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Efficient Solution of the Electronic Eigenvalue Problem Using Wavepacket Propagation

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ABSTRACT: We report how imaginary time wavepacket propagation may be used to efficiently calculate the lowest-lying eigenstates of the electronic Hamiltonian. This approach, known as the relaxation method in the quantum dynamics community, represents a fundamentally different approach to the solution of the electronic eigenvalue problem in comparison to traditional iterative subspace diagonalization schemes such as the Davidson and Lanczos methods. In order to render the relaxation method computationally competitive with existing iterative subspace methods, an extended short iterative Lanczos wavepacket propagation scheme is proposed and implemented. In the examples presented here, we show that by using an efficient wavepacket propagation algorithm the relaxation method is, at worst, as computationally expensive as the commonly used block Davidson–Liu algorithm, and in certain cases, significantly less so.

INTRODUCTION

In most quantum chemistry methods, a computational bottleneck in the calculation of electronic state energies is the diagonalization of the matrix representation of the electronic Hamiltonian operator, $\hat{H}$, represented in some finite N -electron basis. The dimension of the N -electron basis is routinely of the order of 10^5 – 10^8 , rendering the direct, full diagonalization of the electronic Hamiltonian matrix impossible. Instead, iterative subspace diagonalization methods are adopted, in which a handful of the extremum eigenpairs are computed. Among the most widely used iterative diagonalization methods are the Lanczos¹ and Davidson² schemes and, in particular, their block variants.^{3–6} In these methods, the Hamiltonian whose eigenpairs is sought is iteratively projected onto a small dimensional Krylov subspace containing the low-lying eigenstates of interest. In order to generate the Krylov subspace, repeated Hamiltonian matrix–vector multiplications are required to be performed, representing the main computational cost of these methods.

We here consider a different approach to the calculation of electronic states that is based on the idea of wavepacket relaxation,⁷ otherwise known as imaginary time propagation. This is a widely used method in the area of quantum dynamics.^{8–10} There, a guess wavepacket is propagated in negative imaginary time, forcing a collapse to the lowest eigenstate that is nonorthogonal to the initial wavepacket.

Imaginary time propagation has previously been used with great success in the solution of the time-independent Schrödinger equation.^{8–16} With the exception of quantum Monte Carlo schemes, however, previous studies have been applied to grid-based representations of the wave function and commonly employ operator splitting techniques to perform the imaginary time wavepacket propagation.^{11–14} Such methodologies are not applicable to quantum chemistry calculations in

which the wave function is typically expanded in terms of Gaussian basis functions.

It is the aim of this paper to determine a suitable relaxation algorithm for calculating electronic states (both ground and excited) that is applicable to commonly used quantum chemistry methods. Such an algorithm has to be computationally competitive with traditionally used iterative subspace diagonalization schemes to be considered useful. As in these commonly used methods, the bottleneck in a relaxation calculation is the calculation of a large number of Hamiltonian matrix–vector multiplications. As such, the adoption of a wavepacket propagation algorithm that is both applicable to wave functions expanded in terms of Gaussian basis functions and is able to take large time steps is key. To this end, we report the implementation of a new, efficient, modified short iterative Lanczos wavepacket propagation algorithm, termed the extended short iterative Lanczos method. Using this new algorithm, we use the relaxation method to calculate the low-lying excited states of a number of molecules at the second-order algebraic diagrammatic construction (ADC(2)) level of theory. In all cases, we find that the number of rate-limiting Hamiltonian matrix–vector multiplications required by the relaxation method is comparable to, if not smaller than, the number required by the block Davidson–Liu (DL) method. These results suggest that the relaxation method offers a promising alternative framework in which to solve the electronic eigenvalue problem.

METHODOLOGY

The Relaxation Method. We consider an initial guess wavepacket $|\psi(0)\rangle$ whose projection against the lowest

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eigenfunction $|\Psi_0\rangle$ of the electronic Hamiltonian is nonzero: $\langle\Psi_0|\psi(0)\rangle \neq 0$. Next, we make the Wick rotation $t \rightarrow \tau = -it$ and consider the propagation of $|\psi(0)\rangle$ forward in negative imaginary time, τ , using the electronic Hamiltonian:

$$|\psi(0)\rangle \rightarrow |\psi(\tau)\rangle = \exp(-\hat{H}\tau)|\psi(0)\rangle \quad (1)$$

Expanding the propagated wavepacket $|\psi(\tau)\rangle$ in the eigenstates $|\Psi_I\rangle$ of $\hat{H}$, we obtain

$$|\psi(\tau)\rangle = \sum_I C_I \exp(-E_I \tau) |\Psi_I\rangle \quad (2)$$

where

$$C_I = \langle\Psi_I|\psi(0)\rangle \quad (3)$$

From eq 2, we see that by propagating forward in negative imaginary time, τ , followed by renormalization, each eigenfunction $|\Psi_I\rangle$ in the expansion of the guess wavepacket $|\psi(0)\rangle$ is annihilated at a rate inversely proportional to the exponential of its eigenvalue E_I . Thus, as $\tau \rightarrow \infty$, $|\psi(\tau)\rangle/||\psi(\tau)\rangle||$ will converge to the ground state, $|\Psi_0\rangle$. This is the main idea behind the relaxation method.

The calculation of excited states proceeds in sequence, in an analogous manner. First, the ground state $|\Psi_0\rangle$ is calculated. Next, the projected electronic Hamiltonian

$$\hat{H}_\perp^{(0)} = (1 - |\Psi_0\rangle\langle\Psi_0|)\hat{H}(1 - |\Psi_0\rangle\langle\Psi_0|) \quad (4)$$

is used in a subsequent imaginary time propagation, yielding the first-excited state $|\Psi_1\rangle$. In general, the J th excited state is calculated using the projected Hamiltonian $\hat{H}_\perp^{(J-1)}$,

$$\begin{aligned} \hat{H}_\perp^{(J-1)} &= \left(1 - \sum_{I=0}^{J-1} |\Psi_I\rangle\langle\Psi_I|\right) \hat{H} \left(1 - \sum_{I=0}^{J-1} |\Psi_I\rangle\langle\Psi_I|\right) \\ &= \hat{Q}^{(J-1)} \hat{H} \hat{Q}^{(J-1)} \end{aligned} \quad (5)$$

Noting that the projection operator $\hat{Q}^{(J)}$ is idempotent and commutes with $\hat{H}$, we may write

$$\exp(-\hat{H}_\perp^{(J)}\tau) = \exp(-\hat{Q}^{(J)}\hat{H}\hat{Q}^{(J)}\tau) = \exp(-\hat{H}\tau)\hat{Q}^{(J)} \quad (6)$$

which allows for a minimization of the number of orthogonalizations required in the calculation of the excited states.

For the sake notational simplicity, in the following, we only consider the unprojected Hamiltonian, $\hat{H}$, that is used in the calculation of the ground state, understanding that this is to be replaced by $\hat{H}_\perp^{(J-1)}$ when the J th excited state is to be computed.

Wavepacket Propagation Methods. Conceptually, the simplest way to propagate the wavepacket $|\psi(0)\rangle$ forward in negative imaginary time would be to directly integrate the imaginary time Schrödinger equation, i.e., to calculate the quantity

$$\dot{|\psi(0)\rangle} = \frac{\partial|\psi(0)\rangle}{\partial\tau} = \frac{\partial}{\partial\tau} \frac{\partial|\psi(0)\rangle}{\partial t} = -\hat{H}|\psi(0)\rangle \quad (7)$$

and then numerically integrate $\dot{|\psi(0)\rangle}$ to yield $|\psi(\tau)\rangle$.

The problem with this approach is that in commonly used numerical integration methods (e.g., Runge–Kutta or Bulirsch–Stoer (BS) schemes) the ratio of the stepsize to the number of Hamiltonian matrix–vector multiplications required for a given error tolerance is in general small. This can result in a large number of Hamiltonian matrix–vector multiplications and

would render this approach uncompetitive with traditional iterative subspace diagonalization methods.

In order to reduce the number of Hamiltonian matrix–vector multiplications required to accurately take a given stepsize, methods that approximate the imaginary time evolution operator $\hat{U}(\tau) = \exp(-\hat{H}\tau)$ as an expansion in terms of polynomials of the Hamiltonian may be used.¹⁷ Prominent examples include the Chebyshev¹⁸ and short iterative Lanczos (SIL)¹⁹ methods. The requirement of the Chebyshev method that the bounds of the spectrum of $\hat{H}$ be known complicates its use for wavepacket propagation using Gaussian basis sets. Instead, we adopt and extend the SIL algorithm for this purpose.

The Short Iterative Lanczos Algorithm. We first introduce some notation that will aid with the subsequent discussion. Let $\hat{O}_S$ denote the representation of the operator $\hat{O}$ in the set of basis functions S . That is, if $S = \{|f_k\rangle: k = 1, \dots, N\}$, then

$$\hat{O}_S = \sum_{k,l=1}^N |f_k\rangle\langle f_k|\hat{O}|f_l\rangle\langle f_l| \quad (8)$$

In the context of a relaxation calculation, the key idea behind the SIL method¹⁹ is to represent the imaginary time evolution operator $\hat{U}(\tau) = \exp(-\hat{H}\tau)$ in the basis of a small number of Lanczos states $\mathcal{L}^{(N)} = \{|\Lambda_k\rangle: k = 0, 1, \dots, N\}$, which are obtained from the set of Krylov states $\mathcal{K}^{(N)} = \{|K_k\rangle: k = 0, \dots, N\}$,

$$|K_k\rangle = \hat{H}^k |K_0\rangle = \hat{H}^k |\psi(0)\rangle, \quad k = 0, 1, \dots, N \quad (9)$$

via Gram–Schmidt orthonormalization. The imaginary time evolution operator is then approximated by its N th order Lanczos state representation:

$$\begin{aligned} \hat{U}(\tau) &\approx \hat{U}_{\mathcal{L}^{(N)}}(\tau) \\ &= \exp(-\hat{H}_{\mathcal{L}^{(N)}}\tau) \end{aligned} \quad (10)$$

Here, $\hat{H}_{\mathcal{L}^{(N)}}$ denotes the N th order Lanczos state representation of the electronic Hamiltonian:

$$\hat{H}_{\mathcal{L}^{(N)}} = \sum_{k,l=0}^N |\Lambda_k\rangle\langle\Lambda_k|\hat{H}|\Lambda_l\rangle\langle\Lambda_l| \quad (11)$$

It is noted that elements $\langle\Lambda_k|\hat{H}|\Lambda_l\rangle$ form a tridiagonal matrix $\mathbf{H}_{\mathcal{L}^{(N)}}$. Diagonalization of $\mathbf{H}_{\mathcal{L}^{(N)}}$ yields a set of N eigenfunctions and eigenvalues, $|\tilde{\Lambda}_k\rangle$ and $\tilde{E}_k$, respectively, which may then be used to evaluate the operation of $\hat{U}_{\mathcal{L}^{(N)}}(\tau)$ on the wave function $|\psi(0)\rangle$:

$$\hat{U}_{\mathcal{L}^{(N)}}(\tau)|\psi(0)\rangle = \sum_{k=0}^N |\tilde{\Lambda}_k\rangle \exp(-\tilde{E}_k \tau) \langle\tilde{\Lambda}_k|\psi(0)\rangle \quad (12)$$

The standard SIL algorithm is a well-established wavepacket propagation scheme and is known to allow for the use of comparatively long time steps. However, as we detail next, it is possible to modify to the SIL algorithm at little extra cost such that even larger time steps may be taken without a deterioration of accuracy. This modification is of central importance, as it enables this approach to be computationally competitive with standard iterative diagonalization methods.

The Extended Short Iterative Lanczos Algorithm. We here discuss an extension of the standard SIL algorithm, which we term the extended short iterative Lanczos (XSIL) algorithm, that allows for the use of larger time steps. The fundamental idea

behind the XSIL algorithm is to recognize that by including Lanczos states from previous time steps in the Lanczos state representation of $\hat{U}(\tau)$, an effective increase in the dimension of the Krylov subspace used may be achieved without incurring any additional Hamiltonian matrix–vector multiplications. In turn, an increase in the stepsize that may accurately be taken is afforded, decreasing the computational cost to converge a given electronic state.

To understand how the XSIL algorithm results in an increase in the dimension of the Krylov subspace, we consider the propagation of $|\psi(0)\rangle$ to $|\psi(\tau)\rangle$ via n successive subpropagations using a time step $\Delta\tau = \tau/n$. Let $|\psi_m\rangle = |\psi(m\Delta\tau)\rangle$ denote the wave function obtained at the end of the m th time step. Let $\mathcal{K}^{(N;m)} = \{|K_k^{(m)}\rangle: k = 0, 1, \dots, N\}$ denote the set of Krylov states obtained using an initial vector $|K_0^{(m)}\rangle = |\psi_m\rangle$. Analogously, let $\mathcal{L}^{(N;m)} = \{|\Lambda_k^{(m)}\rangle: k = 0, 1, \dots, N\}$ denote the set of Lanczos states obtained from the orthonormalization of the states in the set $\mathcal{K}^{(N;m)}$. In the standard SIL algorithm, propagation of $|\psi_m\rangle$ to $|\psi_{m+1}\rangle$ is performed by representing the evolution operator $\hat{U}(\Delta\tau)$ in the basis $\mathcal{L}^{(N;m)}$, yielding the approximate operator $\hat{U}_{\mathcal{L}^{(N;m)}}(\Delta\tau)$. The key idea behind the XSIL algorithm is to represent $\hat{U}(\Delta\tau)$ in an extended basis $\mathcal{L}_p^{(N;m)}$ that incorporates the Lanczos states from p of the previous time steps:

$$\mathcal{L}_p^{(N;m)} = \mathcal{L}^{(N;m-p)} \cup \mathcal{L}^{(N;m-p+1)} \cup \dots \cup \mathcal{L}^{(N;m)} \quad (13)$$

To understand the advantage of reusing the Lanczos states of previous time steps, consider the use of an extended Lanczos basis $\mathcal{L}_1^{(N;m)}$ incorporating the Lanczos states of the $(m-1)$ th time step in the forward propagation of $|\psi_m\rangle$. The wave function $|\psi_{m-1}\rangle$ of the previous time step may be obtained approximately via the application of $\hat{U}_{\mathcal{L}^{(N;m)}}(-\Delta\tau)$ to $|\psi_m\rangle$. That is, $|\psi_{m-1}\rangle$ may be approximated as a linear combination of the Lanczos states in $\mathcal{L}^{(N;m)}$, or equivalently, as a linear combination of the Krylov states in $\mathcal{K}^{(N;m)}$:

$$\begin{aligned} |\psi_{m-1}\rangle &\approx \sum_{j=0}^N A_j |K_j^{(m)}\rangle \\ &= \sum_{j=0}^N A_j \hat{H}^j |\psi_m\rangle \end{aligned} \quad (14)$$

Using eq 14, the Krylov states in $\mathcal{K}^{(N;m-1)}$ may then be expressed as

$$\begin{aligned} |K_k^{(m-1)}\rangle &= \hat{H}^k |\psi_{m-1}\rangle \\ &\approx \hat{H}^k \sum_{j=0}^N A_j \hat{H}^j |\psi_m\rangle \\ &= \sum_{j=0}^N A_j \hat{H}^{j+k} |\psi_m\rangle \\ &= \sum_{j=0}^N A_j |K_{j+k}^{(m)}\rangle, \quad k = 0, 1, \dots, N \end{aligned} \quad (15)$$

We thus see that the Krylov states in $\mathcal{K}^{(N;m-1)}$, and hence the Lanczos states in $\mathcal{L}^{(N;m-1)}$, contain contributions from Krylov states $|K_k^{(m)}\rangle$ of order $k > N$. Hence, by using the extended Lanczos basis $\mathcal{L}_p^{(N;m)}$, $p \geq 1$, higher-order Lanczos states are effectively incorporated for virtually no extra computational cost.

The Lanczos states corresponding to different time steps are not orthogonal: $\langle \Lambda_j^{(m)} | \Lambda_k^{(n)} \rangle \neq \delta_{jk}$ if $m \neq n$. As such, linear dependencies in the extended Lanczos bases $\mathcal{L}_p^{(N;m)}$ quickly develop. In order to ameliorate numerical problems arising from linearly dependent basis functions, we adopt at each time step a canonical orthogonalization of the extended Lanczos basis $\mathcal{L}_p^{(N;m)}$. This yields a new basis of linearly independent functions $\mathcal{I}_p^{(M;m)} = \{|\Phi_k^{(m)}\rangle: k = 0, 1, \dots, M\}$ of dimension $M+1 \leq (p+1)(N+1)$ that is then used to represent the imaginary time evolution operator. For the sake of brevity, the details of this procedure are given in the Appendix.

The XSIL algorithm that was implemented and used in all of the following calculations is summarized in Algorithm 1 in the Appendix.

RESULTS

Computational Details. To assess the potential usefulness of the relaxation method in the solution of the electronic eigenvalue problem, the low-lying states of a number of small- and medium-sized molecules (allene, benzene, and pyrrole) were calculated at the ADC(2) level of theory within the intermediate state representation.^{20–22} In all cases, the XSIL wavepacket propagation scheme was used. The cc-pVDZ basis was used for all calculations. The convergence criterion used was that the residual norm, $r = \|\hat{H}|\psi\rangle - E|\psi\rangle\|$, be below 10^{-6} . At each time step, $N+1 = 20$ Lanczos states were generated, and the imaginary time evolution operator was represented in a basis derived using the Lanczos states of up to $p = 4$ previous time steps. A constant time step of $\Delta\tau = 200$ au was used for all calculations.

Additionally, all relaxation calculations were also performed using the BS algorithm to perform the imaginary time wavepacket propagation. The purpose of this is to contrast the XSIL relaxation algorithm, which is based upon an efficient representation of the imaginary time evolution operator, $\hat{U}(\tau)$, with a method that directly integrates the imaginary time derivative of the wavepacket. Through comparison to these results, we show that the use of the XSIL propagation algorithm is key to making the relaxation methodology computationally competitive with iterative subspace diagonalization schemes.

To provide a comparison to traditional iterative subspace diagonalization methods, all calculations were repeated using the block DL method used in conjunction with Olsen's preconditioner.²³ We acknowledge that the performance of the block DL method will be sensitive to the specifics of the given implementation. As such, we give the details of the chosen block DL algorithm in Algorithm 2 in the Appendix.

For all calculations, guess wave functions were generated via the diagonalization of the Hamiltonian matrix represented in the basis of the 800 N-electron basis functions corresponding to the smallest on-diagonal elements of the full Hamiltonian matrix.

Test 1: Allene. For allene, the dimension of the ADC(2)/cc-pVDZ Hamiltonian matrix is 93960. For both the SIL relaxation and block DL calculations, three- and ten-state calculations were performed. In the three-state block DL calculation, a block size of

Figure 1. Convergence of the first three excited states of allene calculated at the ADC(2)/cc-pVDZ level of theory: (a) XSIL relaxation and (b) block DL. The total number of Hamiltonian matrix–vector multiplications required for the XSIL and block DL calculations were 140 and 378, respectively.

Figure 2. Convergence of the first 10 excited states of allene calculated at the ADC(2)/cc-pVDZ level of theory: (a) XSIL relaxation and (b) block DL. The total number of Hamiltonian matrix–vector multiplications required for the XSIL and block DL calculations were 560 and 870, respectively.

6 and a maximum subspace dimension of 18 was used. In the ten-state block DL calculation, a block size of 15 and a maximum subspace dimension of 45 was used.

For the XSIL calculations, the number of rate-limiting Hamiltonian matrix–vector multiplications required to converge all states was 140 for the three-state calculation and 560 for the ten-state calculation. This is to be compared to 378 and 870 matrix–vector multiplications for the three- and ten-state block DL calculations, respectively, clearly demonstrating that the XSIL method is competitive with this traditional iterative subspace method.

In Figure 1, we show the residual norm, r , plotted against the iteration number for the three-state XSIL relaxation and block DL calculations. For the XSIL relaxation calculation, rapid convergence of the residual norm, r , for all three states is observed, with a maximum of three iterations being required. A near-linear decrease in $\log(r)$ for all three states with propagation time is observed for all three states. This belies the exponential convergence of the relaxation method, as highlighted in eq 2, and demonstrates its potential power.

An affliction of traditional iterative subspace diagonalization methods is that the rate of convergence for higher-lying states is usually worse than for the lower-lying states. In Figure 1(b) we show the residual norms of the same three excited states of allene during the course of the block DL calculation. While the first two excited states converge at the same rate, almost 2.5 times as many iterations are required to achieve convergence for the third excited state. In contrast, for the XSIL relaxation calculation, convergence of the first two excited states was reached within two iterations. The third excited state required one additional iteration, although it should be noted that by the second iteration the residual norm, r , of this state is close to the convergence threshold of 10^{-6} , and the final iteration takes the residual norm 2 orders of magnitude below this threshold. This result hints that the relaxation method may offer relatively more balanced rates of convergence across different states than the block DL method. This is further illustrated in Figure 2, in which the convergence of the ten-state XSIL relaxation and block DL calculations are shown. Although the rate of convergence for the higher-lying states in the XSIL relaxation calculation is not as uniform as for the first three excited states, convergence of all

Figure 3. Convergence of the first three excited states of pyrrole calculated at the ADC(2)/cc-pVDZ level of theory: (a) XSIL relaxation and (b) block DL. The total number of Hamiltonian matrix–vector multiplications required for the XSIL and block DL calculations were 200 and 408, respectively.

Figure 4. Convergence of the first three excited states of benzene calculated at the ADC(2)/cc-pVDZ level of theory: (a) XSIL relaxation and (b) block DL. The total number of Hamiltonian matrix–vector multiplications required for the XSIL and block DL calculations were 160 and 258, respectively.

states still occurs within three iterations, giving a ratio of the maximum-to-minimum number of iterations of 1.5. In contrast, the ratio of the maximum-to-minimum number of iterations in the corresponding block DL calculation is 2.3.

Test 2: Pyrrole. For pyrrole, the dimension of the ADC(2)/cc-pVDZ Hamiltonian matrix is 569777. The rate of convergence of the three-state XSIL relaxation and block DL calculations are shown Figure 3(a) and (b), respectively. Again, the XSIL relaxation method is found to exhibit good convergence properties, with the convergence of all three states being achieved within a maximum of four iterations. In terms of the number of Hamiltonian matrix–vector multiplications required, the XSIL relaxation method again performs well in comparison to the block DL method, requiring 200 versus 408 multiplications, respectively, to achieve convergence of all states.

Test 3: Benzene. For benzene, the dimension of the ADC(2)/cc-pVDZ Hamiltonian matrix is 1104840. The rate of convergence of the three-state XSIL relaxation and block DL calculations are shown Figures 4(a) and (b), respectively. Similar to the other test cases considered, rapid convergence of the first

three excited states is observed for the XSIL relaxation method, with convergence of all states being achieved within a maximum of three iterations. Again, the number of Hamiltonian matrix–vector multiplications required by the XSIL relaxation calculation compares favorably to that required by the corresponding block DL calculation: 160 versus 258, respectively.

Comparison to the Direct Integration of the Imaginary Time Derivative of the Wavepacket.

We next consider the performance of the XSIL algorithm relative to a wavepacket propagation method that relies on the numerical integration of the imaginary time derivative of the wavepacket, $|\dot{\psi}\rangle$. In particular, we contrast the performances of the XSIL and BS algorithms. All BS relaxation calculations were performed using time step adaptation, with the time step, $\Delta\tau$, and integration order being adjusted to keep the estimated error below threshold. A maximum integration order of 16 was used. In all calculations the use of a maximum time step of $\Delta\tau = 0.2$ au and an error tolerance of 10^{-6} was found to yield optimal rates of convergence. Accordingly, all reported values were obtained from relaxation calculations employing these parameter values.

All the relaxation calculations were repeated using the BS algorithm to perform the imaginary time propagation. The number of Hamiltonian matrix–vector multiplications required to converge all states in each calculation are given in Table 1. In

Table 1. Number of Hamiltonian Matrix–Vector Multiplications Required in Each of Block Davidson–Liu, SIL, XSIL, and Bulirsch–Stoer Calculations Performed for Convergence of All States

Calculation	block Davidson–Liu	SIL	XSIL	Bulirsch–Stoer
Allene, 3-state	378	180	140	9304
Allene, 10-state	870	920	560	–
Pyrrole, 3-state	408	280	200	25878
Benzene, 3-state	258	180	160	10454

the 10-state allene calculation, not all states could be converged, and so these results are excluded. For all other calculations, the numbers of Hamiltonian matrix–vector multiplications required in the BS relaxation calculations are extremely high compared to those required by the XSIL calculations. For the three-state allene, pyrrole, and benzene calculations, the BS relaxation calculations were found to require 66, 129, and 65 times as many Hamiltonian matrix–vector multiplications as the XSIL calculations, respectively. On the basis of these results, we conclude that relaxation calculations that employ the direct integration of imaginary time derivative of the wavepacket are unlikely to prove competitive with traditional iterative subspace diagonalization methods.

SIL versus XSIL Algorithms. Finally, we consider the relative performances of the SIL and XSIL algorithms. To do so, the relaxation calculations for all molecules were also performed using the standard SIL algorithm. The same fixed time step and number of Lanczos states were used in the SIL calculations as in the XSIL calculations. Thus, any increase in the number of iterations, or equivalently the number of Hamiltonian matrix–vector multiplications, required for convergence is diagnostic of a decreased accuracy of the SIL algorithm relative to the XSIL algorithm. The numbers of matrix–vector multiplications required for each calculation are shown in Table 1, together with the numbers required by the block DL calculations. On average, the XSIL calculations were found to afford a 25% saving in the number of Hamiltonian matrix–vector multiplications relative to the SIL calculations. The actual number was, however, found to range significantly, from 39% for the ten-state allene calculation to only 11% for the three-state benzene calculation. However, considering that the XSIL algorithm has essentially the same computational cost as the SIL algorithm, it is still advantageous to use the former even if the associated savings may be expected to vary with the calculation under consideration.

CONCLUSIONS

Iterative subspace diagonalization schemes are central to the methods of solution employed in the majority of quantum chemistry approaches in which a handful of low-lying eigenpairs of the electronic Hamiltonian are required. Variants of the Lanczos and Davidson methods have been the mainstay of such calculations for many years. These methods constitute explicitly time-independent solutions to the time-independent Schrödinger equation. As has been acknowledged for many years, however, the solution of the time-independent Schrödinger equation may also be achieved using time-dependent wavepacket propagation methodologies, namely, the method of relaxation or

imaginary time propagation. Although the relaxation method has been used extensively and successfully in the field of quantum dynamics, its potential use in quantum chemistry calculations has not yet been fully evaluated.

Using an extended SIL (XSIL) algorithm, relaxation calculations were performed at the ADC(2) level for a number of small-to-medium-sized molecules. In all cases, rapid convergence of the XSIL relaxation calculations was observed. To provide comparison to conventional iterative subspace diagonalization methods, all calculations were also performed using the block DL method. In both methods, the rate-limiting steps are the large number of Hamiltonian matrix–vector multiplications that have to be performed. In this respect, the XSIL relaxation method was found to perform well, with an average of half the number of Hamiltonian matrix–vector multiplications being required relative to the block DL calculations. While we acknowledge that the performance of the block DL method will be dependent on the specific details of the implementation and that a multitude of other eigensolvers exist, these results do suggest that the XSIL relaxation method is competitive with traditional iterative subspace diagonalization methods.

Additionally, all relaxation calculations were also performed using the BS algorithm to perform the wavepacket propagations. In all cases, the numbers of rate-limiting Hamiltonian matrix–vector multiplications required were between 1 and 2 orders of magnitude higher than for the XSIL calculations. These results can be taken to be broadly representative of relaxation calculations performed using a wavepacket propagation algorithm based around the direct integration of the imaginary time derivative of the wavepacket. We thus conclude that such methods are to be avoided if a computationally competitive relaxation algorithm is to be constructed.

The results presented here suggest that the relaxation method offers a computationally competitive alternative to traditional iterative subspace diagonalization methods, but only if an efficient wavepacket propagation algorithm is employed. As such, we believe that an impetus for further investigations into the use of the relaxation methodology in quantum chemistry problems is provided.

APPENDIX

Calculation of XSIL Representation of Imaginary Time Evolution Operator

At the m th time step, the basis of N Lanczos states $\mathcal{L}^{(N;m)}$ is generated using the three term Lanczos recursion relation

$$\beta_{i+1}^{(m)}|\Lambda_{i+1}^{(m)}\rangle = \hat{H}|\Lambda_i^{(m)}\rangle - \alpha_i^{(m)}|\Lambda_i^{(m)}\rangle - \beta_{i-1}^{(m)}|\Lambda_{i-1}^{(m)}\rangle \quad (16)$$

where $\alpha_i^{(m)} = \langle \Lambda_i^{(m)} | \hat{H} | \Lambda_i^{(m)} \rangle$ and $\beta_i^{(m)} = \langle \Lambda_{i-1}^{(m)} | \hat{H} | \Lambda_i^{(m)} \rangle$. Next, for a given number of previous time steps, p , the overlap matrix $S_{\mathcal{L}_p^{(N;m)}}$ and Hamiltonian matrix $H_{\mathcal{L}_p^{(N;m)}}$ are constructed:

$$S_{\mathcal{L}_p^{(N;m)}, ni, n'j} = \langle \Lambda_i^{(n)} | \Lambda_j^{(n')} \rangle, \quad n, n' = m - p, \dots, m \\ i, j = 0, \dots, N, \quad (17)$$

$$H_{\mathcal{L}_p^{(N;m)}, ni, n'j} = \langle \Lambda_i^{(n)} | \hat{H} | \Lambda_j^{(n')} \rangle, \\ = \alpha_j^{(n')} \langle \Lambda_i^{(n)} | \Lambda_j^{(n')} \rangle + \beta_{j-1}^{(n')} \langle \Lambda_i^{(n)} | \Lambda_{j-1}^{(n')} \rangle \\ + \beta_{j+1}^{(n')} \langle \Lambda_i^{(n)} | \Lambda_{j+1}^{(n')} \rangle \quad (18)$$


```

1: procedure XSIL( $l, \Delta\tau, N, p, \{\psi_s : s = 1, \dots, l\}$ )
2:   Loop over states:
3:   for  $s = 1, \dots, l$  do
4:     Orthogonalise the guess wavefunction against all previously converged states:
5:      $\psi_s := \psi_s - \sum_{t=1}^{s-1} \psi_t \psi_t^\dagger \psi_s$ 
6:      $\psi_s := \psi_s / \|\psi_s\|$ 
7:     Loop over timesteps:
8:     for  $m = 1, \dots$  do
9:       Compute the Lanczos vectors for the current timestep:
10:       $\Lambda_0^{(m)} := \psi_s$ 
11:      for  $i = 1, \dots, N$  do
12:        if  $i = 1$  then
13:           $q := H \Lambda_{i-1}^{(m)}$ 
14:        else
15:           $q := H \Lambda_{i-1}^{(m)} - \beta_{i-2}^{(m)} \Lambda_{i-2}^{(m)}$ 
16:        end if
17:         $\alpha_{i-1}^{(m)} := q^\dagger \Lambda_{i-1}^{(m)}$ 
18:         $q := q - \alpha_{i-1}^{(m)} \Lambda_{i-1}^{(m)}$ 
19:         $\beta_i^{(m)} := \|q\|$ 
20:         $\Lambda_i^{(m)} := q / \beta_i^{(m)}$ 
21:      end for
22:      Compute the overlap matrix elements:
23:      for  $n = m - p, \dots, m$  do
24:        for  $i, j = 1, \dots, N$  do
25:           $S_{ni,mj} := \Lambda_i^{(n)\dagger} \Lambda_j^{(m)}$ 
26:        end for
27:      end for
28:      Compute the Hamiltonian matrix elements:
29:      for  $n = m - p, \dots, m$  do
30:        for  $i, j = 1, \dots, N$  do
31:           $H_{ni,mj} := \alpha_j^{(m)} S_{ni,mj} + \beta_{j-1}^{(m)} S_{ni,mj-1} + \beta_{j+1}^{(m)} S_{ni,mj+1}$ 
32:        end for
33:      end for
34:      Compute the eigenpairs  $\{\lambda_i, \mathbf{Y}_i : i = 1, \dots, (p+1)(N+1)\}$  of  $\mathbf{S}$ 
35:      Compute the truncated eigenvector matrix  $\bar{\mathbf{Y}} := [\mathbf{Y}_{i_1}, \dots, \mathbf{Y}_{i_M}]$  using the  $M$  eigen-
36:      vectors  $\mathbf{Y}_i$  for which  $\lambda_i \geq \delta$ 
37:      Compute the truncated eigenvalue matrix  $\bar{\boldsymbol{\Lambda}} := \text{diag}(\lambda_{i_1}, \dots, \lambda_{i_M})$  using the the  $M$ 
38:      eigenvalues  $\lambda_i \geq \delta$ 
39:      Compute the transformation matrix  $\mathbf{T} := \bar{\boldsymbol{\Lambda}}^{-\frac{1}{2}} \bar{\mathbf{Y}}$ 
40:      Compute the matrix of linearly independent basis vectors
41:       $\Phi = [\Phi_1, \dots, \Phi_M] := \mathbf{T}[\Lambda_0^{(m-p)}, \dots, \Lambda_N^{(m-p)}, \Lambda_0^{(m-p+1)}, \dots, \Lambda_N^{(m)}]^\dagger$ 
42:      Compute the matrix  $\mathcal{H} := \mathbf{T} \mathbf{H} \mathbf{T}^\dagger$ 
43:      Compute the eigenpairs  $\{\mu_i, \mathbf{Z}_i : i = 1, \dots, M\}$  of  $\mathcal{H}$ 
44:      Compute the matrix of vectors  $\bar{\Phi} = [\bar{\Phi}_1, \dots, \bar{\Phi}_M] := \mathbf{Z}^\dagger \Phi$ 
45:      Propagate the wavefunction forwards one timestep:
46:       $\psi_s := \sum_{i=1}^M \exp(-\mu_i \Delta\tau) \bar{\Phi}_i \bar{\Phi}_i^\dagger \psi_s$ 
47:      Orthogonalise the wavefunction against all previously converged states:
48:       $\psi_s := \psi_s - \sum_{t=1}^{s-1} \psi_t \psi_t^\dagger \psi_s$ 
49:       $\psi_s := \psi_s / \|\psi_s\|$ 
50:      Compute the residual:
51:       $r := \|\mathbf{H} \psi_s - \psi_s^\dagger \mathbf{H} \psi_s\|$ 
52:      Terminate the propagation of  $\psi_s$  if the the residual is below threshold:
53:      if  $r < \delta$  then
54:        exit
55:      end if
56:    end for
57:  end for
58: end procedure

```

Algorithm 1: XSIL relaxation algorithm to calculate the lowest-lying eigenpairs of the Hamiltonian matrix H . The input arguments are the desired number of eigenpairs, l , the time step, $\Delta\tau$, the Krylov subspace dimension, N , the maximum number, p , of previous time steps to include in the construction of the extended Lanczos basis, and a set of orthonormal guess vectors, $\{\psi_s : s = 1, \dots, l\}$.

Then, the overlap matrix $\mathbf{S}_{\mathcal{L}_p^{(N;m)}}$ is diagonalized to yield the eigenvectors $\mathbf{Y}_{\mathcal{L}_p^{(N;m)}}^i$ and eigenvalues $\lambda_{\mathcal{L}_p^{(N;m)}}^i$:

$$\mathbf{S}_{\mathcal{L}_p^{(N;m)}} = \mathbf{Y}_{\mathcal{L}_p^{(N;m)}} \boldsymbol{\Lambda}_{\mathcal{L}_p^{(N;m)}} \mathbf{Y}_{\mathcal{L}_p^{(N;m)}}^\dagger \quad (19)$$

The columns of the matrix $\mathbf{Y}_{\mathcal{L}_p^{(N;m)}}$ corresponding to eigenvalues $\lambda_{\mathcal{L}_p^{(N;m)}}^i$ smaller than a predefined threshold δ are discarded, yielding the rectangular matrix $\bar{\mathbf{Y}}_{\mathcal{L}_p^{(N;m)}}$. The same is done for the corresponding rows and columns of $\boldsymbol{\Lambda}_{\mathcal{L}_p^{(N;m)}}$, yielding the truncated square matrix $\bar{\boldsymbol{\Lambda}}_{\mathcal{L}_p^{(N;m)}}$. The transformation matrix

$\bar{\boldsymbol{\Lambda}}_{\mathcal{L}_p^{(N;m)}}^{-1/2} \bar{\mathbf{Y}}_{\mathcal{L}_p^{(N;m)}}^\dagger$ is then used to generate the basis $\mathcal{I}_p^{(M;m)}$ of orthonormal, linearly independent basis functions $\{|\Phi_k^{(m)}\rangle : k = 0, 1, \dots, M\}$:

$$|\Phi_k^{(m)}\rangle = \bar{\boldsymbol{\Lambda}}_{\mathcal{L}_p^{(N;m)}}^{-1/2} \bar{\mathbf{Y}}_{\mathcal{L}_p^{(N;m)}}^\dagger (|\Lambda^{(m-p)}\rangle, |\Lambda^{(m-p+1)}\rangle, \dots, |\Lambda^{(m)}\rangle)^T \quad (20)$$

as well as the matrix representation of the electronic Hamiltonian in this basis, $\mathbf{H}_{\mathcal{I}_p^{(M;m)}}$:

$$\mathbf{H}_{\mathcal{I}_p^{(M;m)}} = \bar{\boldsymbol{\Lambda}}_{\mathcal{L}_p^{(N;m)}}^{-1/2} \bar{\mathbf{Y}}_{\mathcal{L}_p^{(N;m)}}^\dagger \mathbf{H}_{\mathcal{L}_p^{(N;m)}} \bar{\mathbf{Y}}_{\mathcal{L}_p^{(N;m)}} \bar{\boldsymbol{\Lambda}}_{\mathcal{L}_p^{(N;m)}}^{-1/2} \quad (21)$$


```

1: procedure BLOCK DAVIDSON-LIU USING OLSEN'S PRECONDITIONER( $m, M, \mathbf{V}^{(1)}$ )
2:   for  $k = 1, \dots$  do
3:     Compute the matrix  $\mathbf{W}^{(k)} := \mathbf{H}\mathbf{V}^{(k)}$ 
4:     Compute the Rayleigh matrix  $\mathbf{H}^{(k)} := \mathbf{V}^{(k)T}\mathbf{W}^{(k)}$ 
5:     Compute the  $m$  smallest eigenpairs  $\{\lambda_i^{(k)}, \mathbf{y}_i^{(k)} : i = 1, \dots, m\}$  of  $\mathbf{H}^{(k)}$ 
6:     Compute the Ritz vectors  $\mathbf{x}_i^{(k)} := \mathbf{V}^{(k)}\mathbf{y}_i^{(k)}$  for  $i = 1, \dots, m$ 
7:     Compute the residuals  $\mathbf{r}_i^{(k)} := \lambda_i^{(k)}\mathbf{x}_i^{(k)} - \mathbf{W}^{(k)}\mathbf{y}_i^{(k)}$  for  $i = 1, \dots, m$ 
8:     if  $\|\mathbf{r}_i^{(k)}\| < \epsilon$  for  $\forall i \in \{1, \dots, m\}$  then
9:       exit
10:    else
11:      Compute the preconditioner matrices  $\mathbf{C}_i^{(k)} := (\text{diag}(\mathbf{H}) - \lambda_i^{(k)}\mathbf{1})^{-1}$  for  $i = 1, \dots, m$ 
12:      Compute  $\alpha_i^{(k)} := \frac{\mathbf{x}_i^{(k)T}\mathbf{C}_i^{(k)}\mathbf{r}_i^{(k)}}{\mathbf{x}_i^{(k)T}\mathbf{C}_i^{(k)}\mathbf{x}_i^{(k)}}$ 
13:      Compute new vectors  $\mathbf{t}_i^{(k)} := \alpha_i^{(k)}\mathbf{C}_i^{(k)}\mathbf{x}_i^{(k)} - \mathbf{C}_i^{(k)}\mathbf{r}_i^{(k)}$  for  $i = 1, \dots, m$ 
14:      if  $\dim(\mathbf{V}^{(k)}) \leq M - m$  then
15:         $\mathbf{V}^{(k+1)} := \text{MGS}(\mathbf{V}^{(k)}, \mathbf{t}_1^{(k)}, \dots, \mathbf{t}_m^{(k)})$ 
16:      else
17:         $\mathbf{V}^{(k+1)} := \text{MGS}(\mathbf{x}_1^{(k)}, \dots, \mathbf{x}_m^{(k)}, \mathbf{t}_1^{(k)}, \dots, \mathbf{t}_m^{(k)})$ 
18:      end if
19:    end if
20:  end for
21: end procedure

```

Algorithm 2: Block Davidson–Liu algorithm using Olsen’s preconditioner for the calculation of the lowest-lying eigenpairs of the Hamiltonian matrix $\mathbf{H}$. The input arguments are the blocksize, m , the maximum subspace dimension, M , and an initial matrix of m orthonormal guess vectors $\mathbf{V}^{(1)} := [\nu_1, \dots, \nu_m]$. $\text{MGS}(\cdot)$ denotes the operation of modified Gram–Schmidt orthonormalization.

Finally, diagonalization of $\mathbf{H}_{I_p^{(M;m)}}$,

$$\mathbf{H}_{I_p^{(M;m)}} = \mathbf{Z}_{I_p^{(M;m)}} \boldsymbol{\mu}_{I_p^{(M;m)}} \mathbf{Z}_{I_p^{(M;m)}}^\dagger \quad (22)$$

yields the basis $\tilde{\mathbf{I}}_p^{(M;m)} = \{|\tilde{\Phi}_k^{(m)}\rangle : k = 0, \dots, M\}$ in which $\hat{U}(\Delta\tau)$ is represented, where

$$|\tilde{\Phi}^{(m)}\rangle = \mathbf{Z}_{I_p^{(M;m)}}^\dagger |\Phi^{(m)}\rangle \quad (23)$$

That is, the propagated wavefunction $|\psi_{m+1}\rangle$ is given by

$$\begin{aligned} |\psi_{m+1}\rangle &\approx \hat{U}_{\tilde{\mathbf{I}}_p^{(M;m)}}(\Delta\tau) |\psi_m\rangle \\ &= \sum_{i=0}^M |\tilde{\Phi}_i^{(m)}\rangle \exp(-\mu_{I_p^{(M;m)}}^i \Delta\tau) \langle \tilde{\Phi}_i^{(m)} | \psi_m \rangle \end{aligned} \quad (24)$$

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