Linear scaling Krylov subspace method for large scale \textit{ab initio} electronic structure calculations of metals

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An efficient and robust linear scaling method is presented for large scale \textit{ab initio} electronic structure calculations of a wide variety of materials including metals. The detailed short range and the effective long range contributions to the electronic structure are taken into account by solving an embedded cluster defined in a Krylov subspace, which provides rapid convergence for not only insulators but also metals. As an illustration of the method, we present a large scale calculation based on density functional theory for a palladium cluster with a single iron impurity.

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The development of linear scaling method is a promising direction of extending applicability of \textit{ab initio} electronic structure calculations based on density functional theory (DFT) to large scale realistic systems. In fact, over the last decade, considerable efforts have been devoted to establish efficient and robust linear scaling methods, and successful applications have been reported within non-SCF tight binding (TB) scheme. Nevertheless, within the fully self consistent field (SCF) DFT much improvement is still needed to reduce the error below chemical accuracy (a few milli-Hartree/atom), referred to as milli-Hartree accuracy hereafter, for a wide variety of materials with modest computational cost. In addition, the application to \textit{ab initio} calculations is practically hampered by an intractable feature that an approximate solution of eigenstates by the linear scaling methods often induces instabilities in the SCF calculation. In this paper to overcome these difficulties we present an efficient and robust linear scaling method for a wide variety of materials including metals in which ideas behind two linear scaling methods, divide-conquer (DC) and recursion methods, are unified in a single framework. It is known that the DC method provides rapid convergence for covalent systems such as biological molecules with numerical stability during the SCF calculation. However, the application of the DC method to metals is significantly restricted by requirement of the large size of truncated cluster. On the other hand, the recursion method based on Lanczos algorithms and Green’s functions is one of suitable methods for metals, although the SCF calculation with the recursion method becomes unstable. The main idea behind the recursion method is to employ a Krylov subspace generated by the Lanczos algorithm in evaluating Green’s functions, and this is the reason why the recursion method can provide rapid convergence for metals. Thus, we propose a novel method which possesses the advantages in two methods and overcomes the drawbacks. Let us assume that the basis set consists of nonorthogonal localized functions such as pseudo-atomic orbitals (PAO) and finite elements basis. Through-out this paper we use the PAO χ as basis function to expand one-particle wave functions. The charge density \(\rho(\mathbf{r})\) associated with spin component \(\sigma\) is evaluated via Green’s function \(G\) by

\[
\rho(\mathbf{r}) = \sum_{i\alpha,j\beta} \chi_{i\alpha}(\mathbf{r}) \chi_{j\beta}(\mathbf{r}) n_{i\alpha,j\beta}^{(\sigma)},
\]

where \(i\) is a site index, \(\alpha\) an orbital index, and \(n_{i\alpha,j\beta}^{(\sigma)}\) density matrix given by

\[
n_{i\alpha,j\beta}^{(\sigma)} = -\frac{1}{\pi} \text{Im} \int G_{i\alpha,j\beta}^{(\sigma)} (E + i0^+) f(\frac{E - \mu}{k_B T}) dE
\]

with the Fermi function \(f(x) \equiv 1/[1 + \exp(x)]\). Since only the charge density \(\rho^{(\sigma)}\) and the density matrix \(n^{(\sigma)}\) are required in the conventional DFT, we focus on the evaluation of Green’s functions in later discussion. The spin index \(\sigma\) will hereafter be dropped for simplicity of notation. It is noted that the DC and recursion methods provide different ways of evaluating Green’s functions from a local Hamiltonian \(H\) and overlap \(S\) matrices constructed from the local environment for each atom. By taking into account the rapid convergence as observed in the recursion method and considering that the Krylov subspace for the non-orthogonal basis functions is defined by \(\{|W_0\}, \{S^{-1}H|W_0\}, \{(S^{-1}H)^2|W_0\}, ..., \{(S^{-1}H)^N|W_0\}\), we introduce a Krylov subspace \(U\) for each atom given by

\[
U = W X \lambda^{-1},
\]

where \(W \equiv \{|W_0\}, |W_1\}, |W_2\}, ..., |W_N\}\) and \(X\) are eigenvalues and corresponding eigenvectors of an overlap matrix \(W^T S W\). The \(W\) is generated by the following procedure: (i) \(|R_n\rangle = Q H |W_{n-1}\rangle\), (ii) \(|W_n\rangle = |R_n\rangle - \sum_{m=0}^{n-1} |W_m\rangle \langle W_m | S | R_n\rangle\), (iii) \(|W_n\rangle = S\)-orthonormalized block vector of \(|W_n\rangle\). In this procedure, \(Q\) is the inverse of a local overlap matrix \(S\) constructed from the same truncated cluster as in the construction of the local Hamiltonian \(H\), where the cluster is constructed by
a logically truncation method\textsuperscript{3}. In case the large size of truncated cluster is required for reduction of the computational error, $Q$ can be substituted by an approximate inverse given by $V_{s}^{-1}V_{l}$ with $s = V_{l}SV$ and $V = \{|V_{0}\rangle, |V_{1}\rangle, |V_{2}\rangle, ..., |V_{N}\rangle\}$ which is generated by the following procedure: (I) $|Y_{m}\rangle = S|V_{m-1}\rangle$, (II) $|V'_{m}\rangle = |Y_{m}\rangle - \sum_{p=0}^{m-1} (V_{p})\langle V_{p}|Y_{m}\rangle$ (III) $|V_{m}\rangle = I$-orthonormalized block vector of $|V'_{m}\rangle$. The initial states $|V_{0}\rangle$ and $|W_{0}\rangle$ consist of block I-orthonormalized vectors and its S-orthonormalized vectors, and the optimum choice of $|V_{0}\rangle$ depends on the system as discussed later on. In the generation scheme, we impose only the S-orthogonality between Krylov vectors without assuming any specific form for the representation of the Hamiltonian matrix, while a tridiagonal form of the Hamiltonian matrix is imposed in the Lanczos algorithm\textsuperscript{4, 5}. Although the procedure (i)-(iii) gives a set of S-orthogonal Krylov vectors in principle, the S-orthonormality is not well assured due to round-off error in the Gram-Schmidt orthogonalization. Therefore, the Krylov subspace $U$ is given by an orthogonal transformation Eq. (3). For numerical stability, it is crucial to construct the Krylov subspace $U$ at the first SCF step, and to fix it during subsequent steps. If the Krylov subspace is regenerated at every SCF step, the SCF convergence becomes significantly worse because of fluctuation of the spanned space, which is the reason for the instability inherent in the recursion method coupled with the SCF calculation as discussed later on. By considering a further spatial division of the truncated cluster into a core and the remaining buffer regions, and taking the Krylov subspace representation, the original generalized eigenvalue problem $H = \varepsilon \mu \Sigma \mu$ for the truncated cluster can be transformed to a standard eigenvalue problem $H^{K} b_{\mu} = \varepsilon_{\mu} b_{\mu}$ with

$$H^{K} = U^{\dagger} H U = \begin{bmatrix} H_{c} & H_{cb} \\ H_{bc} & H_{b} \end{bmatrix}$$

where $H_{c}$, $H_{b}$, and $H_{cb}$ are Hamiltonian matrices, represented by the original basis functions $\chi$, for the core and buffer regions, and between the core and buffer regions, respectively. Considering that the Krylov subspace $U$ is decomposed to contributions of the core and buffer regions: $U^{\dagger} = (u_{c}^{\dagger}, u_{b}^{\dagger})$, it is straightforward to see that $H^{K}$ is composed by a short range $H_{s}^{K} = u_{c}^{\dagger} H_{c} u_{c}$ and the other long range contributions $H_{l}^{K}$. Since the required buffer size to satisfy the milli-Hartree accuracy can be large in most cases for metals, therefore, once the long range contributions $H_{l}^{K}$ is calculated at the first SCF step, the matrix is fixed during subsequent steps, while it it possible to update $H_{s}^{K}$ after achieving the self consistency. Then, the standard eigenvalue problem is diagonalized with a updated $H_{s}^{K}$ and the fixed $H_{l}^{K}$ during subsequent steps, which means that the detailed short range contribution to the electronic structure can be taken into account with an effective correction by the long range contribution $H_{l}^{K}$. Thus, the evaluation of Green’s functions is mapped to a cluster problem analogous to the DC method\textsuperscript{3}, but with the effective smaller Hamiltonian $H^{K}$. The core region in this study is defined by a cluster within atoms having non zero overlap $\chi_{i} \chi_{j}\beta$ to the central atom $i$. In this case the required components in the eigenvectors for the evaluation of the charge density Eq. (1) is easily evaluated by a back transform $c_{\mu} = u_{c}\beta$. It is noted that the evaluation of Green’s function and the density matrix Eq. (2) is trivial in the same way as the DC method\textsuperscript{3} since we have the eigenvalues $\varepsilon_{\mu}$ and its corresponding eigenvectors $c_{\mu}$.

In Fig. 1 the absolute error in the total energy and the computational time calculated by three linear scaling methods, the proposed, DC, and recursion methods, are shown as a function of number of atoms in each truncated cluster for bcc lithium bulk. All the calculations in this study were performed by a DFT code, OpenMX\textsuperscript{8, 10}, with a generalized gradient approximation (GGA)\textsuperscript{11} to the exchange-correlation potential. It is found that three methods are equivalent in terms of the accuracy. However, we see that the computational time of the proposed method is remarkably reduced compared to those of the DC and recursion methods. In the proposed method the dimension of the Krylov subspace $W$ and that of the subspace $V$ for the approximate inverse of the overlap matrix are 7 % and 28 % of the total number of basis functions in

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) absolute error, with respect to the band calculation, in the total energy (Hartree/atom) for bcc lithium bulk as a function of atoms in each truncated cluster calculated by three linear scaling methods, (b) computational time (s) for the diagonalization part per MD step. The number of atoms in the core region is 113. The set of numbers in the parentheses means the percentage of the dimension of the subspaces $W$ and $V$ relative to the total number of basis functions in the truncated cluster, respectively.}
\end{figure}
the truncated cluster, respectively. In spite of the considerable reduction of the spanned space, the method gives the same result as that of the DC method, which clearly shows rapid convergence of the proposed method based on the Krylov subspace. The difference between the proposed and recursion methods in the computational time is attributed to the regeneration of the Krylov subspace and the evaluation of Eq. (2) in the recursion method.

To compare the numerical stability, the SCF convergence is shown in Fig. 2 for the conventional band and four linear scaling methods for fcc aluminum. The residual norm of charge density by the band, proposed, and DC methods quickly decreases, while the convergent result is hardly obtained in the proposed method with the regeneration of the Krylov subspace and the recursion method. The comparison between the proposed method and its variant with the regeneration of the Krylov subspace suggests a reason why the recursion method tends to suffer from the numerical instability. The regeneration of the Krylov subspace makes the spanned subspace fluctuate, which means that an eigenvalue problem defined by a different subspace is solved at every SCF step. This fluctuation of the spanned space causes the difficulty in obtaining the SCF convergence for the recursion method. On the other hand, in the proposed method without the regeneration of the Krylov subspace the difficulty is avoided since the spanned space is fixed during the SCF calculation.

In Fig. 3 the absolute error in the total energy calculated by the proposed and DC methods are shown for a wide variety of materials. Several trends in the convergence properties can be found in this comparison. It is obvious that the large truncated cluster is required to satisfy the milli-Hartree accuracy for simple metals such as aluminum and lithium (see also Fig. 1). However, a relatively smaller dimension of the Krylov subspace is enough for the convergence. For the B32-LiAl alloy and the transition metal Fe, the relative dimension of the Krylov subspace required for the convergence increases compared to that for the simple metals. For systems with a finite gap, the total energy converges to the milli-Hartree accuracy even in a small truncated cluster especially for DNA with a periodic double helix structure (650 atoms/unit) consisting of cytosines and guanines, while the dimension of the Krylov subspace for the convergence is comparable to that of the original space defined by the truncated cluster. Therefore, in comparison with the DC method, the proposed method is more efficient especially for metallic systems, and that the efficiency becomes comparable as the covalency and ionicity in the electronic structure increase. The crossing point between the proposed and conventional methods in the computational time is estimated to be about 800 atoms for silicon bulk on the serial computation, while it varies depending on the system and calculation conditions. It is also interesting that the convergence rate with respect to the Krylov subspace dimension depends on the choice of |$V_0$|. For metals and insulators, we find that an optimum choice for |$V_0$| is a set of the basis functions in the central atom and the central atom plus the neighboring atoms, respectively, which may be related to different convergence properties of constituents such as itinerant, $\sigma$, and $\pi$ electrons in the electronic structures [12].

As an illustration of the proposed method, we present a large scale calculation for a truncated octahedral palladium cluster with a single iron impurity, FePd$_{80}$[12]. In the linear scaling calculation the truncated cluster is constructed by atoms within a sphere with a radius of 9.2 Å,
along [100]- and [111]-axes. The total magnetic moment of the cluster is 3.44 (μB). The calculation was performed using six nodes (16 CPUs/node) of a SR11K machine.

and for example in fcc Pd the core and buffer regions contain 55 and 170 atoms under this condition, respectively. The dimension of the Krylov subspace W is 600, and the value corresponds to about 30% of the total number of basis functions in the truncated cluster for fcc Pd. The exact inverse of the local overlap matrix is used for Q. The calculation condition gives 0.00217 and 0.00012 (Hartree/atom) as the absolute error in the total energy for fcc Pd and bcc Fe, respectively, compared to the conventional band calculations.

In summary, an efficient and robust linear scaling method has been developed for a wide variety of materials including metals. Based on the Krylov subspace an embedded cluster problem is solved with an effective Hamiltonian consisting of the detailed short range and the effective long range contributions. The method is regarded as a unified approach connecting the DC and recursion methods, and enables us to obtain convergent results with the milli-Hartree accuracy for a wide variety of materials. The application to a palladium cluster with a single iron impurity clearly shows that the method is a promising approach for realization of linear scaling ab initio calculations for metals.

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FIG. 4: Magnetic moment of Pd atoms in a cluster, Fe8-Pd806, with a central iron impurity as a function of the layer number along [100]- and [111]-axes. The total magnetic moment of the cluster is 3.44 (μB). The calculation was performed using six nodes (16 CPUs/node) of a SR11K machine.