Any order imaginary time propagation method for solving the Schrödinger equation

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The eigenvalue-function pair of the 3D Schrödinger equation can be efficiently computed by use of high order, imaginary time propagators. Due to the diffusion character of the kinetic energy operator in imaginary time, algorithms developed so far are at most fourth-order. In this work, we show that for a grid based algorithm, imaginary time propagation of any even order can be devised on the basis of multi-product splitting. The effectiveness of these algorithms, up to the 12th order, is demonstrated by computing all 120 eigenstates of a model C_{60} molecule to very high precisions. The algorithms are particularly useful when implemented on parallel computer architectures.

I. INTRODUCTION

With the advance of the density functional method of solving diverse solid state physics and quantum chemistry problems, it is of growing importance to solve the Schrödinger equation on a large 3-D mesh with greater than $N = 10^6$ grid points. For such a large mesh, conventional matrix methods are impractical, since even the minimal matrix-vector multiplication would be prohibitively slow. Among $O(N)$ methods, we have previously shown that fourth-order imaginary time propagation provides an effective means of solving the Kohn-Sham and related equations. The use of all forward time-step fourth-order algorithms in solving the imaginary time Schrödinger equation has since been adapted by many research groups.

The lowest $n$ states of the one-body Schrödinger equation

$$H \psi_j(r) = E_j \psi_j(r)$$

with Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) = T + V$$

can be obtained in principle by applying the evolution operator ($\epsilon = -\Delta t$)

$$T(\epsilon) \equiv e^{\epsilon(T+V)}$$

repeatedly on the $\ell$-th time step approximation $\{\psi_j^{(\ell)}(r)\}$ to the set of states $\{\psi_j(r), \ 1 \leq j \leq n\}$,

$$\phi_j^{(\ell+1)} \equiv T(\epsilon)\psi_j^{(\ell+1)}$$

and orthogonalize the states after every step,

$$\psi_j^{(\ell+1)} \equiv \sum_i c_{ji} \phi_i^{(\ell+1)}, \quad (\psi_j^{(\ell+1)}|\psi_i^{(\ell+1)}) = \delta_{ij}. \quad (1.5)$$

The method is made practical by approximating the exact evolution operator by a general product form,

$$T(\epsilon) = \prod_{i=1}^M e^{a_i eT} e^{b_i eV}.$$

The simplest second order decomposition, or the split operator method, is

$$T_2(\epsilon) \equiv e^{\frac{\epsilon}{2}T} e^{\frac{\epsilon}{2}V} = T(\epsilon) + O(\epsilon^3). \quad (1.7)$$

When this operator acts on a state $\psi_j(r)$, the two operators $e^{\frac{\epsilon}{2}V}$ correspond to point-by-point multiplications and $e^{\epsilon T}$ can be evaluated by one complete (forward and backward) Fast Fourier Transform (FFT). Both are $O(N)$ processes. For $T_2(\epsilon), |\epsilon|$ has to be small to maintain good accuracy and many iterations are therefore needed to project out the lowest $n$ states. To achieve faster convergence, one could in principle iterate higher order algorithms at larger time steps. Unfortunately, Sheng and Suzuki have proved that, beyond second order, no factorization of the form
can have all positive coefficients \( \{a_i, b_j\} \). This forward time step requirement is essential for imaginary time propagation because if any \( a_i \) were negative, then the operator \( e^{-a_i \Delta t T} \) would be unbounded, resulting in unstable algorithms corresponding to unphysical backward diffusion in time. To derive forward, all positive time step fourth-order algorithms, Suzuki \(^{10}\) and Chin \(^{11}\) have shown that a correction to the potential of the form \([V, [T, V]] = (\hbar^2/m)|\nabla V|^2\), as first used by Takahashi-Imada \(^{12}\) and later suggested by Suzuki \(^{13}\), must be included in the decomposition process. We have shown \(^{14}\) previously that these forward fourth-order algorithms can achieve similar accuracy at an order-of-magnitude larger step sizes than the second-order splitting \(^{17}\). More recently Bandrauk, Delghanian and Lu \(^{18}\) have suggested that, instead of including such a gradient term, one can use complex coefficients \( \{c_i, b_j\} \) having positive real parts. For real time propagation, their complex time-step algorithms are not left-right symmetric and therefore are not time-reversible. For imaginary time propagation, their fourth-order algorithm \( S_4' \) requires free complete complex-to-complex FFTs, whereas our forward algorithm \( 4A \) only needs two real-to-complex/complex-to-real FFTs \(^{19}\).

### II. Multi-Product Expansion

If the decomposition of \( T(\epsilon) \) is restricted to a single product as in \(^{(1.0)}\), then there is no practical means of implementing a sixth or higher order forward algorithm \(^{15}\). However, if this restriction is relaxed to a sum of products,

\[
e^{(T+V)} = \sum_k c_k \prod_i e^{a_{k,i} \epsilon T} b_{k,i} \epsilon V \tag{2.1}
\]

then the requirement that \( \{a_{k,i}, b_{k,i}\} \) be positive means that each product can only be second order. Since \( T_2(\epsilon) \) is second order with positive coefficients, its powers \( T_2^k(\epsilon/k) \) can form a basis for such a multi-product expansion. Recent work \(^{16}\) shows that such an expansion is indeed possible and takes the form

\[
e^{(T+V)} = \sum_{k=1}^{n} c_k T_2^k \left( \frac{\epsilon}{k} \right) + O(\epsilon^{2n+1}) \tag{2.2}
\]

where the coefficients \( c_k \) are given in closed form for any \( n \):

\[
c_k = \prod_{j=1(\neq i)}^{n} \frac{k_i^2}{k_i^2 - k_j^2} \tag{2.3}
\]

with \( \{k_1, k_2, \ldots k_n\} = \{1, 2, \ldots n\} \). Since the symmetric \( T_2(\epsilon) \) has only odd powers in \( \epsilon \),

\[
T_2(\epsilon) = \exp[\epsilon(T + V) + \epsilon^3 E_3 + \epsilon^5 E_5 + \cdots]
\]

where \( E_i \) are higher order commutators of \( T \) and \( V \), the expansion \(^{(2.2)}\) is just a systematic extrapolation which successively removes each odd order error. Explicitly, for \( n = 2 \) to \( 5 \), we have the following order 4 to order 10 multi-product expansion:

\[
T_4(\epsilon) = -\frac{1}{3} T_2(\epsilon) + \frac{4}{3} T_2^3 \left( \frac{\epsilon}{2} \right) \tag{2.5}
\]

\[
T_6(\epsilon) = \frac{1}{24} T_2(\epsilon) - \frac{16}{15} T_2^2 \left( \frac{\epsilon}{2} \right) + \frac{81}{40} T_2^3 \left( \frac{\epsilon}{3} \right) \tag{2.6}
\]

\[
T_8(\epsilon) = -\frac{1}{360} T_2(\epsilon) + \frac{16}{45} T_2^2 \left( \frac{\epsilon}{2} \right) - \frac{729}{280} T_2^3 \left( \frac{\epsilon}{3} \right) + \frac{1024}{315} T_2^4 \left( \frac{\epsilon}{4} \right) \tag{2.7}
\]

\[
T_{10}(\epsilon) = \frac{1}{8640} T_2(\epsilon) - \frac{64}{945} T_2^2 \left( \frac{\epsilon}{2} \right) + \frac{6561}{4480} T_2^3 \left( \frac{\epsilon}{3} \right) - \frac{16384}{2835} T_2^4 \left( \frac{\epsilon}{4} \right) + \frac{390625}{72576} T_2^5 \left( \frac{\epsilon}{5} \right). \tag{2.8}
\]

Since each \( T_2 \) requires one complete FFT, the above series of \( 2n \)-order algorithms only requires \( n(n+1)/2 \) complete FFTs. Thus algorithms of order 4, 6, 8 and 10 only require 3, 6, 10 and 15 complete FFTs. The low order extrapolation
has been used previously\cite{2,5}. Here, we have a systematic expansion to any even order. Note that Romberg-type extrapolation\cite{2} such as
\begin{equation}
T_0(\epsilon) = -\frac{1}{15}T_4(\epsilon) + \frac{16}{15}T_4^2\left(\frac{\epsilon}{2}\right),
\end{equation}
which triples the number of FFTs in going from order 2n to 2n + 2, is not competitive with Eq. \cite{2,2}'s linear increase of only n + 1 additional FFTs.

Since some coefficients \(c_k\) are negative, this requires that the corresponding product, when acting on state \(\psi_j\), be subtracted. This is doable for a grid based discretization of the wave function, which is just a point-by-point subtraction.

**III. QUANTUM WELL MODEL OF C60**

To demonstrate the workings of this new family of algorithms, we apply them to a model potential with nontrivial geometry, that of a 3D C\(_{60}\) molecule. The effective attraction of the carbon ions is modeled by a potential of the form
\begin{equation}
V(\mathbf{r}) = -\sum_i \frac{V_0}{\cosh(|\mathbf{r} - \mathbf{R}_i|/d)}
\end{equation}
where \(\mathbf{R}_i\) are the locations of the carbon atoms in the C\(_{60}\) cage. The strength \(V_0\) was chosen 1 in units of \(\hbar^2/2m\) and the width of the troughs \(d = 0.05\) a.u. This potential accommodates 120 bound states as needed for a C\(_{60}\) calculation. We have also applied the method in 2D to a square grid of 9\times9 quantum dots described by the same potential. The convergence behavior of the algorithms in both cases are practically identical and need not be discussed separately.

While the above potential is not a realistic description of a C\(_{60}\) molecule, it serves to highlight an important and realistic aspect of any such computation: In the 3D case, the lowest 120 eigenvalues consist of two groups of 60 almost degenerate eigenvalues, one centered around an energy of -5.245 \(\hbar^2/2m\) with an average level spacing of 0.0034 \(\hbar^2/2m\), the other one around -2.992 \(\hbar^2/2m\) with an average level spacing of 0.0077 \(\hbar^2/2m\). Degenerate eigenvalues pose a notorious problem for eigenvalue solvers that contain an orthogonalization step. In this implementation of the algorithm, we use the subspace orthogonalization method described in Ref. \cite{3} which is an application of the Petrov-Galerkin method\cite{1}. We again find that the method works well in the present case; the convergence rates for the highest and the lowest states are the same.

Figs. \ref{fig:fig1} and \ref{fig:fig2} show the convergence of various algorithms for both the lowest and the highest state of the model C\(_{60}\) molecule. To generate the figures, we started with a time step of \(\Delta t = 0.5\) and a set of plane wave initial states in an appropriate box. We then reduced the time step by a factor of 0.9 each time after convergence has been reached, so that the power law behavior can be seen cleanly. In a realistic calculation, it suffices to reduce the time step by a factor 0.5. In other words, the 12th order algorithm can reach the \(10^{-10}\) error level in just two iterations. The reduction factor of 0.5 used here is empirical. Recently, Lehtovaara, Toivanen and Eloranta\cite{1} have suggested that the time step size can be optimally adjusted with added efforts.

While the convergence rate of the eigenvalues verified the order of the algorithms, in practice, it is also useful to monitor the variance of all states with respect to the evolution operator,
\begin{equation}
R_j^E = \sum_k |T_n(\epsilon)\psi_j(\mathbf{r}_k) - e^{iE_j}\psi_j(\mathbf{r}_k)|^2
\end{equation}
Only states with \(R_j^E > \gamma\), where \(\gamma\) is a prescribed error bound, need to be propagated and orthogonalized. As soon as all states have converged at a certain time step \(\epsilon\), their variances with respect to the Hamiltonian,
\begin{equation}
R_j^H = \sum_k |H\psi_j(\mathbf{r}_k) - E_j\psi_j(\mathbf{r}_k)|^2,
\end{equation}
are calculated. If \(R_j^H < \gamma\) for all states \(j\), the iterations are terminated, otherwise the time step is reduced and the whole process is repeated, taking the result of the previous iteration as initial values.

**IV. PARALLELIZATION**

The advantage of high-order propagation methods is particularly compelling on parallel computer architectures: The propagation step \cite{1,3} can be parallelized efficiently without having to abandon the advantage of using FFTs by
simply distributing the states $\psi_j$ across different processors. In such an arrangement, however, the parallelization of the orthogonalization step is notoriously difficult. Let $T_{\text{pro}}$ be the propagation time, \textit{i.e.}, the time it takes to carry out step (1.4) for all states, and $T_{\text{ort}}$ the orthogonalization time. Then, the time $T_{\text{tot}}$ for one iteration step on an ideal machine with $N$ processors is

$$T_{\text{tot}}(N) = T_{\text{pro}}/N + T_{\text{ort}},$$

and the speed up ratio for the “propagation only” and the total time step including orthogonalization for the $j^{\text{th}}$ order algorithm is

$$S_{\text{pro/tot}}^{(j)}(N) = \frac{T_{\text{pro/tot}}(1)}{T_{\text{pro/tot}}(N)},$$

assuming the number of states is larger than the number of processors allocated for the task. The actual speed-up ratio will be less than this ideal since we have neglected communication overhead and other hardware/system specific issues.

Fig. 3 shows the speed up ratio for the C$_{60}$ model calculation in the case of the 2$^{\text{nd}}$, 6$^{\text{th}}$, and 12$^{\text{th}}$ order algorithms on a 256 Itanium$^{18}$ processor Altix$^{19}$ machine for up to twelve threads. We show the two speed-up ratios $S_{\text{pro}}^{(j)}(N)$ and $S_{\text{tot}}^{(j)}(N)$. No particular effort was made to parallelize the orthogonalization step. Evidently, the speed-up of the propagation step alone is a reasonably linear function of the number of threads. The performance improves significantly with the order of the algorithm because the increase computational effort for propagation can be distributed while the cost of communication remained the same.

The 12$^{\text{th}}$ order algorithm can reach about 80 percent of the optimal performance. The actual speed-up is limited by the orthogonalization step; while the 12$^{\text{th}}$ order algorithm can still attain a more than five-fold speed-up, it is hardly worth parallelizing the second order algorithm. The specific speed-up factor for higher order algorithms also depends on the number $n$ of needed eigenstates. In general, the time for propagation is essentially proportional to $n$, whereas the time for orthogonalization goes as $n^2$.

Thus, high order algorithms provide two advantages: they have faster convergence at larger time steps and are more adaptive to parallel computing environments. In the single processor mode, we have determined that the 6$^{\text{th}}$ order algorithm performed the best.

V. CONCLUSIONS

The impressive convergence of our high-order algorithms has a computing cost: One propagation step of the 2$n$-th order algorithm is equivalent to $n(n+1)/2$ propagation steps of the second order algorithm. This cost is compensated by two effects: The first is shown in the figures: The much faster convergence as a function of time step implies that fewer iterations are needed to complete the calculation. The second advantage is less obvious; since orthogonalization is carried out \textit{after} the propagation step (2.2), the relatively costly number of orthogonalization steps is dramatically reduced.

The most likely use of the high-order algorithms will be in real-space implementations of density-functional theory. For realistic systems, one must include non-local pseudo-potentials. We have recently$^{22}$ implemented algorithm 4A using pseudo-potentials of the Kleinman-Bylander form$^{22}$. Calculating the double commutator $[V, [T, V]]$ for such non-local potentials is possible, but the computational cost is twice that of propagating just the potential. Moreover, if the electron density in the vicinity of the ion cores deviates from spherical symmetry, then some approximate treatments may degrade the order of the algorithm. Thus, our new algorithms, without needing the double commutator, should be even more effective for realistic density-functional calculations.

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REFERENCES

1. T. Torsti et al., Physica Status Solidi B 243 (2006) 1016.
2. J. Auer, E. Krotscheck and S. A. Chin, J. Chem. Phys. 115 (2001) 6841.
3. M. Aichinger and E. Krotscheck, Computational Material Science 34, (2005) 188.
4. L. Brualla, K. Sakkos, J. Boronat and J. Casulleras, J. Chem. Phys. 121 (2004) 636.
5. L. Lehtovaara, J. Toivanen, and J. Eloranta, J. Comp. Phys. 221, (2007) 148.
6. G. B. Ren and J. M. Rorison, Phys. Rev. B 77 (2008) 245318.
7. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Chem. Phys. 78 (1982), 301.
8. Q. Sheng, IMA J. Numer. Analysis, 9 (1989) 199.
9. M. Suzuki, J. Math. Phys. 32 (1991) 400.
10. M. Suzuki, in Computer Simulation Studies in Condensed Matter Physics, edited by D. P. Landau, K. K. Mon, and H.-B. Shüttler (Springer, Berlin, 1996), Vol. VIII.
11. S. A. Chin, Phys. Lett. A 226 (1997) 344.
12. M. Takahashi and M. Imada, J. Phys. Soc. Jpn., 53 (1984) 3765.
13. M. Suzuki, Phys. Lett. A 201 (1995) 425.
14. A. D. Bandrauk, E. Dehghanian and H. Lu, Chem. Phys. Lett 419 (2006) 346.
15. S. A. Chin, Phys. Rev. E 71 (2005) 016703.
16. S. A. Chin, “Multi-product Splitting and Runge-Kutta-Nyström Integrators”, arXiv:0809.0914.
17. K. E. Schmidt and M. A. Lee, Phys. Rev. E 51 (1995) 5495.
18. Itanium is a registered trademark of Intel Corp.
19. Altix is a registered trademark of Silicon Graphics inc.
20. www.netlib.org/lapack.
21. E. R. Hernández, S. Janecek, M. S. Kaczmarski, and E. Krotscheck”, Phys. Rev. B 75 (2007) 075108.
22. L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48 (1982) 1425.
FIG. 1: (color online) The convergence of the 2nd to 12th order algorithms for the lowest eigenstate of a model “C_60” molecule are as shown by markers defined in the inset. The dashed lines, as a guide to the eye, are the power laws $\Delta t^n$ for $n = 2, 4, \ldots, 12$. Also shown is the convergence curve for algorithm 4A of Ref. 2. Its characteristic deviation from the $\Delta t^4$ power law behavior at small $\Delta t$ is due to discretization errors in evaluating the double commutator $[V, [T, V]]$. 
FIG. 2: Same as Fig. 1 for the 120th eigenstate of the model C_{60} molecule.
FIG. 3: (color online) The total speed-up time factor $S_{\text{tot}}$ (solid lines) and the propagation only (without orthogonalization) time speed-up factor $S_{\text{pro}}$, as a function of parallel threads, for the 2\textsuperscript{nd}, 6\textsuperscript{th}, and 12\textsuperscript{th} order algorithm (filled squares, circles, and triangles, respectively). Also shown is the “ideal” speed-up factor (dotted line).