

Linear Scaling Method for Phonon Calculations from Electronic Structure

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We present a method for phonon spectrum calculations from electronic structure calculations that scales linearly with system size. It allows computation of the dynamical matrix and phonon structure of systems of unprecedented size. The method is based on (i) use of localized wave functions to describe the electronic states, (ii) truncation of the dynamical matrix beyond a cutoff, and (iii) reconstruction of the spectrum of the sparse dynamical matrix by the maximum entropy approach of Drabold and Sankey. We test the method with a tight-binding Hamiltonian for carbon, on a 216 atom supercell in the diamond structure, and in fullerene balls of up to 3840 atoms.

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One of the best links between experiments in molecular and condensed-matter physics and theoretical simulation is the vibrational density of states (VDOS), directly measured in inelastic neutron scattering and intimately connected to Raman and other spectroscopies. The VDOS carries a wealth of information about dynamics and microstructure. To compute it one needs the equilibrium configuration of the system and accurate interatomic forces, now commonly obtained from electronic structure calculations. In this Letter, we extend this kind of calculation to very large systems by introducing a scheme for computing the dynamical matrix (DM) and the VDOS, whose computational cost scales linearly with the number of atoms under study. A natural approach is to perform a molecular dynamics (MD) simulation at finite temperature and extract the vibrational power spectrum from velocity or position autocorrelations. However, in our scheme, we approximate the DM [1,2], since this contains complete information about the harmonic modes of the system and requires no long simulations to obtain low energy modes.

Conventional electronic structure computations involve an effort proportional to the cube of the number of electrons in the system. This is true when both direct diagonalization or iterative minimization techniques like Car-Parrinello or conjugate gradients are used. This undesirable scaling of the electronic calculations limits the size of the systems that can be studied to a few hundred atoms at most. In recognition of this difficulty, several methods have been proposed which solve the electronic structure problem with an effort proportional to the number of atoms in the system in an approximate way [3]. These methods enable the calculation of accurate forces and electronic structure related properties for systems with a very large number of atoms. However, it is not obvious how such methods can be used to compute the phonon spectrum of a system in $O(N)$ operations. For instance, if the finite differences DM method is used to obtain the vibrational modes, then $3N$ calculations must

be performed (one for the displacement of each atom in each direction in space). Since each calculation requires an $O(N)$ effort, the mere computation of the whole DM would be an $O(N^2)$ task. Besides, one must ultimately diagonalize the DM, which is an $O(N^3)$ operation. The final overall effort would scale therefore as $aN^2 + bN^3$ (where $a \gg b$, since the electronic problem is much more costly than the single diagonalization of the DM, so that the N^2 term dominates for reasonable sizes).

In this work we discuss how to make use of these recent electronic structure order- N methods to compute the phonon spectrum in such a way that the total effort also scales linearly with the system size. The scheme proposed here is compatible with a variety of proposed electronic order- N methods, and we implement it for one in particular: the localized orbital scheme of Ordejón and co-workers [3,4] and by Mauri, Galli, and Car [5]. The key features are as follows: (i) a new band structure energy functional \tilde{E} which, when freely minimized with no orthogonalization constraints, yields the exact ground state energy and a set of orthonormal states defining the ground state subspace, and (ii) description of the system in terms of localized, Wannier-like wave functions (LWF) that are truncated beyond a cutoff radius R_c from their center. When this is done, all the operations necessary to compute and minimize \tilde{E} scale linearly with the size of the system, since for each LWF ψ_i only the matrix elements with overlapping orbitals ψ_j (those closer than $2R_c$) must be calculated (a number independent of the system size). It can also be shown that, once the LWF's have been obtained, the forces on *all* the atoms can also be obtained in $O(N)$ operations.

The method we propose to obtain the phonon spectrum in $O(N)$ operations is based on the finite differences DM approach. We first relax the system to equilibrium (and consequently compute the localized electronic wave functions $\{\psi_j^0\}$). The DM $D_{\alpha I, \beta J}$, defined as $D_{\alpha I, \beta J} = (M_I M_J)^{-1/2} \partial^2 E / \partial u_{\alpha I} \partial u_{\beta J}$ (where E is the total energy

of the system, α and β are Cartesian coordinates on atoms I and J , respectively, and the M 's are ionic masses), is computed by finite differences: Atom I is displaced an amount $\Delta x_{\alpha I}$ in the α direction, and the forces on all the atoms $F_{\beta J}$ are computed. Then, $D_{\alpha I, \beta J} \approx (M_I M_J)^{-1/2} F_{\beta J} / \Delta x_{\alpha I}$, since the force on an atom is the derivative of the total energy with respect to the displacement of that atom: $F_{\beta J} = -\partial E / \partial x_{\beta J}$. During the process of computing the DM, when atom I is displaced, the electronic energy is minimized again to find the new optimized wave functions $\{\psi_j^I\}$. At this point, we introduce the first approximation of our method: Since the functions $\{\psi_j^I\}$ are localized, only those in the neighborhood of atom I will differ significantly from the solutions of the equilibrium system $\{\psi_j^0\}$. Therefore we can, as an approximation, optimize only those functions ψ_j which are close enough to the displaced atom, leaving other functions unchanged. Our criterion is to allow variations in only those wave functions which include the atom that is being displaced. We denote this set of functions as $S_I \equiv \{\psi_j \mid |\mathbf{R}_j - \mathbf{R}_I| < R_c\}$, where \mathbf{R}_j is the center of ψ_j , \mathbf{R}_I is the position of atom I , and R_c is the cutoff radius of the LWF's. This approximation was not taken in Ref. [3] and is essential to reach a linear scaling in the calculation of the DM. Equivalent approximations can be derived for other electronic order- N methods.

To compute the optimized wave functions S_I we minimize the energy functional:

$$\tilde{E} = 2 \sum_{i \text{ or } j \in S_I} H_{ji} Q_{ij} + 2 \sum_{i, j \notin S_I} H_{ji} Q_{ij} = \tilde{E}_1^I + \tilde{E}_2^I, \quad (1)$$

where $H_{ji} = \langle \psi_j | \hat{H} | \psi_i \rangle$ and $Q_{ij} = 2\delta_{ij} - \langle \psi_i | \psi_j \rangle$. The second term in Eq. (1) is constant during minimization (and therefore need not be computed), and we perform a *restricted energy minimization* involving only the first term. The functions $\psi_j \in S_I$ are obtained by minimizing the "local" functional \tilde{E}_1^I . This operation scales as $O(1)$, i.e., does not depend on the size of the system, since if the system size is increased the number of functions included in the set S_I will not increase, provided that the system is large enough. Therefore the solution of the electronic problem for the $3N$ atomic displacements (one per atom per direction in space) takes an $O(N)$ effort.

For each atomic displacement, once the electronic wave functions have been obtained in $O(1)$ operations, we compute the forces on all the atoms in the system. This would lead to an overall $O(N^2)$ task, since for each of the $3N$ atomic displacements we must obtain N forces. Here we introduce the second approximation of our method: Only the forces on atoms closer than a certain cutoff R_f from the displaced atom are computed, the rest of the forces being set to zero. This approximation takes into account the fact that the forces on each atom depend on its local environment, and not on the details of the structure in remote regions. This also reflects the fact that

the DM elements between distant atoms decrease rapidly with distance. Our approximation can therefore be put in terms of imposing a cutoff on the DM: $D_{\alpha I, \beta J} = 0$ if $|\mathbf{R}_I - \mathbf{R}_J| > R_f$, so that the resulting matrix is sparse. Its calculation and storage are both $O(N)$.

Once the DM has been obtained, its diagonalization yields the phonon normal modes and frequencies. This operation scales as $O(N^3)$, so we should avoid it in order to preserve the linear scaling of the method. For systems with up to about 500–600 atoms, however, the direct diagonalization of the DM is still possible with a small effort compared with the cost of the electronic computation. For larger systems, in which diagonalization is not feasible or practical, we propose, as the third major approximation of our method, the use of the maximum entropy (ME) approach of Drabold and Sankey [6], which permits the calculation of the spectral density of states (DOS) of a sparse operator with an $O(N)$ effort. In essence, the method consists of a ME reconstruction of the density of states from the moments of the matrix, which in turn are estimated using a set of random vectors. Its accuracy depends on the number of moments and the number of random vectors used to reconstruct the DOS. While the ME approach produces total and partial DOS, it does not provide us with eigenvectors. Selected eigenvectors can be computed, however, using the Lanczos method [7,8] to obtain selected eigenvectors, also in $O(N)$ operations.

The application of the method to tight-binding formulations (both empirical [9] and *ab initio* [10]) is straightforward, using the techniques described in Ref. [3]. We have implemented it for carbon using the empirical tight-binding model of Xu *et al.* [9]. In order to check the accuracy of our approximations, we have computed the $\mathbf{q} = \mathbf{0}$ phonons of a cubic supercell of 216 carbon atoms in the diamond structure. The Brillouin zone sampling in the electronic calculation was limited to the Γ point. The spectra were broadened with a Gaussian of 15 cm^{-1} FWHM. Figure 1 shows a comparison of the exact results with those of our method for two different values of the cutoff radii: $R_c = R_f = 3.0 \text{ \AA}$ and $R_c = R_f = 4.0 \text{ \AA}$. As expected, the accuracy improves with increasing values of R_c and R_f . For $R_c = R_f = 4.0 \text{ \AA}$, we find essentially perfect agreement with the exact results, with a very small shift towards higher frequencies for the stiffer optical modes. For the $R_c = R_f = 3.0 \text{ \AA}$ the shift is larger, but the agreement is still excellent. We note that most of the error in the calculation has its origin in the use of localized wave functions, and not on the approximations of restricted minimization and cutoff of the DM, as noted by Ordejón *et al.* [3], who studied of the accuracy of the electronic order- N method for phonon calculations. Since the system size is moderate, the spectra were in this case obtained by diagonalizing the dynamical matrix, although the ME method can also be used. The inset in Fig. 1 shows, for the $R_c = R_f = 4.0 \text{ \AA}$ case, the comparison of

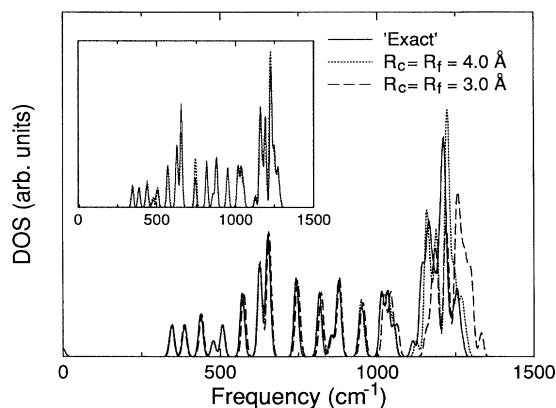


FIG. 1. Phonon DOS for a 216 atom supercell of carbon with the diamond structure. Solid line shows the exact results obtained with no approximations; dotted and dashed lines are the result of our order- N method, for different values of the cutoff radii R_c and R_f . The inset shows a comparison of the results obtained diagonalizing the DM (dotted line), and with ME (full line) for the $R_c = R_f = 4.0 \text{ \AA}$ case.

the diagonalization results with those obtained with the ME method with 100 random vectors and 65 moments. We see that ME provides an excellent representation of the DOS.

We have also computed the vibrational spectra of several large icosahedral carbon fullerenes, from C_{60} to C_{3840} . The structure of the clusters was obtained by dynamical quenching, and is described elsewhere [11]. Their shapes are markedly polyhedral, with nearly flat, graphitelike facets and protruding pentagons, but with smooth, round edges (except for C_{60} , which is perfectly spherical). In the electronic calculation, we use different cutoff radii for the σ -type wave functions ($R_c^\sigma = 4.0 \text{ \AA}$) and for the π -type wave functions ($R_c^\pi = 5.0 \text{ \AA}$). The cutoff in the forces was $R_f = 5.0 \text{ \AA}$. The results are shown in Fig. 2. In all cases, the DOS was calculated from the sparse DM using the ME approach. In order to obtain a fully converged representation of the DOS, for all the clusters larger than C_{240} the ME reconstruction was computed using 100 random vectors and 99 moments. However, the number necessary to obtain a reliable spectrum is much smaller than these values (typically, less than 10 vectors and about 30 moments) and decreases significantly with increasing system size. We should note that, as discussed by Drabold and Sankey [6], the ME reconstruction of the DOS shows a better resolution in the edges of the spectrum than on its center, and therefore the peak width is larger for modes at intermediate frequencies, as is clearly observed in the case of C_{60} . The effort in obtaining the DM and the ME reconstruction of the DOS was *much* smaller (by at least a factor of 10) than that of computing the equilibrium structure of each cluster by MD. This is not the case, however, if the DM and

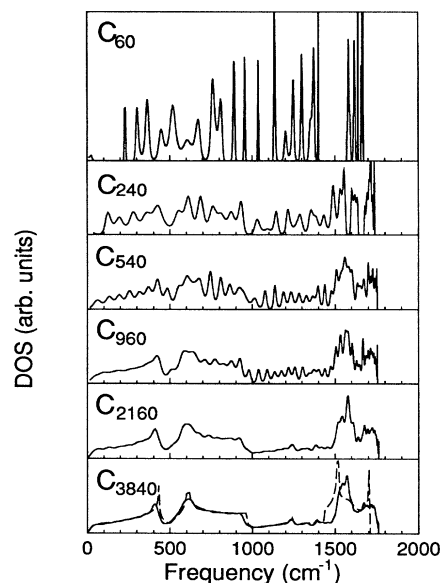


FIG. 2. Phonon DOS for several icosahedral carbon fullerenes, from C_{60} to C_{3840} , obtained with the order- N method. For comparison, superimposed to the C_{3840} spectrum, we also show (dashed line) the results for a perfect single graphite plane, computed exactly.

the phonon DOS are obtained by standard methods (that is, not using the approximations described in this work), where their calculation is, in general, more costly than the atomic relaxation, and becomes more and more expensive as the system size increases, due to the nonlinear scaling discussed above.

Figure 2 clearly shows how the DOS of the fullerenes evolves from the discrete spectrum of C_{60} to a continuum spectrum that resembles the one of a graphite plane (also shown for comparison in Fig. 2). This was expected, given the flat, graphitelike surfaces present in the larger clusters. This is particularly true for the low frequency acoustic modes, and also for the high frequency optical, out-of-plane modes. However, the optical modes above 1500 cm^{-1} are significantly shifted toward higher frequencies in the fullerenes compared to the graphite spectrum. This shift has its origin in the internal stress, which is present in the fullerene structures, that originates from the spherical topology of the clusters.

The present method also allows us to compute the partial DOS for any atom of the system and its decomposition into spatial directions. This can be done in the ME reconstruction, if one obtains the moments using vectors which are zero except for the atom and spatial direction under consideration, as opposed to random vectors (which provide the total DOS). In Fig. 3 we show an example for the C_{2160} fullerene, where we have computed the local density of phonon states for two different atoms: one of them forms part of one of the 12 pentagons of the cluster, and

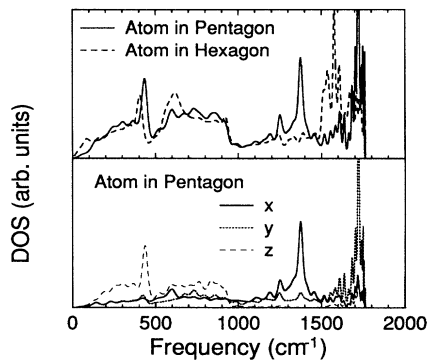


FIG. 3. Local density of states for different atoms and directions of space for the phonons of the C_{2160} fullerene. The top panel shows the density of vibrational states for an atom in a pentagon, and for an atom in a hexagon in the middle of a flat facet. The lower panel shows the density of states of the pentagon atom decomposed in x , y , and z directions.

the other is on a hexagon in the middle of a flat facet. The difference in the dynamics of these two atoms is particularly apparent in the high frequency part of the spectrum. The atom in the pentagon shows a strong peak at about 1370 cm^{-1} , which is not present in the hexagon atom (nor in the graphite DOS), and which is a characteristic stretching mode of the pentagons. This mode is observed in all the fullerenes studied, since all of them contain 12 pentagons. On the other hand, the pentagon atoms do not support the strong optical band at about 1500 cm^{-1} , which is present in the graphitic planes. We have also decomposed the local density of states for the pentagon atom into the three directions of space (z corresponding to the radial direction). We can see that the 1370 cm^{-1} peak corresponds to an in-plane vibration in the x direction, with a large stretching character. The z direction corresponds to out-of-plane vibrations, and therefore has a large DOS on small frequencies, up to 900 cm^{-1} .

In conclusion, we have presented a linear scaling method for the computations of the phonon spectrum from electronic structure, which allows the study of systems with unprecedented size. We have demonstrated the accuracy of the method by applying it to a 216 atom carbon supercell, and proved its power by computing the phonons of clusters of carbon with up to 3840 atoms.

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