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TITLE: THE KERNEL POLYNOMIAL METHOD FOR NON-ORTHOGONAL ELECTRONIC STRUCTURE CALCULATIONS

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THE KERNEL POLYNOMIAL METHOD FOR NON–ORTHOGONAL ELECTRONIC STRUCTURE CALCULATIONS *

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Abstract

The Kernel Polynomial Method (KPM) has been successfully applied to tight-binding electronic structure calculations as an O(N) method. Here we extend this method to nonorthogonal basis sets with a sparse overlap matrix S and a sparse Hamiltonian H. Since the KPM method utilizes matrix vector multiplications it is necessary to apply $S^{-1}H$ onto a vector. The multiplication of S^{-1} is performed using a preconditioned conjugate gradient method and does not involve the explicit inversion of S. Hence the method scales the same way as the original KPM method, i. e. O(N), although there is an overhead due to the additional conjugate gradient part. We show an application of this method to defects in a titanate/platinum interface and to a large scale electronic structure calculation of amorphous diamond.

1 Introduction

Electronic structure calculations are limited by the resources necessary to diagonalize large matrices. The demand on computer memory grows as N^2 and CPU–time as N^3, where N is the dimension of the matrices. A variety of methods at hand use iterative methods requiring only matrix–vector–multiplications (MVMs), and therefore can take advantage of the sparsity of the matrices. Most of these methods use sophisticated variants of the Lanczos method (like e. g. the look-ahead Lanczos algorithm). It is, however, difficult to obtain more than a small percentage of the number of states with such a procedure, since their convergence rate depends on the relative spacing of eigenvalues, which can become extremely small in the center of bands. If one relaxes the constraint of requiring exact eigenvalues and by analogy with experiment is satisfied with the eigenvalue distribution convoluted with a well–defined resolution function, then the kernel polynomial method (KPM) (Silver & Roeder 1994; Wang 1994) and simple variants thereof (Goedecker & Colombo 1994) has been shown to be successful in electronic structure calculations (Silver et al. 1995; Voter et al. 1996). To date all such applications used an orthogonal basis set. However, a large variety of quantum chemical and ab initio LDA calculations work with basis functions that are nonorthogonal, because this allows use of physical intuition in the choice and truncation of basis functions. It therefore becomes necessary to extend the KPM to approximately solve the system

$$H|\Psi>=\lambda S|\Psi> \quad , \tag{1}$$

where H and S are sparse symmetric (hermitian) matrices and S is semi–positive definite. In order to proceed it is necessary to present a short summary of the KPM.

2 The Kernel Polynomial Method

In the KPM the density of states $N(E) = \sum_\lambda \delta(E - E_\lambda)$ is approximated by an expansion in orthogonal polynomials. Depending on the choice of the orthogonal polynomials used the matrix H needs to be

rescaled to X such that the eigenvalue spectrum of X lies in the range in which the polynomials are defined. From now on we will use Chebychev polynomials $T_m(x)$, which are defined in $[-1,1]$. The recursion relation for the Chebychev polynomials is $T_m(x) = 2xT_{m-1}(x) - T_{m-2}(x)$ with $T_0(x) = 1, T_1(x) = x$. The density of states can now be approximated as

$$N(x) = \frac{1}{\pi\sqrt{1-x^2}} \left[\mu_0 + 2 \sum_{m=1}^{\infty} \mu_m T_m(x) \right] \quad , \qquad (2)$$

where the expansion coefficients (moments) are given by

$$\mu_m = Tr\{T_m(\mathbf{X})\} = \int_{-1}^{1} T_m(x) N(x) dx \quad . \qquad (3)$$

In practice one can only calculate a finite number of terms in (2). The truncation effects result in typical Gibbs oscillation. These can be damped out by multiplying with appropriate Gibbs damping factors g_m^M leading to

$$N_K(x) = \frac{1}{\pi\sqrt{1-x^2}} \left[\mu_0 + 2 \sum_{m=1}^{M} \mu_m g_m^M T_m(x) \right] \quad . \qquad (4)$$

The truncation together with the damping corresponds to a convolution of the correct density of states with a finite resolution function or " kernel", whose width decreases with the number of moments M. An alternative is to analyze the truncated series (2) directly using an image reconstruction method like MaxEnt (Silver et al. 1996; Drabold et al. 1993).

In order to generate the moments (3) in time and memory requirements of $O(N)$ one can utilizes a stochastic method by approximating the trace in (3) by a sum over N_r Gaussian random vectors $|r>$:

$$\mu_m = \lim_{N_r \to \infty} \left[\frac{1}{N_r} \sum_r < r|T_m(X)|r > \right] \quad . \qquad (5)$$

The expectation value of $T_m(X)$ is calculated recursively by taking scalar products between $|r>$ and the vectors $|m>$ defined by:

$$|m> = 2X|m-1> - |m-2> \quad , \qquad (6)$$

with $|0> = |r>$ and $|1> = X|r>$.

3 The KPM for Nonorthogonal Basis

In order to extend the KPM to eigenvalue problems described by (1) the straightforward way is to multiply (1) from the left with S^{-1} to obtain

$$S^{-1}H|\Psi> = \tilde{H}|\Psi> = \lambda|\Psi> \quad , \qquad (7)$$

and then to use the conventional KPM described above with $\tilde{H} = S^{-1}H$ as the underlying matrix. However, the inverse of the overlap matrix is neither readily available nor is it in general sparse. But since within the KPM only MVMs are required to generate the moments there is a way out. A MVM in (6) can be written as a linear system of equations like

$$S|x> = H|m-1> \quad , \qquad (8)$$

with unknown $|x>$ and known right–hand side $H|m-1>$. There is a huge variety of methods available to solve such a problem. The typical method for large systems of linear equations with multiple right–hand sides is to generate a Cholesky factorisation of S, $S = LL^H$. Again this is not practical since a Cholesky factorisation takes $O(N^3)$ in CPU–time and doesn't preserve sparsity. Therefore a strictly iterative method is necessary to solve (8). We choose the preconditioned conjugate gradient (PCG) method, because it allows us to control convergence by the choice of the preconditioner. The same preconditioner will be used over and over again, so it pays to obtain a good sparse approximation to S^{-1}. We use an incomplete stabilized Cholesky (ISCHO) factorisation for this purpose. In the ISCHO one performs a Cholesky factorisation, in which one throws away all elements that are not within the sparsity pattern of S, i.e. S is approximated by

$$S \approx \tilde{L}\tilde{L}^H = \tilde{S} \quad . \qquad (9)$$

This renders the usually extremely stable Cholesky algorithm unstable due to the appearance of negative or zero diagonal elements in $\tilde{S}$. We correct this effect by adding a diagonal matrix with small elements of equal size until the resulting $\tilde{S}$ is positive definite. In order to obtain the best possible results from this preconditioner one needs to choose the correction as small as possible to remain close to the original overlap matrix. An additional benefit of this method is that one can choose the solution of $\tilde{S}|x> = H|m-1>$ as a good initial vector for the PCG method. Using preconditioning typically reduces the number of MVMs necessary for the solution of (8) by at least a factor of ten. Combining conventional KPM with this PCG method allows a feasable calculation of the moments for the nonorthogonal eigenvalue problem (1). The memory requirement scales as the number of nonzero matrix elements of S and H and therefore as $O(N)$, if

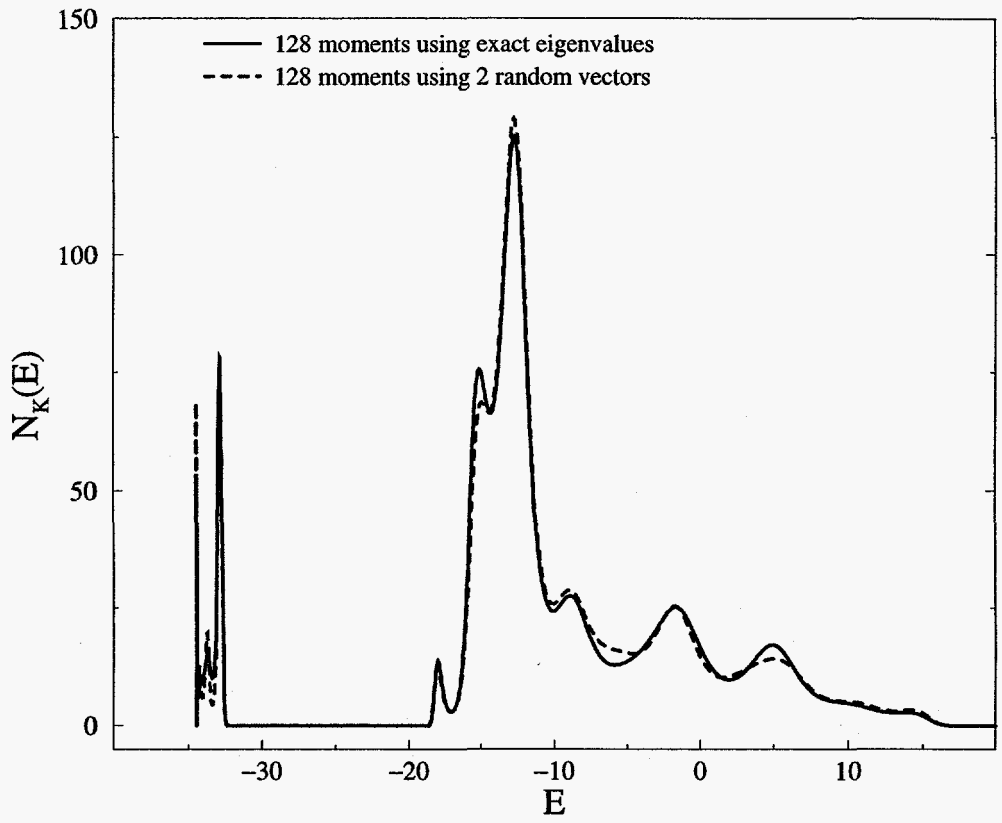

Figure 1: The density of states for an oxygen defect in a lead titanate/platinum interface calculated from a convolution of exact eigenvalues and from the extended KPM method described in the text. Unphysical states at high energies are a relic of the extended Hückel method and are not shown. 128 moments were calculated and the MaxEnt reconstruction method was used for the reconstruction of the DOS from the moment expansion.

they are sparse. The number of MVMs needed as compared to orthogonal KPM is multiplied by the number of MVMs performed within the PCG to solve the system of equations (8). For the examples below this was a factor of about thirty. Although this appears large the method is intrinsically $O(N)$ (for sparse matrices). The matrix dimension at which the KPM is more efficient is $N \approx 1000$ (if one wants the total energy at the Fermi level accurate up to four digits).

4 Applications

As an application where the electronic (ferroelectric) properties are of interest, an oxygen defect in a lead titanate/platinum interface is considered. A 127 atom model is implemented which constructs an interface between a lead titanate crystal and the (100) face of a platinum surface, which consists of 16 titanium (Ti) atoms, 12 lead (Pb) atoms, 43 oxygen (O) atoms, and 56 platinum (Pt) atoms. The extended Hückel (R. Hoffmann, 1963; R. Hoffmann, 1988) implementation of the tight-binding method, a semi-empirical quantum chemical approach, was used to construct (G. Landrum, 1995) the overlap and Hamiltonian matrices. Periodic boundary conditions were utilized in the x and y directions (parallel to the interface) and free surfaces were used in the z direction. The basis set consists of 9 orbitals (one s, three p, five d) per Ti and Pt atom, and 4 orbitals (one s, three p) per Pb and O atom. For the 127 atom model, the resulting matrices are of order 868 and the Fermi level is determined