Efficient and Accurate Linear Algebraic Methods for Large-scale Electronic Structure Calculations with Non-orthogonal Atomic Orbitals

H. Teng¹, T. Fujiwara¹,2, T. Hoshi³,2, T. Sogabe⁴,2, S.-L. Zhang⁵,2, and S. Yamamoto⁶,2

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

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The need for large-scale electronic structure calculations arises recently in the field of material physics and efficient and accurate algebraic methods for large simultaneous linear equations become greatly important. We investigate the generalized shifted conjugate orthogonal conjugate gradient method, the generalized Lanczos method and the generalized Arnoldi method. They are the solver methods of large simultaneous linear equations of one-electron Schrödinger equation and maps the whole Hilbert space to a small subspace called the Krylov subspace. These methods are applied to systems of fcc Au with the NRL tight-binding Hamiltonian (Phys. Rev. B 63, 195101 (2001)). We compare results by these methods and the exact calculation and show them equally accurate. The system size dependence of the CPU time is also discussed. The generalized Lanczos method and the generalized Arnoldi method are the most suitable for the large-scale molecular dynamics simulations from the view point of CPU time and memory size.

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I. INTRODUCTION

In recent years, molecular dynamics (MD) simulations with electronic structure calculations in nano-scale structures have attracted much attention. One needs a large size of systems of several hundred thousands atoms with a few hundred pico-seconds (or more longer time) process in order to investigate characteristics of nano-scale systems such as phenomena of competition between different physical principles or phenomena of the multi-physics, e.g. energy competition between the strain field and chemical bonds. Several requirements for large-scale MD simulation with electronic structure calculations are contradictory to each other, e.g. total energy accuracy vs. larger system size or longer physical time of processes.

There are several approaches for large-scale MD simulations: (a) the Fermi operator expansion, (b) the divide-and-conquer method and (c) the minimization method (the density matrix minimization or the wavefunction minimization). Another classification may be the one according as the basis set of wavefunctions: (a) the plane wave basis set and switching between the real-space and k-space representation and (b) localized orbitals or tight-binding basis set. Computation with “massively parallel machine” is also an important issue.

An important aspect is development of novel algebraic algorithm for extra-large scale systems. The most general and important algorithm may be the linear algebra solving simultaneous linear equations

\[(z - H)x = b,\]  

where \(H\) is self-adjoint or real symmetric matrix, \(b\) is a given vector, \(z = \varepsilon + i\eta\), \(\varepsilon\) is an energy parameter and \(\eta\) is an infinitesimally small positive number, respectively. Solutions of Eq. (1) relate to the standard eigenvalue problem \((\varepsilon - H)x = 0\). We developed the subspace diagonalization method and the shifted conjugate orthogonal conjugate gradient (COCG) method. Then the methods were applied to the fracture propagation and surface formation in Si crystals with the tight-binding Hamiltonian based on an orthogonal basis set. On the other hand, since its Hamiltonian is described by the tight-binding Hamiltonian based on a non-orthogonal basis set, the problem of the formation of Au multishell helical nanowires was solved by the exact diagonalization method.
real symmetric matrix $S$;

$$(zS - H)x = b,$$  \hspace{1cm} (2)

which relates to the generalized eigen-value problem $(zS - H)x = 0$. We will investigate efficient methods of solving Eq. (2) with a complex energy variable $z$ when the matrix size of $H$ and $S$ is huge. Several algebraic algorithms will be discussed and directly applied to a tight-binding Hamiltonian based on non-orthogonal atomic orbitals in large-scale systems.

The structure of the present paper is as follows. In Section III the idea of non-orthogonal atomic orbitals and physical properties (e.g. the band energy, the local/partial density of states, numbers of occupied electron states, the chemical potential et al.) are summarized. Sections III IV and V explain three different algorithms of large-scale linear equations, i.e. the generalized shifted conjugate orthogonal conjugate gradient method (GsCOCG), the generalized Lanczos method and the generalized Arnoldi method which generate the Krylov subspace from the whole Hilbert space. In these sections, numerical examples are presented by using the NRL tight-binding Hamiltonian. The generalized Lanczos method becomes applicable to actual large systems with a high accuracy if one use the modified Gram-Schmidt reorthogonalization to maintain the orthogonality of generated basis vectors. In Section VII we compare the CPU-times of each algorithm and discuss the applicability to large-scale electronic structure calculations and MD simulations. Section VIII is conclusions. The examples without reorthogonalization in the generalized Lanczos method are shown and discussed in Appendix A. Appendix B is devoted to discuss the consistency between the total energy and force.

II. THEORETICAL BACKGROUND

A. Non-orthogonal basis set and S-orthogonalization

We define two sets of wavefunctions, $\{\phi_i(r)\}$ and $\{\psi_\alpha(r)\}$, where $\{\phi_i(r)\}$ is the non-orthogonal (normalized) basis set (e.g. atomic orbitals and ‘i’ denotes an atomic site and energy level), and $\{\psi_\alpha(r)\}$ is the orthonormalized basis set. Then the overlap matrix $S_{ij}$ and the Hamiltonian matrix $H_{ij}$ are defined as

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int \phi_i^* \phi_j \, dr, \quad S_{ii} = 1,$$  \hspace{1cm} (3)

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle = \int \phi_i^* \hat{H} \phi_j \, dr,$$  \hspace{1cm} (4)

where $\hat{H}$ is the Hamiltonian operator. The orthonormal basis set $\{\psi_\alpha(r)\}$ can be expanded in terms of $\{\phi_j\}$ as

$$\psi_\alpha(r) = \sum_i \phi_i(r) w_i^{(\alpha)},$$  \hspace{1cm} (5)

and the orthogonality relation is expressed as

$$\langle \psi_\alpha | \psi_\beta \rangle = \sum_{ij} w_i^{(\alpha)*} w_j^{(\beta)} S_{ij}$$ $$\equiv (w^{(\alpha)}, w^{(\beta)})_S = \delta_{\alpha \beta},$$  \hspace{1cm} (6)

where $w^{(\alpha)} = (w_1^{(\alpha)}, w_2^{(\alpha)}, \cdots,)^T$. We call the representation $(w^{(\alpha)}, w^{(\beta)})_S$ the “S-product” and the relation Eq. (7) the “S-orthogonalization” of basis vectors $w^{(\alpha)}$.

When $\psi_\alpha(r)$ satisfies the Schrödinger equation

$$\hat{H} \psi_\alpha(r) = \varepsilon_\alpha \psi_\alpha(r),$$  \hspace{1cm} (8)

coefficients $\{w_i^{(\alpha)}\}$ should be elements of an eigen-vector of a simultaneous linear equation in the $\phi$-representation:

$$\sum_i H_{ij} w_i^{(\alpha)} = \varepsilon_\alpha \sum_i S_{ij} w_i^{(\alpha)}$$  \hspace{1cm} (9)

or, in matrix-vector form,

$$H w^{(\alpha)} = \varepsilon_\alpha S w^{(\alpha)}.$$  \hspace{1cm} (10)

Matrices $H = (H_{ij})$ and $S = (S_{ij})$ are self-adjoint in $\phi$-representation.

B. Green’s function and local/partial density of states represented by the non-orthogonal basis set

The Green’s operator $\hat{G}$ is defined as

$$\hat{G}(z) = \{(z + i\eta)\hat{1} - \hat{H} \}^{-1},$$  \hspace{1cm} (11)

where $\hat{1}$ is the identity operator and $z = \varepsilon + i\eta$. Elements of the Green’s function matrix can, then, be written as

$$G_{ij}(z) = \langle \phi_i | \hat{G}(z) | \phi_j \rangle = \{S(zS - H)^{-1}S\}_{ij}$$ $$= \sum_{k,l} S_{ik} \{ \sum_{\alpha} w_k^{\alpha*} \frac{1}{z - \varepsilon_\alpha} w_l^{\alpha} \} S_{lj}. \hspace{1cm} (12)$$

The local (partial) densities of states is expressed in the $\phi$-representation as follows:

$$D_{ij}(\varepsilon) = -\frac{1}{\pi} \text{Im}(G(z)S^{-1})_{ij}.$$  \hspace{1cm} (14)

The normalization of the Green’s functions and the local/partial density of states (DOS) is then

$$\left(-\frac{1}{\pi}\right) \int_{-\infty}^{\infty} d\varepsilon \text{Im}G_{ij}(z) = \langle \phi_i | \phi_j \rangle = S_{ij}, \hspace{1cm} (15)$$

$$\int_{-\infty}^{\infty} d\varepsilon D_{ii}(\varepsilon) = 1.$$  \hspace{1cm} (16)
C. Total band energy and Green's function

1. Density matrix and energy density matrix

In the simulation process, the density matrix \( \rho_{ij} \) and the energy density matrix \( \pi_{ij} \) appear repeatedly in the calculation of the Mulliken charge, the total energy and forces, whose definition may be

\[
\rho_{ij} = \left( -\frac{1}{\pi} \right) \text{Im} \int d\varepsilon \sum_{\alpha} f(\varepsilon_\alpha) \frac{w_i^{(\alpha)*} w_j^{(\alpha)}}{z - \varepsilon_\alpha},
\]

(17)

\[
\pi_{ij} = \left( -\frac{1}{\pi} \right) \text{Im} \int d\varepsilon \sum_{\alpha} f(\varepsilon_\alpha) \frac{w_i^{(\alpha)*} w_j^{(\alpha)}}{z - \varepsilon_\alpha},
\]

(18)

where \( f(\varepsilon) \) is the Fermi-Dirac function \( f(\varepsilon) = \{1 + \exp((\varepsilon - \mu)/\tau)\}^{-1} \), where \( \mu \) and \( \tau \) are the chemical potential and temperature.

Moreover, any physical property can be expressed by using the density matrix as

\[
\langle X \rangle = \left(-\frac{2}{\pi}\right) \int d\varepsilon f(\varepsilon) \sum_{ij} X_{ij} \text{Im}(S^{-1}G(z)S^{-1})_{ji},
\]

(19)

The expressions Eqs. (27) and (28) and also (29) are satisfied not only in the whole Hilbert space but also in the mapped subspace in which we construct approximate eigen-states.

Now we have obtained three different expressions Eqs. (21) ~ (23) for \( N_{\text{tot}} \) and Eqs. (26) ~ (28) for \( E_{\text{tot}} \). These expressions normally give different values, because we usually use finite values of the energy interval, \( \eta \) and approximate eigen-states in the mapped subspace. Fortunately, if the formula \( \sum_{ij} \rho_{ij} H_{ji} = \sum_{ij} S_{ij} \pi_{ji} \) is satisfied, the consistency between the total band energy and the force can be kept as shown in Appendix B.

III. GENERALIZED SHIFTED COCG METHOD

We developed the shifted COCG method for large-scale linear equations.\(^{14,15,21}\) It was shown that the convergence behavior can be monitored by observing the behavior of the “residual norm”. The shifted COCG method is generalized for Eq. (2) in this section.

A. Definition of the problem

The eigen-value problem of stationary Schrödinger equation is equivalent to the scattering problem;

\[
(z \hat{1} - \hat{H}) \psi(r) = \chi(r),
\]

(30)

where \( z = \varepsilon + i \eta \) and \( \varepsilon \) is an energy parameter of incident waves. The wavefunction \( \psi(r) \) is expanded by the set of non-orthogonal atomic orbitals \( \{\phi_j\} \);

\[
\psi(r) = \sum_j \phi_j(r) x_j(z).
\]

(31)

Substituting Eq. (31) into Eq. (30), one obtains generalized linear equations

\[
(z S - H) x(z) = b,
\]

(32)

where the \( j \)-th component of the vector \( b \) is \( b_j = \langle \phi_j | \chi \rangle \).

The solution of the linear equation \( x(z) \) is then

\[
x(z) = (z S - H)^{-1} b = S^{-1} G(z) S^{-1} b
\]

(33)

with a help of Eq. (12). By setting a vector \( b \) as

\[
b = e_j = (0, 0, \cdots, 0, 1_j, 0, 0 \cdots)^t,
\]

(34)
we can get the corresponding solution \( x^j(z) \) as
\[
  x^j(z) = S^{-1}G(z)S^{-1}e_j.
\] (35)

The product of \( e_i \) and \( x^j \) (not \( S \)-product), the \( i \)-th element of a vector \( x^j \), is identical just to the energy-component of the density matrix \( \rho_j(z) \):
\[
  \rho_{ij}(z) = -\frac{1}{\pi} \text{Im} \left[ e_i^\dagger \cdot x^j(\varepsilon + i\eta) \right],
\] (36)

which relates to the local DOS as
\[
  D_{ij}(\varepsilon) = \sum_k S_{ik} \rho_{ki}(\varepsilon).
\] (37)

Then the density matrix and the energy density matrix are given by the integrations of \( \rho_{ij}(\varepsilon) \) as
\[
  \rho_{ij} = \int d\varepsilon f(\varepsilon) \rho_{ij}(\varepsilon),
\] (38)
\[
  \pi_{ij} = \int d\varepsilon \varepsilon f(\varepsilon) \rho_{ij}(\varepsilon).
\] (39)

It should be noticed here that there is no quantities of eigen-energies in the Krylov subspace and, we should use the calculation procedure through \( \rho_{ij}(\varepsilon) \) rather than the calculation of Eqs. (13) and (20). Their resultant values depend on the interval of energy mesh-points for the energy integration and a fictitious finite value of \( \eta \).

**B. Generalized shifted conjugate orthogonal conjugate gradient (GsCOCG) method**

For non-orthogonal basis set, we can generalize the shifted COCG procedure, named the generalized shifted COCG (GsCOCG) method. The linear equations of the ‘seed’ energy \( \sigma_s \) and the ‘shift’ energy \( \sigma \), respectively, are written down as
\[
  (S^{-1}A + \sigma_s 1)x = S^{-1}b, \quad (40)
\]
\[
  (S^{-1}A + \sigma 1)x^{(i)} = S^{-1}b, \quad (41)
\]
where the matrix \( A \) is defined as
\[
  A = z_{\text{ref}} S - H
\] (42)

with an arbitrary reference energy \( z_{\text{ref}} = \varepsilon_{\text{ref}} + i\eta \), \( 1 \) is the unit matrix and \( b = e_j \). The seed energy and the ‘shift energy’ are given as \( \varepsilon_s = \varepsilon_{\text{ref}} + \sigma_s \) and \( \varepsilon = \varepsilon_{\text{ref}} + \sigma \).

Following the procedure of the shifted COCG method we try to find iterative \( n \)-th solutions \( x_n \) in the Krylov subspace defined
\[
  K_n(S^{-1}A + \sigma_s 1, S^{-1}b) = \text{Span}\{S^{-1}b, S^{-1}AS^{-1}b, (S^{-1}A)^2S^{-1}b, \ldots, (S^{-1}A)^nS^{-1}b\}.
\] (43)

This yields the residual vector \( r'_n = S^{-1}b - (S^{-1}A + \sigma_s 1)x_n \) to be a
\[
  r'_n \perp K_n((S^{-1}A + \sigma_s 1)^\dagger, b^*),
\] (44)

where \( B^\dagger \) is the Hermitian conjugate matrix of \( B \) and \( b^* \) is the complex conjugate vector of \( b \). The actual algorithms may be as follows. Under the initial conditions
\[
  x_0 = p_{-1} = 0, \quad (45)
\]
\[
  r_0 = b, \quad (46)
\]
\[
  \alpha_{-1} = 1, \quad \beta_{-1} = 0, \quad (47)
\]

and a definition \( r'_n = S^{-1}r_n \), we evaluate the following equations for the ‘seed’ energy \( \sigma_s \) iteratively for \( n = 0, 1, 2, \ldots \):
\[
  p_n = r'_n + \beta_{n-1} p_{n-1},
\]
\[
  \alpha_n = \frac{(r'_n, r'_n)^S}{(p_n, S^{-1}(A + \sigma_s S)p_n)^S},
\]
\[
  x_{n+1} = x_n + \alpha_n p_n,
\]
\[
  r_{n+1} = r_n - \alpha_n(A + \sigma_s S)p_n,
\]
\[
  r'_{n+1} = S^{-1}r_{n+1},
\]
\[
  \beta_n = \frac{(r'_{n+1}, r'_{n+1})^S}{(r'_n, r'_n)^S}.
\] (48)

Important point here is our use of \( r'_n = S^{-1}r_n \). In actual procedure, we employ a form \( r_n = S\pi r_n \) at each iteration step by CG method. Since the overlap matrix \( S \) is real symmetric positive definite and sparse, the convergence of CG iteration can be fast.

The basic theorem of the Krylov subspace is the invariance of the subspace under an energy shift \( \sigma \). The other very basic theorem is the collinear residual. (52)
\[
  r_n = \frac{1}{\pi_n^\sigma} r_n.
\] (49)

Owing to these theorems, once we solve the set of equations for the ‘seed’ energy \( \sigma_s \), we can obtain the results for any shift energy \( \sigma \) only by scalar multiplications. The recurrence equations for shift energies are given (all the quantities are denoted by the superscript \( \sigma \)), with initial values \( \pi_{n-1} = \pi_0^\sigma = 1 \), as follows;
\[
  \pi_{n+1}^\sigma = \left( 1 + \alpha_n (\sigma - \sigma_s) \right) \pi_n^\sigma + \frac{\beta_{n-1}}{\alpha_{n-1}} \alpha_n (\pi_n^\sigma - \pi_{n-1}^\sigma)
\] (50)

and
\[
  x_{n+1}^\sigma = x_n^\sigma + \alpha_n^\sigma p_n^\sigma
\] (51)

with
\[
  \alpha_n^\sigma = \frac{\pi_n^\sigma}{\pi_{n+1}^\sigma} \alpha_n,
\]
\[
  \beta_{n-1}^\sigma = \left( \frac{\pi_{n-1}^\sigma}{\pi_n^\sigma} \right)^2 \beta_{n-1},
\]
\[
  p_n^\sigma = \frac{1}{\pi_n^\sigma} r'_n + \beta_{n-1}^\sigma p_{n-1}^\sigma.
\]
Partial densities of states are shown in Fig. 1 for a system of Au 864 atoms by NRL tight-binding Hamiltonian in comparison with those by the exact calculations. In order to see the behavior of the peak positions and the tail of the peaks, the figures are drawn in the logarithmic scale. Two lines of GsCOCG and the exact calculation overlap each other almost completely and one can recognize an excellent agreement between the two different calculations.

FIG. 1: (Color on line) Partial density of states for a system of Au 864 atoms by NRL tight-binding Hamiltonian, normalized to unity. (a) s-orbitals, (b) p-orbitals and (c) d-orbitals. Comparison is for GsCOCG and the exact calculation, which are almost identical to each other. Parameters in GsCOCG calculations are \(\eta = 10^{-3}\) Ry, \(\tau = 5\eta\). The energy interval of mesh-points is \(10^{-4}\) Ry. See Figs. 4, 5 and 7 for comparison.

C. Residual norm and convergence behavior

The useful characteristic property of GsCOCG method is the capability of monitoring the norm of residual vectors. The residual vectors for the seed and shift equations with an energy \(\varepsilon_k\) (with \(b = e_j\) and \(\sigma_k = \varepsilon_k - \varepsilon_{\text{ref}}\)) are \(r_n^{(s,j)}\) and \(r_n^{(k,j)}\), respectively, and the ‘mapped’ residual vectors for the seed and shift equations \(r_n^{(s,j)} = S^{-1}r_n^{(s,j)}\) and \(r_n^{(k,j)} = S^{-1}r_n^{(k,j)}\). We usually need only elements of the density matrix among near-sited orbital pairs connected by non-zero elements of the Hamiltonian or overlap matrices and the convergence monitoring is necessary for these components. Therefore, in order to monitor the convergence behavior, we adopt the “residual norm” defined as

\[
\| r_n^{(s/k,j)} \|_2^2 = \sum_i |e_i^s \cdot r_n^{(s/k,j)}|^2.
\]

Furthermore, since the residual norm is different among different energy points, the average quantity (‘average
residual norm”) should be defined as

\[ R_n^{(j)} = \frac{1}{N_{ene}} \sum_{k} r_{n}^{(k,j)} \| r_{n}^{(k,j)} \|_{2}^{2} \]

where \( N_{ene} \) is the number of energy points.

The convergence behavior of the residual norm for different seed energies is shown in Fig. 2a. The convergence at the energy of the low DOS is very fast, because the eigen-state can be constructed by a small number of basis states. The convergence of the averaged norm is shown in Fig. 2b, which confirms numerically the fact that the average residual norm (and all the physical quantities) does not depend sensitively on the choice of a seed energy.

D. Seed-switching technique

When one chooses a seed energy in an energy range of rapid convergence, the spectra at majority energy points have not been converged yet and one should restart the calculation with a new seed energy as seen in Fig. 2a. The most desirable seed energy may be the one of the largest (partial) DOS because the convergence at these points is the most slowest.

However, even if one chooses a starting seed energy in the highest DOS region and the residual norm at the seed energy reaches the convergence criterion, it often happens that there still remain several energy points/regions where the residual norm has not been small enough. Fortunately the shifting energy does not need any additional heavy computational task but several scalar manipulation as Eq. (50). Because of this property of shifting energy, a choice of a seed energy \( \sigma_{s} \) can be arbitrary. As shown in Fig. 2b, even if we start with an improper seed energy and switch a seed, the total iteration times for desired convergence over whole energy range is not very different. The seed-switching is very efficient technique to avoid restarting the calculation from the beginning with a new seed energy.\(^{16,25}\) One chooses a new seed energy \( \sigma_{new} \) and can continue the calculation without discarding the information of the previous calculation with the old \( \sigma_{s} \) by using the shift property. Figure 3 shows the behavior of the residual norms in the seed-switching process.

IV. GENERALIZED LANCZOS PROCESS AND DENSITY OF STATES

The three-term recursive relation used in GsCOCG method leads us to the generalization of the Lanczos method.\(^{18,19,26}\) As far as we know, the generalization of the Lanczos method was presented first in Ref. 18. In this section, we will stress that the generalized Gram-Schmidt reorthogonalization process makes G-Lanczos method practically useful and also the use of Eqs. (18) and (20) gives very efficient and accurate results.

A. Generalized Lanczos process

First we define a matrix \( \mathcal{H} \) as

\[ \mathcal{H} \equiv S^{-1} H, \]  

which is not self-adjoint but still satisfies the quasi-Hermitian property in the S-product;

\[ (v, \mathcal{H}u)_{S} = (\mathcal{H}v, u)_{S}. \]
We can construct the three-term procedure of the Lanczos process \((n = 0, 1 \cdots)\) as\(^{18,19}\)

\[
\mathcal{H} u^n = a_n u^n + b_{n+1} u^{n+1} + b_n u^{n-1},
\]

where
\[
a_n = (u^n, \mathcal{H} u^n)_S, \\
b_{n+1}^2 = ( (\mathcal{H} - a_n) u^n - b_n u^{n-1}, (\mathcal{H} - a_n) u^n - b_n u^{n-1})_S, \\
u^{n+1} = \{ (\mathcal{H} - a_n) u^n - b_n u^{n-1} \} / b_{n+1}
\]

with conditions \(b_0 = 0, b_n \geq 0\) and then the vectors \(\{ u^m \}\) satisfy the S-orthogonality
\[
(u^n, u^m)_S = \delta_{nm}.
\]

This process we call the generalized Lanczos (G-Lanczos) process (method). It is well-known that the orthogonality relation is broken for larger \(n\) in the Lanczos method and this is also the case here. We adopt the modified Gram-Schmidt reorthogonalization process in order to keep the S-orthogonality. (See the results without the modified Gram-Schmidt reorthogonalization process in Appendix A)

We then stop the Lanczos process up to \(n = N\) and assume \(u^m = 0\) \((m = N + 1, N + 2, \cdots)\). This procedure constructs the Krylov subspace

\[
K_N(\mathcal{H}, b) = \{ b, \mathcal{H} b, \mathcal{H}^2 b, \cdots, \mathcal{H}^N b \}
\]

and the matrix \(\mathcal{H}\) is transformed in this subspace to a matrix of a tridiagonal form.

Starting with a natural basis \(u^0 = e_{j_0}\), one generates vectors \(u^n\) in the Krylov subspace and each vector corresponds to an orthonormalized linear combination of atomic orbitals (LCAO):

\[
u^m \mapsto \varphi^m (r) = \sum_j \phi_j (r) u_j^m.
\]

The normalized eigen-states in the generated Krylov subspace is denoted by

\[
\psi^n (r) = \sum_{n=0}^{N} \varphi^n (r) Q_n^{(a)} = \sum_j \phi_j (r) w_j^n,
\]

which satisfies the Schrödinger equation

\[
\sum_{m} \mathcal{H}_{nm} Q_m^{(a)} = \varepsilon_{n} Q_n^{(a)},
\]

where \(\mathcal{H}_{nm} = (u^n, \mathcal{H} u^m)_S = (u^n)^j \mathcal{H} u^m\).

**B. Numerical test with NRL Hamiltonian for fcc Au**

Chemical potential \(\mu\) can be evaluated by using Eqs. \((21) \sim (23)\) in the generalized Lanczos method. Calculation of the Green’s function uses Eq. \((13)\) having a double summation of atomic sites and orbitals and it consumes a long CPU time. On the contrary, the calculation of the density of states by Eq. \((14)\) costs less CPU time. The computational efficiency will be discussed later in Section VII. Here in this subsection, we show several evaluated values, the density of states, the integrated density of states as functions of energies for a system of gold 864 atoms of fcc structure described by the tight-binding Hamiltonian constructed by Mehl and Papaconstantopoulos.\(^{24}\)

Several evaluated values and consistency between them are summarized in Table I. The parameters in the generalized Lanczos method are \(N = 50\), the convergence criterion \(\delta = 10^{-6}\text{Ry}\) in the inner CG process of \(r' = S^{-1} r\). In GsCOCG, the imaginary small energy \(\eta = 10^{-3}\text{Ry}\), the total number of the energy integration mesh-points is 3,000, and the convergence criterion \(\delta = 10^{-6}\text{Ry}\) in the inner CG and outer iteration procedures. The difference of the calculated total energy is of the order of \(10^{-2} \sim 10^{-3}\text{Ry}\). The scale of the band energy is 1 Ry and the relative error may be of \(10^{-3}\). The bold numbers in Table I are a set of consistent values in each case.

![FIG. 4: (Color on line) Partial density of states (pDOS), normalized to unity, and integrated density of states (IDOS) for a system of Au 864 atoms by NRL tight-binding Hamiltonian.](image)
TABLE I: The generalized Lanczos process applied to a system of 864 atoms of fcc Au and comparison with that by GsCOCG. The Hamiltonian is the NRL tight-binding form. The chemical potential and the total energy are in Ry unit and \( N_{\text{atom}} \) is the number of atoms in the system.

| \( N_{\text{tot}}/2N_{\text{atom}} \) | G-Lanczos | GsCOCG |
|---|---|---|
| Eq. (21) | \( \mu \) by Eq. (21) | 0.3010 8669 |
| | \( \mu \) by Eq. (22) | 0.2926 6528 |
| | \( \mu \) by Eq. (23) | 0.2870 0985 |
| Eq. (24) | \( N_{\text{tot}}/2N_{\text{atom}} \) | 5.5000 0000 |
| | \( E_{\text{tot}}/2N_{\text{atom}} \) by Eq. (21) | 5.4869 9705 |
| | \( \rho \) by Eq. (17) | 5.4674 0401 |
| | \( \rho \) by Eq. (18) | 5.4654 0739 |
| | \( \pi \) by Eq. (20) | 5.4999 9999 |
| Eq. (25) | \( \pi \) by Eq. (20) | 5.5135 2184 |

\[ H, \text{ as } 19, 27 \]

\[
l^{n+1} = H u^n \quad (62)
\]

\[
k^{n+1} = l^{n+1} - \sum_{m=0}^{n} u^{m} (u^{m}, l^{n}) S \quad (63)
\]

\[
u_{n+1} = \frac{k^{n+1}}{(k^{n+1}, k^{n+1})^{1/2}}. \quad (64)
\]

This is the Arnoldi process and we call it the generalized Arnoldi (G-Arnoldi) method. The generalized Arnoldi method generates the Krylov subspace

\[
K_{N+1}(H; b) = \text{Span}\{b, Hb, H^2b, \ldots, H^N b\}
\]

\[
= \text{Span}\{u^0, u^1, u^2, \ldots, u^N\}. \quad (65)
\]

The generated vector \( u^m \) corresponds to orthonormalized LCAO

\[
\varphi^m(r) = \sum_j \phi_j(r) u^m_j \quad (66)
\]

as in G-Lanczos method. An eigen-function \( \psi^\alpha(r) = \sum_n \varphi^n(r) Q_n^{(\alpha)} \) satisfies the Schrödinger equation

\[
\sum_m \tilde{H}_{nm} Q_m^{(\alpha)} = \varepsilon_\alpha Q^{(\alpha)}_n \quad (67)
\]

where \( \tilde{H}_{mn} = \langle \varphi^m | \tilde{H} | \varphi^n \rangle = \langle u^m | H | u^n \rangle \) and \( \tilde{H} \) is an upper Hessenberg matrix. We can say that this procedure is a kind of generalization of the subspace diagonalization of the Krylov subspace developed before.

V. GENERALIZED ARNOLDI PROCESS AND DENSITY OF STATES

A. Generalized Arnoldi process

We can construct the Krylov subspace, starting with a natural basis \( u^0 = e_j \alpha \), by using the Hamiltonian matrix

\[
H, \text{ as } 19, 27
\]
TABLE II: The generalized Arnoldi process applied to a system of 864 atoms of fcc Au and comparison with that by GsCOCG. The Hamiltonian is the NRL tight-binding form. The chemical potential and the total energy are in Ry unit and $N_{\text{atom}}$ is the number of atoms in the system.

|                  | G-Arnoldi | GsCOCG |
|------------------|-----------|--------|
| $\mu$ by Eq.(21) | 0.3039 0679 | 0.3066 0832 |
| $\mu$ by Eq.(22) | 5.5000 0002 | 5.5000 0000 |
| $\mu$ by Eq.(23) | 5.5176 0887 | — |

The peak positions are deviated slightly from those by the exact calculation, which one could make smaller with increasing a dimension $N$ of the Krylov subspace.

VI. COMPARISON AMONG GsCOCG, G-LANCZOS METHOD AND G-ARNOLDI METHOD

A. Convergence

The dimension of the Krylov subspace in GsCOCG, G-Lanczos or G-Arnoldi methods equals to $N + 1$ where $N$ is the maximum iteration step. GsCOCG method is very accurate method if one achieves the iteration to have enough small residual norm (e.g. $\delta = 10^{-6}$Ry). In Fig.2, we have shown the convergence behavior of the residual norms with different seed energies and until much smaller convergence region. One should use the same iteration criteria both in the inner CG and outer procedures in GsCOCG method. It sometimes happens that the resultant DOS shows an un-physical behavior, e.g. negative values of DOS, if one stops the iteration steps before enough convergence in GsCOCG method. On the other hand, G-Lanczos and G-Arnoldi methods never give such un-physical DOS even if one stops at small iteration step because of the expression of Eq.(13). Furthermore, the first $N$ moments are preserved correctly in the energy spectra of G-Lanczos method. In the spectrum of the present model by the exact calculation, we observe about forty prominent peaks and then we use $N = 50$ in the calculations of G-Lanczos and G-Arnoldi procedures. This is presumably the reason why the peak positions and detailed profiles in the spectra of G-Lanczos method show excellent agreement with those of the exact calculation. G-Lanczos method needs the Gram-Schmidt reorthogonalization and also it is necessary to have enough convergence in the inner CG procedure. G-Arnoldi method does not need such reorthogonalization procedure since one solve the eigen-value problem in that subspace.

In condensed matters, the width of the valence and/or conduction bands $W$ may be of the order of 1Ry. Then, when the number of atoms is $N_{\text{atom}}$, we can estimate...
TABLE III: Chemical potential and the total energy (in Ry unit) of systems of 864 and 256 atoms of fcc Au by three different methods. The values of $\rho$ in the G-Lanczos and G-Arnoldi methods are evaluated by Eq. (18).

| Method      | System | $\mu$    | $E_{\text{tot}}/2N_{\text{atom}}$ |
|-------------|--------|----------|-----------------------------------|
|             |        | Eq. (22) | Eq. (27)                          |
| G-Lanczos   | 864    | 0.2926   | 0.1364 7104 0.1358 7639           |
| (864 atoms) | (256 atoms) |             |                                    |
| G-Arnoldi   | 864    | 0.2928   | 0.1351 4434 0.1346 6195           |
| (864 atoms) | (256 atoms) |             |                                    |
| GsCOCG      | 864    | 0.3006   | -0.1436 4084 -0.1433 1925         |
| (864 atoms) | (256 atoms) |             |                                    |

The separation of each energy level as of the order of $W/(9 \times N_{\text{atom}})$. Presumably 10% of this separation would be enough accuracy in the energy scale. In our present case, with $N_{\text{atom}} \approx 1,000$, the convergence criterion can be chosen as $0.1 \times W/(9 \times N_{\text{atom}}) \approx 0.1 \times 1/9,000 \approx 10^{-5}$ Ry. We also observed that the maximum iteration steps are almost the same for the convergence criterion $\delta = 10^{-5}$ and $\delta = 10^{-6}$ in GsCOCG and G-Lanczos methods. This is the reason why we choose $\delta = 10^{-6}$ Ry.

We compare the results of the chemical potential and the total band energy of systems of 256 and 864 atoms in Table III. The difference of the chemical potential $\mu$ is of the order of $10^{-3}$ Ry, and that of the total band energy $E_{\text{tot}}$ is of the order of $10^{-4}$ Ry. The level separation in 256 atom system can be estimated as $1.0/(9 \times 256) \approx 4 \times 10^{-4}$ Ry and that in 864 atom system $10^{-4}$ Ry. The difference in the chemical potential of two systems of different sizes is due to the difference of total number of levels which changes the value of the chemical potential sensitively. On the other hand, the difference of $E_{\text{tot}}$ is just the quantity related to the overall spectrum and we can see an excellent convergence of the results of $N = 50$.

Figure 6 shows the actual convergence behavior of IDOS by G-Lanczos and G-Arnoldi method. The agreement between the results by G-Lanczos or G-Arnoldi methods and those by the exact calculation is excellent both for systems of 864 atoms and that of 256 if we adopt $N = 50$. The most apparent difference appears in the IDOS curves of exact calculation of systems of 256 atoms and 865 atoms in the mid energy region, and the calculated results by our present methods present this difference with complete fidelity.

B. CPU times

We summarize, in Tables IV, the CPU times (by using single CPU of the standard workstation) for (s-orbitals) $D_{ii}$ of the generalized Lanczos and the generalized Arnoldi methods with Eq. (14), that of GsCOCG with Eq. (27), and that of the exact diagonalization method for the NRL Hamiltonian of fcc Au system of 256 and 864 atoms. The total number of orbitals equals to nine times of the total number of atoms (1 s, 3 p’s and 5 d’s). We use, in the inner CG process of the generalized Lanczos (G-Lanczos) method, the convergence criterion $\delta = 10^{-6}$ Ry. Two numbers in the row of the CPU time are referred to those of $N = 50$ and $N = 100$, respectively, for G-Lanczos and G-Arnoldi methods, though the results of $N = 100$ almost coincide with those of $N = 50$. For GsCOCG (with shifted 3,000 energy points), the data shown here are those of $\delta = 10^{-6}$ Ry both for in the inner and outer iteration processes. The repeated time of the inner CG process ($S^{-1}x$ part) in GsCOCG and G-Lanczos method is $10 \sim 11$. (Repeated time of 25 $\sim 27$ is needed for $\delta = 10^{-18}$ Ry.)

The system size dependence of the CPU time is linear for the generalized Arnoldi (G-Arnoldi) method and the generalized Lanczos (G-Lanczos) method, bilinear for GsCOCG method and cubic for the exact calculation. The generalized Arnoldi method is extremely efficient in electronic structure calculations of extra-large systems with several hundred thousands atoms.

C. Applicability to large-scale electronic structure calculations and MD simulations

In the exact calculation and GsCOCG method, calculations of physical properties, such as the density matrix, the energy density matrix, and chemical potential,
TABLE IV: CPU times by using a standard single CPU workstation, for (a) a system of gold 256 atoms (Au256) and (b) gold 864 atoms (Au864) by NRL tight-binding Hamiltonian.\textsuperscript{23}

| (a) Au 256 | CPU-times (s) |
|------------|---------------|
| G-Arnoldi  | main part     | 0.52          |
|            | total         | 1.59          |
| G-Lanczos  | inner CG      | 2.04          |
|            | main part     | 2.89          |
|            | total         | 3.92          |
| GsCOCG     | seed          | 13.67         |
|            | shifted       | 7.53          |
|            | total         | 21.20         |
| Exact      |               | 57.60         |

| (b) Au 864 | CPU-times (s) |
|------------|---------------|
| G-Arnoldi  | main part     | 1.94          |
|            | total         | 3.00          |
| G-Lanczos  | inner CG      | 7.93          |
|            | main part     | 10.87         |
|            | total         | 11.93         |
| GsCOCG     | seed          | 140.89        |
|            | shifted       | 108.36        |
|            | total         | 249.15        |
| Exact      |               | 2111.51       |

We have investigated the accuracy and efficiency by showing numerical data with different numerical procedures. GsCOCG is very accurate with less consumption than the exact diagonalization but may not be appropriate for long MD-step simulations. The generalized Lanczos method becomes applicable to actual large systems with the modified Gram-Schmidt reorthogonalization to maintain the orthogonality of generated basis vectors. Then, the generalized Arnoldi method and the generalized Lanczos method are accurate and efficient, and their CPU times depend linearly upon the system size. Therefore, these two methods would be the most suitable to the large-scale electronic structure calculations and MD simulations. A crucial point we should point out finally is the fact that G-Lanczos and G-Arnoldi methods do not adopt any numerical integration in energy which leads additional numerical error.

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Appendix A: Re-orthogonalization by modified Gram-Schmidt method

The three-term recursive relation in the generalized Lanczos method guarantees theoretically the automatic

VII. CONCLUSION

require the numerical integration as in Eqs. (21), (20), (28), and (39). Therefore, in order to keep high accuracy, the integration needs fine energy mesh points. On the other hand, the generalized Lanczos or the generalized Arnoldi methods use the simple summation of the eigen-states in the mapped subspace in Eqs. (22), (23), (38) and (39). Therefore, in order to keep high accuracy, the integration needs fine energy mesh points. On the other hand, the generalized Lanczos or the generalized Arnoldi methods use the simple summation of the eigen-states in the mapped subspace in Eqs. (22), (23), and (17) ~ (20). These two methods do not consume the CPU time and give stable values of the density matrix and the energy density matrix.

The CPU times per one MD-step are, for the present models, a few seconds by the generalized Lanczos method and the generalized Arnoldi method. From the above comparison among various viewpoints, we can conclude that the generalized Lanczos method or the generalized Arnoldi method are very suitable to large-scale electronic structure calculations and MD simulation of several tens of thousands atoms and a long MD-steps. On the other hand, GsCOCG method can give excellently rigorous results with more CPU times and may be applicable to problems of a fixed atomic configuration (but not for the MD simulation).

GsCOCG method is based on the three-term recursive equations and we need store three generated vectors at each recursive process. Of course, when the size of the Hamiltonian and overlap matrices are extremely large and the memory size becomes a serious obstacle, (though much smaller consumption than the exact diagonalization method, ) we should invent other method of much faster convergence and smaller cost of memory size.

The convergence criterion \( \delta = 10^{-5} \) might corresponds to the range of neighboring 1,000 atoms, as already discussed, and we do not observe any clear difference between results by the present methods and the exact calculations. Even when we should discuss some physics of nano-scale systems, the electronic structure is determined by some nearby surroundings. This idea we call near-sitedness.\textsuperscript{23} Even when we have to deal with a much larger systems, we can use smaller interaction range than the system size due to the near-sitedness. Presumably more serious problem of the system size in some specific problems, for examples, entire calculation of nano-device or the electron-strain field interaction such as fracture propagation\textsuperscript{22} and dislocation.\textsuperscript{23}
S-orthogonalization. However, the orthogonality is broken in the numerical calculation procedure. This problem causes several troubles such as the existence of constant background of error in the spectrum, appearance of “ghost” structure in spectrum due to erroneous mixing of states and a broken normalization of the partial density of states.

Figure 7 shows the examples of this broken orthonormality, in a system of 256 atoms of fcc Au by using the NRL Hamiltonian. One can see the “ghost” peaks (e.g. at $\varepsilon \simeq 1.8$Ry in (a-1), at $\varepsilon \simeq 1.25 \sim 1.3$Ry in (b-1) and (c-1)) and broken normalization (e.g. in (a-2) and (b-2)). These problems are solved by the re-orthogonalization with the modified Gram-Schmidt method.

**Appendix B: Consistency between the total energy minimum and a vanishing force**

We should construct our eigen-states in a small subspace and a certain numerical error is unavoidable in evaluated total energy and force. Even in that case, the consistency between the total band energy minimization and an vanishing atomic force is the most important in the electronic structure calculation in equilibrium atom configuration. In the framework of the tight-binding model, the force (due to band energy) acting on an atom $I$ is evaluated by a formula

$$F_I = -2 \sum_{ij} \left( \rho_{ij} \frac{\partial H_{ij}}{\partial R_I} - \pi_{ij} \frac{\partial S_{ij}}{\partial R_I} \right),$$  
(B1)

which can be rewritten, with only an assumption of the eigen-state property Eq. (8) in the mapped subspace, as

$$F_I = -2 \frac{\partial}{\partial R_I} \left\{ \sum_{ij} (\rho_{ij} H_{ij}) - \sum_{ij} (\pi_{ij} S_{ij}) \right\} - \frac{\partial}{\partial R_I} \sum_{\alpha} f(\varepsilon_{\alpha}) \varepsilon_{\alpha}. $$  
(B2)

Therefore, calculated atomic and electronic configuration of the minimum total energy is consistent with that of vanishing atomic force, if the identity $\sum_{ij} (\rho_{ij} H_{ij}) = \sum_{ij} (\pi_{ij} S_{ij})$ is satisfied always in any atomic configuration. It should be noticed that the above equality is satisfied in the mapped subspace as described in [11]. It is important in actual calculating procedure that we should use the consistent pair of equations as Eqs. (18) and (20) or Eqs. (19) and (20).

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* Present address: Institute of Mechanics, Chinese Academy of Sciences, Beijing, China

† Corresponding author: fujiwara@coral.t.u-tokyo.ac.jp

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