Large scale electronic structure calculations using the Lanczos method

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Abstract

The orthogonality requirement in either iterative diagonalization or conjugate gradient approaches to the single particle Schrödinger equation $\hat{H}\psi = E\psi$ leads to an overall $N^3$ scaling of the effort with the number $N$ of atoms. We show that the Lanczos method circumvents this problem even when applied to all occupied states. Our implementation shows that the method is stable, exact, scales as $N^2$ for $N$ around a few hundreds, and is thus optimally suited for such mid-size (100 – 1000 atoms) quantum systems. The analogy between the basic Lanczos equations and Anderson’s localization in a disordered one-dimensional tight-binding chain is pointed out and used to gain some insights into improved convergence and stability of the method. For a 900-atom Si cluster tested here using pseudopotentials and a plane wave basis, the Lanczos method is about an order of magnitude faster than the state-of-the-art preconditioned conjugate gradient method using the same pseudopotentials and basis set.

1. Introduction

While recent developments in computational strategies [1] enable first principles electronic structure calculations for systems with up to 100 atoms, rapid experimental advances are constantly shifting interest to quantum systems with an ever increasing number of atoms. Examples include the $\geq$ 1000-atom quantum dot and quantum wire structures [2], as well as superlattices and quantum wells [3]. The effort in state-of-the-art $\hat{H}\psi = E\psi$ electronic structure algorithms scales as $N^3$, where $N$ is the number of atoms in the system. Recently [4], we have demonstrated that one could find exact eigenfunctions of $\hat{H}\psi = E\psi$ in a desired “energy window” (e.g., $E$ around the band gap of insulators and semiconductors) in a linear-in-$N$ scaling. This is very useful for energy level calculations of large quantum systems [5], but not for total energy calculations that require all occupied eigensolutions. Although there are several promising proposals for total-energy electronic structure method with a linear-in-size ($N$) scaling of the effort [6-10], these are still in their formative stages and the cross-over size of their cost with respect to the conventional ($N^3$-scaling) methods is yet unknown. Here we present a method for finding all exact occupied eigenstates of a given Schrödinger equation based on the Lanczos algorithm [11]. The effort scales as $N^2$ for $N$ around a few hundreds of atoms (basis set size around 30 000) and is an order of magnitude faster than the state-of-the-art preconditioned conjugate gradient method [1]. Although for large $N$ (perhaps > 1000), the Lanczos method could be less effective than the currently proposed [6–10] linear scaling meth-
ods, our proposed method appears competitive for mid-range system sizes (100–1000 atoms). Using this method, a plane-wave calculation for a Si$_{617}$H$_{316}$ cluster (having 1392 occupied states and 30 000 basis functions) takes 2.5 Cray-YMP cpu hours for a given total potential $V(r)$, while our implementation of the preconditioned conjugate gradient is estimated to take 23 cpu hours for the same problem. Thus, the present method makes electronic structure calculations of all occupied states of a few hundred to one thousand atom quantum systems affordable.

We use the Kohn–Sham formalism [12] in which the total energy of a system with external potential $V_{\text{ext}}(r)$ (e.g. the ionic potential) is:

$$E_{\text{tot}} = \begin{aligned} &\sum_{\text{occupied}} \left[ -\frac{\hbar^2}{2m} \right] \int \psi_i \nabla^2 \psi_i \, d^3r \\
+ &\int V_{\text{ext}}(r) \rho(r) \, d^3r \\
+ &\frac{e^2}{2} \int \frac{\rho(r) \rho(r')}{|r-r'|} \, d^3r d^3r' \\
+ &E_{\text{xc}}[\rho(r)] + E_{\text{ion}}[\{R_{\text{atom}}\}] \end{aligned}$$

(1)

where $E_{\text{ion}}$ is the ion–ion Coulomb repulsion energy of the atomic configuration $\{R_{\text{atom}}\}$, $E_{\text{xc}}[\rho(r)]$ is the total exchange and correlation energy of the electronic charge density $\rho(r)$ given by the occupied single-particle wavefunctions $\psi_i(r)$:

$$\rho(r) = \sum_{\text{occupied}} |\psi_i(r)|^2.$$  

(2)

The wavefunctions can be obtained from the single particle self-consistent Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_i(r) = E_i \psi_i(r),$$

(3)

where $V(r)$ is the self-consistently determined total potential:

$$V(r) = V_{\text{ext}}(r) + \frac{e^2}{2} \int \frac{\rho(r')}{|r-r'|} \, d^3r' + \frac{\delta E_{\text{xc}}[\rho(r)]}{\delta \rho(r)}.$$

The preconditioned conjugate gradient (PCG) method is an effective method for solving Eqs. (3) and (4). Since however, the PCG method requires performing orthogonalization (a $N^3$ operation), it is limited to systems with fewer than about 100 atoms. Here, we concentrate on solving Eq. (3) for a given $V(r)$. Self-consistency can be subsequently obtained by repeating this step and generating $V(r)$ from Eq. (4) using the solutions $\{\psi_i(r)\}$ of Eq. (3).

We expand $\psi$ in a plane wave basis:

$$\psi_i(r) = \sum_G a_i(G)e^{-iG\cdot r},$$

(5)

where $G$ is the reciprocal lattice vector of the system and $a_i(G)$ are the expansion coefficients to be determined. Then, for a given $V(r)$, Eq. (3) is a linear equation of the variables $a_i(G)$, where its dimension is the number of reciprocal lattice vector $\{G\}$; for the largest systems studied here, this is $\sim$30 000. In what follows we will assume that one can compute efficiently the matrix-by-vector product $H\psi_i$ [e.g. using fast Fourier transform (FFT)], so individual matrix elements $H_{G_1,G_2} = \langle \exp(-iG_1\cdot r) \rangle H \langle \exp(-iG_2\cdot r) \rangle$ need not be computed. [Using the FFT, a single multiplication $H\psi_i$ scales as $N \ln(N)$, so it is much faster than explicit matrix multiplication using the matrix elements $H_{G_1,G_2}$.]

It has been previously suggested [13,14] that the Lanczos algorithm could be an efficient way to solve for the eigenstates of large linear systems. However, although the Lanczos method has been recently used to calculate some ($\sim 30$) of the lowest eigenstates of large systems [15], total energy Lanczos calculations (requiring all occupied eigenstates) have apparently not been widely used. Indeed, the alleged instability of the basic Lanczos scheme [11] and the success of iterative diagonalization [16] and the conjugate gradient method [17] in electronic structure calculations seem to have discouraged testing of the Lanczos method for large scale total energy calculations. To examine these paradigms, we will first introduce the Lanczos method and discuss the “Lanczos phenomena”. This analysis (described in section 2) and the unexpected anal-
ogy between Lanczos convergence and the Anderson localization problem then suggest a particular implementation of the Lanczos approach, discussed in section 3. Section 4 describes applications to Si quantum dots and section 5 compares the method to the preconditioned conjugate gradient method, while section 6 provides a summary.

It is useful to illustrate some of the Lanczos phenomena on a concrete system. In what follows, we will use large Si quantum dots as examples. Here, the total potential \( V(r) \) will be taken as a superposition
\[
V(r) = \sum_{\text{atom}} \mathbf{V}_{\text{atom}}(r - \mathbf{R}_{\text{atom}})
\]
of spherically symmetric empirical pseudopotentials \( \mathbf{V}_{\text{atom}}(r) \) [5]. Our basic algorithm does not depend on this choice. The Si atoms have a bulk-like configuration and are arranged in a shape of a rectangular box; all surface dangling bonds are saturated by hydrogen atoms. We consider four quantum boxes: Si\(_{47}\)H\(_{52}\), Si\(_{47}\)H\(_{116}\), Si\(_{32}\)H\(_{204}\) and Si\(_{61}\)H\(_{116}\). We use a plane wave basis (Eq. (5)) with 5520, 11 012, 18 794 and 29 982 orbitals for the four clusters, respectively. We apply periodic boundary conditions on each unit cell that contains the quantum structure surrounded by vacuum. The action of \( \hat{H} \) on \( \psi \) is executed using FFT’s with a real-space grid of up to 54 x 54 x 80. Figures 1–5 illustrate various “Lanczos phenomena”, to be discussed below, on the Si\(_{47}\)H\(_{52}\) quantum dot.

2. Lanczos method and Lanczos phenomena

The Lanczos method [11,13,14] starts with a random wavefunction \( \psi_1 \), then iteratively generates “Lanczos vectors” \( \{ \psi_i \} \) from
\[
\beta_{i+1} \psi_{i+1} = \hat{H} \psi_i - \alpha_i \psi_{i-1} - \beta_i \psi_i
\]
where \( \hat{H} = -\hbar^2/2m \nabla^2 + V(r) \) is the Hamiltonian of the system (Eq. (3)), \( \alpha_i \) is given by \( < \psi_i | \hat{H} | \psi_i > \) and \( \beta_{i+1} \) is determined by the normalization condition \( < \psi_{i+1} | \psi_{i+1} > = 1 \). At the start of the iterations, we have \( \beta_1 = 0 \). Using induction, it is easy to show from Eq. (6) that, for the exact (e) Lanczos algorithm, \( \psi_i \) is orthogonal to all previous Lanczos vectors, i.e:
\[
< \psi_i^\dagger | \psi_j^\dagger > = \delta_{i,j}.
\]

Thus, the exact \( \psi_i \) represents an orthonormal basis which tridiagonalizes (Eq. (6)) the original Hamiltonian \( \hat{H} \). The element of this matrix \( H^T_i \) are defined by \( < \psi_i^\dagger \hat{H} | \psi_j^\dagger > \). However, if we only have \( \psi_i \) with a finite precision, \( H^T \) can be defined by Eq. (6) and written as:
\[
H^T = \begin{pmatrix}
\alpha_1 & \beta_2 & \beta_3 & \cdots & \beta_M \\
\beta_2 & \alpha_2 & \beta_3 & \cdots & \beta_M \\
\beta_3 & \alpha_3 & \ddots & \vdots & \vdots \\
\vdots & \vdots & \ddots & \alpha_M & \cdots \\
\beta_M & \beta_M & \cdots & \cdots & \alpha_M
\end{pmatrix}
\]

All eigenvalues \( \{ E_i \} \) of this tridiagonal matrix can be obtained by standard techniques [14,18] with an effort proportional to \( O(M) \), where \( M \) is the dimension of \( H^T \). Then, the individual eigenfunctions \( \{ b_i \} \) of \( H \) can be calculated using “inverse iteration” [14] of \( H^T \) around the energy \( E_i \). This is a very fast, \( O(M) \) operation for each eigenfunction \( \{ b_i \} \). Finally, the eigenfunctions of \( \hat{H} \) can be constructed from the eigenfunction of \( H^T \) as
\[
\psi_i(r) = \sum_{i}^M b_i^\dagger \psi_i(r).
\]

The above arguments are valid only for the exact Lanczos algorithm, i.e., when there are no round off errors in the numerical implementation. In practice, round off errors always exist, so some of the above equations, especially the orthogonality condition of Eq. (7), are not satisfied. In the following, we will discuss some properties of the finite precision Lanczos algorithm. These properties are referred to as “Lanczos phenomena”. We will identify here a number of problems with the Lanczos method. Cures will then be offered in our algorithm described in section 3.

2.1. Amplification of end-of-spectrum states

As the number of Lanczos iterations \( M \) increases, the eigenstates at the two ends of the
spectrum ("end-of-spectrum states") are the first to converge. This is because there is a hidden driving mechanism which amplifies the amplitudes of the end-of-spectrum states. To see this effect, let's first write $u_i$ and $u_{i+1}$ as sums of the eigenstates of $H$, i.e., $u_i = \sum_l c_l^i \psi_l$ and $u_{i+1} = \sum_l c_l^{i+1} \psi_l$. Substituting these into the Lanczos iterative equation (6), we have:

$$c_l^{i+1} = \frac{1}{\beta_{i+1}} \left[ (E_l - E_i) - \beta_i \right] c_l^i,$$

(10)

where, $E = \sum_l E_l c_l^i$ is the average eigenvalue of $u_i$. So if at the beginning of the iterative sequence, all $c_l^i$ have the same order of magnitude, then $(E_l - E_i)$ will have the largest value for the end-of-spectrum states $l$. Thus, the amplitude $c_l^i$ of these states will increase exponentially as a function of iteration history $i$, until they are large enough to begin to change $E_l$. After this, their amplitudes will decrease because the factor $(E_l - E_i)$ becomes small for these $l$. In this discussion, we have ignored the effect of the $\beta_i$ term in Eq. (10). But this term will not change the qualitative picture. This is confirmed in Fig. 1, which depicts the amplitude of the $\psi_l(r)$ component in $u_i(r)$ vs the iteration index $i$. We see that first $< \psi_l | u_i >$ increases exponentially as a function of $i$ and subsequently it decays. Because these end-of-spectrum $\psi_l$'s appear in $u_i$ with large amplitudes, we can expect that $\psi_l$ can be accurately represented by some linear combinations of $u_l$. In other words, these $\psi_l$'s have converged.

2.2. Loss of orthogonality among $\{u_i\}$

Because of the mechanism discussed in section 2.1 and because of numerical round off errors, the orthogonality condition (7) does not hold in actual finite-precision computations. The exact Lanczos algorithm constrains the process, so the previous $(j < i)$ $u_j$ will not have any components in the newly generated $u_i$. However, in finite precision calculations, there is always a small, but finite admixture of $u_j$ into $u_i$. This admixture will be amplified exponentially by the driving mechanism described in section 2.1, and will eventually lead to the violation of the orthogonality (Eq. (7)). This violation of the orthogonality is illustrated in Fig. 2, which depicts $< u_l | u_i >$ versus $i$. After $i > 180$, this overlap becomes large. This loss of orthogonality seems to have led to the belief [11] that the Lanczos algorithm breaks down unless one explicitly reorthogonalizes $u_i$ to all the previous $u_j$'s, (a rather expensive operation). However, as will be shown in section 2.3 below, the Lanczos algorithm without explicit reorthogonalization does work despite of the failure of Eq. (7).

2.3. Loss of orthogonality does not prevent finding accurate eigenstates

Let us just ignore for a moment the failure of Eq. (7) and go ahead and diagonalize the tridiagonal matrix $H^T$ of Eq. (8), finding its eigenstates $\{b_i^l\}$. Then, $\{b_i^l\}$ satisfies:

$$\beta_i b_{i-1}^l + \alpha_i b_i^l + \beta_{i+1} b_{i+1}^l = E_i b_i^l$$

for $1 < i < M$

and

$$\beta_M b_{M-1}^l + \alpha_M b_M^l = E_M b_M^l.$$

(11)

Now, using these coefficient $\{b_i^l\}$ to construct from Eq. (9) the wavefunction $\psi_i(r)$, and applying $H$ to this $\psi_i(r)$ using Eqs. (6) and (11), we find

$$H \psi_i = E_i \psi_i + \beta_{M+1} b_M u_{M+1}.$$

(12)

We see that if $b_M$ is very small, $\psi_i$ is a numerically accurate eigenstate of $H$. Equation (12) does not depend on the orthogonality condition of Eq. (7). If we had an orthogonal basis $\{u_i\}$, then a normalized $\{b_i^l\}$ would have guaranteed a normalized $\psi_i$. Thus, the loss of orthogonality means that $\psi_i$ is no longer normalized. However, as long as the norm of $\psi_i$ is much larger than $b_M$, this is not a real problem (since then the second term in Eq. (12) can be ignored). Thus, as will be demonstrated in our later numerical tests, accurate eigenstates of the original Hamiltonian $H$ can be obtained from Eq. (9). The reason for the smallness of $b_M$ is discussed next.
Fig. 1. The amplitude of the end-of-spectrum states $\psi_i(r)$ in the Lanczos wavefunction $u_i(r)$. The amplitude increases from $i = 1$ to $i = 25$, then it decreases from $i = 25$ to $i = 50$. At $i = 100$, $\psi_i(r)$ is converged. The next and other peaks are duplicates of $\psi_i(r)$ discussed in section 2.5. These are also indications of the failure of orthogonality among the different $u_i(r)$. The system studied is Si$_{47}$H$_{52}$.

Fig. 2. The overlap coefficient $\langle u_1(r)|u_i(r)\rangle$. Note how $u_i(r)$ loses its orthogonality (i.e., nonzero overlap) with $u_1(r)$ after about $i = 200$ iterations. Note also that the first peak (indicated by an arrow at $i = 180$) is caused by the first duplicate of $\psi_1(r)$, shown in Fig. 1 ($i = 180$). The system studied is Si$_{47}$H$_{52}$. 
2.4. **Anderson localization in $b_i$ is the reason for the convergence of $\psi_l$**

To understand why $b_M$ can be so small, consider Eq. (11). Notice that this equation is isomorphic with the linear chain tight binding equation [19,20] for the eigenfunction $\{b'_i\}$. In the linear chain problem one considers a single orbital per atom, where $i$ is the atomic position and $\alpha_i$ and $\beta_i$ are, respectively, the diagonal ("on-site") and the off-diagonal nearest neighbor "hopping" Hamiltonian matrix element. Thus, the Lanczos iteration index $i=1,...,M$ is analogous to atomic positions in a chain and the Lanczos coefficients $\alpha$ and $\beta$ are analogous to tight-binding matrix elements. Fig. 3 shows the value of $\alpha_i$ and $\beta_i$ calculated from the Lanczos procedure of Eq. (6) for our test system $\text{Si}_{47}\text{H}_{52}$. We see that there are significant random fluctuations in the Lanczos value of $\alpha_i$ and $\beta_i$ as a function of the iteration index $i$. Thus, Eq. (11) represents a random one-dimensional tight-binding system. For such a system, it is well known that all eigenstates are localized with exponentially decaying tails ("Anderson localizations") [19]. The decay length is determined by the magnitude of the randomness: the larger the randomness, the smaller the decay length, (and thus the faster the Lanczos convergence rate of the corresponding eigenstates). If site $i$ on which localization occurs is far from site $M$, then $b'_M$ will be small and $\psi_l$ will be well converged. The coefficients $\{b'_i\}$ of typical converged eigenstates $\psi_l$ ($l = 1$ and $l = 10$) are shown in Fig. 4. The localizations and the tails of $\{b'_i\}$ are clearly seen. Because of the mechanism discussed in section 2.1, the localization site of the end-of-spectrum states always occurs at small position index $i$. Thus, these states will be converged even for small $M$. In practice, soon after $M$ passes the localization site $i$ of $\{b'_i\}$, the wavefunction $\psi_l$ and its eigenvalue $E_l$ will converge. On the other hand, for a given $M$, there are eigenstates of Eq. (11) which have a
Fig. 4. The expansion coefficients \{b_i\} of the basis \{u_i(r)\} [Eq. (9)], for (a) \psi_i(r), and (b) \psi_{10}(r). The dimension of the tridiagonal matrix $H^T$ used to calculate \{b_i\} is $M = 1000$. The localization of \{b_i\} is apparent from the exponential decay (straight line for $\ln(b_i)$) around the localization sites (the peak positions of $\ln(b_i)$). Note that \{b_i\} has a much shorter decay length than \{b_i^{10}\}. The multiple peaks are a result of the coupling between the duplicates of \psi_i(r). Because the last duplicate (centered around $i = 1000$) for \{b_i^{10}\} has not been fully converged, there is no coupling to this state. Thus, this emerging (yet unconverged) duplicate does not spoil the convergence of the previously converged duplicates. The system studied is Si$_{47}$H$_{52}$.

Localization site $i$ close to $M$, so these eigenstates have large $b_{M}^i$ value. These eigenstates are not well converged and their eigenvalues are scattered throughout the spectrum. However, because of their large $b_{M}^i$ value, their eigenvalues are very sensitive to a change in $M$. Thus, their eigenvalues will change as we replace $M$ by, e.g. $M - 1$. This is useful as a criterion to identify these spurious states. [The absolute amplitude of $b_{M}^i$ is not used to judge the convergence, because the normalization of $\psi_i$ constructed from Eq. (9) can be very different from unity.]

2.5. The occurrence of eigenvalue duplicates

Another consequence of the "driving mechanism" (section 2.2) and the lose of orthogonality (section 2.2), is that the Lanczos procedure will produce many duplicates of a single eigenstate. In the language of the one-dimensional random system, one can say that there are many localized states with degenerate eigenvalues. The occurrence of duplicates is illustrated in Fig. 1 and Fig. 4. Note that $b_i^l$ in Fig. 4 decays to machine precision $\epsilon$ ($= 10^{-13}$) before it increases again to generate the next duplicate. The duplicates are generated at almost equal intervals $d_l$ determined by:

$$d_l \equiv -2\lambda_l \ln \epsilon,$$

where $\lambda_l$ is the decay length of state $\{b_i^l\}$. From Anderson's model [19], we know that $\lambda_l$ depends on the magnitude of the randomness of $\alpha_i, \beta_i$ and the eigenvalue $E_l$. The smaller $E_l$, the
shorter is $\lambda_i$, thus the more often it repeats itself. This is confirmed in Fig. 4 by the much shorter decay length of $\{b_i^\dagger\}$ relative to that of $\{b_i^{10}\}$.

In actual calculation, the duplicate states can be easily recognized by noting their nearly identical eigenvalues. Thus, only a single $\{b_i^\dagger\}$ and $\psi_i$ will be calculated from these identical eigenvalues. However, if the original Hamiltonian $H$ supports truly degenerated states, this procedure will clearly miss one partner of a degenerate set. This problem will be solved in our algorithm (see below) by restarting the Lanczos iteration several times with different starting random wavefunctions $u_1$.

A related concern is whether a yet un converged duplicate of $E_i$ which is just emerging, (i.e. the localization site of this new duplicate is very close to $M$), could spoil the convergence of the previously converged states of $E_i$. Considering the picture of a one-dimensional random system and actual numerical tests, we find that the already converged eigenvalue $E_i$ will not be shifted by the newly emerging duplicate. Furthermore, the amplitude $\{b_i^\dagger\}$ of the newly emerging state can be coupled to the previously converged states only after the new state has been fully converged. This is illustrated in Fig. 4(b).

Another concern is that with all converged states generating their duplicates at a rate given by Eq. (13), could it be that after a while, the procedure will produce only duplicates of old states rather than new states. Fortunately, this does not happen, as illustrated in Fig. 5. We see that, while the duplicates can account for more than half of the total number of converged eigenstates, the number of unique converged states (without counting the duplicates) increases steadily almost as a linear function of the number $M$ of Lanczos iterations. In the example shown in Fig. 5, there are two slopes: a larger slope for the states below the energy gap in the spectrum (i.e., the band gap of Si$_{47}$H$_{52}$), and a smaller slope for the higher energy states. Of course, after all the eigenstates of the original Hamiltonian have been generated, further iterations can only produce duplicates.

Finally, the ultimate test of accuracy and convergence of an eigenstate $\psi_i$ is to apply on it the original Hamiltonian $H$ and examine the ful-

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**Fig. 5.** The Number of converged eigenvalues as functions of the Lanczos iteration index $i$. Since this system has 120 occupied states, most of the occupied states should have already converged around $i \sim 1000$. The system studied is Si$_{47}$H$_{52}$. 
fillment of the Schrödinger equation (3). This check will be used in our following algorithm.

3. The algorithm for electronic structure calculations

Based on our analysis of the Lanczos phenomena described in the previous section, we next present our Lanczos scheme for calculating all the occupied eigenstates \( \{ \psi_i(r) \} \) of Schrödinger equation (3). This algorithm will cure most problems identified in section 2. The algorithm is summarized in Fig. 6, and explained step by step in what follows.

**Step (i):** Start with a randomly selected wavefunction \( \psi_1(r) \) (constructed from choosing random coefficients of a given basis), and generate the Lanczos wavefunction \( \psi_i(r) \) according to Eq. (6), without any reorthogonalization among the members of \( \{ \psi_i(r) \} \). If this is the first sweep of steps (i)–(vi) \( (N_{\text{sweep}} = 1) \), skip the following. If this is not the first sweep — so there are \( N_{\text{tot}} \) converged eigenstates \( \{ \psi_i(r) \} \) from previous sweeps — then orthogonalize each \( \psi_i(r) \) to all \( \{ \psi_1(r) \} \) by subtracting the component of each \( \psi_i(r) \) from \( \psi_1(r) \), i.e. \( \psi_i(r) - \sum_j <\psi_j | \psi_i> \psi_j \).

If disk space allows, store all generated \( \{ \psi_i \} \) on disk for later use. If not, discard the old \( \psi_i \).

**Step (ii):** At some Lanczos iteration \( i = N_t \) (e.g. every 50 or more Lanczos steps), diagonalize the tridiagonal Lanczos matrix \( H_T \) of Eq. (8) using standard programs (e.g. the LAPACK routines) and obtain the eigenvalues \( \{ E_i(N_t) \} \) without calculating the eigenvectors. Next, reduce the dimension of \( H_T \) by one and repeat the diagonalization of \( H_T \), finding the set \( \{ E_i(N_t - 1) \} \). Compare \( \{ E_i(N_t) \} \) with \( \{ E_i(N_t - 1) \} \), keeping the eigenvalues that have changed by less than \( \epsilon_i \), where \( \epsilon_i \) is a desired convergence criterion (e.g. \( 1 \times 10^{-6} \) Hartree). For eigenvalues that are degenerated within \( \epsilon_i \), keep only a single copy. Denote these eigenvalues as \( \{ E_i^c(N_t) \} \). Then calculate the number \( N_c(N_t) \) of \( E_i^c(N_t) \)'s which are below the Fermi energy, (the latter can be obtained for insulator from calculations on a small system). If \( N_c(N_t) \) is larger than a desired percentage (e.g. 98%) of the total number \( N_{\text{occ}} \) of occupied states, then go to step (iii). If not, continue step (i).

**Step (iii):** Using \( \{ E_i^c(N_t) \} \) as the input energies, and applying the inverse iteration method to the tridiagonal matrix \( H_T \) (using standard programs, e.g. the LAPACK routine), calculate \( N_c(N_t) \) eigenfunctions of \( H_T \), \( \{ b_i^c \} \) in the basis of the Lanczos vector \( \{ u_i(r) \} \). As can be seen

![Fig. 6. Flow chart describing the Lanczos procedure for large scale electronic structure calculation. See section 3 for details.](image-url)
from Fig. 4, most of the eigenstates have been converged far before \( N_t \) is reached, so for each \( E_t \), it is worth doing a few (5 to 10) inverse iterations for different matrix dimensions \( M (< N_t) \), and examining whether the eigenvalue that resulted from the inverse iteration has changed from \( E_t(N_t) \) (within a tolerance limit \( \epsilon_t \), which can be much smaller than \( \epsilon_t \) and close to the machine precision). Choose the smallest \( M \) for which \( E_t \) does not change beyond \( \epsilon_t \), and denote this as \( M_t \). Then, \( \{ b_{il} \} \) (which has \( M_t \) terms \( i \)) are the coefficients based on the \( M_t \)-dimensioned matrix \( H^T \).

**Step (iv):** generate \( \psi_t \) from \( \{ b_{il} \} \) and \( \{ u_i \} \). If \( \{ u_i \} \) is stored on disk, retrieve \( \{ u_i \} \) from disk. If it is not, recalculate \( \{ u_i \} \) exactly as in step (i). While \( u_i \) are retrieved or recalculated one by one, construct the \( N_c(N_t) \) \( \psi_i(r) \)'s from Eq. (9) and from the \( \{ b_{il} \} \) and \( M_t \) obtained in step (iii). Because of the nonorthogonality of \( \{ u_i \} \), the \( \psi_i(r) \) from Eq. (9) is not normalized. So, at the end this step, normalize all \( \psi_i(r) \)'s.

**Step (v):** check the accuracy of the \( N_c(N_t) \) \( \psi_i \)'s generated in step (iv) by evaluating the error

\[
\delta_i \equiv \| \psi_i(H - E_t)^2 | \psi_i > |^{1/2}.
\]

If \( \delta_i < \epsilon_t \), accept \( \psi_i \), else, discard it. If there are two eigenstates whose \( E_t \)'s are within the order of their \( \delta_i \)'s, then orthogonalize them using the Gram–Schmidt scheme [18]. The error of the resulting wavefunction then needs to be checked again. Upon completion of step (v), we will have \( N_c(N_{\text{sweep}}) \) newly converged eigenstates. This brings the total number of converged eigenstates to \( N_c(N_{\text{sweep}}) = N_c(N_{\text{sweep}} - 1) + N_c(N_{\text{sweep}}) \).

**Step (vi):** if \( N_c(N_{\text{sweep}}) \) is less than \( N_{\text{occ}} \), go to step (i) and begin another sweep \( N_{\text{sweep}} = N_{\text{sweep}} + 1 \). If \( N_c(N_{\text{sweep}}) \) equals \( N_{\text{occ}} \), stop.

We close this section by a number of comments on the algorithm:

1. More recent sweeps \( (N_{\text{sweep}} > 1) \) operate similarly as the first sweep, except that the already converged states \( \psi_t \) have been removed from the spectrum of their effective Hamiltonian \( H^T \). As a result, the Lanczos iteration of later sweeps have a faster convergence than that of the first sweep. Typically, one needs three or four sweeps to get all the occupied eigenstates. The number of Lanczos iterations and the number of converged eigenstates generated at each sweep decay as a geometrical series.

2. The Lanczos procedure described here is stable. It guarantees that each converged eigenstate \( \psi_t \) is accurate to within a given tolerance \( \epsilon_t \). Since we use consecutive sweeps (steps (i)–(vi)), the procedure also guarantees that all occupied eigenstates (irrespective to whether they are degenerate or not) are found. (An eigenstate missed from the first sweep can be found in subsequent sweeps.)

3. All eigenstates are mutually orthogonal simply because they are found to be numerically accurate eigenstates of the hermitian Hamiltonian \( \hat{H} \). Possible nonorthogonality among degenerate, or nearly degenerate states is avoid by explicit orthogonalizations in steps (i) and (v).

4. The procedure works optimally for systems without explicit symmetry, thus without too many degenerated states. Otherwise, the first sweep cannot generate the majority of the eigenstates, and the procedure will be slow. One obvious solution for systems with explicit symmetry is to use group theory to break the original Hamiltonian \( \hat{H} \) into several blocks, and then apply the current procedure to diagonalize each block. Another solution is to apply, at the end of step (v), the symmetry operations on each newly converged eigenstate \( \psi_t \), to see whether it can generate new (but energy degenerate) states. If it can, add them as converged eigenstates.

5. For a typical nonsymmetric system, we find in our numerical tests that the first sweep can generates more than 90% of the total number of occupied eigenstates. Thus, the total number of Lanczos iterations in subsequent sweeps (which need explicit orthogonalization to the previously converged eigenstates \( \psi_t \)) is about 1/10 of the number of Lanczos iterations in the first sweep. Thus, practically speaking, the whole procedure can be considered as a Lanczos scheme without reorthogonalization.

### 4. Applications to Si quantum dots

We now apply the above Lanczos scheme to Si quantum dots described at the end of the In-
The quantum dots studied here have approximate rectangular shapes, and all surface dangling bonds are passivated by hydrogen atoms. The symmetry of the pure Si skeleton is destroyed by the tilting of the surface H atoms. The pseudopotentials used for Si and H were given in ref. [5]. We use $\epsilon_i = 1 \times 10^{-6}$ Hartree as our convergence criterion. We do not store on disk the Lanczos wavefunctions $u_i$ in step (i), but regenerated them in step (iv). The charge density contour plot of the Si$_{617}$H$_{316}$ system calculated by the current method is shown in Figs. 7 and 8 in two different planes. Hydrogen atoms are evident at the periphery of the cluster. In Fig. 7 [(110) plane] we see clearly the Si–Si bonds. Figs. 7 and 8 also demonstrate that the charge density of the interior atoms is very close to that of bulk Si. At the surface, we find charge transfer that leads to the formation of strong Si–H bonds.

The time consumed by the different parts of the algorithm is given in Table 1 for the four systems considered here. For the Si$_{617}$H$_{316}$ system, this method takes about 2.5 Cray YMP cpu hours to calculate all 1392 occupied states. For this system, 41% of the time is spent on generating the Lanczos wavefunction $u_i$. This is a $N^2$ operation, where $N$ is the size of the system. Thus, if $\{u_i(r)\}$ are stored on disk in step (i) instead of being regenerated in step (iv), 20% of the total time can be saved. About 28% of the time is spent on the constructing $\psi_i(r)$ using Eq. (9) and 20% of the time is spent on orthogonalizing $u_i(r)$ to previously converged $\psi_i(r)$ during the Lanczos iteration of $N_{\text{sweep}} > 1$. Both of these terms scale as $N^3$. About 9% of the time is spent on using standard Lapack routines to diagonalize the tridiagonal matrix $H^T$ and solve its inverse iteration. This corresponds roughly to a $N^2$ scaling. The remaining 2% of the time accounts for all other operations. The whole procedure scales between $N^2$ and $N^3$, as shown in
Table 1
Time analysis (in Cray YMP cpu seconds) of the Lanczos method. "cpu for constructing $\psi_I"$ denotes the time consumed by constructing $\psi_I$ using Eq. (9) in step (iv). "cpu for orth." denotes the time consumed by making the $u_i$ orthogonal to the converged $\psi_I$ in the other-than-first sweeps. "cpu for diag. and inv. $H^T$" denotes the time used to get the eigenvalues of $H^T$ and to solve the inverse iteration to get the coefficients $\{b_i\}$.

<table>
<thead>
<tr>
<th></th>
<th>Si$<em>{47}$H$</em>{52}$</th>
<th>Si$<em>{147}$H$</em>{116}$</th>
<th>Si$<em>{329}$H$</em>{204}$</th>
<th>Si$<em>{617}$H$</em>{316}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>760</td>
<td>1392</td>
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<td>48 x 48 x 72</td>
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<td>33 Mb</td>
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<td>8986</td>
</tr>
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<td>300</td>
<td>1650</td>
<td>3686</td>
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<td>2521</td>
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<tr>
<td>cpu for orth.</td>
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<td>430</td>
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<tr>
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<td>807</td>
</tr>
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</tr>
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<td></td>
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<td></td>
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<tr>
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<td>661</td>
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<tr>
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<td>6</td>
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<td>86</td>
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<td></td>
<td>1</td>
<td>5</td>
<td>13</td>
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<tr>
<td>cpu of each sweep</td>
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<td>2161</td>
<td>6730</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>72</td>
<td>567</td>
<td>1975</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>26</td>
<td>76</td>
<td>281</td>
</tr>
</tbody>
</table>

Fig. 9. For smaller size systems, the $N^2$ scaling of calculating $H u_i$ dominates the computing time. At $N \approx 1000$ atoms we find a cross-over of the $N^2$ to the $N^3$ scaling. Thus this method works best for systems with 100–1000 atoms.

One practical limitation is the run time memory. This is caused by the need to store in memory all the converged eigenstates $\{\psi_I(r)\}$. This aspect is the same as the conventional method (e.g. conjugate gradient method). The coefficient $\{b_i\}$ (30% of $\{\psi_I(r)\}$, in terms of memory space) can be stored on disk without slowing down the speed of the calculation. The possibility of storing $\{\psi_I(r)\}$ on the disk depends on (i) how rapidly one can retrieve them from disk, and (ii) how accurate would the orthogonalization of $u_i(r)$ to $\{\psi_I(r)\}$ be if this is only enforced every few Lanczos steps. This is left for future testing when memory space is not enough for truly large system calculations. In our example involving the 1392 occupied states of the Si$_{617}$H$_{316}$ cluster, the memory needed is
To test whether this procedure is stable, we have repeated the calculation of the largest system \( \text{Si}_{617}\text{H}_{316} \) using different starting random wavefunctions \( u_1(r) \) in the Lanczos iteration (Eq. (6)). The two sets of the eigenvalues \( \{E_l\} \) show a one-to-one correspondence, so no eigenstate is missed. The largest difference between the two sets of eigenvalues is \( < 1 \times 10^{-10} \) Hartree. The mean square difference of the charge density \( \rho(r) \) (on real space grid \( r \)) of these two runs is 0.0001\%, indicating very accurate convergence. The sum of the eigenvalues (which is used for total energy calculations) differs by less than \( 1 \times 10^{-10} \) Hartree. For most purposes, this accuracy is (more than) sufficient. Although the least converged eigenstates has a convergence error \( \delta_t \) (defined in step (v)) close to \( \epsilon_t \), most eigenstates have much smaller convergence errors, i.e. close to machine precision. This and our numerical tests show that using a smaller \( \epsilon_t \) does not affect much the computing time. The orthogonalization among different eigenstates \( \psi_l \) was checked explicitly by calculating \( \langle \psi_l | \psi_{l'} \rangle \) for \( l \neq l' \). The largest value found for this overlap element is \( 3 \times 10^{-5} \) and occurs for the least converged eigenstates. For most states, however, this quantity is much smaller (i.e. close to the machine precision).

5. Comparisons with the preconditioned conjugate gradient method

We applied the preconditioned conjugate gradient (PCG) algorithm to the two smallest systems \( \text{Si}_{47}\text{H}_{52} \) and \( \text{Si}_{147}\text{H}_{116} \), using identical conditions and numerical techniques as in the Lanczos method for evaluation of the wavefunction \( \psi_l(r) \) and for its multiplication by the Hamiltonian \( \hat{H} \). Also, an identical convergence criterion \( \epsilon_t = 1 \times 10^{-6} \), is used in both methods. The resulting computing times are shown in Table 2. We found that the eigenvalues calculated by the PCG method exhibit a one-to-one correspondence to their Lanczos counterparts, to within the convergence limit of \( 1 \times 10^{-6} \) Hartree. The total charge density \( \rho(r) \) calculated by PCG is within 0.0001\% of the Lanczos results. For systems larger than \( \text{Si}_{147}\text{H}_{116} \), the computational times denoted by "E" in Table 2 have been estimated from the known scaling of the orthogonalization part \( (N^3 \text{ scaling}) \) and the \( H \psi(r) \) part \( (N^2 \text{ scaling}) \). It can be seen from Table 2 that for systems larger than \( \text{Si}_{47}\text{H}_{52} \) (the smallest considered), the computational time of PCG is dominated by the orthogonalization time. Thus, the cross-over size from \( N^2 \) to \( N^3 \) scaling for the PCG method is at \( N \approx 100 \) atoms, compared to the 1000 atom cross-over size for the Lanczos method (Table 1 and Fig. 9). Also, Table 2 shows that for the smallest and the largest system, respectively, the Lanczos method is faster than the PCG method by a factor of 4 and 9. This is also illustrated in Fig. 9.

To understand why the Lanczos method is faster than the PCG method, recall that the conjugate gradient method is related to Lanczos method by the fact that both explore the same subspace. So, if only one or a few lowest eigenfunctions are needed, the conjugate gradient method should be more efficient because the preconditioning technique can be applied to the conjugate gradient method but not to the Lanczos method. However, if many eigenstates are needed, as in our examples, then the PCG method is less effective since it searches for each eigenstates independently (except for the orthogonalizations). This is analogous to starting a new Lanczos iteration series for each eigenstates. A set of Lanczos wavefunction \( \{u_i(r)\} \) contain not only the informations of the lowest eigenstate \( \psi_1(r) \), but also for other higher energy eigenstates. So, using \( \{u_i(r)\} \) for just one eigenstate is not economical, compared with having a longer series of \( \{u_i(r)\} \) and diagonalizing \( H^T \) of Eq. (8) to get all the eigenstates at once. In our examples, to get \( N \) occupied eigenstates, we need approximately \( 10N \) Lanczos iterations for the two smallest systems. For the same system, using the PCG method with preconditioning, getting each eigenstates requires about 30 conjugate gradient steps (line minimizations). Furthermore, note that each conjugate gradient step is more expensive than a Lanczos iteration step. More importantly, because of the independence
Table 2
Time analysis of the preconditioned conjugate gradient (PCG) method and the Lanczos method. “total num. of PCG iter.” is the total number of PCG line minimization steps. We use $1 \times 10^{-6}$ Hartree as the convergence criterion. “cpu of $H\psi_i$” is the time of applying $H$ to the wavefunction $\psi_i$, which is a $N^2$ operation. This step also includes the time of other $N^2$ scaling operations (e.g. operations like: $\psi_i(r) = a\psi_i(r) + \beta \rho_i(r)$). “cpu of orth.” is the time of Gram-Schmidt’s explicit orthogonalization among $\{\psi_i\}$. This is a $N^3$ operation. Note that only the Si$_{47}$H$_{52}$ and Si$_{147}$H$_{116}$ quantum dots are actually calculated by the PCG method. The PCG computing times of other two systems indicated by “E” are estimated from their above noted scalings. All four quantum dots were actually calculated by the Lanczos method. All times are in Cray YMP cpu seconds.

<table>
<thead>
<tr>
<th></th>
<th>Si$<em>{47}$H$</em>{52}$</th>
<th>Si$<em>{147}$H$</em>{116}$</th>
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<th>Si$<em>{617}$H$</em>{316}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>total num. of PCG iter.</td>
<td>31</td>
<td>32</td>
<td>32 (E)</td>
<td>32 (E)</td>
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<td>total cpu time for LANCZOS</td>
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<td>471</td>
<td>2804 (E)</td>
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</tr>
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<td>1080</td>
<td>4900 (E)</td>
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<tr>
<td>cpu of orth. in PCG</td>
<td>95</td>
<td>1470</td>
<td>12900 (E)</td>
<td>69200 (E)</td>
</tr>
</tbody>
</table>

of the searches of different eigenstates in the conjugate gradient method, the wavefunctions do not share any information, so their mutual orthogonality is not guaranteed, and has to be enforced explicitly. As Table 2 shows, this becomes the most time consuming part of the PCG algorithm. On the other hand, the Lanczos algorithm diagonalizes the tridiagonal matrix $H^T$ of Eq. (8) and gets all eigenstates at the same time. Thus, the eigenstates “avoid each other” automatically. This leads to the orthogonalization among $\{\psi_i(r)\}$ without explicit enforcement. As a result, the algorithm is close to an $N^2$ scaling.

The above Lanczos algorithm is for all occupied state calculations. Not surprisingly, it is an order of magnitude slower than our novel method [4] used to calculate a few states around a given energy. If the band edge states (the top of valence band and the bottom of conduction band) are all that one wants, the above Lanczos method is not the best algorithm.

6. Conclusions

In order to utilize the Lanczos algorithm, several Lanczos phenomena have been explored in details. In particular, an unexpected relation was found between Lanczos convergence and one-dimensional Anderson localization. The understanding of the mechanism of exponential amplification of the end-of-spectrum states is discussed. Based on the insights into the Lanczos algorithm gained from this analysis, a Lanczos scheme is presented for large system total energy electronic structure calculations. Details of this algorithm are given. The programming of this method is no more complicated than that of the conjugate gradient method. This method is stable, all occupied eigenstates are guaranteed to be found and each eigenstate is guaranteed to be accurate to within a prescribed convergence limit. Thus, unlike other proposed schemes for large system calculations [6–10], the current approach is exact. For a few hundred atom system, this method scales as $N^2$. When $N > 1000$, the scaling changes to $N^3$. For the largest system tested here, this method is 9 times faster than the widely used preconditioned conjugate gradient method. Using this method, the charge density and 1392 eigenstates of a 933 atom quantum dot Si$_{617}$H$_{316}$ has been calculated within two and a half Cray YMP cpu hours. Thus, 100 – 1000 atom system total energy plane wave calculations become affordable by this method.

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References