A New Order-N Method to Calculate the Local Density of States

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(April 2, 1997)

We present a rigorous and general method to extract the local density of states $\rho_i(\omega)$ of a system from its time response to a specified external perturbation. This method which does not involve any truncation of interactions is order-N when the matrix is sparse. In a single run it gives $\rho_i(\omega), \rho_i(2\omega), .., \rho_i(n\omega), ..$ concurrently, which enhances the total efficiency by two decades. Application to a lattice dynamics problem of 4096 SiC particles in a supercell with dynamical matrix generated from an appropriate interatomic potential shows excellent agreement with exact phonon dispersion calculations; the accelerated algorithm yields a full LDOS spectrum for each supercell $\mathbf{k}$-point in 15 minutes on a desktop workstation. Results showing the effects of an antisite-pair defect are given for which methods requiring lattice periodicity can not be used.

In the current search for $\mathcal{O}(N)$ methods[1,2] for analyzing the energetics of condensed matter systems, techniques have been proposed which involve either some kind of localization (truncation of interaction shells) or a statistical approach, or both[1,2]. The goal in all cases is to treat large systems (N atoms) without performing $\mathcal{O}(N^3)$ computations such as matrix diagonalization. In this communication we present a novel method for calculating the local density of states (LDOS) of a system (which could be the tight-binding Hamiltonian in an electronic structure problem or the dynamical matrix in lattice dynamics), by exploiting a fundamental relation between the LDOS and the time response of the system to a prescribed external perturbation; it does not involve any truncation of interaction shells, is of $\mathcal{O}(N)$, and is made demonstrably robust by introducing a combination of projection and filtering techniques.

Basic definitions of LDOS and DOS are, respectively,

$$\rho_i(\omega) = \sum_n \delta(\omega - \omega_n)|\langle i|n\rangle|^2 \qquad (1)$$

$$\rho(\omega) = \sum_n \delta(\omega - \omega_n) = \sum_i \rho_i(\omega) \qquad (2)$$

where $\omega_n, |n\rangle$'s are the eigenvalues and eigenkets of the system, and i denotes local coordinate. They are the most important characteristics in analyzing a large, aperiodic system. For extensive motivations and applications see references[3,4].

Many existing methods[3,4] obtain the LDOS by calculating the Green's function in real space,

$$\mathbf{G}(z = \omega + i\varepsilon) = \frac{1}{z - H} = \sum_n \frac{|n\rangle\langle n|}{\omega + i\varepsilon - \omega_n} \qquad (3)$$

$$\rho_i(\omega) = -\frac{1}{\pi}\mathrm{Im}_{\varepsilon\to 0^+} G_{ii}(\omega + i\varepsilon) \qquad (4)$$

which in essence is to replace the δ-function of (1) by a sharp Lorentzian $\varepsilon/\pi(x^2 + \varepsilon^2)$. The resolvent matrix of (3) can be efficiently evaluated[3,5] for block-tridiagonal systems using iterative procedures in which convergence is monitored by going to increasing number of interacting shells.

Physically, the Green's function corresponds to the response ("displacement") of the system to an external perturbation ("force"). Consider lattice dynamics problem,

$$\ddot{\mathbf{u}}(t) = -\mathbf{D}\mathbf{u}(t) + \mathbf{f}(t) \tag{5}$$

where $\mathbf{u}(t)$ are atomic displacements and $\mathbf{f}(t)$ the external force (both being column vectors), and $\mathbf{D}$ is the dynamical matrix. Let $\mathbf{f}(t) = \mathbf{f}e^{-i\omega t}$, $\mathbf{u}(t) = \mathbf{u}e^{-i\omega t}$, then

$$\mathbf{u} = -\frac{1}{w^2 - \mathbf{D}}\mathbf{f} = -\mathbf{G}(\omega^2)\mathbf{f} \tag{6}$$

So $G_{ii}(\omega^2)$ corresponds to applying unit perturbation force on atom i and measuring the displacement of i. Thus one can obtain $G_{ii}(\omega^2)$ by directly integrating[6] (5). Because $\mathbf{G}(\omega^2)$ is closely related to the LDOS, perhaps one can get the LDOS from a similiar experiment.

For a one-dimensional problem

$$\ddot{u}(t) = -\omega_0^2 u(t) + \delta(t); \qquad u(t) = 0 \quad \text{for} \quad t < 0 \tag{7}$$

the solution is $G(t) = \theta(t)\omega_0^{-1}\sin\omega_0 t$, where $\theta(t)$ is the Heaviside step-function. Generalizing this to multi-dimensional systems, one has

$$\mathbf{G}(t - t') = \sum_n \frac{\sin\omega_n(t - t')}{\omega_n}\theta(t - t')|n\rangle\langle n| \tag{8}$$

Consider next applying instead a sinusoidal perturbation force with frequency ω on atom i after $t = 0$,

$$f_i(t) = \sin(\omega t)\theta(t), \qquad f_{j\neq i}(t) \equiv 0 \tag{9}$$

Then,

$$u_i(t) = \sum_n |\langle i|n\rangle|^2 \int_0^t \frac{\sin\omega_n(t - t')}{\omega_n}\sin\omega t' dt'$$
$$= \sum_n \frac{|\langle i|n\rangle|^2}{2\omega_n}\left(\frac{\sin\omega t + \sin\omega_n t}{\omega + \omega_n} - \frac{\sin\omega t - \sin\omega_n t}{\omega - \omega_n}\right) \tag{10}$$

In the limit of large t the last term becomes

$$\frac{\sin\omega t - \sin\omega_n t}{\omega - \omega_n} \approx 2\pi\delta(\omega - \omega_n)\cos(\omega t) \tag{11}$$

which can be regarded as the resonance response to the perturbation. We can project out its amplitude by multiplying $u_i(t)$ with $\cos\omega t$ and integrate from 0 to $T = 2k\pi/\omega$, where k is a positive integer, such that

$$\int_0^T \sin\omega t\cos\omega t dt \equiv 0 \tag{12}$$

From (10) we then have

$$\begin{aligned}&\int_0^T u_i(t)\cos\omega t dt\\&=\sum_n \frac{|\langle i|n\rangle|^2}{2\omega_n}(\frac{1}{\omega+\omega_n}+\frac{1}{\omega-\omega_n})\int_0^T \sin\omega_n t\cos\omega t dt\\&=\sum_n \frac{|\langle i|n\rangle|^2}{2\omega_n}\cdot\frac{2\omega}{\omega^2-\omega_n^2}\cdot -2\omega_n\frac{\sin^2(\omega_n T/2)}{\omega^2-\omega_n^2}\\&=\sum_n \frac{-2|\langle i|n\rangle|^2}{\omega^3(1+\omega_n/w)^2}\cdot\frac{\sin^2(k\pi(1-\omega_n/\omega))}{(1-\omega_n/\omega)^2}\end{aligned}\tag{13}$$

In view of the identity

$$\lim_{\alpha\to\infty}\frac{\sin^2\alpha x}{\pi\alpha x^2}=\delta(x)\tag{14}$$

(which is also the representation of δ-function in deriving Fermi's Golden Rule), we obtain the fundamental connection underlying our method,

$$\rho_i(\omega)=-\frac{2\omega^2}{\pi^2}\lim_{k\to\infty}\frac{1}{k}\int_0^{\frac{2k\pi}{\omega}}u_i(t)\cos\omega t dt\tag{15}$$

Our approach should be clear by now. By numerically integrating[6] the equation of motion (5) subject to a prescribed perturbation (9), one obtains $u_i(t)$, which is then integrated with $\cos\omega t$ up to nodes $T=2k\pi/\omega$. The limit of the integral at large k gives $\rho_i(\omega)$. Because at each timestep we only need to multiply $\mathbf{D}$ by a column vector $\mathbf{u}(t)$ to calculate the force, which in the case of local interactions must be a sparse matrix, the method will be then strictly $\mathcal{O}(N)$. The method is also exact in the sense that in the absence of numerical error, we know exactly what is replacing the δ-function of (1) (see (13)) for each finite k. There is no arbitrary truncation of interaction shells involved.

The main computational cost of this method is in $\mathbf{Du}$ multiplication. Applying perturbations on i and calculating the integral (15) cost very little. It turns out that one can extract $\rho_i(\omega)$'s at multiples of a certain base frequency α from a single displacement trajectory calculation as follows. Consider the perturbation

$$f_i(t)=\sum_{m'=1}^{M}A(m')\sin(m'\alpha t)\theta(t),\qquad f_{j\neq i}(t)\equiv 0\tag{16}$$

where $\{A(m)\}$ are arbitrary constants. Referring to (10) and invoking linear superposition, we get

$$\begin{aligned}u_i(t)=&\sum_n\frac{|\langle i|n\rangle|^2}{2\omega_n}\sum_{m'=1}^{M}A(m')\\&\left(\frac{\sin m'\alpha t+\sin\omega_n t}{m'\alpha+\omega_n}-\frac{\sin m'\alpha t-\sin\omega_n t}{m'\alpha-\omega_n}\right)\end{aligned}\tag{17}$$

If we let $T=2k\pi/\alpha$, a node of the *base frequency*, and integrate $u_i(t)$ with a specific frequency channel $\cos(m\alpha t)$, such that

$$\int_0^T \sin(m'\alpha t)\cos(m\alpha t)dt \equiv 0 \quad \text{for any} \quad m' \tag{18}$$

one has instead of (13),

$$\begin{aligned} &\int_0^T u_i(t)\cos(m\alpha t)dt \\ &= \sum_n -|\langle i|n\rangle|^2 \left(\sum_{m'=1}^{M} \frac{2A(m')m'\alpha}{m'^2\alpha^2-\omega_n^2}\right)\frac{\sin^2(\omega_n T/2)}{m^2\alpha^2-\omega_n^2} \end{aligned} \tag{19}$$

In the limit of large k, factoring out a common $(m^2\alpha^2 - \omega_n^2)^{-1}$ from the bracket would lead to a δ-function in the last term by (14), and only the $m' = m$ term survives. So in the end, just like (15), we arrive at

$$\begin{aligned} &\rho_i(\omega = m\alpha) \\ &= -\frac{2(m\alpha)^2}{\pi^2}\lim_{k\to\infty}\frac{1}{A(m)mk}\int_0^{\frac{2k\pi}{\alpha}} u_i(t)\cos(m\alpha t)dt \end{aligned} \tag{20}$$

It can be shown that at finite k, the line-widths of the sharply peaked functions in (19) which replace the δ-functions of (1) are uniform for all m:

$$\Delta\omega = \frac{\alpha}{k} \tag{21}$$

which means that the quality of convergence is the same for all channels in a calculation.

Eq.(5) differs in its *explicit form* from the usual equation of motion solved in a molecular dynamics simulation. Because of this, we can construct a high-precision integration scheme that allows stepsize 10^3 times larger than those of the conventional methods while the cost of each step only increases by 5 times (for the order-12 case). The method is a generalization of the Verlet algorithm[6]:

$$\begin{aligned} &\mathbf{u}(t+\Delta t) + \mathbf{u}(t-\Delta t) \\ &= 2\mathbf{u}(t) + (\Delta t)^2\ddot{\mathbf{u}}(t) + \frac{(\Delta t)^4}{12}\mathbf{u}^{(4)}(t) + \frac{(\Delta t)^6}{360}\mathbf{u}^{(6)}(t) + ... \end{aligned} \tag{22}$$

Because $\ddot{\mathbf{u}}(t) = -\mathbf{D}\mathbf{u}(t) + \mathbf{f}(t)$, so

$$\begin{aligned} \mathbf{u}^{(4)}(t) &= -\mathbf{D}\ddot{\mathbf{u}}(t) + \ddot{\mathbf{f}}(t) \\ \mathbf{u}^{(6)}(t) &= -\mathbf{D}\mathbf{u}^{(4)}(t) + \mathbf{f}^{(4)}(t) \\ &... \end{aligned} \tag{23}$$

are exact and can be *evaluated* successively with only the initial knowledge of $\mathbf{u}(t)$. Thus the trajectory can be integrated to arbitrarily high order, as in our case using $\{\mathbf{u}(t), \ddot{\mathbf{u}}(t), .., \mathbf{u}^{(10)}(t)\}$, to the 12th order. We can also numerically integrate (20) up to the same order of accuracy using integration by parts:

$$\begin{aligned} &\int_t^{t+\Delta t} u_i(t')\cos(m\alpha t')dt' \\ &= \Big[\frac{u_i(t')\sin(m\alpha t')}{m\alpha} + \frac{\dot{u}_i(t')\cos(m\alpha t')}{(m\alpha)^2} \end{aligned} \tag{24}$$

$$-\frac{\ddot{u}_i(t')\sin(m\alpha t')}{(m\alpha)^3}-\frac{u_i^{(3)}(t')\cos(m\alpha t')}{(m\alpha)^4}+...$$

$$\left.-\frac{u_i^{(10)}(t')\sin(m\alpha t')}{(m\alpha)^{11}}-\frac{u_i^{(11)}(t')\cos(m\alpha t')}{(m\alpha)^{12}}\right]\Bigg|_t^{t+\Delta t}$$

The odd-ordered derivatives can be determined from even-ordered ones to the same accuracy through Taylor expansion. Notice that in (24) by stopping the series at $u_i^{(11)}$ it is equivalent to approximating $u_i(t')$ in the range $(t, t+\Delta t)$ by a continuous 11th-order polynomial, so the end-point derivatives should be entirely determined from the start-point ones.

In applying this method we found that the most efficient way to calculate the full LDOS spectrum is to set $k=1$ and let α be the desired resolution (see (21)). It is best in the sense that all ω_n's of the system shall be covered by the main peak of one channel or the other and so minimum information is lost. On the other hand setting $k=1$ can induce interference between nearby channels which is significant between m and $m\pm1, m\pm2$. Referring to (19), let us define

$$N_{m,m'}(\omega)=\frac{\sin^2(\pi\omega)m'}{(m^2-\omega^2)(m'^2-\omega^2)} \tag{25}$$

where $\omega=\omega_n/\alpha$ is the reduced eigenfrequency; for a given ω its contribution to the $k=1$ result of the mth channel is proportional to $\sum_{m'=1}^{M} A_{m'}N_{m,m'}(\omega)$ (see (19)), in which only the $A_mN_{m,m}(\omega)$ term is needed. All others are noise functions that though give zero drift ($\int_0^{+\infty} N_{m,m'}(\omega)d\omega=0$ for $m'\neq m$), they impair the resolution. However, we can choose an $\{A_m\}$ series such that all noise functions with $m'-m$ being odd are cancelled out, by noticing that A_m can be complex but $N_{m,m'}(w)$ is always real ("time-reversal symmetry"). If we assign *alternating "parities"* to each channel by letting $\mathrm{Im}A_m=(-1)^m(\mathrm{Re}A_m)$, and correspondingly extract the final result after a $[\mathrm{Re}+(-1)^m\mathrm{Im}]$ operation, it can be shown that the noise influence is reduced to

$$A_{m-2}N_{m,m-2}(\omega)+A_{m+2}N_{m,m+2}(\omega)+... \tag{26}$$

because neighbouring channels always have different "parities". Furthermore there will be cancellations if A_{m-2} and A_{m+2} are of the same sign. Combining the above we arrive at the following amplitude series

$$\begin{cases}\mathrm{Re}A_m=(-1)^{(m\ \mathrm{div}\ 2)} & \text{i.e.,}++--++--\\ \mathrm{Im}A_m=(-1)^m(\mathrm{Re}A_m) & \text{i.e.,}+--++--+\end{cases} \tag{27}$$

There is another issue. We want $f_i(t)$ (see (16)) to be well behaved in time from the stand-point of numerical integration. (27) does not satisfy this criterion because at $t=\pi/2\alpha$ there will be a sharp peak in $f_i(t)$ which is proportional to M and with even higher derivatives. Such resonances are due to the long-range order in $\{A_m\}$ irrespective of its detailed repeat pattern. We eliminate this problem by noticing that the noise cancellation scheme of (26) depends only on *short-range order* in $\{A_m\}$. If we multiply $\{A_m\}$ by a slowly varying "spin-wave":

$$B_m = e^{i\phi_m} A_m, \qquad \phi_{m+1} = \phi_m + \xi_m \Delta\theta \tag{28}$$

where ξ_m is a random number taking equally possible values ± 1 and $\Delta\theta$ is a very small angle, then long-range order will be destroyed whereas short-range order remains. We will then use $\{B_m\}$ as the amplitude series and later "decode" the mth channel result by multiplying $e^{-i\phi_m}$, before the $[\mathrm{Re} + (-1)^m \mathrm{Im}]$ operation.

The present algorithm is found to be generally robust except at very low frequencies, where the first few channels usually diverge due to the accumulation of round-off error. We can avoid this problem by applying a rigid shift transformation on the dynamical matrix $\mathbf{D} \to \mathbf{D} + \omega_{shift}^2 \mathbf{I}$ such that all eigenfrequencies are outside the divergence region, and use the new matrix instead. In the end we transform back to $\rho_i(\omega)$.

The method proposed here can be used to calculate the LDOS of any *positive definite* Hermitian matrix. For a general Hermitian matrix such as the electronic tight-binding Hamiltonian, we can use the method after shifting the spectrum to the positive axis. There is also an entirely parallel construction using the Schrodinger equation as evolution dynamics which does not require the matrix to be positive definite, this possibility will be explored in future work.

We have calculated the vibrational LDOS of Si and C in β-SiC (zinc blende structure) using the above method. As a test, we first considered the perfect crystal for which exact phonon dispersion results can be readily obtained. The dynamical matrix is generated from an appropriate many-body interatomic potential[7]. Each atom has 4 nearest and 12 second-nearest neighbours and so total of 51 non-vanishing entries on a column of $\mathbf{D}$. We have taken a 4096-particle cubic supercell with periodic boundary conditions and randomly sampled 25 $\mathbf{k}$-points in the simple cubic BZ of this supercell. For each of these $\mathbf{k}$-points, we have 12288 eigenvalues. Given that the spectrum of β-SiC covers 0 to 35 THz ($=\omega_{max}$), we have on the average 350 eigenvalues per THz. We choose the base frequency to be 0.125 THz and turn on all multiple channels up to 35 THz, with $\omega_{shift} = 2$ THz, for which a crude estimate gives a relative variance of $(350 \times 0.125 \times 25)^{-\frac{1}{2}} = 3\%$ for each channel's result. The "spin-wave" encoding in (28) has $\Delta\theta = \pi/10$. The derivatives of $\mathbf{u}(t)$ are given at $t = 0^+$ according to the analytic formula, and a stepsize of $\omega_{max}\Delta t = 2\pi/3$ is being used to do the order-12 numerical integration which gives satisfactory convergence. The crystal is equivalent in three directions and so we only pick x. Fig.1 shows a comparison of the LDOS of Si and C. Plotted in smooth solid lines are results from exact phonon dispersion calculations by diagonalizing 6×6 matrices in the $\mathbf{k}$-space of the fcc unit cell, after randomly sampling 100,000 $\mathbf{k}$-points. Results obtained from our method are shown in circles. The agreement is seen to be excellent, down to the very low frequency region, with sharp resolution of the band gap and critical points. The computational speed for this full LDOS spectrum calculation is 15 minutes per supercell **k**-point on a desktop DEC $\alpha-$workstation, taking into view that we are treating a huge matrix (12288×12288) with 51 non-vanishing entries on each column. The efficiency stems from the multi-channel idea and the high-precision integration scheme. Memory requirement is minimal. Also, the algorithm is so simple that it can be easily vectorized or transported to a parallel platform.

Fig.2 shows the result of switching a nearest neighbour pair of Si and C in the above supercell, thus generating an antisite-pair defect. The configuration was then relaxed using the conjugate gradient method. The LDOS is calculated for the switched Si atom in the direction of this bond ((111) direction). All parameters remain unchanged except ω_{max} = 40 THz. The most conspicuous effect is the splitting of the optical LDOS and the generation of two gap modes at 23.2 and 25.9 THz.

We would like to thank S. Y. Wu and C. S. Jayanthi for helpful discussions which inspired this work, and our colleague Lisa Porter for her code which generates the Tersoff dynamical matrix. This work has been supported in part by the Air Force Office of Scientific Research. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the ACS.

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FIG. 1. LDOS of Si and C in a perfect crystal of β-SiC: exact phonon dispersion results (solid lines) and the present method (circles).

FIG. 2. LDOS of Si in (111) direction after introduction of an antisite-pair defect (dashed lines). Also shown for comparison are the perfect crystal results from exact phonon dispersion calculations (solid lines) and from the present method (dash-dot lines).