An order-$N$ electronic structure theory with generalized eigenvalue equations and its application to a ten-million-atom system

T Hoshi$^{1,2}$, S Yamamoto$^3$, T Fujiwara$^4$, T Sogabe$^{2,5}$ and S-L Zhang$^{2,6}$

1 Department of Applied Mathematics and Physics, Tottori University, Tottori 680-8550, Japan
2 Core Research for Evolutional Science and Technology, Japan Science and Technology Agency (CREST-JST), Japan
3 School of Computer Science, Tokyo University of Technology, Katakura-machi, Hachioji, Tokyo 192-0982, Japan
4 Center for Research and Development of Higher Education, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
5 School of Information Science and Technology, Aichi Prefecture University, Nagakute-cho, Aichi 480-1198, Japan
6 Department of Computational Science and Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

E-mail: hoshi@damp.tottori-u.ac.jp

Received 19 November 2011, in final form 10 January 2012
Published 30 March 2012
Online at stacks.iop.org/JPhysCM/24/165502

Abstract
A linear algebraic theory called the ‘multiple Arnoldi method’ is presented and realizes large-scale (order-$N$) electronic structure calculations with generalized eigenvalue equations. A set of linear equations, in the form of $(zS - H)x = b$, are solved simultaneously with multiple Krylov subspaces. The method is implemented in a simulation package ELSES (www.elses.jp) with tight-binding-form Hamiltonians. A finite-temperature molecular dynamics simulation is carried out for metallic and insulating materials. A calculation with $10^7$ atoms was realized by a workstation. The parallel efficiency is shown up to 1024 CPU cores.

1. Introduction

Large-scale electronic structure calculation, with $10^3$ atoms or more, plays a crucial role in nanoscience and is realized by an order-$N$ theory, in which the computational cost is proportional to the system size. References on the order-$N$ electronic structure theory can be found in a recent paper [1]. In this paper, a method, called the ‘multiple Arnoldi method’, is presented for generalized eigenvalue equations, or large-scale electronic structure theory with non-orthogonal (atomic) bases. The method is applicable both to metals and insulators and the molecular dynamics (MD) simulations were carried out for up to ten-million-atom systems with tight-binding-form Hamiltonians. The present method is a theoretical extension of a previous one, the diagonalization method in the Krylov subspace, [2, 3], since the present method will be reduced to the previous one in the case with orthogonal bases.

This paper is organized as follows; the theory is summarized in section 2. In section 3, numerical examples appear and the method is compared with several existing ones with non-orthogonal bases [1]. The summary is given in section 4.

In this paper, the $j$th unit vector is denoted as $e_j \equiv (0, 0, 0, \ldots, 1_j, 0, 0, 0, \ldots, 0_M)^T$. The inner product between the two vectors of $f \equiv (f_1, f_2, \ldots)^T, g \equiv (g_1, g_2, \ldots)^T$ is...
written as $f^Tg = \sum_i f_i g_i$. The unit matrix is denoted as $I$.
The representation with atomic orbitals is considered and the
suffix $i$ for a component of a vector indicates the composite
suffix for the atom and orbital ($s, p_x, p_y, p_z, \ldots$).

2. Theory

A key concept of the present method is the Krylov subspace
that is defined as a linear (Hilbert) space of

$$K_m(A; b) \equiv \text{span}\{b, Ab, A^2b, \ldots, A^{m-1}b\}$$  \hspace{1cm} (1)

with a given square matrix $A$ and a given vector $b$. Krylov subspace
is a common mathematical foundation for iterative
linear algebraic algorithms, such as the conjugate-gradient
(CG) algorithm.

A generalized eigenvalue equation is written as

$$H\Phi_k = \varepsilon_k S\Phi_k.$$  \hspace{1cm} (2)

Here the Hamiltonian and overlap matrices are denoted as $H$
and $S$, respectively. They are sparse real-symmetric $M \times M$
matrices and $S$ is positive definite. The eigenvalues and vectors
are denoted as $\varepsilon_k$ and $\Phi_k$, respectively.

A basic equation for large-scale electronic structure
theory is the set of linear equations

$$\varepsilon_j S - H x_j = e_j$$ \hspace{1cm} (3)

among the unit vectors $\{e_j = 1, e_2, e_3, \ldots, e_M\}$. A matrix
element of the Green’s function, $G \equiv (\varepsilon S - H)^{-1} \notag$, is given
as $G_{ij} = e_j^T x_i$.

In the present method, the solution of equation (3) is given
within the multiple Krylov subspace of

$$\mathcal{L}_\nu^K \equiv K_p(H; e_j) \oplus K_q(H; S^{-1}e_j),$$ \hspace{1cm} (4)

where $p, q$ are positive integers and $\nu \equiv p + q$. The dimension
of the subspace, $\nu$, is chosen to be much smaller than that of
the original matrices. The case with $q = 0$ is the generalized
Arnoldi method in [1].

The two initial vectors of $e_j$ and $s_j \equiv S^{-1}e_j$, in equation (4)
satisfy a ‘duality’ relation of $e_j^T S e_j = 1$. A formulation with
the dual vectors reduces a generalized eigenvalue equation
into a standard one [4]. An efficient numerical treatment of
$S^{-1}e_j$ is required for a large-scale calculation, since the explicit
matrix-inversion procedure of $S$ is costly, as the matrix-diagonalization
procedure. In the present method, the vector of $s_j := S^{-1}e_j$ is calculated by an inner CG loop, in
which the linear equation of $S x_j = e_j$ is solved iteratively
with the standard CG method. This inner loop converges fast, typically with $\nu_{CG} = 10$–30 iterations, since the overlap
matrix is sparse and nearly equal to the unit matrix ($S \approx I$) [1].

The whole procedures are carried out in the following two
stages. First, the bases of the subspaces

$$\mathcal{L}_\nu^K \equiv \text{span}\{u^{(1)}_1, u^{(1)}_2, \ldots, u^{(1)}_\nu\},$$ \hspace{1cm} (5)

are generated so as to satisfy the ‘$S$-orthogonality’

$$(u^{(1)}_m)^T S u^{(1)}_n = \delta_{mn}.$$ \hspace{1cm} (6)

With a given initial vector of $l_1 := e_j$, the

nth basis ($u_n$), for $n \geq 1$ and $n \neq p + 1$ is generated in the
following three procedures;

$$u_n := \frac{I_n}{\sqrt{\langle l_n | S l_n \rangle}}$$ \hspace{1cm} (6)

$$k_n := H u_n$$ \hspace{1cm} (7)

$$l_{n+1} := k_n - \sum_{m=1}^{n} u_m q_{mn}$$ \hspace{1cm} (8)

with $q_{mn} \equiv u^*_m S l_n$. The modified Gram–Schmidt procedure
appears in equation (8), so as to satisfy the ‘$S$-orthogonality’
of $u^*_m S l_{n+1} = 0$ for $m = 1, 2, \ldots, n$. For $n = p + 1$, equation (7) is replaced by

$$k_{p+1} := S^{-1} e_j.$$ \hspace{1cm} (9)

The $S^{-1}$-vector multiplication in equation (9) is realized by the
inner CG loop explained above.

Second, subspace eigenvectors $v^{(0)}_\nu \in \mathcal{L}^{(0)}_\nu$

$$v^{(0)}_\nu = \sum_{n} v^{(0)}_{\nu n} C^{(0)}_{nu}$$ \hspace{1cm} (10)

and subspace eigenvalues $\varepsilon^{(0)}_\nu$ are introduced so that the residual vector $r^{(0)}_\nu \equiv (H - \varepsilon^{(0)}_\nu S) v^{(0)}_\nu$ is orthogonal to the subspace ($r^{(0)}_\nu \perp \mathcal{L}^{(0)}_\nu$). The above principle is known as the
Galerkin principle in numerical analysis [5]. Consequently, a standard eigenvalue equation appears with a reduced ($\nu \times \nu$
Hamiltonian matrix of $(H^{(1)})_{\nu \nu} \equiv u^{(0)}_\nu S u^{(0)}_\nu$. The derived
eigenvalue equation is solved, so as to determine $\varepsilon^{(0)}_\nu$ and $C^{(0)}_{nu}$.

The solution vector is determined as

$$x_j(z) := G^{(0)}(z) e_j$$ \hspace{1cm} (11)

where the matrix $G^{(0)}$, called the ‘subspace Green’s function’,

$$G^{(0)} \equiv \sum_{\alpha} v^{(0)}_{\nu \alpha} v^{(0)T}_{\nu \alpha}$$ \hspace{1cm} (12)

is defined as.

The above calculation will be exact, when the subspace $\mathcal{L}^{(0)}_\nu$
comes to the complete space ($\nu \rightarrow \infty$).

The density matrix and the energy density matrix

$$\rho_{ij} := \sum_{\alpha} f(\varepsilon^{(0)}_\alpha) e^*_\alpha v^{(0)T}_{\nu \alpha} e_j$$ \hspace{1cm} (13)

$$\pi_{ij} := \sum_{\alpha} f(\varepsilon^{(0)}_\alpha) e^*_\alpha v^{(0)T}_{\nu \alpha} v^{(0)}_{\nu \alpha} e_j$$ \hspace{1cm} (14)

are calculated, where the occupation number $f(\varepsilon)$ is the
Fermi–Dirac function with the given values of the temperature
(level-broadening) parameter and the chemical potential $\mu$.
The chemical potential is determined by the bisec tion method,
so that the total electron number is the correct one.

The electronic structure energy ($E_{\text{elec}}$) and its derivative
with respect to the $K$th atom position ($F_K$) are required for a
MD simulation. They are decomposed into the partial sums as

$$E_{\text{elec}} \equiv \text{Tr}[\rho H] = \sum_{j} E^{(0)}_{\text{elec}}$$ \hspace{1cm} (15)
where the partial sums are defined by

\[ E_{\text{elec}}^{(i)} = \sum_i \rho_{ij} H_{ji} \]

The components of \( \rho_{ij} \) or \( \pi_{ij} \) are required only for the selected \((i, j)\) pairs that satisfy \( H_{ij} \neq 0 \) or \( S_{ij} \neq 0 \), respectively. The value of \( F_{K}^{(j)} \) in equation (18) is contributed only within a local region where the atom positions of the \( i \)th and \( j \)th bases are equal to or near the \( k \)th atom position \( \mathbf{R}_k \), because the value of \( (\partial H_{ji}/\partial \mathbf{R}_k) \) or \( (\partial S_{ji}/\partial \mathbf{R}_k) \) is non-zero only for the local region.

The calculation work flow is summarized as

\[ \{ \mathbf{u}_n^{(j)} \} \Rightarrow \{ \mathbf{v}_n^{(j)}, \mathbf{e}_n^{(j)} \} \Rightarrow (\text{bisection}) \Rightarrow \mu \]

\[ \Rightarrow \{ f(\mathbf{v}_n^{(j)}) \} \Rightarrow \{ \rho_{ij}, \pi_{ij} \} \Rightarrow \{ E_{\text{elec}}^{(i)}, F_{K}^{(j)} \} \]

where the procedures in a curly parenthesis \{ \cdots \} are carried out independently among the running index \( j \), as a parallel computation. In the bisection procedure, the total electron number with a trial value of the chemical potential is summed up among the bases and the summation is made parallel with the basis index \( j \).

Several calculations with the charge-self-consistent (CSC) formulation [6] were also carried out. At each MD step, an iterative loop is required for the self-consistency of the change distribution. Since the overlap matrix is unchanged within the iterative loop, the inner CG loop for \( S^{-1} \mathbf{e}_j \) is required only once at one MD step and gives a tiny fraction of the total computational cost.

3. Examples and discussion

Several numerical examples are calculated by the multiple Arnoldi method. We choose \( p = q = \sqrt{v}/2 \) \((v: \text{even})\) in the following calculations, except where indicated, so as to investigate the examples systematically among different values of the subspace dimension \( v \), with a significant contribution by the second term in equation (4).

Figure 1(a) shows the electronic structure energy \( E_{\text{elec}} \) for bulk gold with 864 atom. The tight-binding-form Hamiltonian in [7] was used and contains \( s, p \) and \( d \) orbitals. The electronic structure energy was calculated with the subspace dimensions of \( v = 2, 4, 10, 20, 30, 50, 100 \). The calculated energy agrees for \( v = 30, 50, 100 \) within deviations less than 0.01 eV/atom. In general, the use of the multiple Krylov subspaces \((p, q \geq 1)\) reproduces several properties. (i) In the fully filled limit \((f(\epsilon) \rightarrow 1)\), a physical quantity is contributed by all the eigenstates and is expressed by

\[ \langle X \rangle \equiv \sum_k \Phi_k^\dagger X \Phi_k = \text{Tr}[S^{-1}X]. \]

(20)

3. Examples and discussion

The proof is based on a ‘projection’ theorem: in the fully filled limit, the density matrix of equation (13) is reduced to \( \Omega^{(j)} S \mathbf{r}^{(j)} = \mathbf{r}^{(j)} \). If a vector \( \mathbf{r}^{(j)} \) is included in the subspace \( \mathbf{r}^{(j)} \subset \mathbf{L}^{(j)} \), the ‘projection’ theorem of \( \Omega^{(j)} S \mathbf{r}^{(j)} = \mathbf{r}^{(j)} \) holds.
polymer. The calculation of DOS requires a finer calculation condition \((\nu = 300 \text{ and } N_{RP} = 1000)\) than that for the density matrix, since the DOS profile is an energy resolved quantity. The result by the exact diagonalization method is also shown and one finds that the present method reproduces the overall spectrum precisely. Moreover, when the eigenvalues are assumed to be non-degenerated, the calculated Green’s function can be decomposed into the contributions of individual eigenstates and the individual eigenvalues can be estimated\(^9\). For example, the highest-occupied (HO) and lowest-unoccupied (LU) levels were estimated and are indicated by the arrows in figure 2. These values agree excellently, within less than 3 meV, with those in the exact diagonalization method. The agreement is also found on a couple of levels near the HO and LU levels. It is noteworthy that a state located near a band edge, such as the HO and LU states, is reproduced with a smaller subspace dimension \((\nu)\) than the one located within the band, as a general property of the subspace theory [10].

An MD simulation was carried out also for a gold nanowire—a metal. The same conditions of \(\nu\) and \(N_{RP}\) were used as in the polymer simulation. The simulation by the present method reproduces the formation process of helical gold nanowire, as does that by the exact diagonalization method among calculations of the conjugated polymer.

A ten-million-atom calculation was realized for a bulk silicon by a work station with two six-core Xeon CPUs (X5650), the calculation did not work with smaller numbers of cores, because of insufficient memory. The parallel efficiency is almost ideal, since the measure for the efficiency is obtained as \(\alpha = T(32)/T(1024) \times (1024/32) = 0.994\), where \(T(n)\) is the elapsed time with \(n\) cores per MD step. The dominant part of the elapsed time is that for the electronic structure calculation with the work flow of equation (19) and the remaining parts contain the file IO and other procedures. The parallel efficiency only for the electronic structure calculation is higher (\(\alpha = 1.00\)) than that for the whole elapsed time. The high parallel efficiency appears, because only vector quantities in small data sizes, such as the force on atoms \((F_i)\), are communicated among the nodes. Matrix quantities \((H, S, p, \pi)\) in much larger data sizes are not communicated among the nodes [14]. The required elements of \(H\) and \(S\) are calculated redundantly among the nodes and the elements of \(\rho_{ij}\) and \(\pi_{ij}\) are calculated and used only within the procedures made parallel by the index \(j\), as shown in equation (19).

Finally, the efficiency of the present method is compared with the other subspace methods proposed in [1] or the references therein; the generalized shifted conjugate-orthogonal conjugate-gradient (gSCOCG) method and generalized Lanczos (gLanczos) method. In these methods, a Krylov subspace of \(K_{\rho}(S^{-1}H; b)\) is used for an initial vector \(b\). Then the inner CG loop for the \(S^{-1}\)-vector multiplication appears at every step of the recurrence relation, unlike equation (7), and requires \(v_{CG}\) time matrix–vector multiplications. The present method gives, therefore, a faster performance, when the computational cost is dominated by the matrix–vector multiplications, than those in the MD simulations of the present paper. For example, the measured \(N\)-atom system, whereas the exact diagonalization method consumes an \(O(N^3)\) cost. In figure 3(a), the calculation has the order-N scaling property with up to 10 629 120 atoms\(^10\). Figure 3(b) shows the parallel efficiency of the present method with the ten-million-atom system, among 32–1024 cores.

Each eigenlevel is assigned from the inverse function of the integrated DOS, \(\eta = \eta(n)\), as follows. The integrated DOS is assumed to be the integration of smoothed delta functions of non-degenerated levels \((\sum k(e - e_k))\). The energy integration in the region of \(\eta(k - 1) < e < \eta(k)\) is assigned to be the contribution of the \(k\)th eigenstate. The \(k\)th eigenlevel is estimated to be \(e_k^\eta := \eta(k - 1/2)\) as the central peak position of the smoothed delta function.

\(^9\) Each eigenvalue is assigned from the inverse function of the integrated DOS, \(\eta = \eta(n)\), as follows. The integrated DOS is assumed to be the integration of smoothed delta functions of non-degenerated levels \((\sum k(e - e_k))\). The energy integration in the region of \(\eta(k - 1) < e < \eta(k)\) is assigned to be the contribution of the \(k\)th eigenstate. The \(k\)th eigenlevel is estimated to be \(e_k^\eta := \eta(k - 1/2)\) as the central peak position of the smoothed delta function.

\(^10\) A ten-million-atom calculation was realized for a bulk silicon by a perturbation method of the Wannier state (figure 10 of [13]). Its applicability, however, is severely limited, unlike the present method, since the Wannier states are constructed from the occupied states and the method is applicable only to insulating systems. Moreover the perturbation theory requires reliable initial states as unperturbed wavefunctions.
computational time in the gLanczos method with the same subspace dimension ($\nu$) is six times larger than that of the present one or the benchmark data with $1.4 \times 10^5$ atoms in figure 3(a). The faster performance of the present method, however, may not hold when the number of the subspace dimension ($\nu$) is much larger than those in the present paper ($\nu \rightarrow M$) and the cost is dominated by the procedure of calculating the subspace eigenvectors of equation (10) for the given reduced matrix. This is because, in the present method, the reduced $\nu \times \nu$ matrix is dense and the procedure consumes an $O(\nu^3)$ cost. The subspace methods with the subspace of $K_\nu(S^{-1}H,b)$ avoid the $O(\nu^3)$ cost, since the reduced matrix is tridiagonal. In conclusion, one should use the present method first with a moderate number of the subspace dimension ($\nu = 10^1 – 10^2$) and, if one finds a serious demand for a much larger number of $\nu$, one may use another method as explained above. In addition, the gSCOCG and gLanczos methods have several advantages. The energy momenta are conserved by the $\nu$th order in the two methods and the calculation by the gSCOCG method is robust against numerical rounding errors, even without the explicit modified Gram–Schmidt orthogonalization procedure or the long recurrence of equation (8) [1]. The absence of the long recurrence saves both the CPU time and memory costs, among the calculation with a large subspace dimension.

4. Summary

The ‘multiple Arnoldi method’ is presented for large-scale (order-$N$) electronic structure calculation with non-orthogonal bases. The test calculations were carried out with up to $10^7$ atoms. The present paper shows the potential of the present method, since the method is applicable both to metals and insulators and shows an ideal parallel efficiency. The method is implemented in a simulation package ELSES (www.elses.jp).

Acknowledgments

This research was supported partially by Grant-in-Aid (KAKENHI, Nos 20103001–20103005, 23104509, 23540370), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. The parallel computation in figure 3(b) was carried out using the supercomputer of the Institute for Solid State Physics, University of Tokyo. The supercomputers at the Research Center for Computational Science, Okazaki were also used. The authors thank Y Zempo (Hosei University) and M Ishida (Sumitomo Chemical Co., Ltd) for providing the structure model of the amorphous-like polymer.

References

[1] Teng H, Fujiwara T, Hoshi T, Sogabe T, Zhang S-L and Yamamoto S 2011 Phys. Rev. B 83 165103
[2] Takayama R, Hoshi T and Fujiwara T 2004 J. Phys. Soc. Japan 73 1519
[3] Hoshi T and Fujiwara T 2006 J. Phys.: Condens. Matter 18 10787
[4] Artacho E and Milán del Bosch L 1991 Phys. Rev. A 43 5770
[5] Bai Z, Demmel J, Dongarra J, Ruhe A and van der Vorst H 2000 Templates for the Solution of Algebraic Eigenvalue Problems (Philadelphia: SIAM)
[6] Elstner M, Porezag D, Jungnickel G, Elsner J, Haug M, Frauenheim Th, Suhai S and Seifert G 1998 Phys. Rev. B 58 7260
[7] Mehlig M J and Papaconstantopoulos D A 1996 Phys. Rev. B 54 4519
[8] Kirchhoff F, Mehlig M J, Papanicolaou N I, Papaconstantopoulos D A and Khan F S 2001 Phys. Rev. B 63 195101
[9] Elstner M, Porezag D, Jungnickel G, Elsner J, Haug M, Frauenheim Th, Suhai S and Seifert G 1998 Phys. Rev. B 58 7260
[10] Takayama R, Hoshi T, Sogabe T, Zhang S-L and Fujiwara T 2006 Phys. Rev. B 73 165108
[11] Iguchi Y, Hoshi T and Fujiwara T 2007 Phys. Rev. Lett. 99 125507
[12] Hoshi T and Fujiwara T 2009 J. Phys.: Condens. Matter 21 272201
[13] Hoshi T, Iguchi Y and Fujiwara T 2005 Phys. Rev. B 72 075323
[14] Geshi M, Hoshi T and Fujiwara T 2003 J. Phys. Soc. Japan 72 2880