Quantum Molecular Dynamics: Representation & Solution

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How to represent & solve Kohn-Sham equations in QMD?

Representation: Plane-Wave Basis

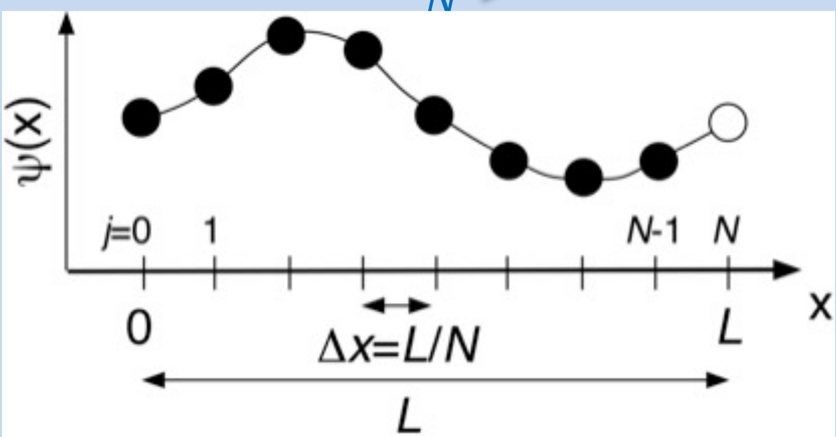
- **Pseudopotentials result in slowly varying wave functions that can be represented on a regular grid, which in turn can be represented as a linear combination of plane waves, *i.e.*, Fourier transform**

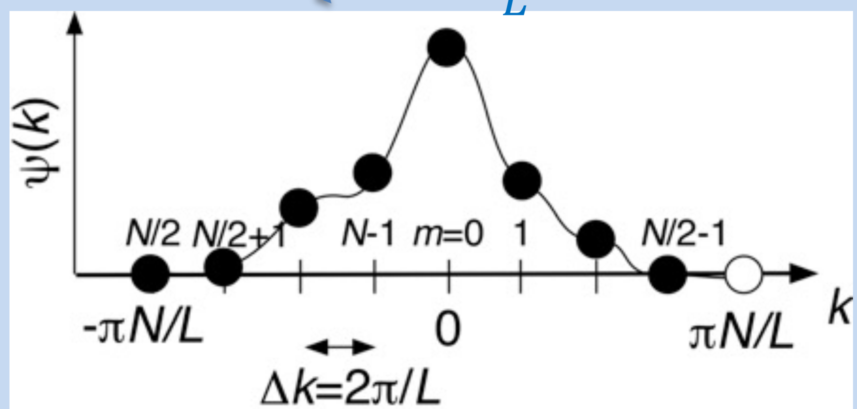
$$\psi(\mathbf{r}_j) = \sum_{\mathbf{k}_n} \psi_{\mathbf{k}_n} \exp(i\mathbf{k}_n \bullet \mathbf{r}_j)$$

$x_j = \frac{jL}{N}$

1D example

$k_n = \frac{2\pi n}{L}$



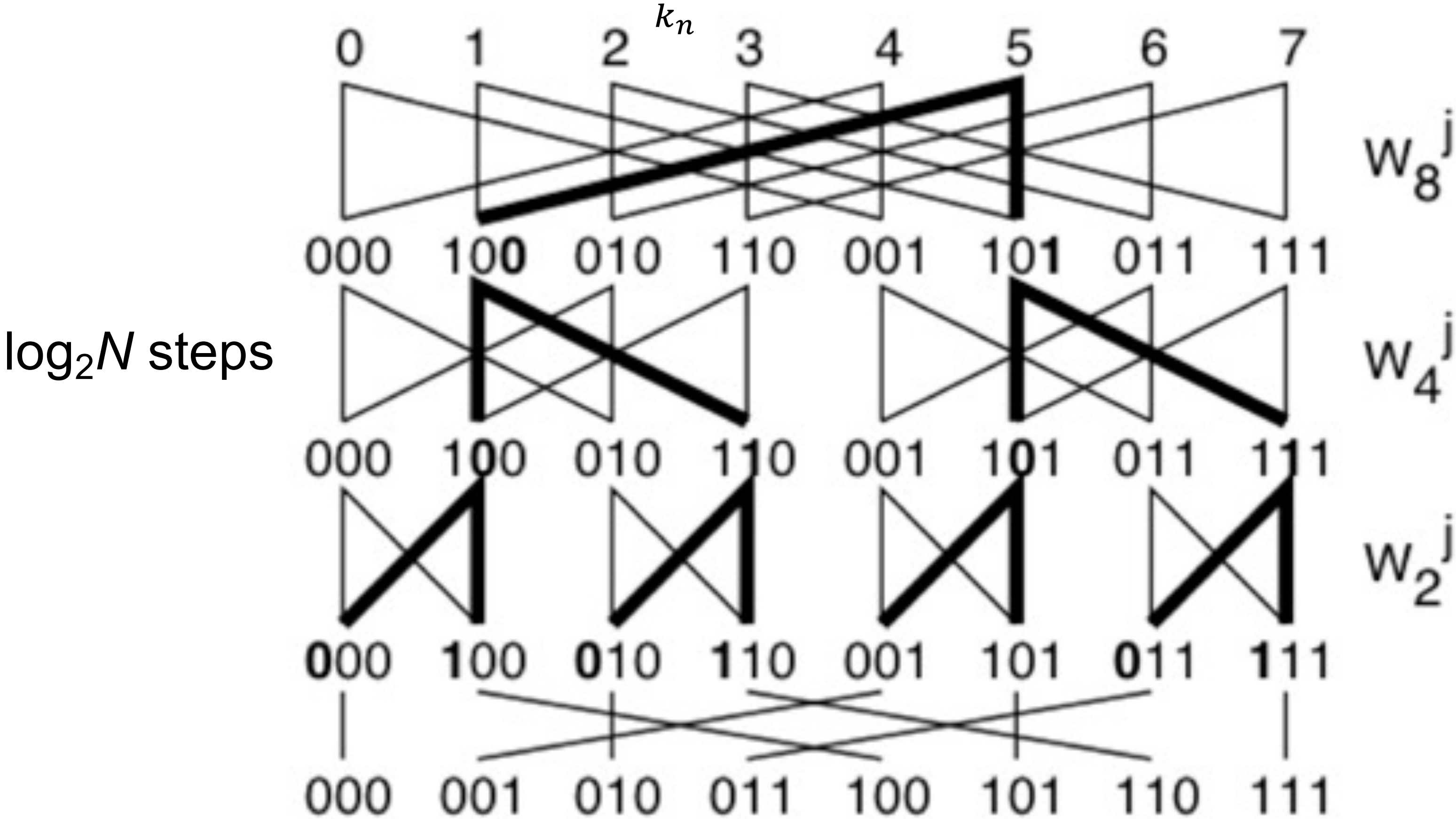


See "Fourier transform as a resolution of unity in a vector space"
https://aiichironakano.github.io/phys516/03QD-slide.pdf

Numerics: Fast Fourier Transform

- ***O*(*N*log*N*) fast Fourier-transform (FFT) algorithm is typically used to perform Fourier transform**

$$\psi(x_j) = \sum_{k_n} \psi_{k_n} \exp(i k_n x_j)$$

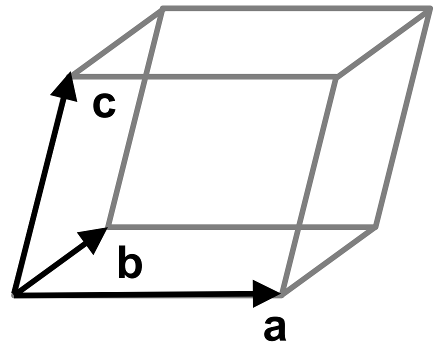


Butterfly (hypercube) data-exchange network

See "divide-&-conquer and FFT"
https://aiichironakano.github.io/phys516/03QD-slide.pdf

Periodic Solid

- **Consider a periodic solid with the unit cell spanned by vectors a, b & c**



- **Fourier transform of a periodic function**

$$u(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{G}} \exp(i\mathbf{G} \bullet \mathbf{r})$$

$$\mathbf{G} = \frac{2\pi}{\mathbf{a} \bullet (\mathbf{b}\times\mathbf{c})} [l(\mathbf{b}\times\mathbf{c}), m(\mathbf{c}\times\mathbf{a}), n(\mathbf{a}\times\mathbf{b})] \quad (l, m, n \in \mathbb{Z})$$

- **Bloch's theorem**

n: band index

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \bullet \mathbf{r})\, u_{n,\mathbf{k}}(\mathbf{r})$$

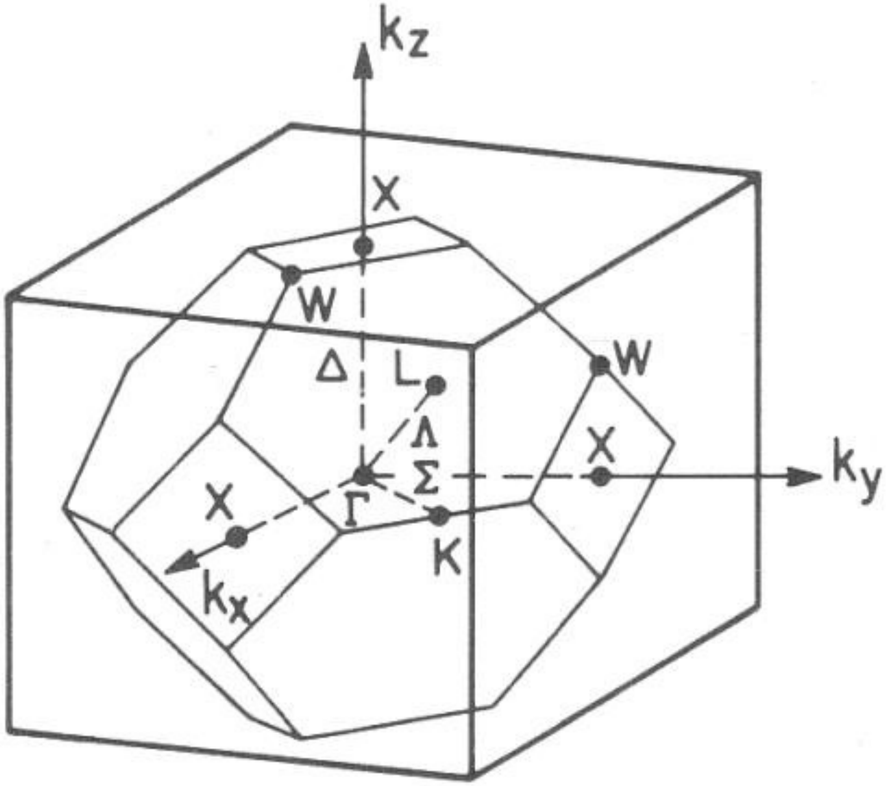
$$= \sum_{\mathbf{G}} u_{n,\mathbf{k}}(\mathbf{G}) \exp(i(\mathbf{k} + \mathbf{G}) \bullet \mathbf{r})$$

k ∈ first Brillouin zone in the reciprocal space

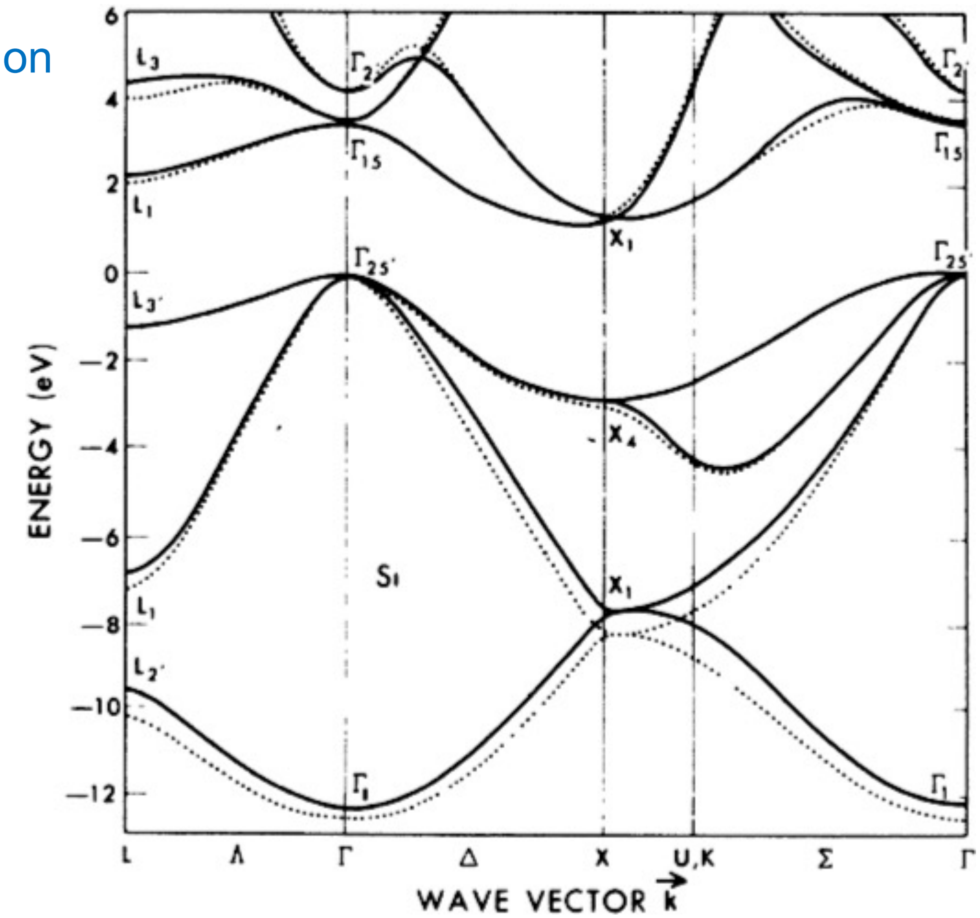
Electronic Bands: Infinite Lattice

- **Bloch theorem:** $\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \bullet \mathbf{r})u_{n,\mathbf{k}}(\mathbf{r})$

band index   periodic function



Brillouin zone of Si crystal



Kohn-Sham energy

J. R. Chelikowsky & M. L. Cohen, *Phys. Rev. B* 10, 5095 ('74)

See notes on (1) plane-wave basis & (2) supercell

QMD Algorithm

time $t = 0$

coordinates & velocities of atoms, $\{\vec{R}_I(t)\}, \{\vec{V}_I(t)\}$

minimize energy functional $E\left[\{\psi_n\}, \{\vec{R}_I(t)\}\right]$

by conjugate-gradient method

atomic force $\vec{F}_I(t) = -\dfrac{\partial E\left[\{\psi_n\}, \{\vec{R}_I(t)\}\right]}{\partial \vec{R}_I(t)}$

new coordinates and velocities of atoms at time $t + \Delta t$

$$\{\vec{R}_I(t + \Delta t)\}, \{\vec{V}_I(t + \Delta t)\}$$

by integrating Newton's equations of motion

$$M_I \frac{d^2 \vec{R}_I(t)}{dt^2} = \vec{F}_I(t)$$

$t \leftarrow t + \Delta t$

Molecular Dynamics Modes

- **Structural optimization, *e.g.*, quasi-Newton method, see** https://aiichironakano.github.io/phys760/MNK.pdf
  - **Relax atomic positions $\{\mathbf{R}_I\}$ to minimize the energy**
    $$\{\mathbf{R}_I^*\} = \mathrm{argmin}_{\{\mathbf{R}_I\}}\left(\min_{\{\psi_n(\mathbf{r})\}} E[\{\psi_n(\mathbf{r})\},\{\mathbf{R}_I\}]\right)$$

- **Molecular dynamics**
  - **Follow atomic trajectories by numerically integrating Newton's second law of motion**
    $$M\frac{d^2}{dt^2}\mathbf{R}_I = -\left\langle \Psi_0 \middle| \frac{\partial h(\mathbf{r},\mathbf{R}(t),t)}{\partial \mathbf{R}(t)} \middle| \Psi_0 \right\rangle$$
  - **Microcanonical (NVE), canonical (NVT) & isobaric (NPT) ensembles are supported**

    Martyna *et al.*, *Mol. Phys*. **87**, 1117 ('96)

For classical molecular dynamics, see PHYS 516 (*Methods of Computational Physics*, https://aiichironakano.github.io/phys516/02MD-slide.pdf) & MASC 575 (*Basics of Atomistic Simulation of Materials*)

Self-Consistent Field Iteration

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H,xc}}[\rho(\mathbf{r})]\right)\psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$$

Given $\rho(\mathbf{r})$, iteratively obtain $\{\psi_n, \epsilon_n\}$, *e.g.*, by preconditioned conjugate gradient

Given $\{\psi_n, \epsilon_n\}$, determine μ and compute $\rho(\mathbf{r})$

$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2\, \Theta(\mu - \epsilon_n)$$

Chemical potential

$$N = \int d\mathbf{r}\rho(\mathbf{r})$$

Self-Consistent Field Iteration

initial wave function $\{\psi_n | n = 1, \ldots, N_{\mathrm{band}}\}$ & charge ρ

↓

solve $\nabla^2 V_{\mathrm{Hartree}}(\vec{x}) = -4\pi e^2 \rho(\vec{x})$

set up the electronic potential, $V = V_{\mathrm{ion}} + V_{\mathrm{Hartree}} + V_{\mathrm{xc}}$

↓

unitary transformation to diagonalize $\int d^3 x \psi_m(\vec{x}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{x}) \right\} \psi_n(\vec{x})$

↓

iterative improvement of $\{\psi_n\}$ & orthonormalization

↓

calculate new ρ from updated $\{\psi_n\}$

if not converged

Orthogonalization by Matrix Decomposition

- **Gram-Schmidt orthonormalization: The orthonormal basis set Q = [$\mathbf{q}_1 \ldots \mathbf{q}_m$] is obtained starting from an arbitrary set of *m* vectors, S = [$\mathbf{s}_1 \ldots \mathbf{s}_m$] as**

$$
\begin{aligned}
&\mathbf{q}_1 = \mathbf{s}_1 / |\mathbf{s}_1| \\
&\text{for} \quad i = 2 \quad \text{to} \quad m \\
&\qquad \mathbf{q}'_i = \mathbf{s}_i - \sum_{j=1}^{i-1} \mathbf{q}_j \left(\mathbf{q}_j \bullet \mathbf{s}_i \right) \\
&\qquad \mathbf{q}_i = \mathbf{q}'_i / |\mathbf{q}'_i| \\
&\text{endfor}
\end{aligned}
$$

Projection!

$$\overbrace{\sum_{j=1}^{i-1} |q_j\rangle\langle q_j|}^{\hat{P}} \; |s_i\rangle$$

- **The Gram-Schmidt procedure amounts to QR decomposition, S = QR, where R is an $m \times m$ right-triangle matrix**

$$
\begin{array}{cc}
 & m \\
n & \begin{bmatrix} \mathbf{s}_1 & \mathbf{s}_2 & \mathbf{s}_3 & \mathbf{s}_4 \end{bmatrix}
\end{array}
=
\begin{array}{cc}
 & m \\
n & \begin{bmatrix} \mathbf{q}_1 & \mathbf{q}_2 & \mathbf{q}_3 & \mathbf{q}_4 \end{bmatrix}
\end{array}
\begin{array}{cc}
m & \\
\begin{bmatrix}
|\mathbf{q}'_1| & \mathbf{q}_1 \bullet \mathbf{s}_2 & \mathbf{q}_1 \bullet \mathbf{s}_3 & \mathbf{q}_1 \bullet \mathbf{s}_4 \\
0 & |\mathbf{q}'_2| & \mathbf{q}_2 \bullet \mathbf{s}_3 & \mathbf{q}_2 \bullet \mathbf{s}_4 \\
0 & 0 & |\mathbf{q}'_3| & \mathbf{q}_3 \bullet \mathbf{s}_4 \\
0 & 0 & 0 & |\mathbf{q}'_4|
\end{bmatrix} & m
\end{array}
$$

$$\therefore \mathbf{s}_i = |\mathbf{q}'_i| \mathbf{q}_i + \sum_{j=1}^{i-1} \mathbf{q}_j \left(\mathbf{q}_j \bullet \mathbf{s}_i \right)$$

Hasegawa *et al.*, *SC* ('11)

- **For higher parallelization, Cholesky decomposition (BLAS3) is used instead**
  https://aiichironakano.github.io/phys516/Cholesky.pdf

Charge Mixing

- **Fixed-point charge mapping in self-consistent field iteration**
  $\rho_{\mathrm{in}}(\mathbf{r}) \mapsto v_{\mathrm{Hxc}}(\mathbf{r}) \mapsto \{\psi_n(\mathbf{r})\} \mapsto \rho_{\mathrm{out}}(\mathbf{r})$
- **Directly using $\rho_{\mathrm{out}}(\mathbf{r})$ as $\rho_{\mathrm{in}}(\mathbf{r})$ in the next iteration step often destabilizes numerical iteration**
- **Charge mixing**
  $\rho_{\mathrm{in}}^{i} \leftarrow \sum_{j=1}^{n} \alpha_i \, \rho_{\mathrm{in}}^{i-j}$
- **Determine the mixing coefficients α_i in order to minimize the residual**
  $R[\rho_{\mathrm{in}}(\mathbf{r})] \equiv \rho_{\mathrm{out}}[\rho_{\mathrm{in}}] - \rho_{\mathrm{in}}$
- **See note on** Pulay charge mixing

P. Pulay, *Chem. Phys. Lett.* **73**, 393 ('80)

Conjugate-Gradient Minimization of Energy Functional

i: iteration index; n: band index

"gradient" $$g_n^{(i)} = -\frac{\delta E\left[\left\{\psi_n^{(i)}\right\},\{\vec{R}_I(t)\}\right]}{\delta\psi_n^{(i)}} + \varepsilon_n^{(i)}\psi_n^{(i)} \equiv -H\psi_n^{(i)} + \varepsilon_n^{(i)}\psi_n^{(i)}$$

$$\varepsilon_n^{(i)} = \int d^3r\psi_n^{(i)*}H\psi_n^{(i)}$$

"preconditioning" $\tilde{g}_n^{(i)} = \hat{P}g_n^{(i)}$

"conjugate gradient" $h_n^{(i)} = \tilde{g}_n^{(i)} + \beta h_n^{(i-1)}, \beta = \int d^3r g_n^{(i)} \bullet g_n^{(i)} / \int d^3r g_n^{(i-1)} \bullet g_n^{(i-1)}$

"new wave function" $\psi_n^{(i+1)} = C(\lambda)\left(\psi_n^{(i)} + \lambda h_n^{(i)}\right)$

with constraint $\int d^3r\psi_n^{(i+1)*}\psi_m = 0 \ \ (m \le n)$

$i \leftarrow i+1$ if $\left|\varepsilon_n^{(i+1)} - \varepsilon_n^{(i)}\right| > \varepsilon$

See lecture on iterative minimization (https://aiichironakano.github.io/phys516/QD2CG.pdf**) & notes on** (1) conjugate-gradient (CG) method, (2) CG electronic-state solver, (3) CG DFT solver & (4) 2D electron example

Real-Space Grid as a Basis

- **Wave functions & electron density are represented by numerical values on real-space grid points**

- **Finite difference expansion for the kinetic-energy operator**

$$\left.\frac{\partial^2 \psi_n}{\partial x^2}\right|_{\mathbf{r}_{ijk}=(x_i,y_j,z_k)} = \sum_{l=-L}^{L} C_l \psi_n(x_i + lh, y_j, z_k) + O(h^{2L+2})$$

(short-ranged operation)

The calculations are performed completely in "real space"

↓

- **Suitable for systems with vacuum (*e.g.*, clusters, surfaces)**
- **Efficient implementation on parallel computers**

J.R. Chelikowsky, N. Troullier & Y.Saad, *Phys. Rev. Lett*. **72**, 1240 ('94)

Acceleration of Convergence

Preconditioning

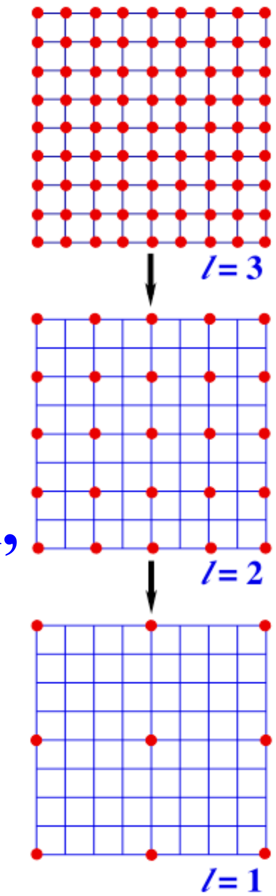
Enhanced convergence rate of short wavelength components of the residual

$$
\begin{array}{rl}
 & (H-\varepsilon)(\psi+\delta)=0 \\
-) & (H-\varepsilon)\psi=-g \\
\hline
 & (H-\varepsilon)\delta=g
\end{array}
\Rightarrow \quad \delta \leftarrow (H-\varepsilon)^{-1}g
$$

approximately invert?

$$\tilde{g}_n(x_i, y_j, z_k) = \hat{P} g_n^{(i)}$$

$$= \sum_{l_1=-1}^{1} \sum_{l_2=-1}^{1} \sum_{l_3=-1}^{1} c_{l_1 l_2 l_3} g_n(x_i + l_1 h, y_j + l_2 h, z_k + l_3 h)$$



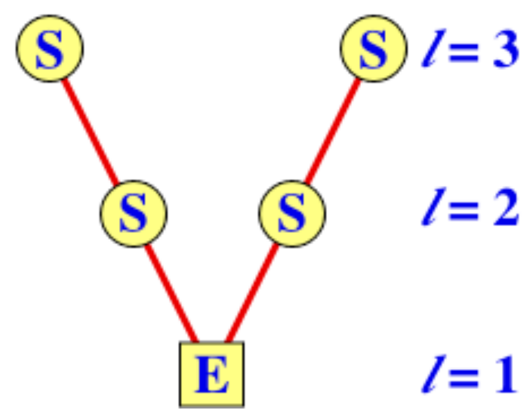
Multigrid method [Brandt '77, Bernholc *et al*. '96, Beck, '00]

To reduce long wavelength components of the residual,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\varphi = g_n^{(i)}$$

$$\psi_n^{(i)} \leftarrow \psi_n^{(i)} + \varphi$$

on a coarse grid



Iterative Solution of Linear Systems

$$Ax = b$$

$$A = \underset{L}{\begin{bmatrix} & & & \\ X & & & \\ X & X & & \\ X & X & X & \end{bmatrix}} + \underset{D}{\begin{bmatrix} X & & & \\ & X & & \\ & & X & \\ & & & X \end{bmatrix}} + \underset{U}{\begin{bmatrix} & X & X & X \\ & & X & X \\ & & & X \\ & & & \end{bmatrix}}$$

- **Fixed-point equation**

$$x = D^{-1}[-(L+U)x + b]$$

- **Jacobi iteration**

$$x^{(n+1)} = D^{-1}[-(L+U)x^{(n)} + b]$$

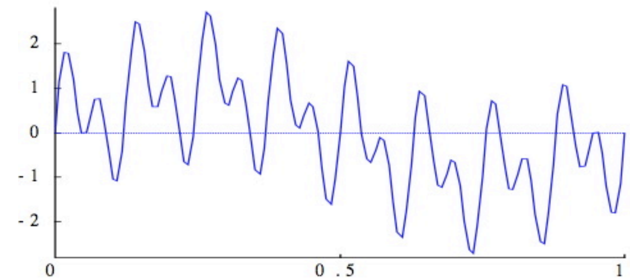
$$x_i^{(n+1)} = \frac{1}{a_{ii}}\left(-\sum_{\substack{j=1\\(j\neq i)}}^{N} a_{ij}x_j^{(n)} + b_i\right)$$

- **Over (under) relaxation: $\Delta > 1$ ($\Delta < 1$)**

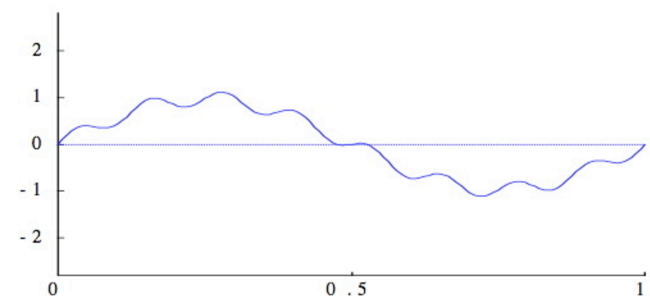
$$x_i^{(n+1)} = \frac{1}{a_{ii}}\left(-\sum_{\substack{j=1\\(j\neq i)}}^{N} a_{ij}x_j^{(n)} + b_i\right)$$

$$= x_i^{(n)} + \frac{1}{a_{ii}}\left(-\sum_{j=1}^{N} a_{ij}x_j^{(n)} + b_i\right) \rightarrow x_i^{(n)} + \frac{\Delta}{a_{ii}}\left(-\sum_{j=1}^{N} a_{ij}x_j^{(n)} + b_i\right)$$

- Initial error:

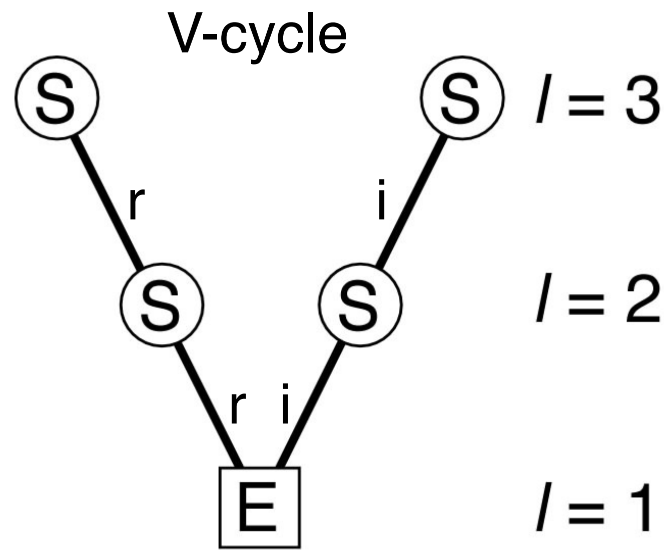


- Error after 35 iteration sweeps:



Multigrid Method

- **Residual equation:** $$\begin{array}{r} A^{(l)}(\psi + e) = 0 \\ -)\,A^{(l)}\psi = r \\ \hline A^{(l)}e = -r \end{array}$$

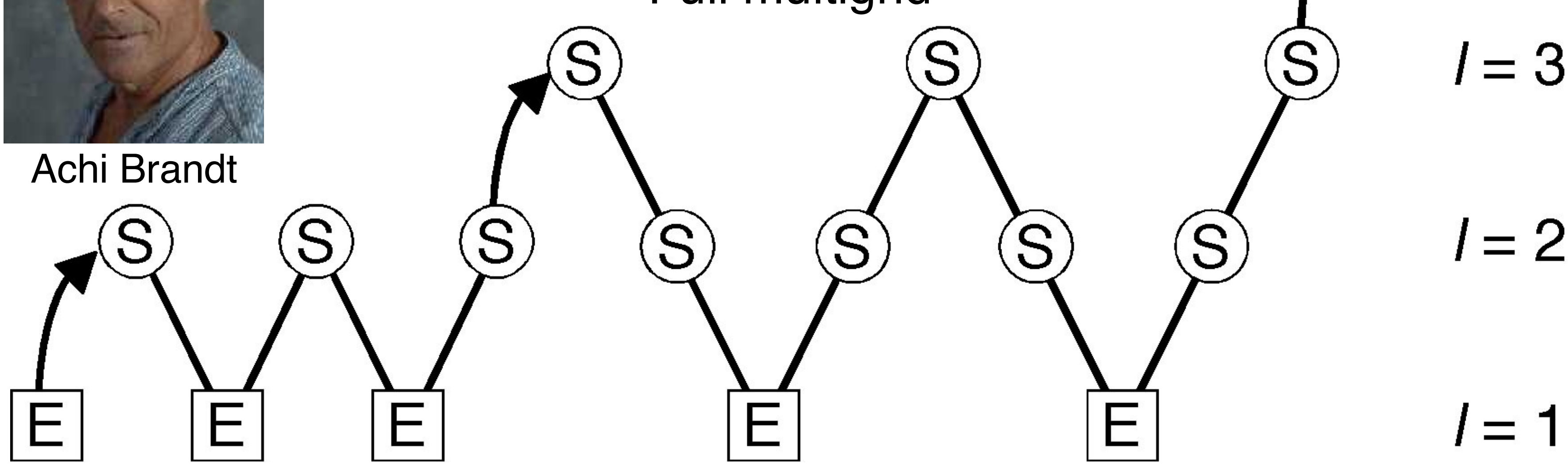


- **Smoothing:** $e \leftarrow \left[1 + Z^{(l)}A^{(l)}\right]e + Z^{(l)}r$

- **Coarsening of residual & interpolation of error**

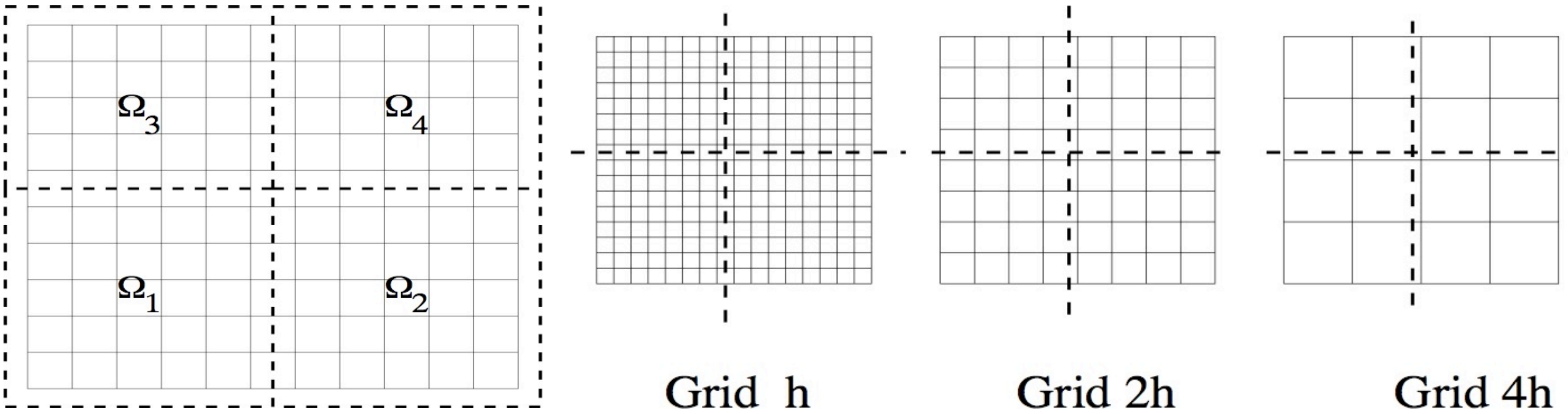
Achi Brandt

r: restrict (to coarser grid)
i: interpolate (to finer grid)



Parallel Multigrid Method

- **Domain decomposition with boundary-layer caching**



- **2D computational & communication costs (isogranular or weak scaling)**

$N \times N$ grids each on $P \times P$ processors: $T(N^2P^2, P^2) = a \log NP + bN + cN^2$

Speedup $$S_{P^2} = \frac{N^2P^2T(N^2,1)}{N^2T(N^2,P^2)} = \frac{P^2(cN^2)}{a\log NP + bN + cN^2} = \frac{P^2}{1 + \frac{b}{cN} + \frac{a}{cN}\log NP}$$

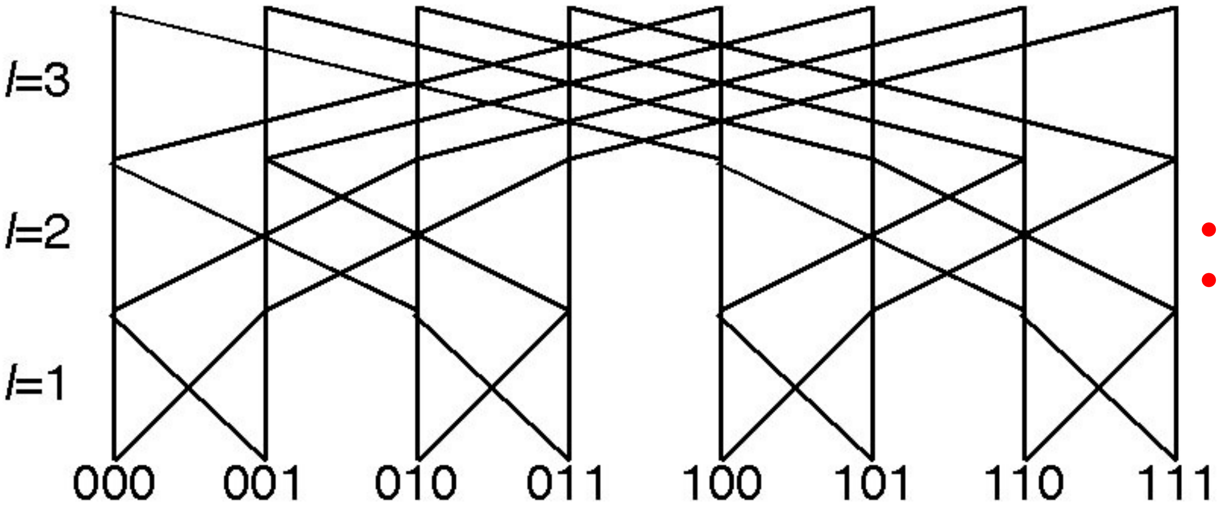
Parallel efficiency $$E_{P^2} = \frac{S_{P^2}}{P^2} = \frac{1}{1 + \frac{b}{cN} + \frac{a}{cN}\log NP}$$ Highly scalable!

Nakano *et al.*, *Comput. Phys. Commun.* **83**, 181 ('94)

For the definition of parallel efficiency, see https://aiichironakano.github.io/cs596/MPI-Pi.pdf

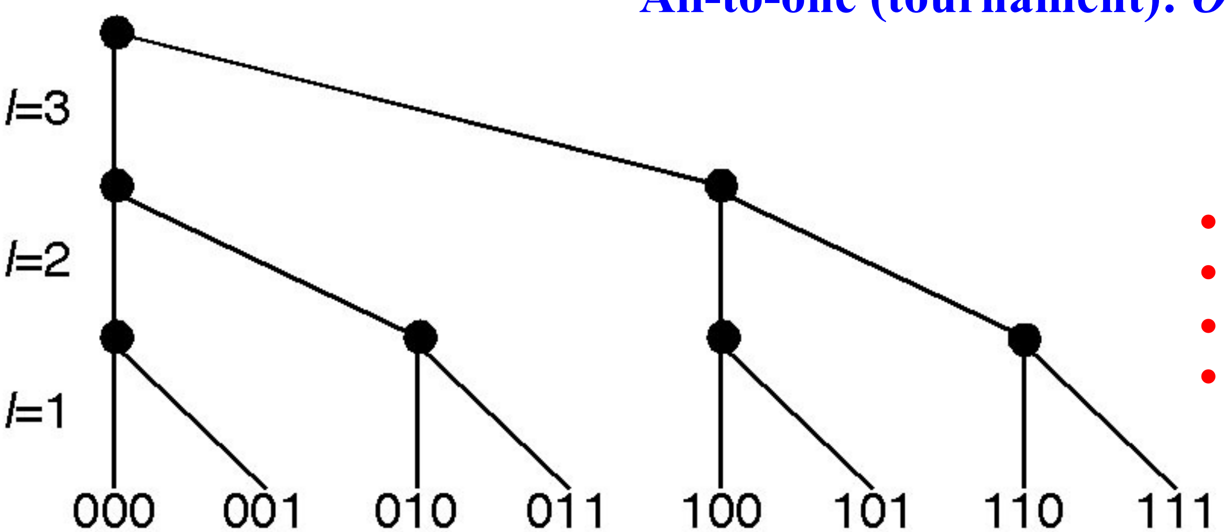
Global Communications

All-to-all (hypercube): $O(N\log N)$



- **Quicksort**
- **Fast Fourier transform**

All-to-one (tournament): $O(N)$



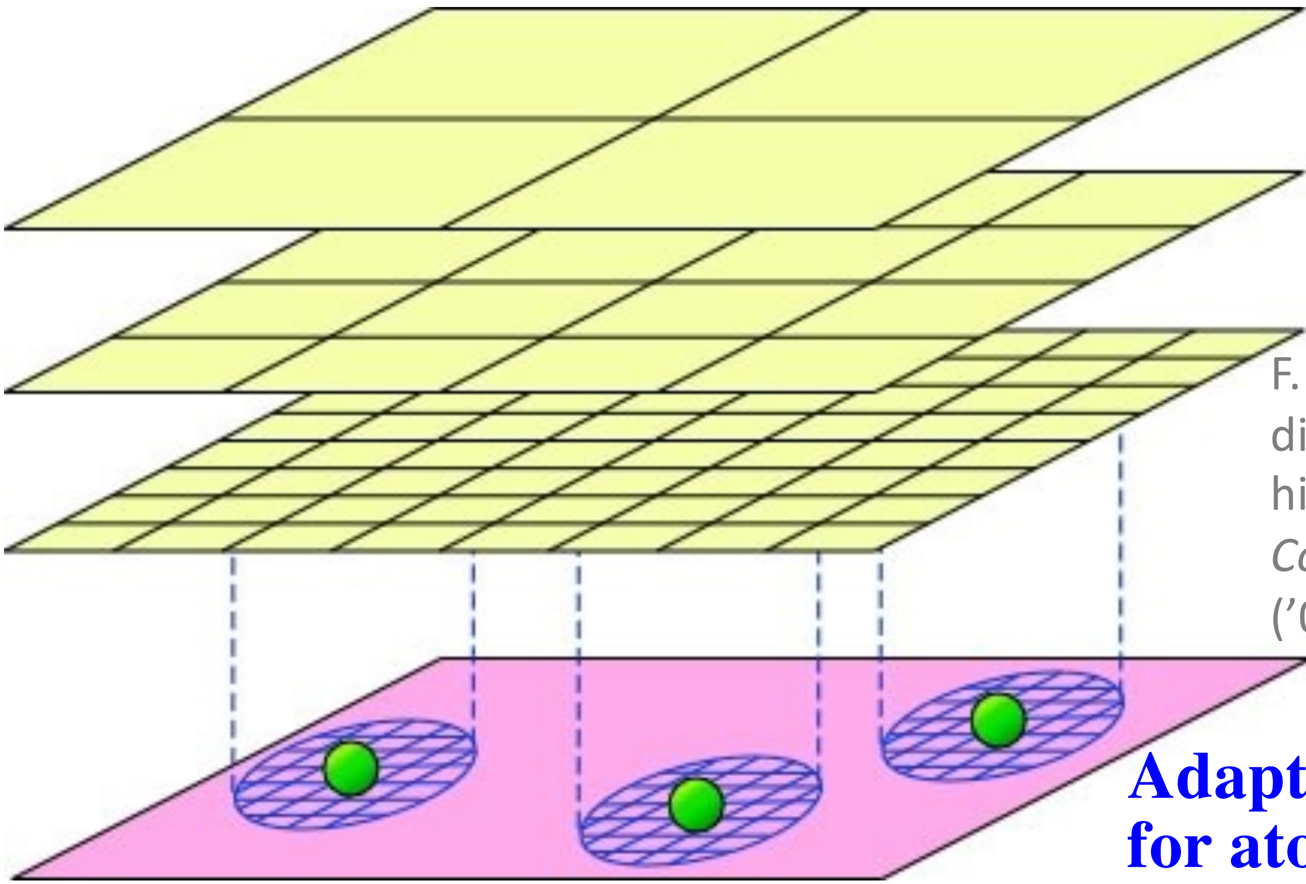
- **Global reduction**
- **Fast multipole method**
- **Multigrid method**
- **Wavelets**

See note on multigrid preconditioned CG

Real-Space DFT on Hierarchical Grids

Efficient parallelization of DFT: real-space approaches

- **High-order finite difference** [Chelikowsky, Troullier, Saad, ’94]
- **Multigrid acceleration** [Bernholc *et al*., ’96; Beck, ’00]
- **Double-grid method** [Ono, Hirose, ’99] **~ obsolete, with PAW**
- **Spatial decomposition/divide-&-conquer**



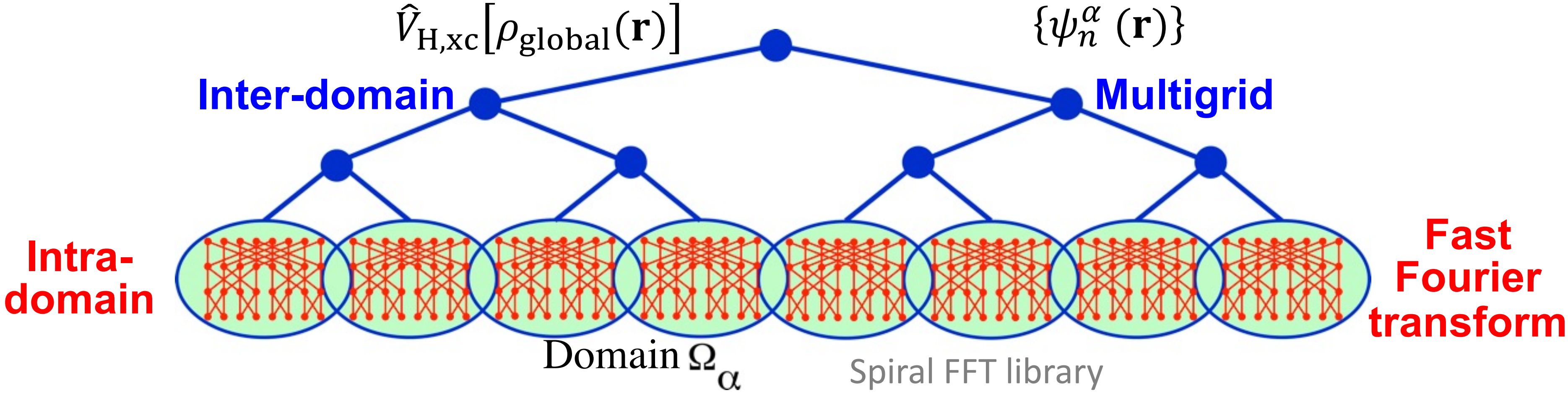
Multigrid acceleration of preconditioned conjugate gradient

F. Shimojo *et al*., “Embedded divide-and-conquer algorithm on hierarchicalreal-space grids,” *Comput. Phys. Commun*. **167**, 151 (’05)

Adaptive high-resolution grid for atomic pseudopotentials

Hierarchical Computing

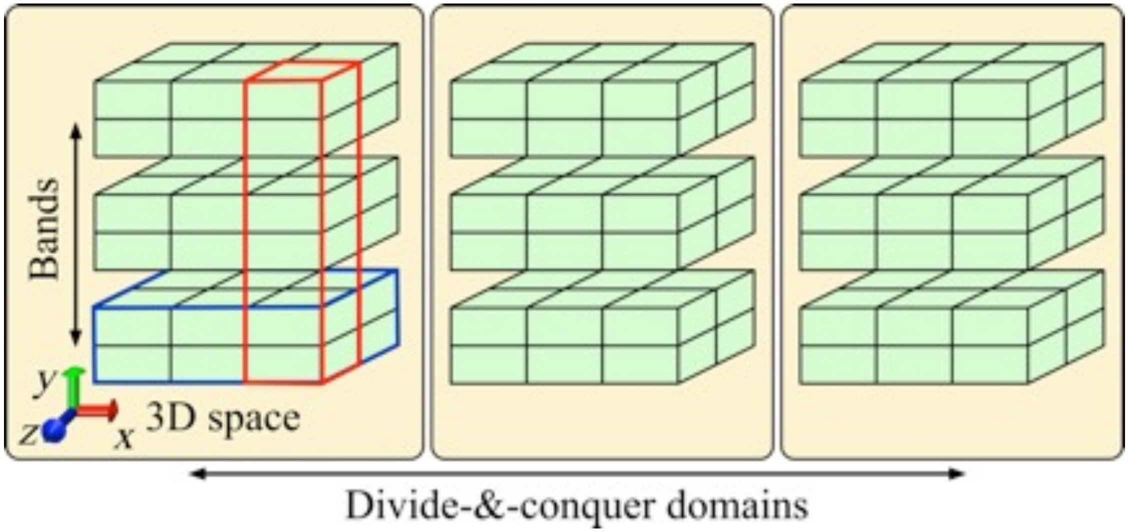
- **Globally scalable (real-space multigrid) + locally fast (plane wave) electronic solver**



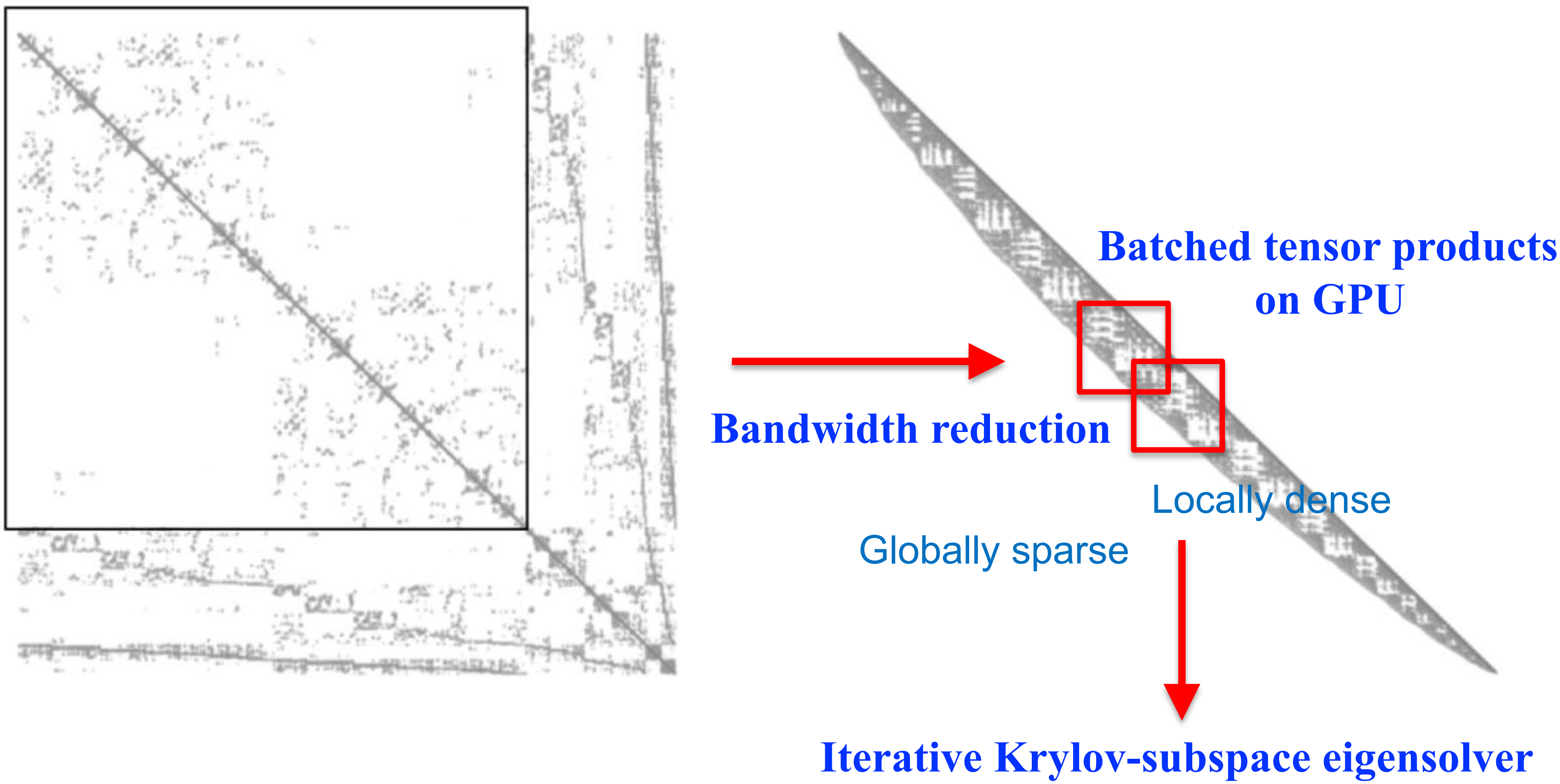
Spiral FFT library
[M. Puschel *et al.*, *Proc. IEEE* **93**, 232 ('05)]

cf. globally- sparse-yet-locally-dense eigensolver [J. H. Lam *et al.*, *Nature Commun*. **15**, 3479 ('24)]

- **Hierarchical band (*i.e.*, Kohn-Sham orbital) + space + domain (BSD) decomposition**



Globally-Sparse Yet Locally-Dense Eigensolver



- **250-fold speed-up over state-of-the-art for 2.4M atom molecular vibrational modes**

J. H. Lam *et al*., *Nature Commun*. **15**, 3479 ('24)

Finite-Element DFT

- **DFT calculation using a higher-order adaptive spectral finite-element (FE) basis outperforms that with the plane-wave basis for larger (*e.g.*, > 10,000 electrons) systems: see DFT-FE code** [S. Das *et al*., *Comput. Phys. Commun*. **280**, 108473 ('22); https://github.com/dftfeDevelopers/dftfe]
- **2023 Gordon-Bell award: 659.7 Pflop/s (43.1% of the peak) by the DFT-FE code for 619,124 electrons on 8,000 GPU nodes of the Frontier supercomputer** [S. Das *et al*., *Proc. Supercomputing, SC* ('23)]