Local Density of States (LDOS):

$$\rho_i(\omega) = \sum_n \delta(\omega - \omega_n)|\langle i|n\rangle|^2 \tag{0.1}$$

Total Density of States (DOS):

$$\rho(\omega) = \sum_n \delta(\omega - \omega_n) = \sum_i \rho_i(\omega) \tag{0.2}$$

Green's function:

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

Real Space Green's Function (RSGF) method:

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

- $G(z)$ (the "resolvent matrix") can be efficiently evaluated for block-tridiagonal systems using iterative methods (matrix operations).
- Convergence is achieved by going to larger and larger number of interacting shells.
- Except for 1D and pseudo-1D systems, efficiency deteriorates due to progressively increasing block size.

Our method ("Multi-Channel Perturbation Method"?):

- Bypass matrix operations.
- Order-N when matrix is sparse.
- Measure the entire spectrum in one run.
- No arbitary truncation of interaction shells.
- Theoretical error control.

---

perturbation:

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

response:

$$u_i(t)$$

An identity:

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

Rationale:

- **What's Green's function?**

Green's function corresponds to the response ("displacement") of the system to an external perturbation ("force").

Example of lattice dynamics:

$$\ddot{\mathbf{u}}(t) = -\mathbf{D}\mathbf{u}(t) + \mathbf{f}(t) \tag{0.3}$$

where $\mathbf{D}$ is the dynamical matrix. Let $\mathbf{f}(t) = \mathbf{f}e^{-i\omega t}$, $\mathbf{u}(t) = \mathbf{u}e^{-i\omega t}$, then

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

$\Rightarrow$ By doing simulations via equation of motion (0.3), we can get $\mathbf{G}(\omega^2)$.

$\Rightarrow$ Because $\mathbf{G}(\omega^2)$ and LDOS are closely related, *maybe* we can get the LDOS from a similiar experiment.

Idea Experiment – Single-Channel Perturbation:

Add monochromatic sinusoidal perturbation force on atom i at $t > 0$,

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

The real-time Green's function:

$$G(t) = \frac{\sin \omega_0 t}{\omega_0}\theta(t) \qquad \text{(1D)}$$

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

The response is

$$\begin{aligned} u_i(t) &= \langle i| \int \mathbf{G}(t-t') * \mathbf{f}(t')dt'\rangle \\ &= \sum_n \frac{|\langle i|n\rangle|^2}{2\omega_n}\left(\frac{\sin \omega t + \sin \omega_n t}{\omega + \omega_n} - \frac{\sin \omega t - \sin \omega_n t}{\omega - \omega_n}\right) \end{aligned} \tag{0.4}$$

In the limit of large t,

$$u_i(t) \;\; \textit{approximately} \;\; \longrightarrow \sum_n -\frac{|\langle i|n\rangle|^2}{2\omega_n} \cdot 2\pi\delta(\omega - \omega_n)\cos(\omega t)$$

Rigorously, by using a representation of the δ-function (which's also the one used in deriving Fermi's Golden Rule),

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

We can show that the *resonance amplitude* of i due to perturbation on i — which was shown above to be proportional to the LDOS, can be filtered out by multiplying $\cos\omega t$ and integrate up to node $T = 2k\pi/\omega$, where k is a large integer. Thus we arrive at the central result

$$\boxed{\rho_i(\omega) = -\frac{2\omega^2}{\pi^2} \lim_{k\to\infty} \frac{1}{k} \int_0^{\frac{2k\pi}{\omega}} u_i(t) \cos\omega t dt} \tag{0.5}$$

- So the procedure would be

1. Add perturbation on i and do "MD" using equation of motion

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

2. Integrate $u_i(t)$ using formula (0.5) to get $\rho_i(\omega)$.

Multi-Channel Perturbation:

- Observation:
  - Major cost in computing $\mathbf{Du}(t)$ at each step.
  - Adding perturbation and doing integration cost very little.

Question: *Is it possible to get many channels of frequency information out of a single "MD" run?*

It turns out that *we can*, on condition that all frequencies are multiples of a certain *base frequency* α, and that the integration is up to a node of the base frequency.

Perturbation:

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

The interference effect between channels completely vanishes in the limit of large k:

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

Several Points:

- $\mathbf{Du}(t)$ multiplication is $\mathcal{O}(N)$ when $\mathbf{D}$ is sparse, $\mathcal{O}(N^2)$ when $\mathbf{D}$ is dense.
- Memory requirement is minimal.
- Measure the full spectrum.
- Equation of motion can be entirely *fictitious*. If we replace $\mathbf{D}$ by electronic tight-binding Hamiltonian H, the only difference is to replace ω by $\sqrt{\omega}$.
- Even at finite k, we know exactly what the δ-functions are replaced by, which will give a theoretical account of the error. One conclusion is that the linewidth is **uniform** for all channels:

$$\Delta\omega = \frac{\alpha}{k} \tag{0.6}$$

High-Precision Integration Scheme:

Due to the *explicit* form of the equation of motion, we can come up with a high-precision integration scheme that allows timestep 1000 to 2000 times larger than those of the conventional methods ($\omega_{max}\Delta t \sim 2\pi/3!$), while the cost of each step only increases by 5 times (for the order-12 case). The idea is a generalization of the Verlet algorithm:

$$\mathbf{u}(t+\Delta t) + \mathbf{u}(t-\Delta t) = 2\mathbf{u}(t) + (\Delta t)^2\ddot{\mathbf{u}}(t) + \frac{(\Delta t)^4}{12}\mathbf{u}^{(4)}(t) + \frac{(\Delta t)^6}{360}\mathbf{u}^{(6)}(t) + ...$$

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

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

are exact and can be *evaluated* successively with only the initial knowledge of $\mathbf{u}(t)$. The integration could be done to the same order of accuracy using integration by parts,

$$\begin{aligned}\int_t^{t+\Delta t} u_i(t')\cos(m\alpha t')dt' = & \left[\frac{u_i(t')\sin(m\alpha t')}{m\alpha} + \frac{\dot{u}_i(t')\cos(m\alpha t')}{(m\alpha)^2}\right. \\ & - \frac{\ddot{u}_i(t')\sin(m\alpha t')}{(m\alpha)^3} - \frac{u_i^{(3)}(t')\cos(m\alpha t')}{(m\alpha)^4} + ... \\ & \left.\left. - \frac{u_i^{(10)}(t')\sin(m\alpha t')}{(m\alpha)^{11}} - \frac{u_i^{(11)}(t')\cos(m\alpha t')}{(m\alpha)^{12}}\right]\right|_t^{t+\Delta t}\end{aligned}$$

Error Analysis:

• In measuring the full spectrum it is most convienient to let $k = 1$ and α be the desired resolution of your measurement. Usually $\alpha = \omega_{max}/M, M \sim 300$.

• $\Rightarrow$ 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 no information is lost. On the other hand the non-ideal $k = 1$ condition can induce strong interference between nearby channels: m and $m \pm 1, m \pm 2$.

At $k = 1$, what's actually happening?

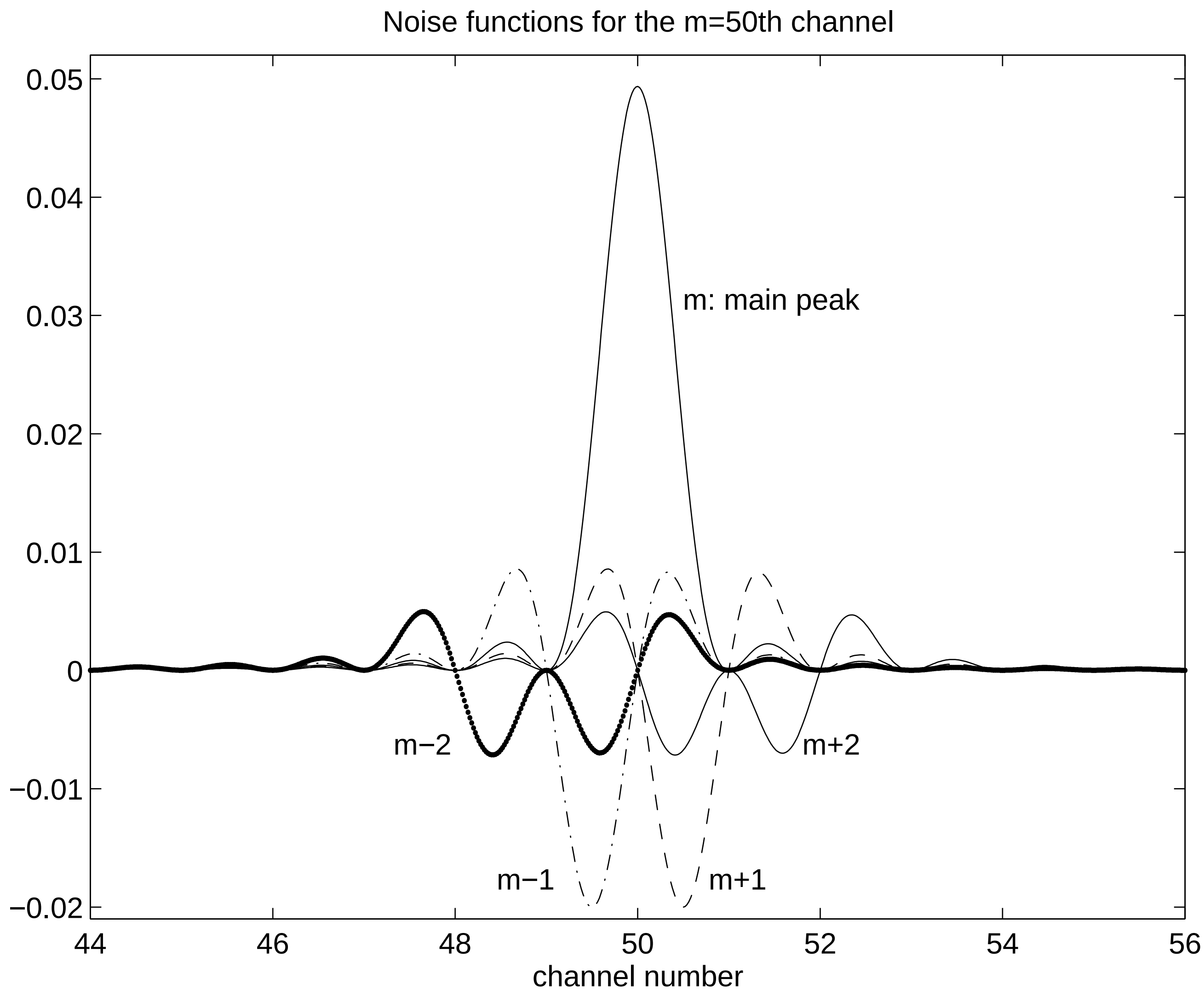
$$\delta(\omega_n - m\alpha) \to \left\{ \sum_{m'=1}^{M} A_{m'} N_{m,m'} \left(\frac{\omega_n}{\alpha}\right) \right\} \cdot \frac{4m}{A_m \pi^2 \alpha}$$

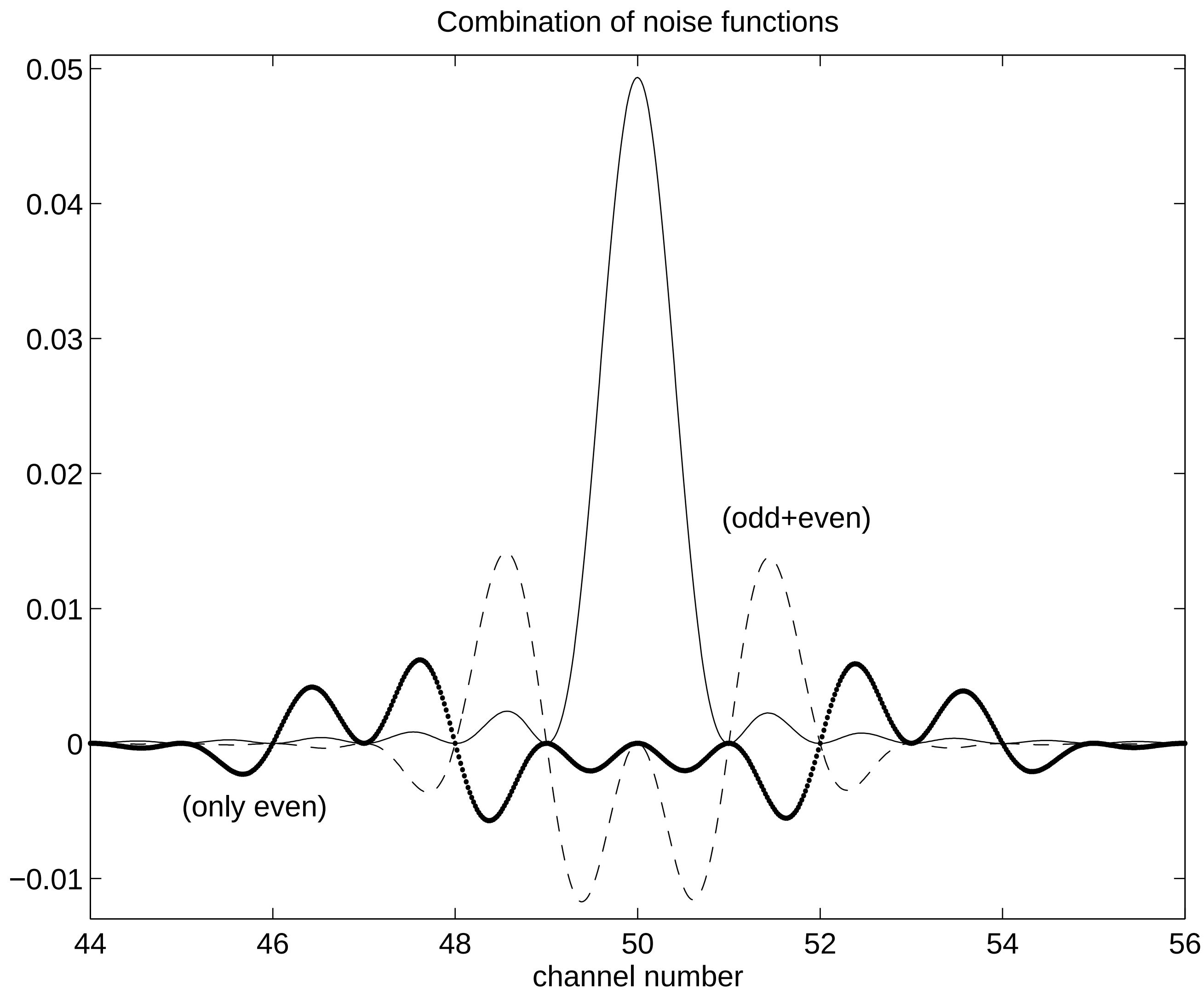
$$N_{m,m'}(\omega) = \frac{\sin^2(\pi\omega) m'}{(m^2 - \omega^2)(m'^2 - \omega^2)}$$

in which only the $m' = m$ term is needed. All others are noise functions that although give zero net drift:

$$\int_0^{+\infty} N_{m,m'}(\omega) d\omega = 0 \quad \text{for} \quad m' \neq m.$$

they impair the resolution power.


Noise functions for the m=50th channel
0.05
0.04
0.03
0.02
0.01
0
−0.01
−0.02
44
46
48
50
52
54
56
channel number
m: main peak
m−2
m+2
m−1
m+1


Combination of noise functions
0.05
0.04
0.03
0.02
0.01
0
−0.01
(odd+even)
(only even)
44
46
48
50
52
54
56
channel number

Question: *Can we design an $\{A_m\}$ series that globally decrease the effect of noise?*

• "Time-reversal" symmetry:

Notice that $A_{m'}$ can be any complex number while $N_{m,m'}(\omega)$ is always real.

⇒ *Assign alternating "parities" to different channels*

$$\mathrm{Im}A_m = (-1)^m \mathrm{Re}A_m$$

⇒ *Observe that*

mth channel real response:	$.. + (\mathrm{ReA_{m-1}})N_{m,m-1}(\omega) + (\mathrm{ReA_m})N_{m,m}(\omega) + (\mathrm{ReA_{m+1}})N_{m,m+1}(\omega) + ..$
mth channel imaginary response:	$.. + (\mathrm{ImA_{m-1}})N_{m,m-1}(\omega) + (\mathrm{ImA_m})N_{m,m}(\omega) + (\mathrm{ImA_{m+1}})N_{m,m+1}(\omega) + ..$

⇒ *If we use*

(mth channel real response) + $(-1)^m \times$ (mth channel imaginary response)

then **all odd-distanced noise functions would be cancelled out** because the two channels have different "parity". Furthermore there will be cancellations if A_{m-2} and A_{m+2} are of the same sign. So we arrive at the following amplitude series,

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

There is another issue: we want $f_i(t)$ to be well-behaved in time such that it does not contain very high blips that will destroy the numerical integration.

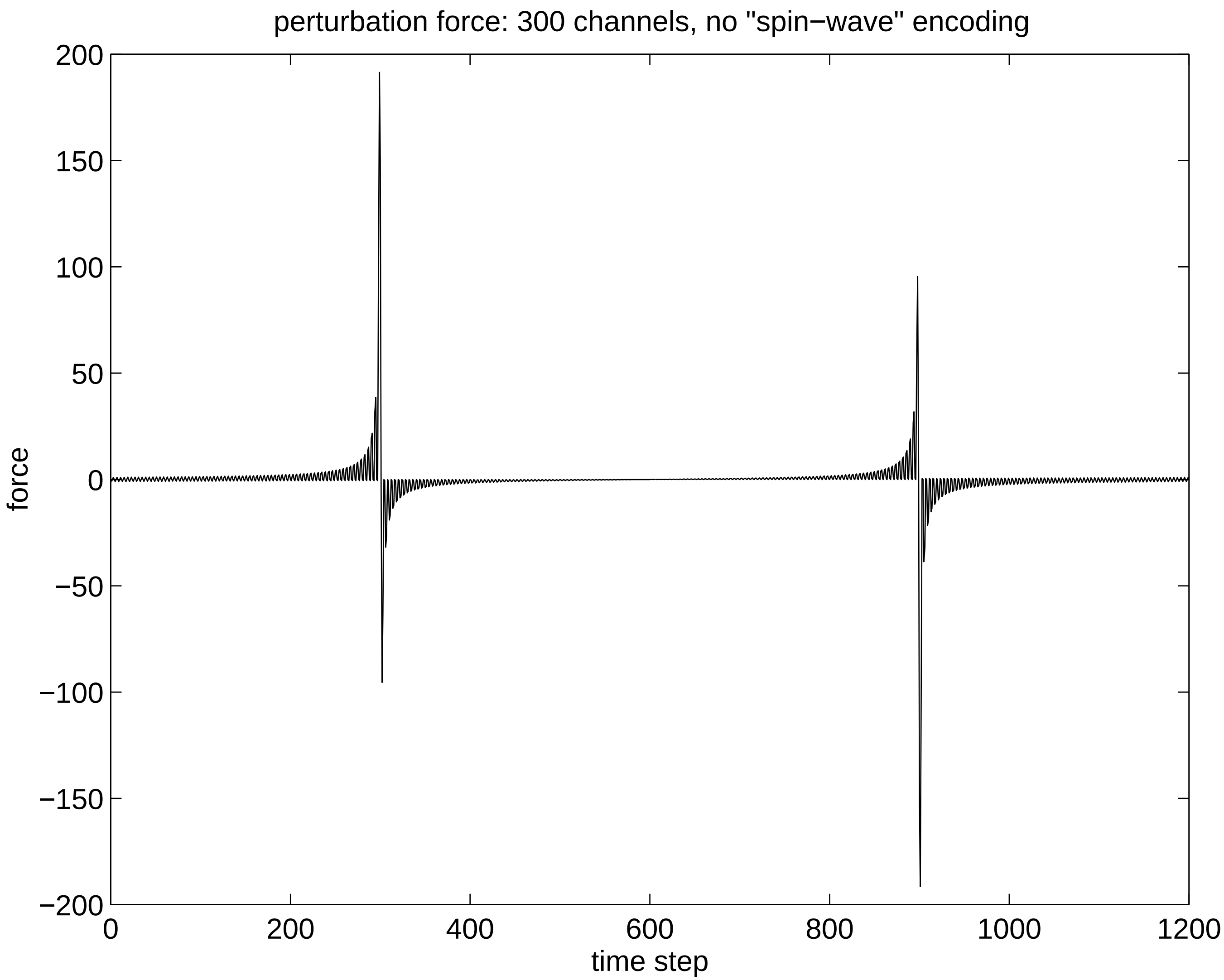
• The above $\{A_m\}$ doesn't work well in this sense because at $t = \pi/2\alpha$ there will be a sharp resonance in $f_i(t)$ that's proportional to M and with even higher derivatives. Such resonances are due to the long-ranged order in $\{A_m\}$ irrespective of its detailed repeat pattern.

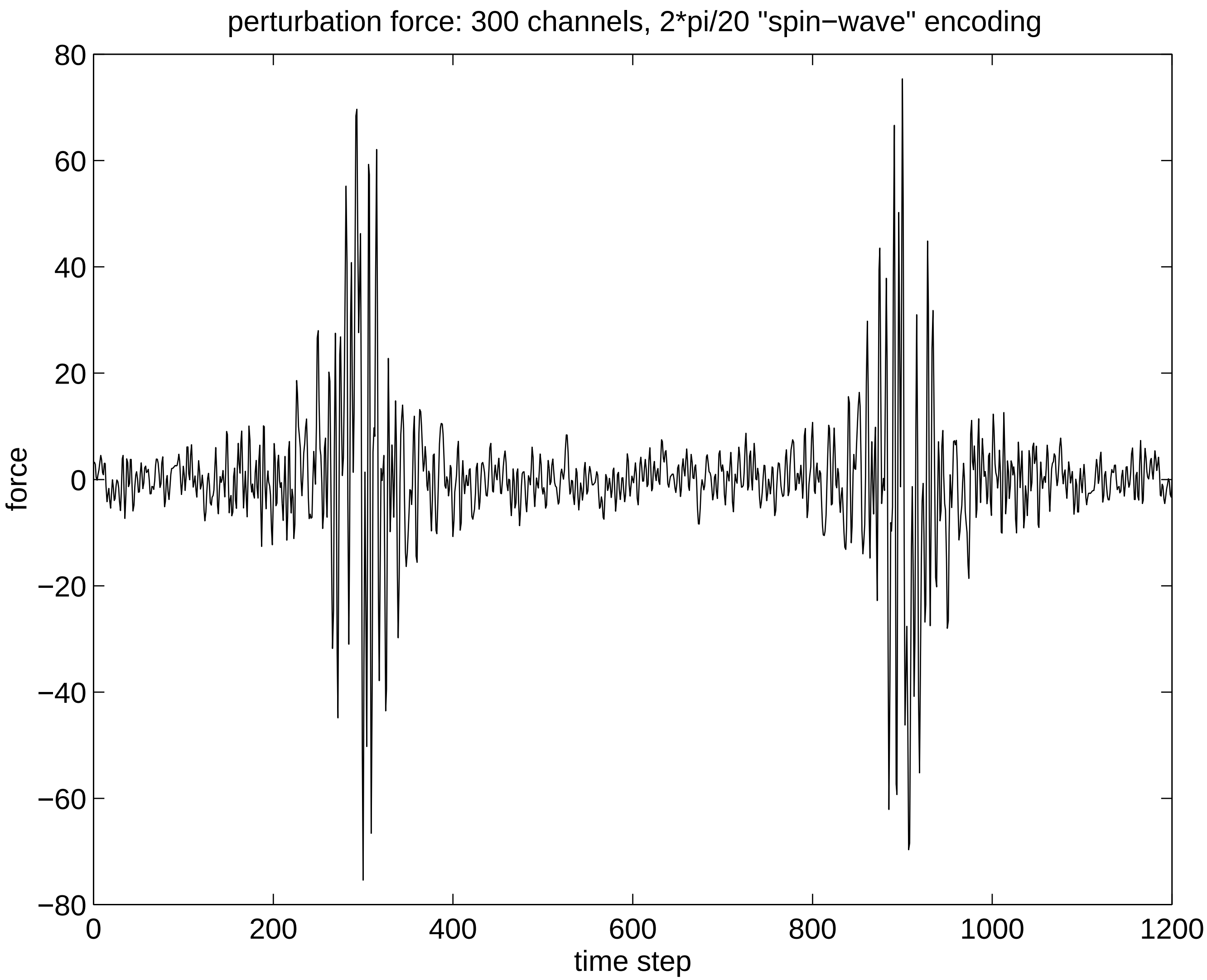
⇒ We can improve the situation by multiplying $\{A_m\}$ by a slowly varying "spin-wave":

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

where ξ_m is a random number taking equally possible value ± 1 and $\Delta\theta$ is a constant small angle.
⇒ long-ranged order destroyed
⇒ short-ranged order remains such that previous error cancelling scheme still works.

• We will use $\{B_m\}$ as the amplitude series and in the end just "decode" the mth channel result by multiplying $e^{-i\phi_m}$.


perturbation force: 300 channels, no "spin−wave" encoding
force
time step
200
150
100
50
0
−50
−100
−150
−200
0
200
400
600
800
1000
1200


perturbation force: 300 channels, 2*pi/20 "spin−wave" encoding
force
time step
80
60
40
20
0
−20
−40
−60
−80
0
200
400
600
800
1000
1200

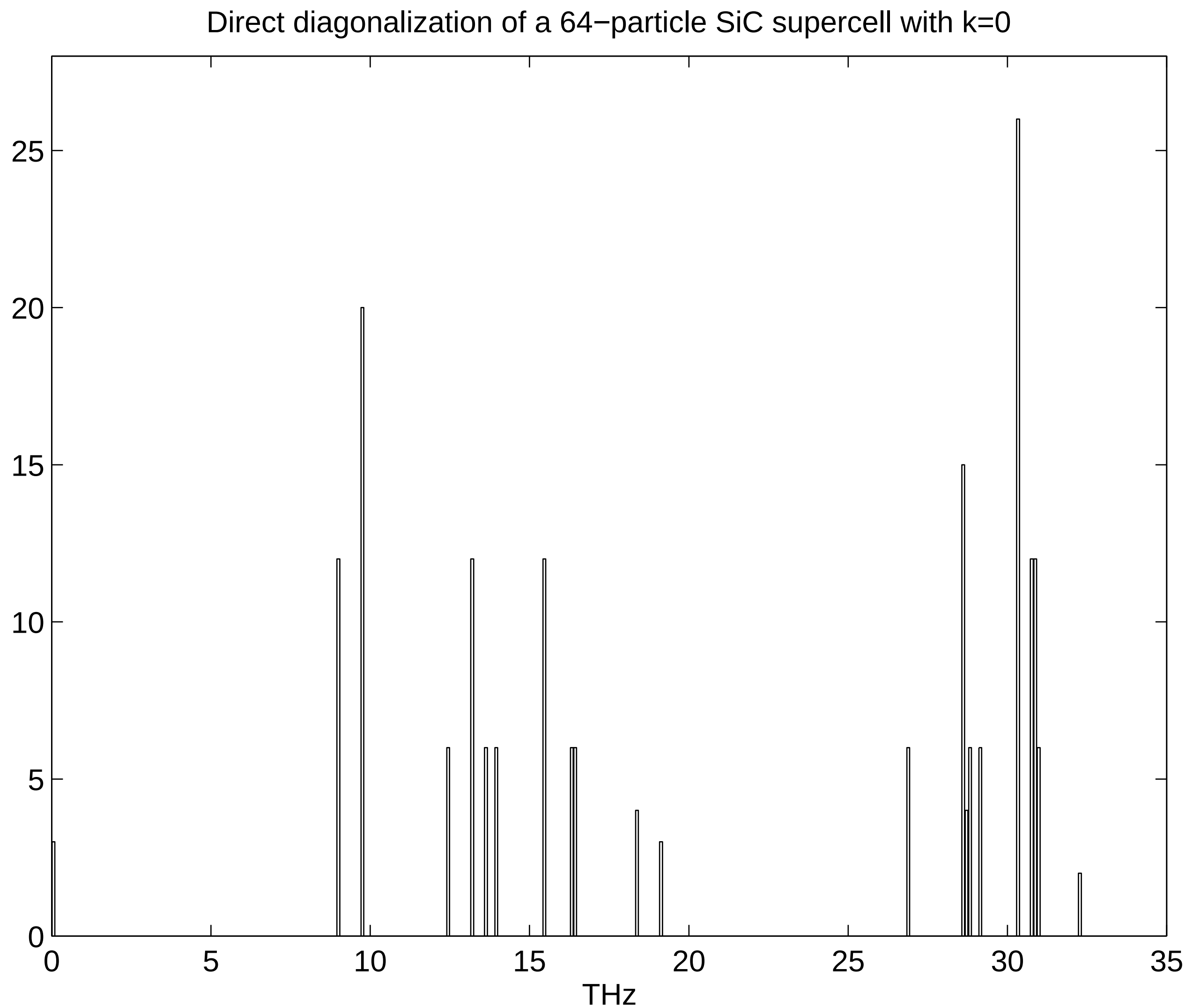
• The algorithm is generally **robust** except at very low frequencies, where the first few channels usually diverge. We can solve the problem by doing a *rigid shift transformation* on the dynamical matrix

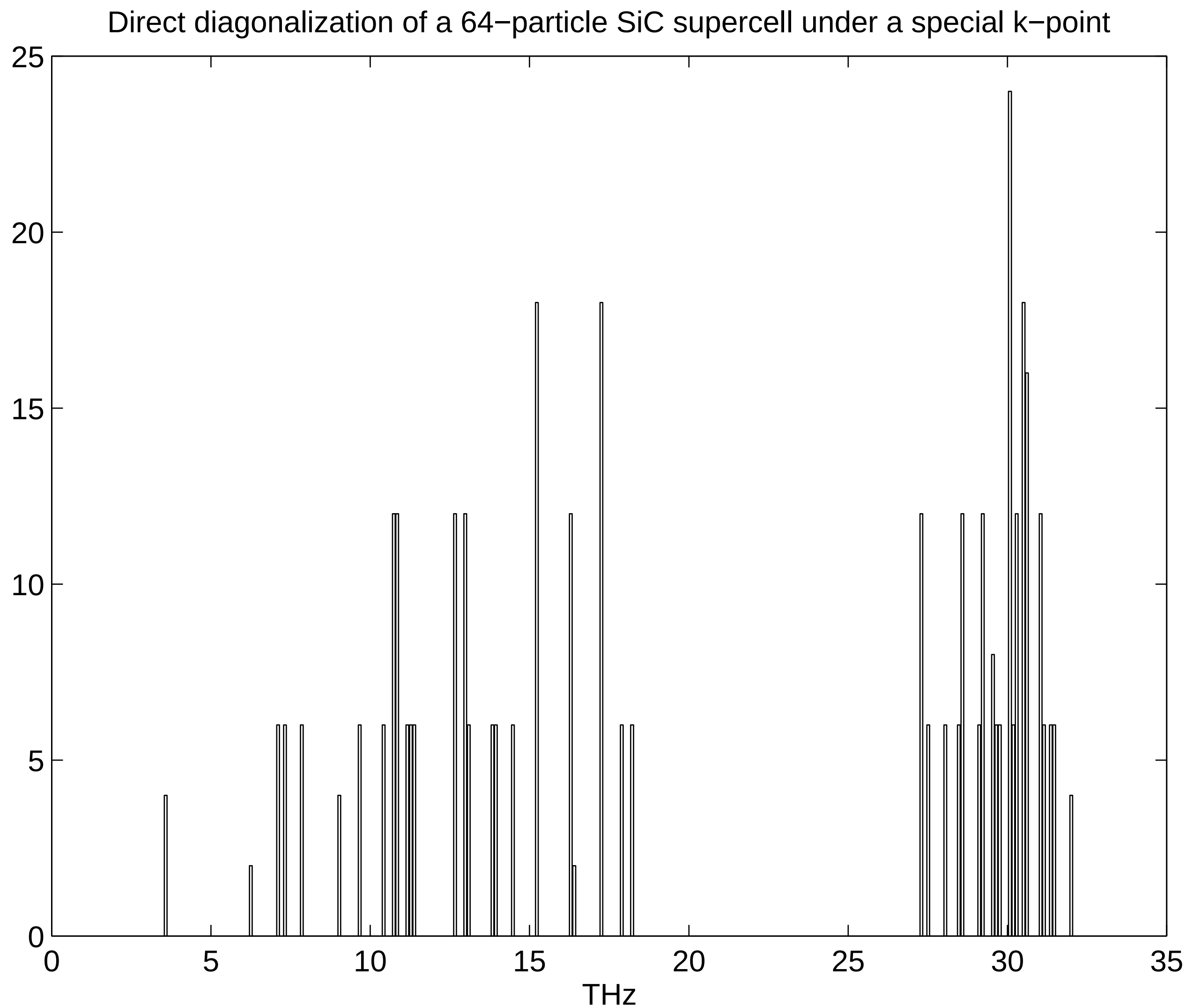
$$\mathbf{D} \rightarrow \mathbf{D} + \omega_{shift}^2 \mathbf{I}$$

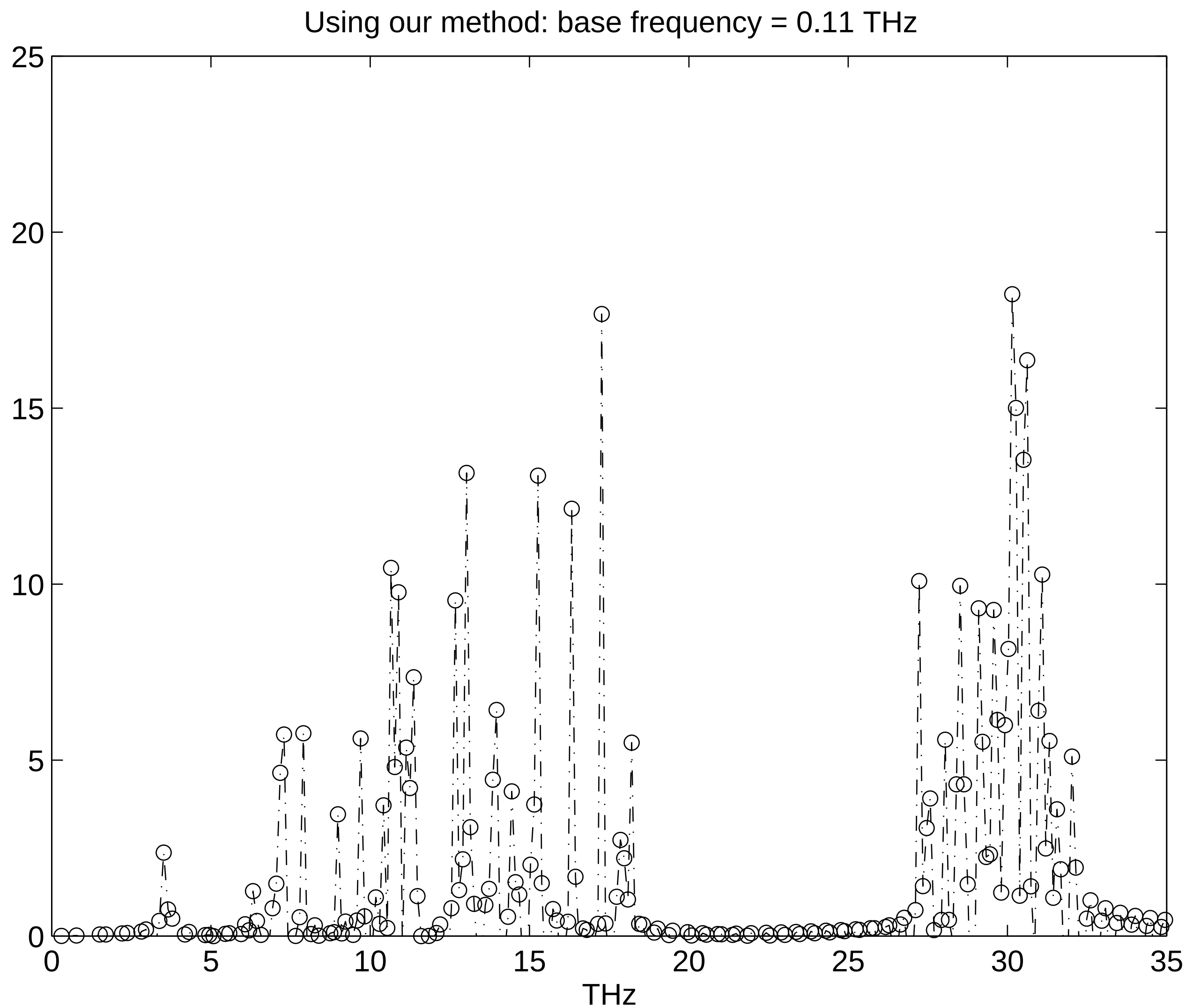
such that all meaningful channels are outside the divergence region, and *use the new matrix* instead. In the end we just do a simple transformation back to $\rho_i(\omega)$:

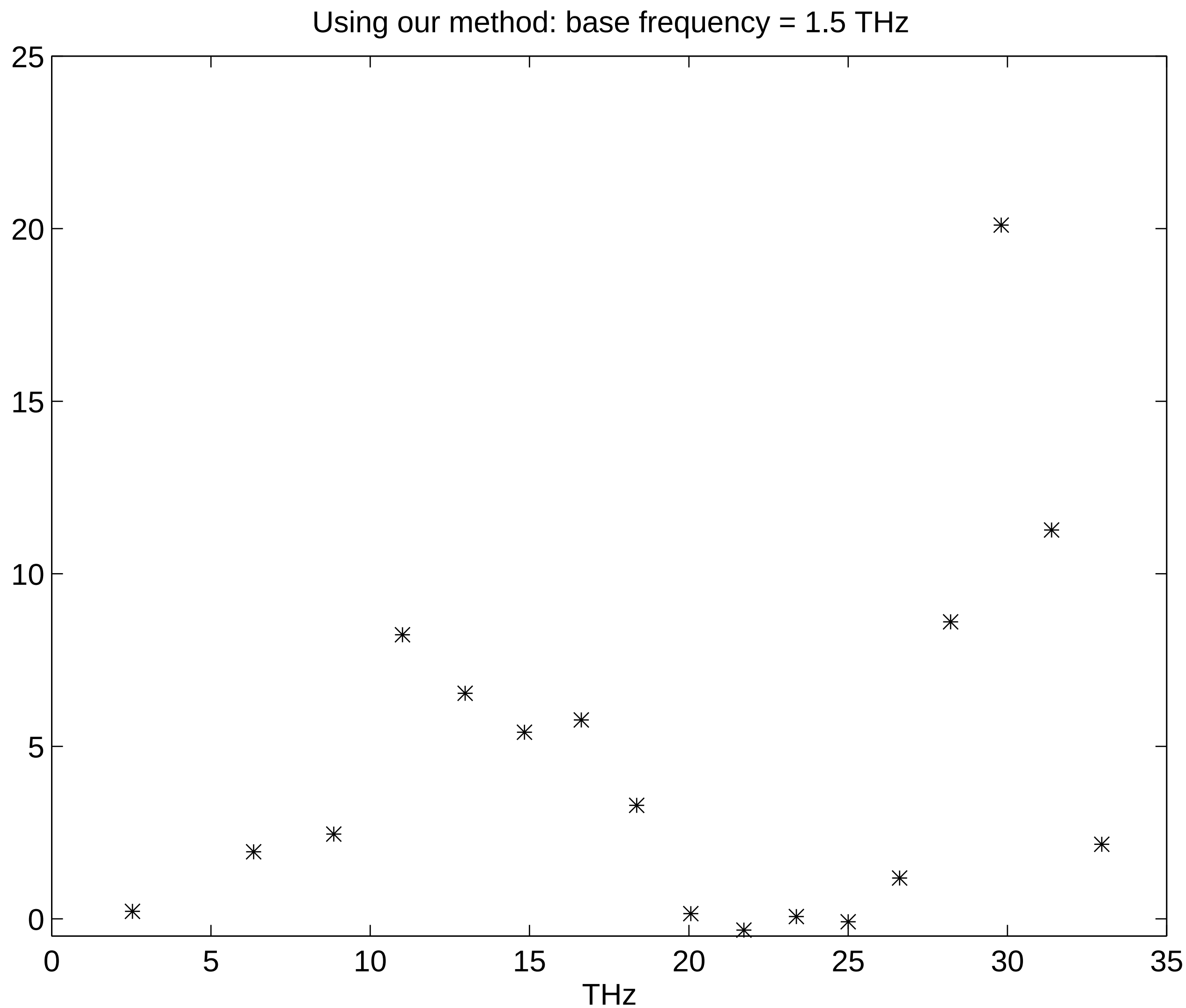
$$\omega'^2 = \omega^2 + \omega_{shift}^2 \qquad \rho_i(\omega) = \frac{\omega}{\omega'} \rho_i'(\omega')$$

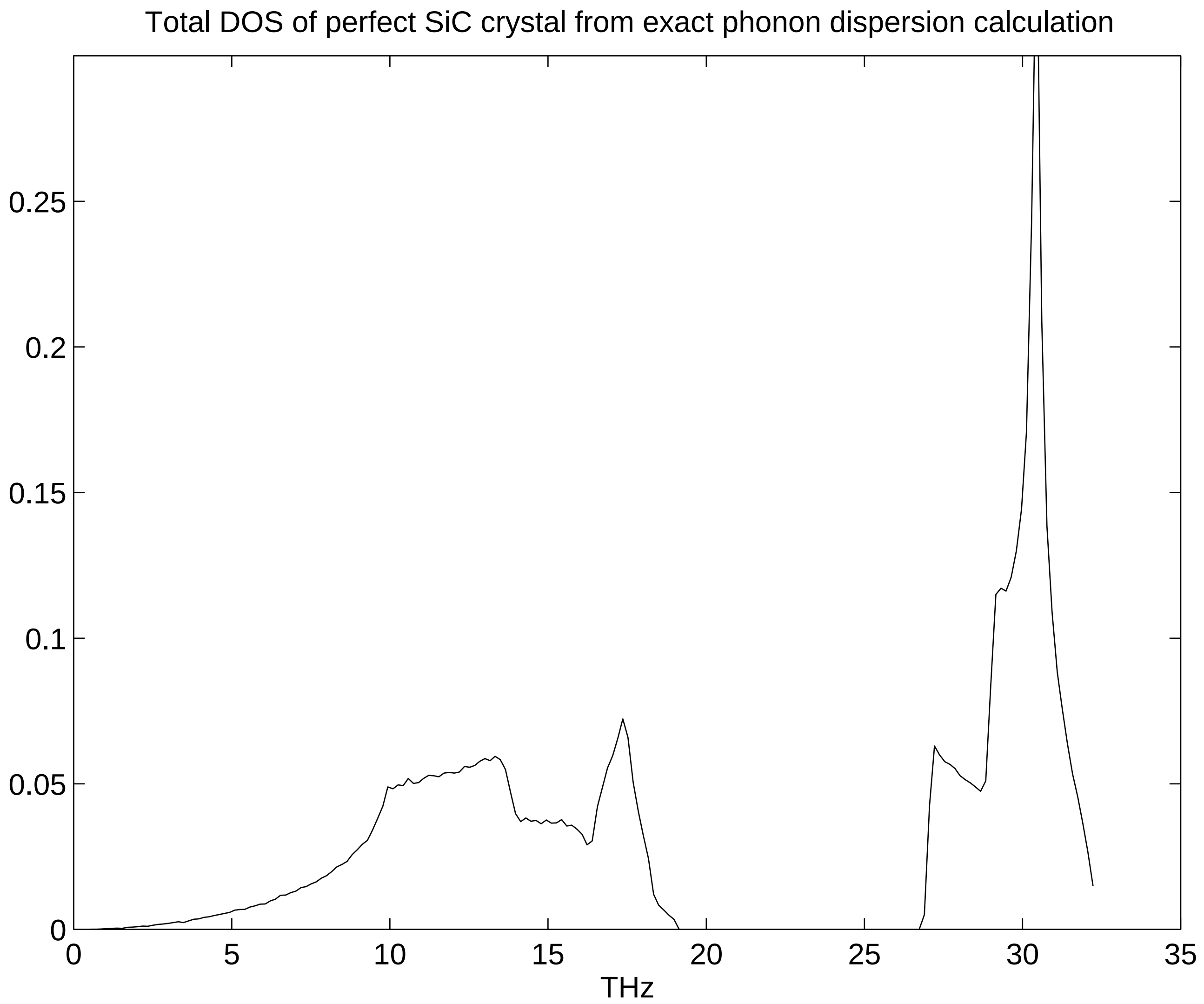
Test on a small matrix: We studied the dynamical matrix of a SiC supercell with 64 particles inside in perfect crystalline order. First shown is the result of direct diagonalization of this real matrix (the "Γ-point"). A better representation is given after we impose a supercell **k**-wavevector $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\frac{2\pi}{A}$ on the dynamical matrix, which is a special **k**-point given by Baldereschi for the simple-cubic BZ (of the supercell). Direct diagonalization of this new matrix shows that the zero-modes are now shifted. We apply our method on this 192×192 Hermitian matrix and compare with the exact results. Two extremes are shown: one is very small α, the other is rather large α.


Direct diagonalization of a 64−particle SiC supercell with k=0
0
5
10
15
20
25
0
5
10
15
20
25
30
35
THz


Direct diagonalization of a 64−particle SiC supercell under a special k−point
25
20
15
10
5
0
0
5
10
15
20
25
30
35
THz


Using our method: base frequency = 0.11 THz
25
20
15
10
5
0
0
5
10
15
20
25
30
35
THz


Using our method: base frequency = 1.5 THz
25
20
15
10
5
0
0
5
10
15
20
25
30
35
THz


Total DOS of perfect SiC crystal from exact phonon dispersion calculation
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
30
35
THz

LDOS of Si and C in perfect crystal:

Solid line from exact phonon dispersion calculations by diagonalizing 6×6 matrices in the $\mathbf{k}$-space of the unit cell (zinc-blend structure, fcc lattice). A total number of 100,000 $\mathbf{k}$-points were randomly sampled to give the two smooth curves.

Our method:

- A 4096-particle supercell is being used, which means a 12288×12288 Hermitian matrix for each supercell $\mathbf{k}$. *"The bigger, the merrier!"*

- Dynamical matrix from three-body Tersoff potential. Each particle has 4 nearest and 12 second-nearest neighbours and so total of 51 non-vanishing entries in a column of $\mathbf{D}$.

- $\alpha = 0.125$ THz, $w_{max} = 35$ THz; $\omega_{shift} = 2$ THz.

- time step: $\omega_{max}\Delta t = 2\pi/3$; "spin-wave" encoding: $\Delta\theta = \pi/10$.

- A total number of 25/30 supercell $\mathbf{k}$-points were randomly sampled for Si/C.

Facts:

- High quality results, up to the very low frequency region, with very sharp resolution of the band gap and critical points.

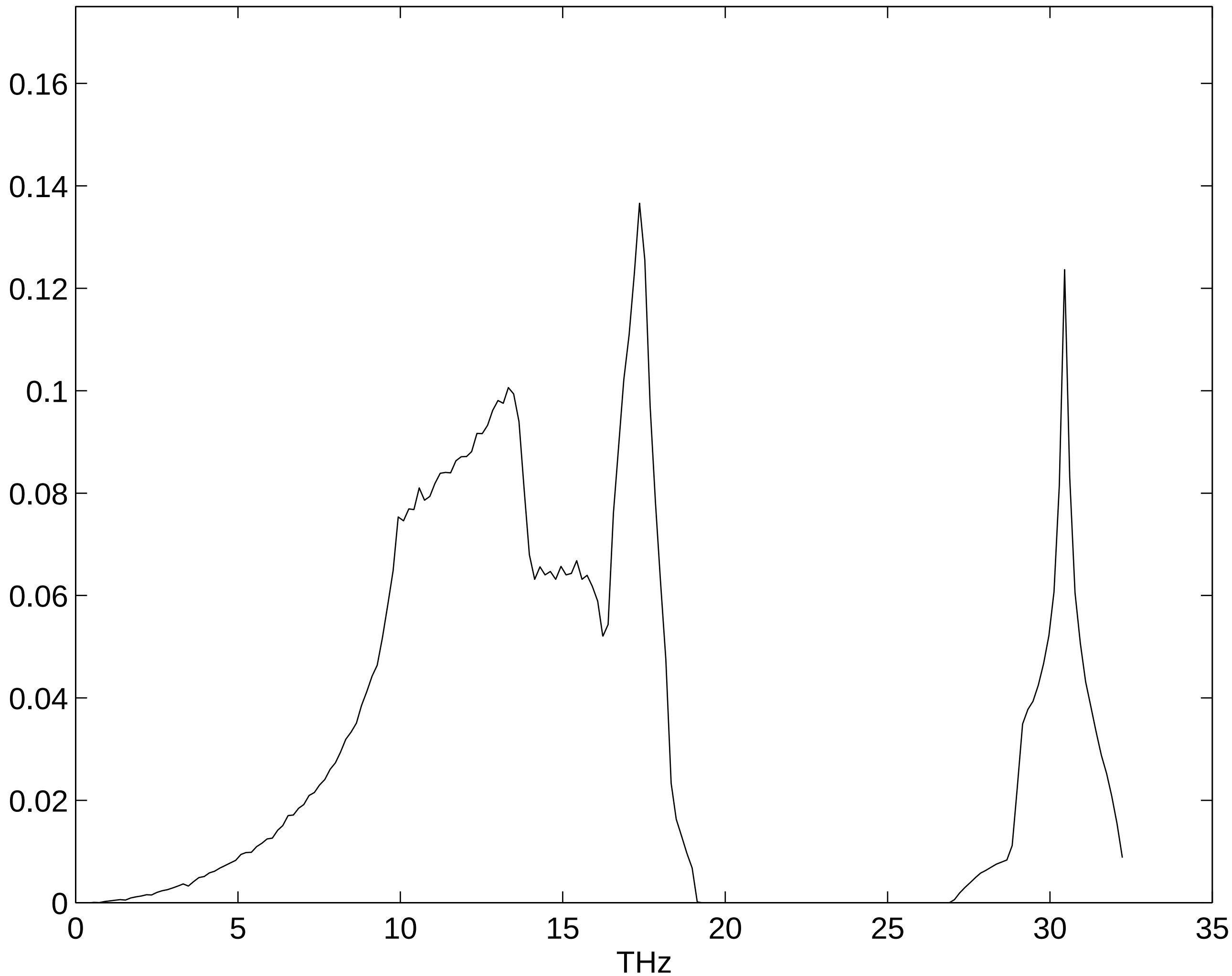
- The speed is 20 *minutes* per supercell **k**-point for a full LDOS spectrum calculation on a desktop DEC $\alpha-$workstation, for this *very large* system. *!!@*?!.♡♡!*

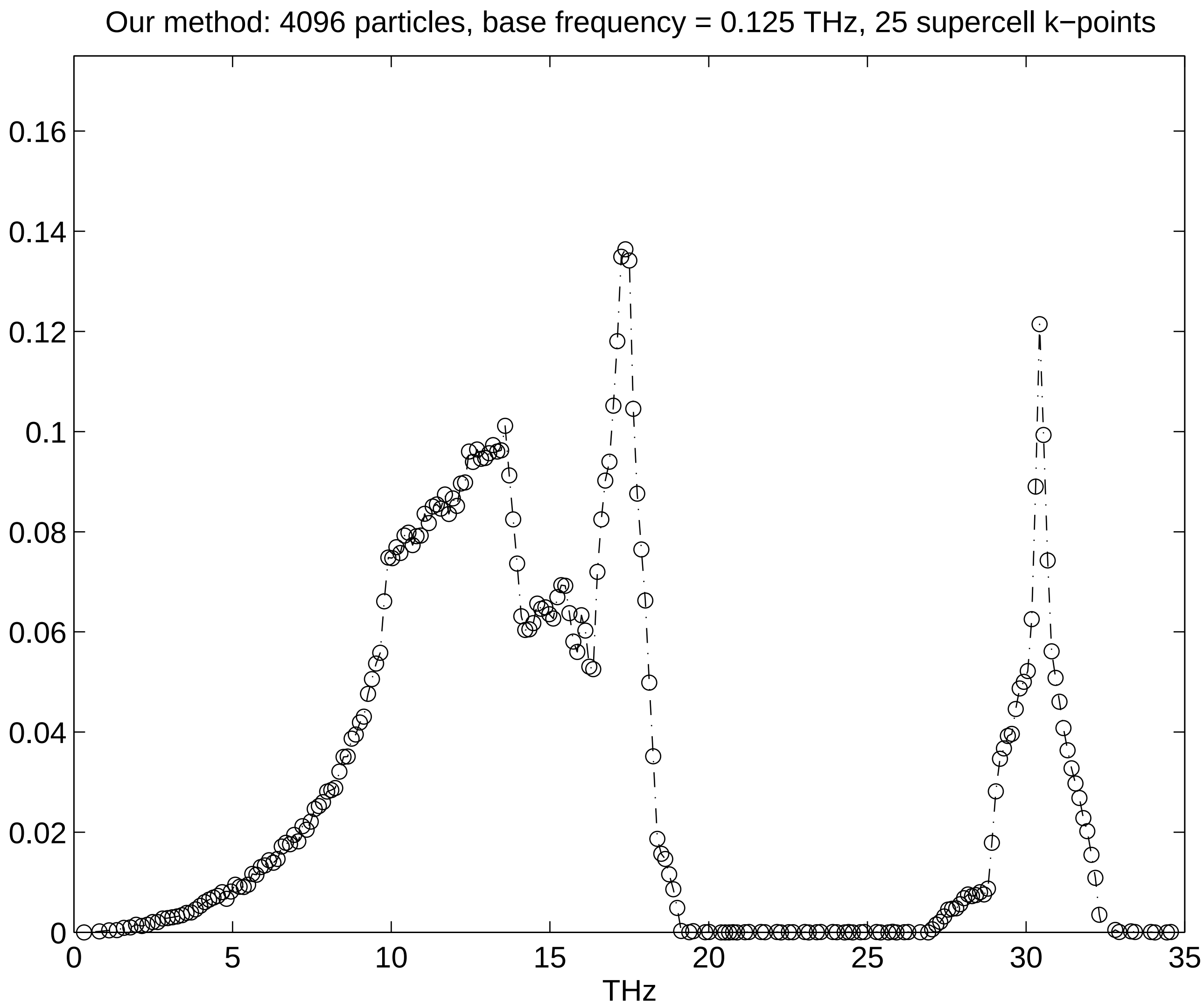
- One-loop structure can be easily vectorized.

Defect calculations:

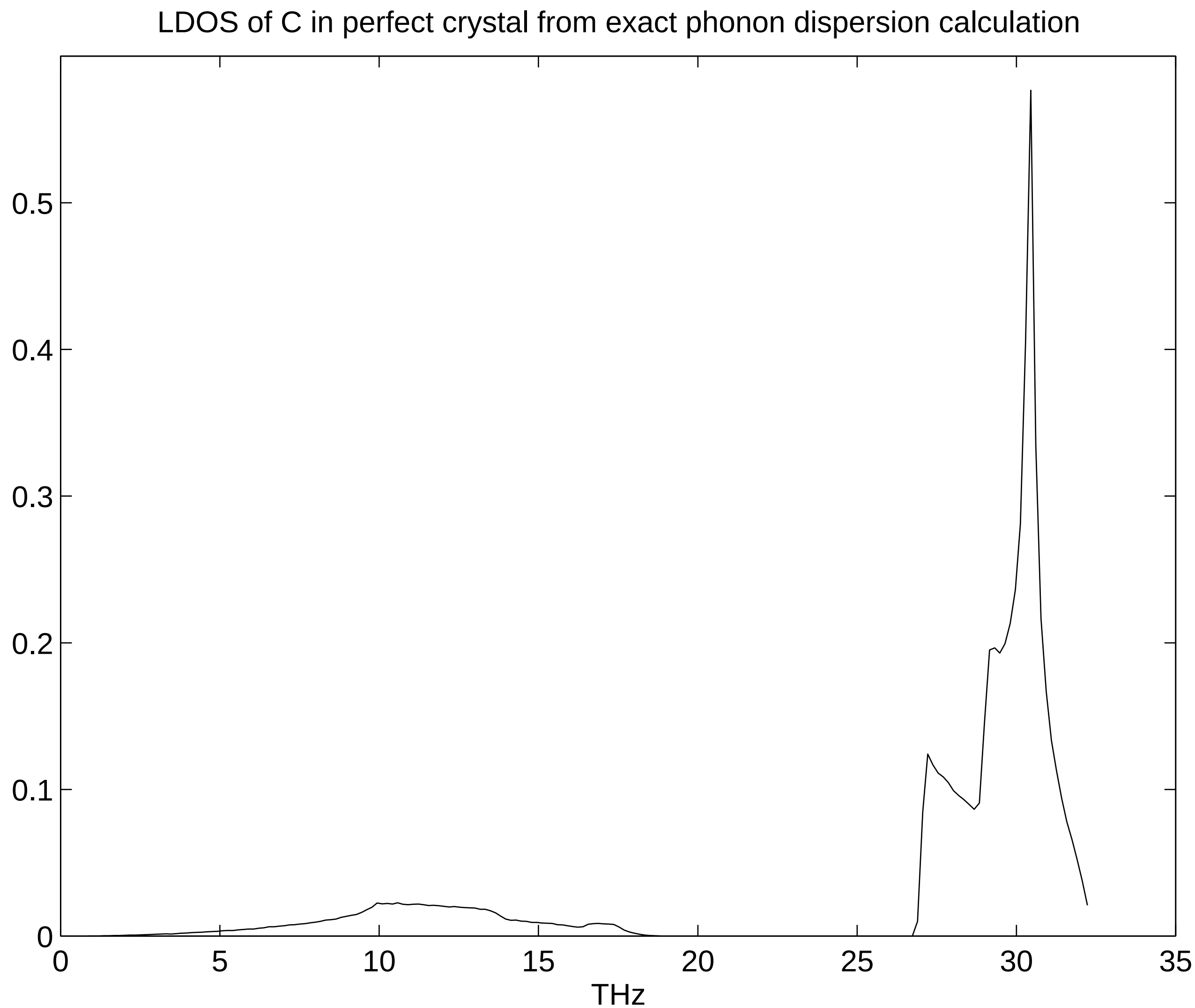
Switch a nearest-neighbour pair of Si and C in the above supercell, thus generating an antisite-pair defect. The configuration was relaxed by the conjugate gradient method. LDOS is calculated for the switched two atom in the direction of their bond. All parameters remain unchanged except $\omega_{max} = 40$ THz. Observe the splitting of the optical branch and the generation of two gap modes at 23.2 and 25.9 THz.

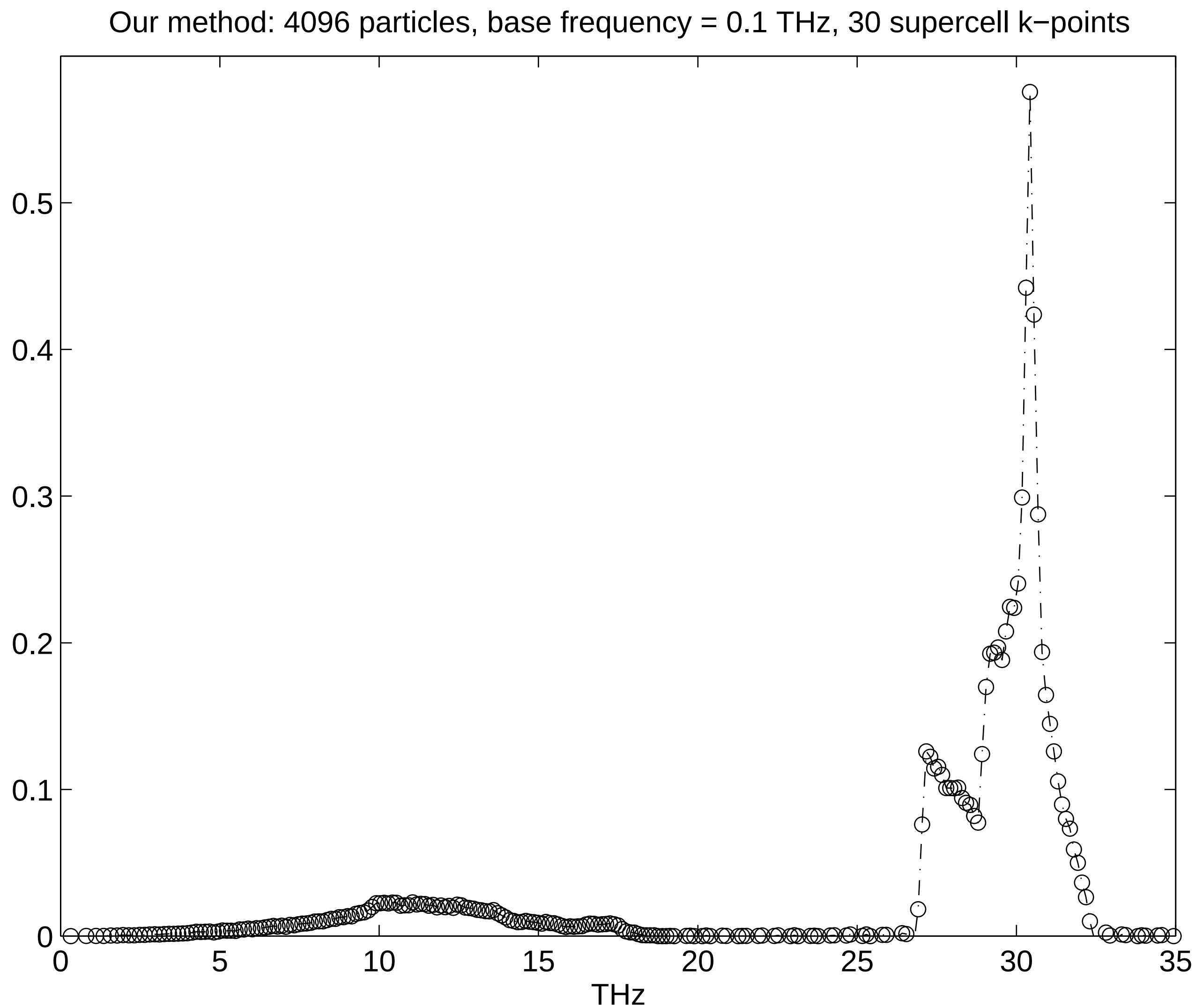
LDOS of Si in perfect crystal from exact phonon dispersion calculation

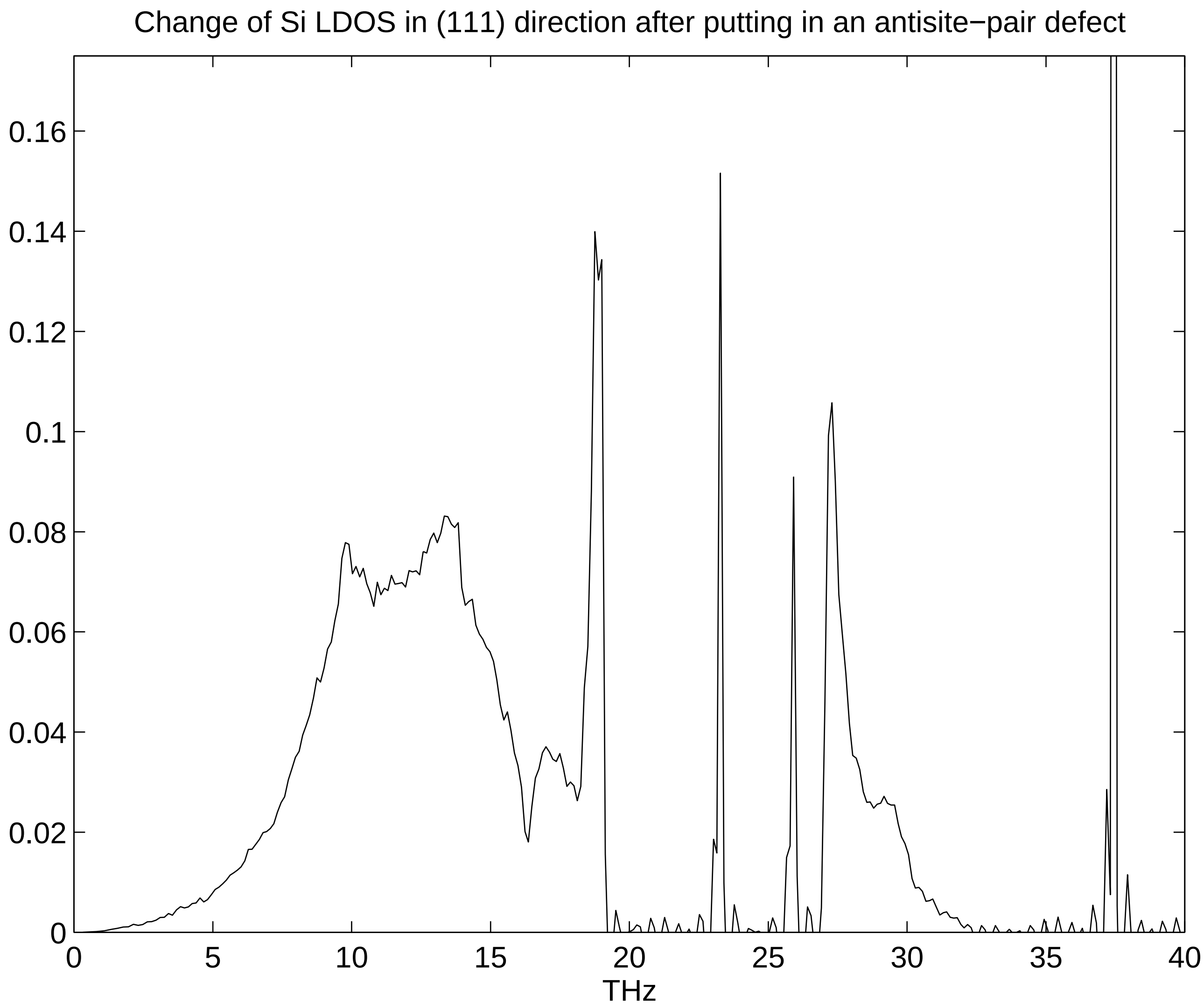


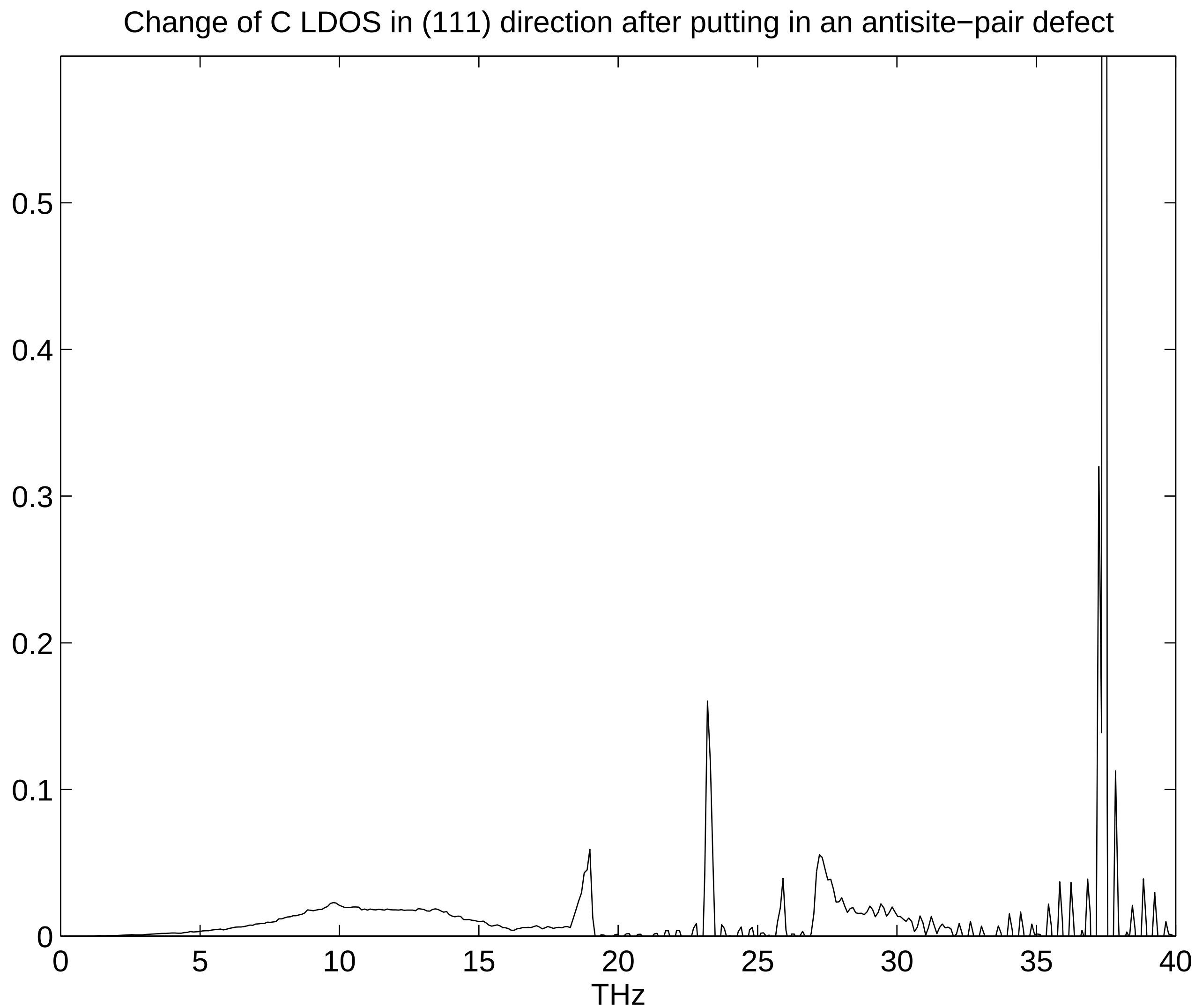


Our method: 4096 particles, base frequency = 0.125 THz, 25 supercell k−points
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
25
30
35
THz


LDOS of C in perfect crystal from exact phonon dispersion calculation
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
THz


Our method: 4096 particles, base frequency = 0.1 THz, 30 supercell k−points
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
THz


Change of Si LDOS in (111) direction after putting in an antisite−pair defect
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
25
30
35
40
THz


Change of C LDOS in (111) direction after putting in an antisite−pair defect
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
40
THz