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Quadratic Padé approximant method for calculating densities of states

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We suggest that the use of quadratic Padé approximants is a superior method of calculating the local density of states from a knowledge of the corresponding moments of the Hamiltonian. As a demonstration, very accurate values are obtained for most energy values in the cases of a bcc lattice and a binary alloy on a simple cubic lattice using the tight-binding model.

The calculation of the electron or phonon density of states (DOS) $n(E)$ is fundamental to many problems in the theory of condensed matter.[1] In inhomogeneous systems a more basic quantity is the local density of states corresponding to the site $|\vec{r}\rangle$,

$$\rho(\vec{r},E)=\int d\vec{k}\,\langle\vec{r}|\psi_{\vec{k}}\rangle\langle\psi_{\vec{k}}|\vec{r}\rangle\delta(E-E_{\vec{k}}) \ , \qquad (1)$$

where $|\psi_k\rangle$ are the eigenstates of the Hamiltonian H with energy $E_{\vec{k}}$. The density of states is obtained by integrating $\rho(\vec{r},E)$ over $\vec{r}$.

One way to calculate the local density is through its relation with the local Green's function

$$\begin{aligned}G(\vec{r},E)&=\langle\vec{r}|(E-H)^{-1}|\vec{r}\rangle\\&=\int_S dE'\rho(\vec{r},E')(E-E')^{-1} \ , \qquad (2)\end{aligned}$$

where S is the spectrum of eigenvalues $E_{\vec{k}}$ of H lying on the real axis in the energy plane. It is obtained from $G(\vec{r},E)$ by means of the formula

$$\rho(\vec{r},E)=(2\pi i)^{-1}\lim_{\epsilon\to 0^+}[G(\vec{r},E+i\epsilon)-G(\vec{r},E-i\epsilon)] \ , \quad (3)$$
$$E\in S \ .$$

In practical calculations, especially when periodicity is absent, we often replace the infinite system by a finite cluster[2] or terminate an approximate scheme at a certain stage.[3,4] In either case, the continuum spectrum of the infinite system is replaced by a set of discrete poles in the usual available methods. Numerical evaluation of $G(\vec{r},E)$ at or near these poles becomes inaccurate.

Several evaluation methods involve a knowledge of the moments.[3,4] Now $G(\vec{r},E)$ may be expanded as

$$G(\vec{r},E)=\sum_{k=0}^{\infty}\mu_k E^{-(k+1)} \ , \qquad (4)$$

where the moments are given by

$$\mu_k=\int_S dE\rho(E)E^k=\langle\vec{r}|H^k|\vec{r}\rangle \ . \qquad (5)$$

The problem is to extrapolate the function $G(\vec{r},E)$, analytic in the complex E plane cut along S from the expansion (4) about $E=\infty$ to values of E near S. One approach is equivalent to using the $[n/n]$ Padé approximant[5] to $G(\vec{r},E)$

$$G(\vec{r},E)\approx[n/n]=Q_n(E)/P_n(E) \ , \qquad (6)$$

where $Q_n(E)$ and $P_n(E)$ are polynomials of degrees $n-1$ (in this case) and n, respectively, so that

$$Q_n(E)-G(\vec{r},E)P_n(E)=O(E^{-(n+1)}), \quad E\approx\infty \ . \qquad (7)$$

To calculate $Q_n(E)$ and $P_n(E)$ the first $2n$ moments are needed.

Equation (6) may be written as

$$G(\vec{r},E)\approx\sum_{j=1}^{n}\nu_j(E-E_j)^{-1} \ , \qquad (8)$$

where $E_j\in S$ are the zeros of $P_n(E)$, which leads to the approximation

$$\rho(\vec{r},E)\approx\sum_{j=1}^{n}\nu_j\delta(E-E_j) \ . \qquad (9)$$

In practice, n is often around 30. Thus, $\rho(\vec{r},E)$ is represented by a weighted distribution of 30 or so δ functions. Physical features in the true local density of states comparable to or finer than the spacings of these δ functions are obscured. Various methods[4,6] have been suggested to smooth out this crude approximation, but none of them converges very fast when $n\to\infty$. Very often additional information is needed to help in carrying out a smoothing scheme, the more so when S consists of more than one band.[7]

The more familiar method of expressing the Green's function in the form of a truncated continued fraction[3,4] is mathematically the same as the Padé approximant summarized above.

For all periodic systems (including alloys), $\rho(\vec{r},E)$ will be an analytic function of E except possibly for certain branch points, some of which may be in S (at band edges and internal Van Hove singularities). Thus, $G(\vec{r},E)$ will have an analytic continuation in E to another Riemann sheet by passing S either from above or below. There may well be similar properties in systems for which the requirement of periodicity is removed.

The purpose of this Rapid Communication is to point out that, in these circumstances, an extension of (6), the quadratic Padé approximant[8] (QPA), may be a much superior method of estimating $G(\vec{r},E)$ near S and so finding $\rho(\vec{r},E)$ much more accurately.[9]

In the $[n,n,n]$ QPA to $EG(\vec{r},E)$ three polynomials $P_1(E)$, $P_2(E)$, $P_3(E)$, of degree n, are constructed from the first $3n+2$ moments so as to satisfy

$$\begin{aligned}P_1(E)+EG(\vec{r},E)P_2(E)+[EG(\vec{r},E)]^2P_3(E)&\\=O(E^{-(2n+2)}), \quad E\approx\infty \ . \qquad (10)\end{aligned}$$

Equating to zero the coefficients of E^n, $E^{n-1}, \ldots,$

$E^{-(2n+1)}$ gives $3n+2$ linear equations for the coefficients in the polynomials. Alternatively, the polynomials may be found with less work with the help of a four-term recurrence relation.[10,11] The QPA to $G(\vec{r},E)$ is obtained by solving (10) with $O(E^{-(2n+2)})$ replaced by zero, so that we have

$$G(\vec{r},E)\approx\frac{-P_2\pm(P_2^2-4P_1P_3)^{1/2}}{2EP_3}\ . \tag{11}$$

Mathematical analysis[9] suggests that, in the present case, (11) will give a good approximation to $G(\vec{r},E)$ throughout the plane cut along S, including points on S itself, except near to the branch points in S. The limiting values of $G(\vec{r},E)$ as S is approached from above and below are different, and this is to be accounted for by using both signs of the square root in (11). Thus, it is predicted that on S

$$R(E)=P_2^2(E)-4P_1(E)P_3(E) \tag{12}$$

will be negative so that, using (11), we have

$$\rho(\vec{r},E)\approx\frac{1}{\pi E}\left|\frac{[-R(E)]^{1/2}}{2P_3(E)}\right|\ . \tag{13}$$

Unlike (9), this is a continuous function of E.

As a test case we have applied the method to the electronic local DOS for the bcc lattice in the tight-binding approximation with nearest-neighbor interaction only.[12] As in this case all sites are equivalent, the index $\vec{r}$ will be omitted. We have evaluated (13) for values of n up to 15. It is found that the only two real zeros of $R(E)$ lie very close to the band edges $E=\pm 8$, where E is given in units of the nearest-neighbor interaction energy. Even for $n=5$ these points are given to nine significant figures. The result of the calculation of $\rho(E)$ using $n=15$ is shown in Fig. 1.

In this example there is a logarithmic Van Hove[1,13] singularity at $E=0$. In the complex E plane this is indicated by the position of the zeros of $R(E)$ and $P_i(E)$, $i=1,2,3$. They all [except for the two real zeros of $R(E)$] lie on the imaginary axis or extremely close to it. The zeros of $R(E)$ (except for the two real ones) are found to occur in pairs, the members of each pair separated by a very small amount.

The DOS has an accuracy that varies gradually to nine significant figures as one moves away from the band center. Even at a distance as close as $E=0.4$ to the logarithmic singularity at $E=0$, the density of states is better than four significant figures. We have been using as a comparison the accurate results of Morita and Horiguchi[13] obtained using numerical evaluation of a multiple integral representation of the DOS. The difference between QPA results and the Morita-Horiguchi results is too small to be seen in the figure.

For a second example we chose a binary alloy which consists of atoms of types A and B placed alternately on a simple cubic lattice. In the tight-binding model the site energies of the A and B types were taken to be $E_A=8$ and $E_B=10$ and the energy of interaction between nearest neighbors was unity. Such a system has two bands:

$$S=2.917\,237\,47<E<8,\quad 10<E<15.082\,762\,53\ . \tag{14}$$

There are Van Hove singularities at $E=6.7639$, 11.2361.

For $n=15$, zeros of $R(E)$ occur which represent the outer band edges to nine figures and the inner edges [one of which is $(E-a)^{-1/2}$ in nature] to four figures. The result of the calculation of $\rho(E)$ for an A-type site using $n=15$ is shown in Fig. 2.

The local DOS for the binary alloy (at either site) may be generated from the DOS for the simple cubic lattice,[14] and thus exact values can be calculated for comparison. It appears that the QPA results are most accurate in the part of S outside the Van Hove singularities, say $E<6.4$ or $E>11.6$, where the error is in the range 10^{-4}–10^{-8}. The Van Hove singularities are signaled by the presence of spurious oscillations. In between these singularities, say $7.4<E<10.6$, the error is of order 10^{-2} or less.

We have also calculated the density of states of other cubic lattices, the diamond lattice and the two-dimensional square lattice in the tight-binding model with results of similar accuracy.

QPA is not restricted to the tight-binding model. It is based on the knowledge of the lower moments. The latter can be obtained by direct matrix multiplications in the general case, but to make use of the full advantage of the scheme, it is best applied to systems with a sparse Hamil-

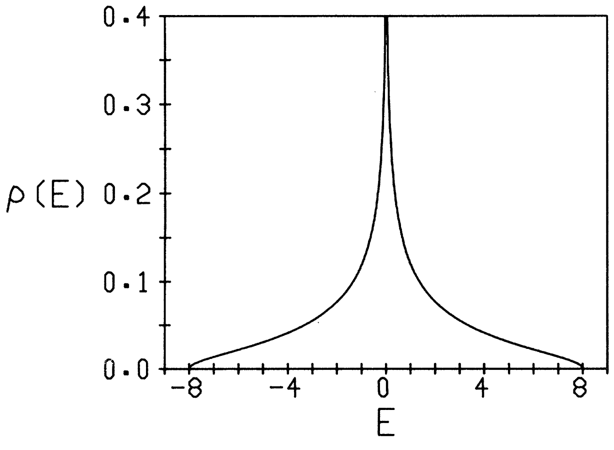

FIG. 1. Local density of states computed using the QPA method with $n=15$ for the bcc lattice with a tight-binding Hamiltonian with nearest-neighbor interaction of strength 1, site energies of zero.

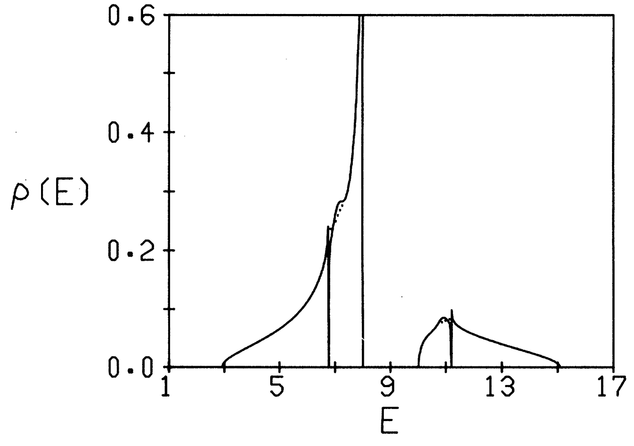

FIG. 2. Local density of states at a site of type A computed using the QPA method with $n=15$ for an AB binary alloy on a simple cubic lattice. The tight-binding Hamiltonian with nearest-neighbor interactions of strength 1 has been used, with site energies $E_A=8$, $E_B=10$. Exact results are represented by dashed lines.

tonian matrix, or systems with certain symmetry. We know of no other method based on moments for calculating the DOS which can produce results of accuracy at all comparable with those reported here, especially in the case of multiband spectra, where, without special efforts, the band-gap edges are fairly precisely determined.

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