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LETTER TO THE EDITOR

An efficient technique for obtaining eigenvectors of a Hamiltonian in a basis of non-orthogonal orbitals

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Abstract. A technique is developed for solving the large-scale generalised eigenproblem $Ab = EBb$, where A and B are real symmetric and block tridiagonal or band form matrices; B is positive definite. In physics this technique can be used to calculate the eigenvectors of a large electronic system in a basis of non-orthogonal orbitals.

In physics and engineering, many problems can be expressed as a generalised eigenproblem. For example, one chain or many coupled chain systems provide an expansion of the Hamiltonian in a basis of non-orthogonal orbitals which require a solution of the eigenproblem

$$Hb = ESb \tag{1}$$

where H is a Hamiltonian, E and b are an eigenvalue and an eigenvector respectively, S is an overlap matrix and $S_{ij} \neq \delta_{ij}$. In a disordered system we need to solve unusually large-scale systems. Some methods are available [1, 2] to solve equation (1), but how to solve the large-scale generalised eigenproblem is still unresolved.

In the present letter a technique is developed for solving the generalised eigenproblem

$$Ab = EBb \tag{2}$$

where A and B are real symmetric and block tridigonal or band form matrices; B is positive definite. We also point out the condition under which this method can be used to handle electronic systems in a basis of non-orthogonal orbitals.

One way to solve equation (2) is to rewrite it as a classical eigenproblem, for example, using the Cholesky factorisation:

$$B = LL^{\mathrm{T}}$$

or to write (2) as:

$$(B^{-1}A)b = Eb. \tag{3}$$

However, there are some disadvantages of this method. If A, B are of very high order, this may introduce a storage problem. In the calculation of B^{-1}, it is easy to induce a large error. Furthermore, the matrix $B^{-1}A$ is no longer of sparse form and even A, B are block tridiagonal or band form. So this method can only be used to solve small matrices.

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In this letter we directly solve equation (2) using the fact that the leading principal minors $\det(A_r - EB_r)$ $(r = 1, 2, \ldots)$ form a Sturm sequence. Then the jth eigenvalue E_j can be determined by a bisection method to the desired degree of accuracy. By using the method developed by Zheng [3, 4] the eigenvector $\boldsymbol{b}$ can be calculated.

In practice this procedure is as follows. For real symmetric block tridiagonal matrices A and B:

$$(A - EB)\boldsymbol{b} = 0$$

$$A - EB = \begin{pmatrix} A_{11} - EB_{11} & A_{12} - EB_{12} & & 0 & \\ A_{21} - EB_{21} & A_{22} - EB_{22} & A_{23} - EB_{23} & & \\ & A_{32} - EB_{32} & A_{33} - EB_{33} & A_{34} - EB_{34} & \\ 0 & & & \ddots & \\ & & & A_{m,m-1} - EB_{m,m-1} & A_{mm} - EB_{mm} \end{pmatrix}$$

$$\boldsymbol{b} = \begin{pmatrix} \boldsymbol{b}_1 \\ \boldsymbol{b}_2 \\ \vdots \\ \boldsymbol{b}_m \end{pmatrix} \qquad \boldsymbol{b}_i = \begin{pmatrix} b_{i1} \\ b_{i2} \\ \vdots \\ b_{iN_i} \end{pmatrix}$$

where A_{ii}, B_{ii} are $N_i \times N_i$ submatrices; $A_{ij} = A_{ji}$, $B_{ij} = B_{ji}$, and A_{ij}, B_{ij} are $N_i \times N_j$ submatrices. B is positive definite. $\Sigma_{i=1}^{m} N_i = N$. If $N_i = n$ for $i = 1, 2, \ldots, m$, the A, B are of band form.

Let $\eta(M)$ be the number of negative eigenvalues of matrix M. For a real parameter x:

$$\eta(A - xB) = \eta \sum_{i=1}^{m} (U_i) \tag{4}$$

$$U_1 = A_{11} - xB_{11}$$

$$U_i = A_{ii} - xB_{ii} - (A_{i,i-1} - xB_{i,i-1}) U_{i-1}^{-1} (A_{i-1,i} - xB_{i-1,i})$$

$$i = 2, 3, \ldots, m.$$

Then, by bisection, the eigenvalue E_j can be determined.

The eigenvector $\boldsymbol{b}$ is determined by:

$$(A - E_j B)\boldsymbol{b} = 0.$$

Let

$$D = (A - E_j B). \tag{5}$$

For $\boldsymbol{b}_k \neq 0$, equation (5) can be divided into three equations:

$$\begin{pmatrix} D_{11} & D_{12} & & & 0 & \\ D_{21} & D_{22} & D_{23} & & & \\ & & \ddots & & & \\ 0 & & & & & \\ & & & D_{k-1,k-1} & D_{k-1,k-1} & \end{pmatrix} \begin{pmatrix} \boldsymbol{b}_1 \\ \boldsymbol{b}_2 \\ \vdots \\ \boldsymbol{b}_{k-1} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ -D_{k-1,k}\boldsymbol{b}_k \end{pmatrix} \tag{6}$$

$$D_{k,k-1} \cdot \boldsymbol{b}_{k-1} + D_{kk} \cdot \boldsymbol{b}_k + D_{k,k+1} \cdot \boldsymbol{b}_{k+1} = 0 \tag{7}$$

$$\begin{pmatrix} D_{k+1,k+1} & D_{k+1,k+2} & & & \\ D_{k+2,k+1} & D_{k+2,k+2} & D_{k+2,k+3} & & \\ & & \ddots & & \\ & & & D_{m,m-1} & D_{m,m} \end{pmatrix} \begin{pmatrix} \boldsymbol{b}_{k+1} \\ \boldsymbol{b}_{k+2} \\ \vdots \\ \boldsymbol{b}_m \end{pmatrix} = \begin{pmatrix} -D_{k+1,k}\boldsymbol{b}_k \\ 0 \\ \vdots \\ 0 \end{pmatrix}. \tag{8}$$

The relations between $\boldsymbol{b}_k$ and $\boldsymbol{b}_{k+r}$, $r = \pm 1, \pm 2, \ldots$, are:

$$\begin{aligned} \boldsymbol{b}_{k\pm 1} &= -\Delta^{\pm}_{k\pm 1} \cdot D_{k\pm 1,k} \cdot \boldsymbol{b}_k \\ \boldsymbol{b}_{k\pm 2} &= -\Delta^{\pm}_{k\pm 2} \cdot D_{k\pm 2,k\pm 1} \cdot \boldsymbol{b}_{k\pm 1} \\ &\vdots \\ \boldsymbol{b}_m &= -\Delta^{\pm}_{m} \cdot D_{m,m-1} \cdot \boldsymbol{b}_{m-1} \end{aligned} \tag{9}$$

where

$$\Delta^{\pm}_i = (D_{ii} - D_{i,i\pm 1} \cdot \Delta^{\pm}_{i\pm 1} \cdot D_{i\pm 1,i})^{-1}. \tag{10}$$

$\boldsymbol{b}_k$ is determined by equation (7).

For $b_{kl} \neq 0$, let $b_{kl} = 1$ then we obtain the b_{kl}, $l = 1, 2, \ldots, l-1, l+1, \ldots, N_k$ by using equations (7) and (9). After determining $\boldsymbol{b}_k$, all $\boldsymbol{b}_{k\pm r}$, $r = \pm 1, \pm 2, \ldots$ can be obtained by equations (9) and (10). The choice of k,l is the key [3, 4].

In some physics problems the Hamiltonian in the basis of non-orthogonal orbitals is a block tridiagonal matrix or band form matrix. In most cases the matrix is real symmetric. That means that in equation (1) H, S are real symmetric, block tridiagonal or band form. But is the overlap matrix S the positive definite or not?

From Gershgorin's theorem, every eigenvalue λ of matrix S satisfies at least one of the equations:

$$|S_{ii} - \lambda| < \sum_{j \neq i} |S_{ij}| \qquad i = 1, 2, \ldots. \tag{11}$$

It is very easy to prove that if

$$S_{ii} > 0 \qquad S_{ii} > \sum_{j \neq i} |S_{ij}| \qquad i = 1, 2, \ldots \tag{12}$$

then all eigenvalues of matrix S are positive. For such cases the above method can be used to solve equation (1).

Because in electronic tight-binding systems, the conditions $|S_{ii}| \gg |S_{ij}|$ and $S_{ii} > 0$ are always satisfied, so in most cases the conditions (12) are fulfilled and S is positive definite. Maybe in some particular situations the off-diagonal elements of S are large enough that it is necessary to check the inequalities (12) when we use this method.

In order to check this method we choose a two coupled chains model. $H_{ii} = \varepsilon_i$, ε_i being a random number distributed uniformly in the interval $[-W/2, W/2]$ and $W = 1.0$. The nearest-neighbour hopping elements are $H_{ij} = 1.0$, the nearest-neighbour overlap elements are $S_{ij} = 0.2$ for the intra-chain and $S_{ij} = 0.1$ for the inter-chain. $S_{ii} = 1.0$ and $S_{ij} = 0$, $H_{ij} = 0$ for others. The chain length is L and the total number of atoms is $N = 2L$, $L = 5 \times 10^{-3}$.

Because $S_{ii} > 0$, $S_{ij} \geqslant 0$ and $S_{ii} > \Sigma_{j \neq i} S_{ij}$, S is positive definite. We can use this procedure. The density of state of the two-chains diagonal random system is shown in figure 1, calculated by equation (4) and formula:

$$\rho(x) = \{\eta[H - (x + \Delta x)S] - \eta[H - xS]\}/(N\Delta x).$$

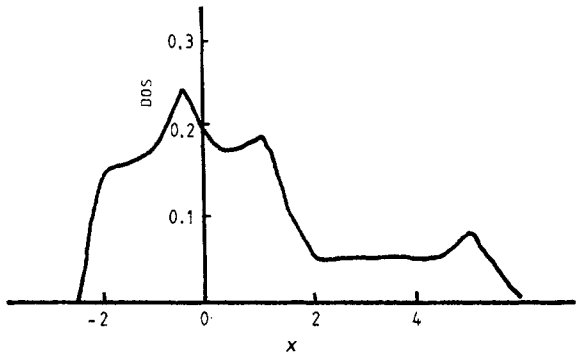

Figure 1. The density of states (DOS) of two coupled chains with $N = 2 \times 5000$.

In figures 2 and 3 two eigenvectors are shown. Two states are localised. One is in the band medium, the other is in the band tail. The above calculation only requires an Altos microcomputer.

The sample calculation demonstrates that this method is efficient and can be used to handle large-scale electronic systems in a basis of non-orthogonal orbitals using an Altos or Vax computer. That means that we have a technique to compute the electronic properties of polymer or biological long-molecule chains.

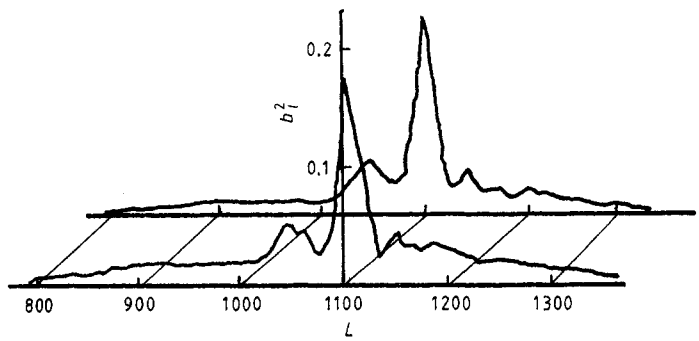

Figure 2. The square of components of eigenvector for $E_j = 0.000\,345$.

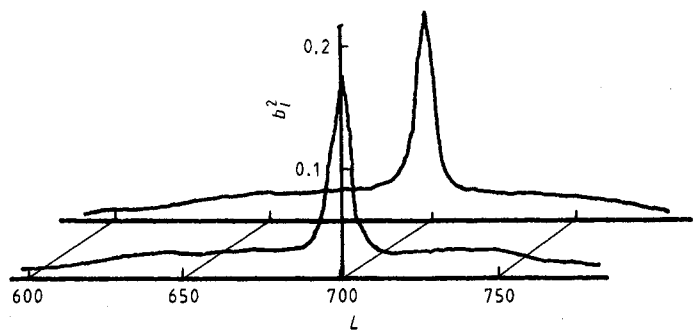

Figure 3. The square of components of eigenvector for $E_j = -2.109\,375$.

In summary, to combine the theory of Sturm sequence and the method developed by Zheng, a procedure for the solution of the generalised eigenproblem is developed. This procedure is particularly useful for high-order band form matrices. After checking the positive definite property of the overlap matrix S, the method can be used to compute the electronic properties of polymer or biological long-chain molecules. This programme of research work is now under active consideration.

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