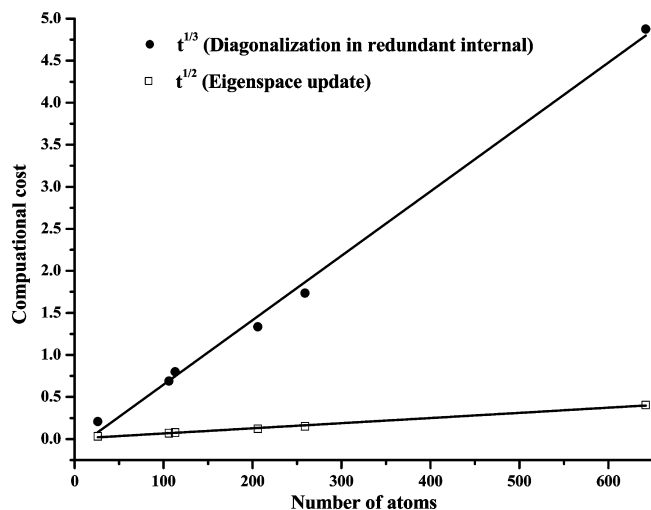


Figure 2. Comparison of computational costs using diagonalization in the redundant coordinate and eigenspace update. The computational cost of a single optimization step is plotted against the number of atoms.

Hessian eigenvalue. In the following discussion, we refer to a *geometry step* as the procedure including (1) forming the Wilson **B** matrix; (2) obtaining the nonredundant eigenspace (section II.B), (3) Hessian update, and (4) diagonalization or eigenspace update (section II.A); and (5) solving the RFO equation. For semiempirical and force field methods, the computational cost of the analytical gradient is not considered to be a computationally expensive step.

In the ESU approach, the Hessian eigenspace is usually an approximation and requires a number of optimization steps to converge to the true value. Figure 1 shows the convergence of the Hessian eigenspace using the ESU method and direct diagonalization of the updated Hessian, compared to the true analytical Hessian. It is known that the Hessian update scheme is able to converge to the true Hessian within a few geometry steps. Built on the Hessian update scheme, the Hessian eigenspace update method (section II.A) adds an additional degree of approximation. Therefore, the convergence behavior of the ESU approach is slower than the diagonalization-based method, but only by a few geometry steps. Nevertheless, the gain in computational speed owing to the $O(N^2)$ scaling and the nonredundancy is promising for large scale systems.

Table 1 lists relative computational costs for geometry optimizations using the ESU method for a select set of molecules compared to those obtained with full diagonalization in the redundant internal coordinate. The computational cost is evaluated using the total CPU time of geometry steps of the Hessian diagonalization-based RFO approach as the unit reference. For smaller molecules, such as hydrazobenzene, there are no savings in the overall computational cost. Although the computational cost for geometry steps is reduced, the approximate nature of the Hessian eigenspace in ESU leads to several additional optimization steps compared to the diagonalization-based RFO approach. As a result, additional computational cost incurs, arising from additional SCF

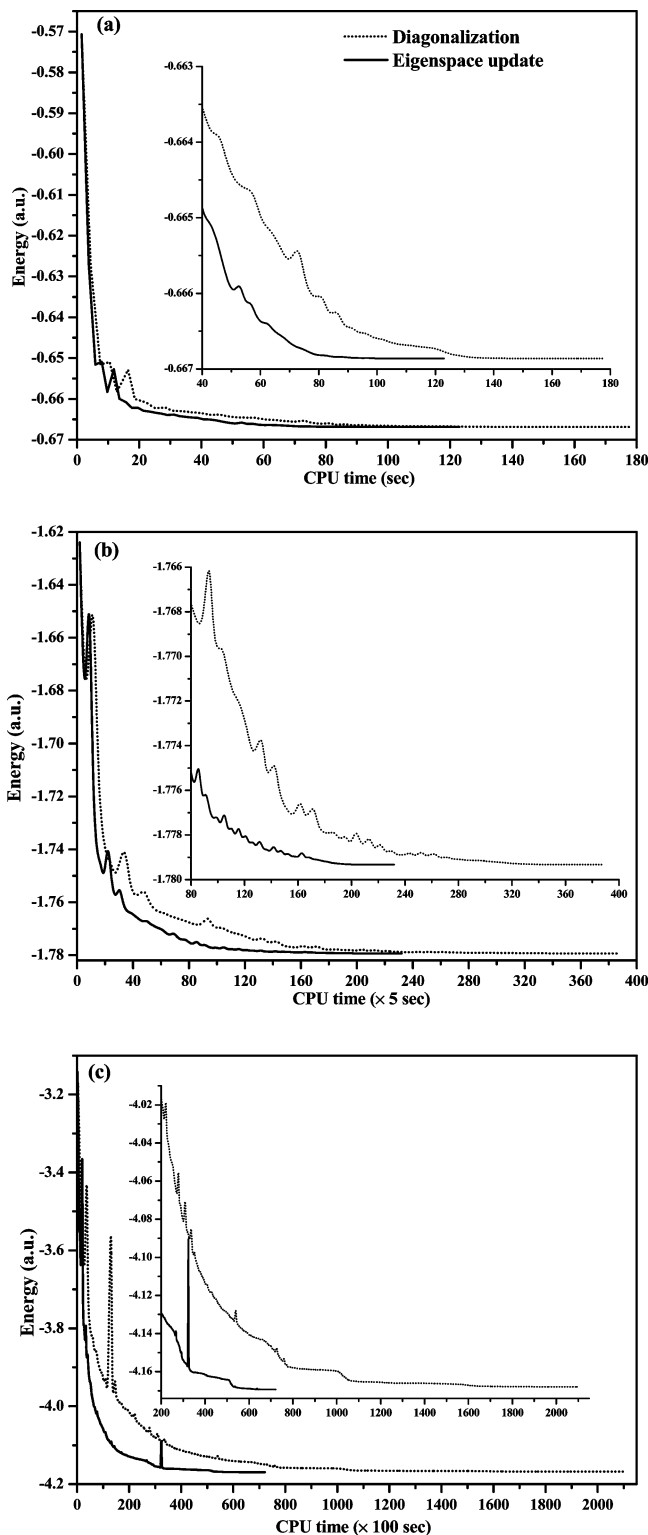


Figure 3. Comparison of optimizations using diagonalization in redundant space and eigenspace update methods for (a) taxol, (b) 25-alanine chain, and (c) crambin at the AM1 level of theory. See Table 1 regarding the evaluation of computational cost.

steps, and therefore the application of ESU for small molecules is not particularly advantageous.

On the other hand, as the molecular size increases, the cost for geometry steps becomes dominant in computational cost for semiempirical self-consistent field (SCF) or force

field energy calculations. In Table 1, we include test cases of large-scale molecules, such as taxol, alanine chains, and crambin. Because of excessive nuclear and electronic degrees of freedom, and numerous undesirable shallow potential wells on the PES, these molecules are often difficult and computationally expensive to optimize. As the nuclear degrees of freedom increase, the computational cost of the ESU-based method is noticeably less expensive than the conventional approach using full diagonalization in redundant coordinates. For the 25-alanine chain case, a ~60% computational saving is observed. In this case, the total computational cost for SCF iterations in the ESU-based method is slightly (~1%) more expensive than the conventional approach due to a slightly larger number of geometry steps. Therefore, such a large computational savings in the ESU-based method can be ascribed to the efficient eigenspace update algorithm in nonredundant internal coordinate space introduced herein. Although we cannot make a direct comparison for the largest test case, crambin, as the two methods converge to different minima,²⁷ a factor of 3 in computational cost is definitely noticeable.

To further understand the computational performance of the ESU approach, we plot in Figure 2 the computational cost of a single geometry step as a function of the number of atoms. It is clear that ESU is an $O(N^2)$ method while the diagonalization-based approach exhibits an $O(N^3)$ scaling. As the molecular sizes increase, the advantage of using an $O(N^2)$ approach becomes highly appreciated. Figure 3a–c illustrate optimization processes of selected large-sized molecules: taxol, alanine-25, and crambin at the AM1 level of theory. It shows that the ESU method takes a similar optimization pathway as diagonalization in the redundant-space-based RFO approach but has the advantage of being much more efficient.

IV. Conclusion

This paper presents a geometry optimization method using an eigenspace update approach. This method takes advantage of previously computed eigenvectors for obtaining eigenspaces of the transformation **G** matrix and the Hessian matrix and exhibits an $O(N^2)$ scaling. This method shows an encouraging efficiency for geometry optimization, with up to a factor of 3 savings in computational cost for large-sized molecular systems. The optimization pathways are similar to those using conventional diagonalization in the redundant-space-based RFO approach. An even more promising implementation of the ESU method would be combination direct inversion in the iterative subspace algorithm (DIIS), as exemplified by the energy-represented DIIS²³ and the simultaneous DIIS methods.²⁷

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