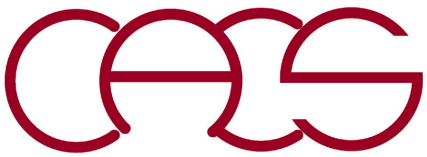
Quantum Molecular Dynamics: Representation & Solution

Aiichiro Nakano

Collaboratory for Advanced Computing & Simulations
Department of Computer Science
Department of Physics & Astronomy
Department of Quantitative & Computational Biology
University of Southern California

Email: anakano@usc.edu

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

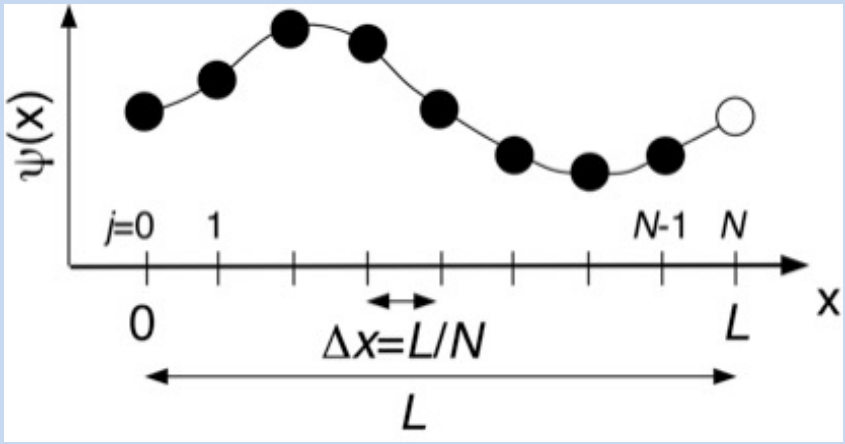


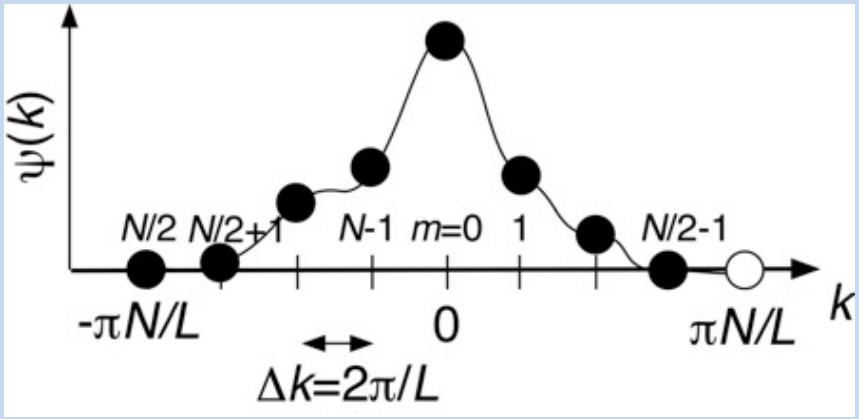
Representation: Plane-Wave Basis

- **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**

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

1D example



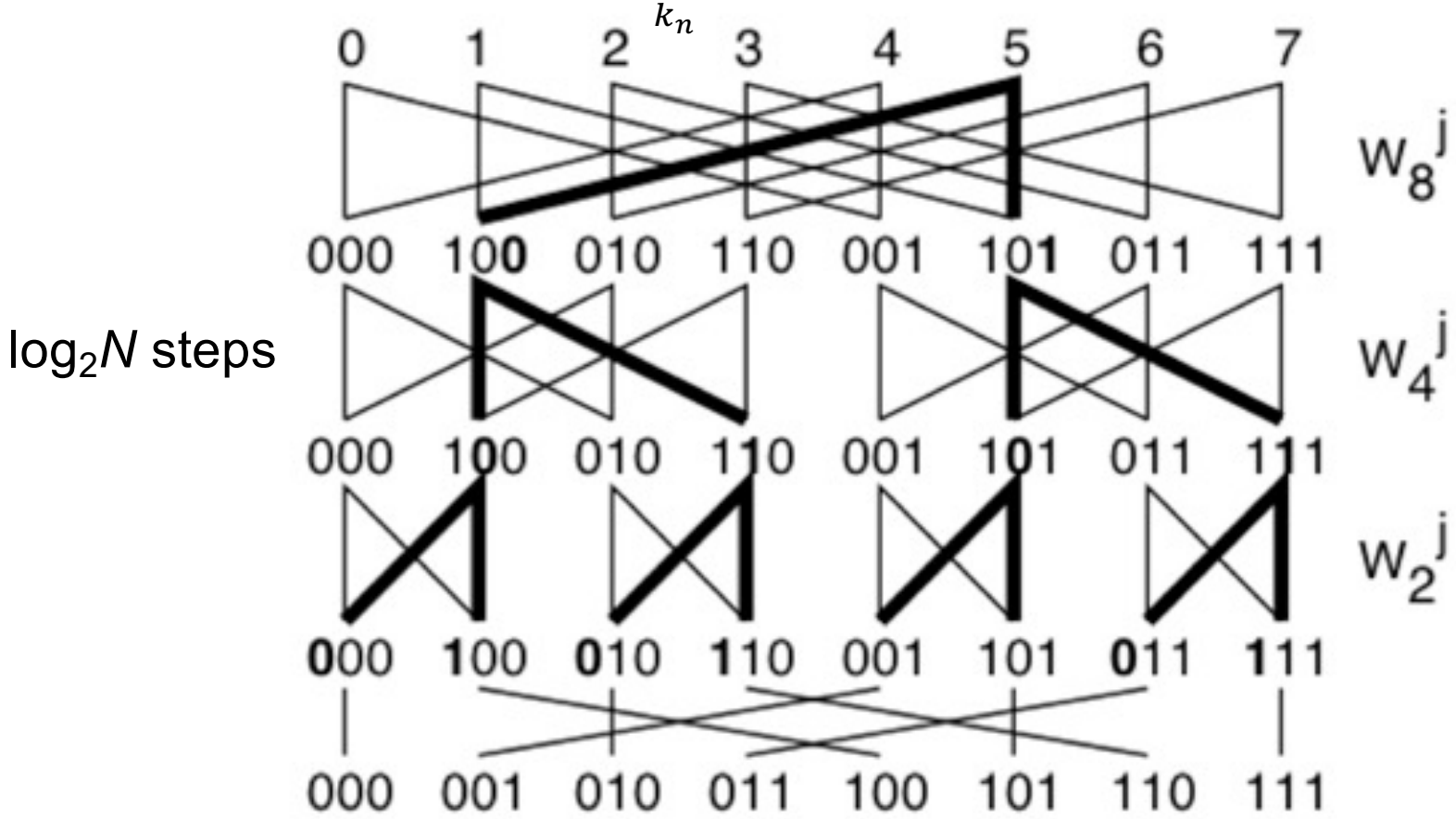


$$x_j = \frac{jL}{N};\ k_n = \frac{2\pi n}{L}$$

Numerics: Fast Fourier Transform

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

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



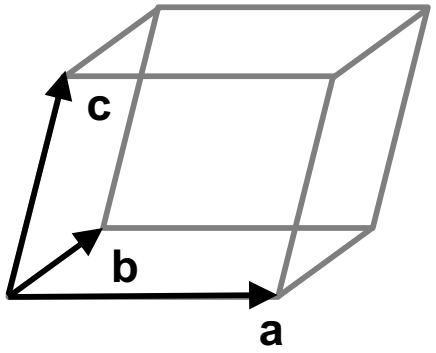
Butterfly (hypercube) data-exchange network

See PHYS 516 lecture on quantum dynamics

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**

band index

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

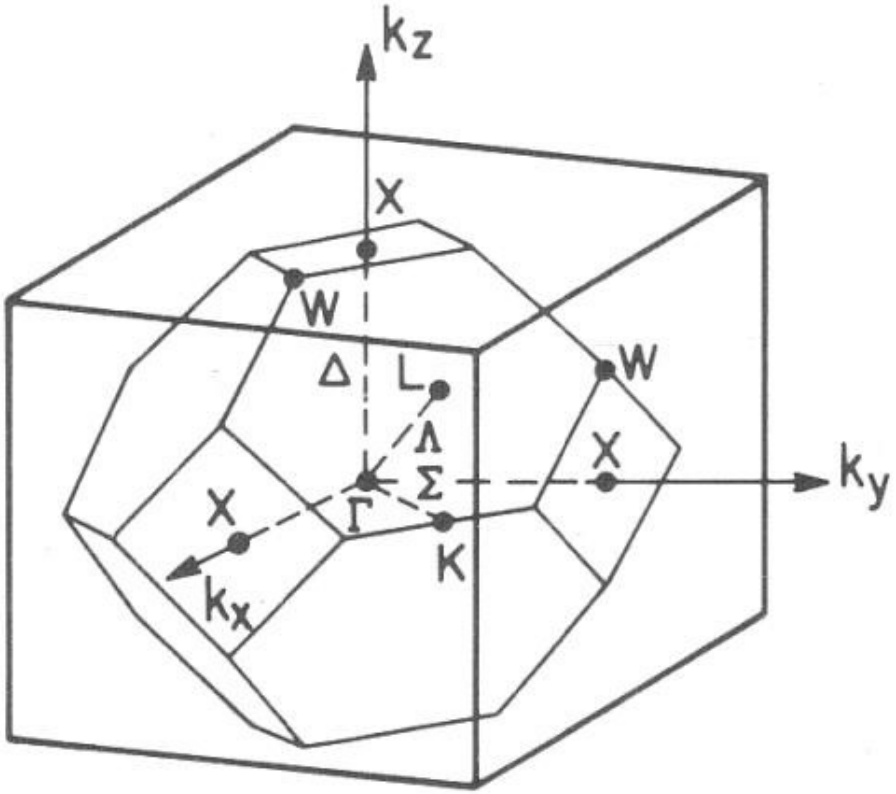
$$= \sum_{\mathbf{G}} u_{n,\mathbf{k}}(\mathbf{G}) \exp(i(\mathbf{k} + \mathbf{G}) \bullet \mathbf{r})$$

$\mathbf{k} \in$ first Brillouin zone in the reciprocal space

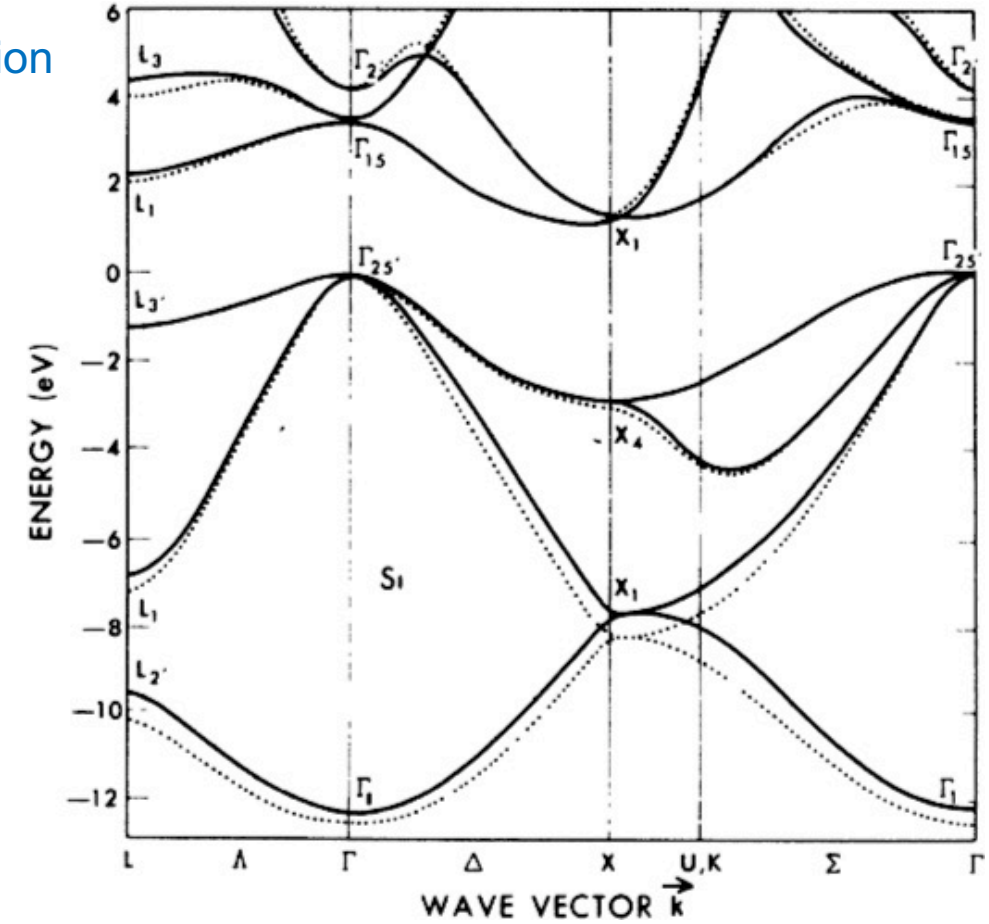
Electronic Bands: Infinite Lattice

- **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**
    $\{\mathbf{R}_I^*\} = \text{argmin}_{\{\mathbf{R}_I\}}\left(\min_{\{\psi_n(\mathbf{r})\}} E[\{\psi_n(\mathbf{r})\},\{\mathbf{R}_I\}]\right)$

- **Molecular dynamics**
  - > **Follow atomic trajectories by numerically integrating Newton's second law of motion**
    $$M\frac{d^2}{dt^2}\mathbf{R}_I = -\left\langle\Psi_0\left|\frac{\partial h(\mathbf{r},\mathbf{R}(t),t)}{\partial\mathbf{R}(t)}\right|\Psi_0\right\rangle$$
  - > **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

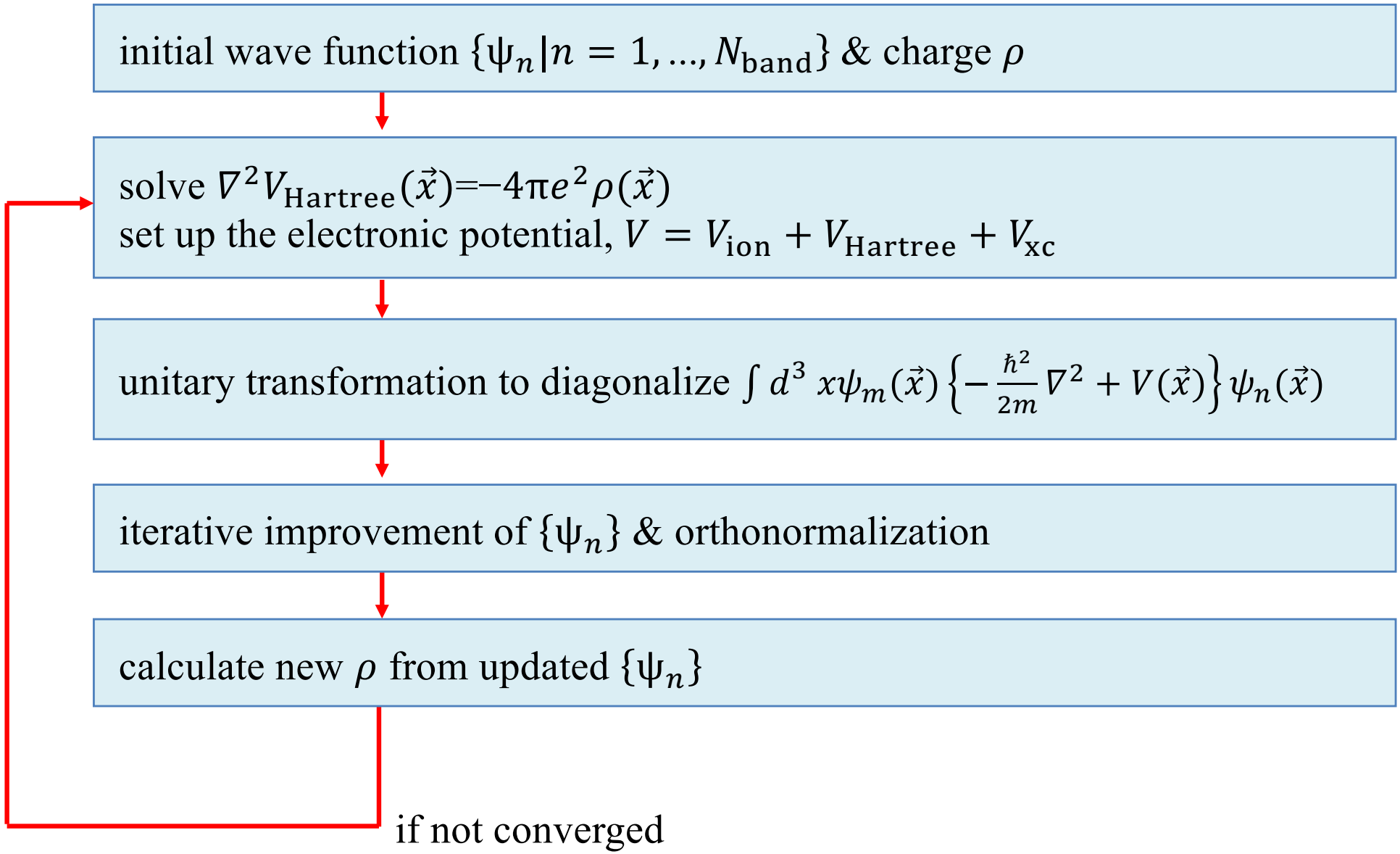
Given $\{\psi_n, \epsilon_n\}$, determine μ and compute $\rho(\mathbf{r})$

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

Chemical potential

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

Self-Consistent Field Iteration



Orthogonalization by Matrix Decomposition

- **Gram-Schmidt orthonormalization: The orthonormal basis set $Q = [q_1 \ldots q_m]$ is obtained starting from an arbitrary set of m vectors, $S = [s_1 \ldots s_m]$ as**

$$\mathbf{q}_1 = \mathbf{s}_1 / |\mathbf{s}_1|$$

for $i = 2$ to m

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

$$\mathbf{q}_i = \mathbf{q}'_i / |\mathbf{q}'_i|$$

endfor

Projection!

$\hat{P}$ $|s_i\rangle$

$\sum_{j=1}^{i-1} \widetilde{|q_j\rangle\langle q_j|}$

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

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

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

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**
  $\rho_{\text{in}}(\mathbf{r}) \mapsto v_{\text{Hxc}}(\mathbf{r}) \mapsto \{\psi_n(\mathbf{r})\} \mapsto \rho_{\text{out}}(\mathbf{r})$
- **Directly using $\rho_{\text{out}}(\mathbf{r})$ as $\rho_{\text{in}}(\mathbf{r})$ in the next iteration step often destabilizes numerical iteration**
- **Charge mixing**
  $\rho_{\text{in}}^{i} \leftarrow \sum_{j=1}^{n} \alpha_i \, \rho_{\text{in}}^{i-j}$
- **Determine the mixing coefficients α_i in order to minimize the residual**
  $R[\rho_{\text{in}}(\mathbf{r})] \equiv \rho_{\text{out}}[\rho_{\text{in}}] - \rho_{\text{in}}$
- **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

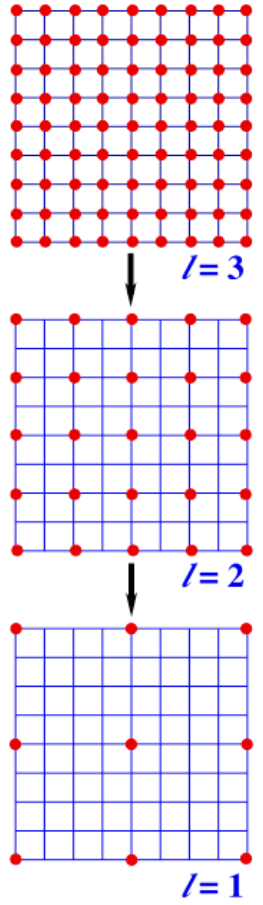
Preconditioning

Enhanced convergence rate of short wavelength components of the residual

$$(H-\varepsilon)(\psi+\delta)=0$$
$$-)\ (H-\varepsilon)\psi=-g$$
$$(H-\varepsilon)\delta=g \quad \Rightarrow \quad \delta \leftarrow (H-\varepsilon)^{-1}g$$

approximately invert?

$$\tilde{g}_n(x_i,y_j,z_k)=\hat{P}g_n^{(i)}$$
$$=\sum_{l_1=-1}^{1}\sum_{l_2=-1}^{1}\sum_{l_3=-1}^{1}c_{l_1l_2l_3}g_n(x_i+l_1h,y_j+l_2h,z_k+l_3h)$$

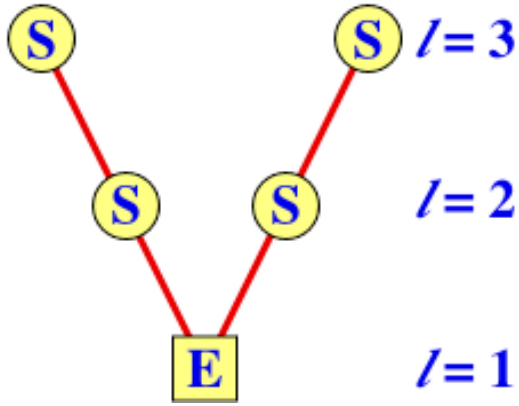


Multigrid method [Brandt '77, Bernholc *et al*. '96, Beck, '00]

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

$$Ax = b$$

$$A = L + D + U$$

$$\begin{bmatrix} & & \\ X & & \\ X & X & \\ X & X & X \end{bmatrix} + \begin{bmatrix} X & & & \\ & X & & \\ & & X & \\ & & & X \end{bmatrix} + \begin{bmatrix} & X & X & X \\ & & X & X \\ & & & X \\ & & & \end{bmatrix}$$

- **Fixed-point equation**

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

- **Jacobi iteration**

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

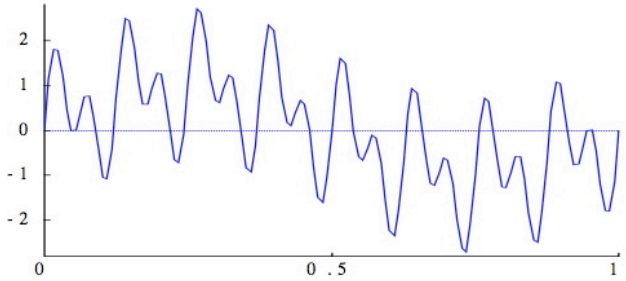
$$x_i^{(n+1)} = \frac{1}{a_{ii}}\left(-\sum_{\substack{j=1 \\ (j\neq i)}}^{N} a_{ij}x_j^{(n)} + b_i\right)$$

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

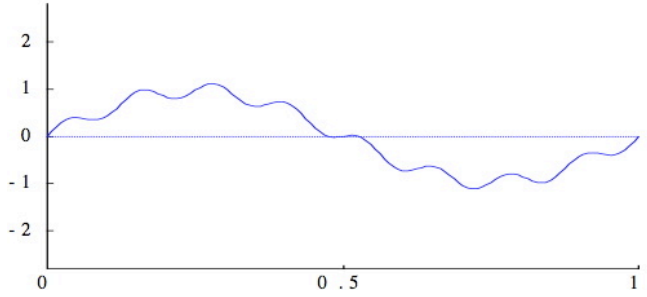
$$x_i^{(n+1)} = \frac{1}{a_{ii}}\left(-\sum_{\substack{j=1 \\ (j\neq i)}}^{N} a_{ij}x_j^{(n)} + b_i\right)$$

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

- Initial error:



- Error after 35 iteration sweeps:

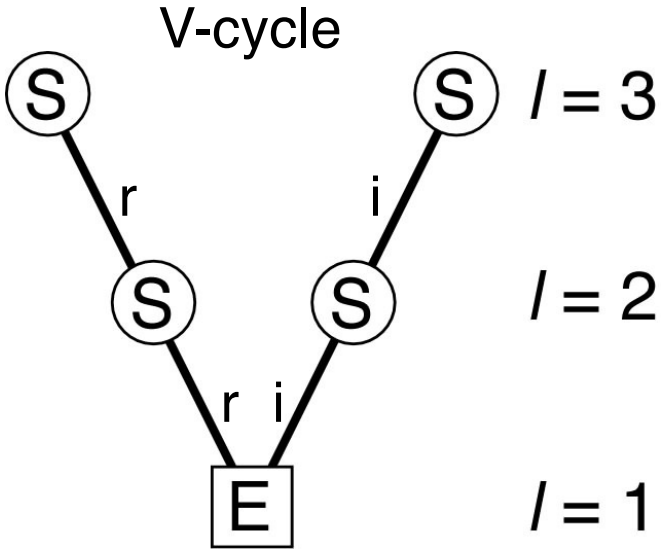


Multigrid Method

- **Residual equation:** $A^{(l)}(\psi + e) = 0$

$$\frac{-)A^{(l)}\psi = r}{A^{(l)}e = -r}$$

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



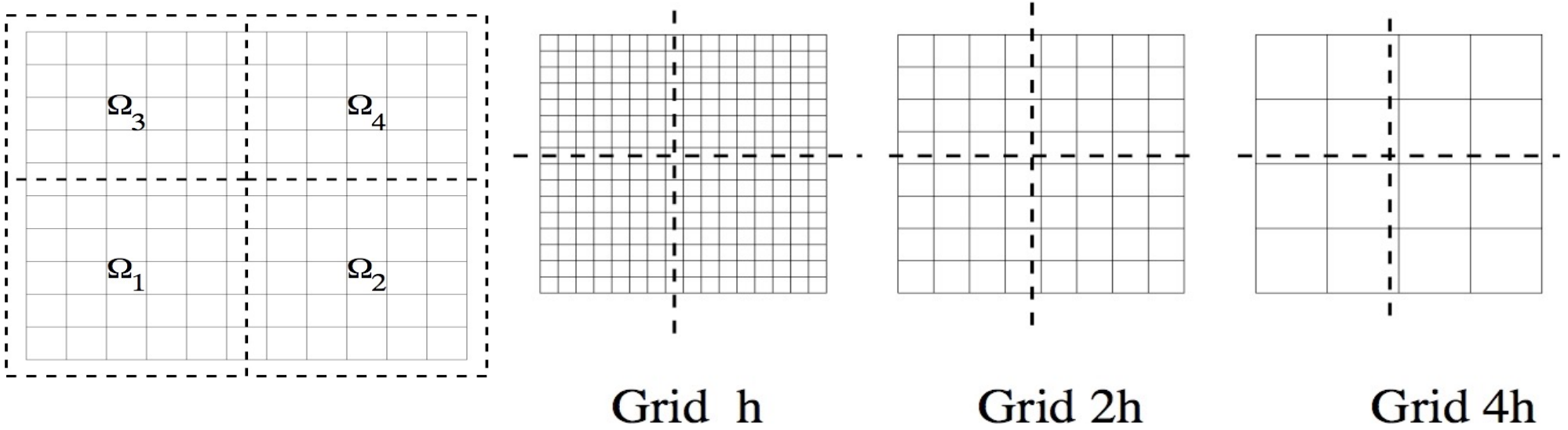
- **Coarsening of residual & interpolation of error**

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: $T(N^2P^2, P^2) = a \log NP + bN + cN^2$

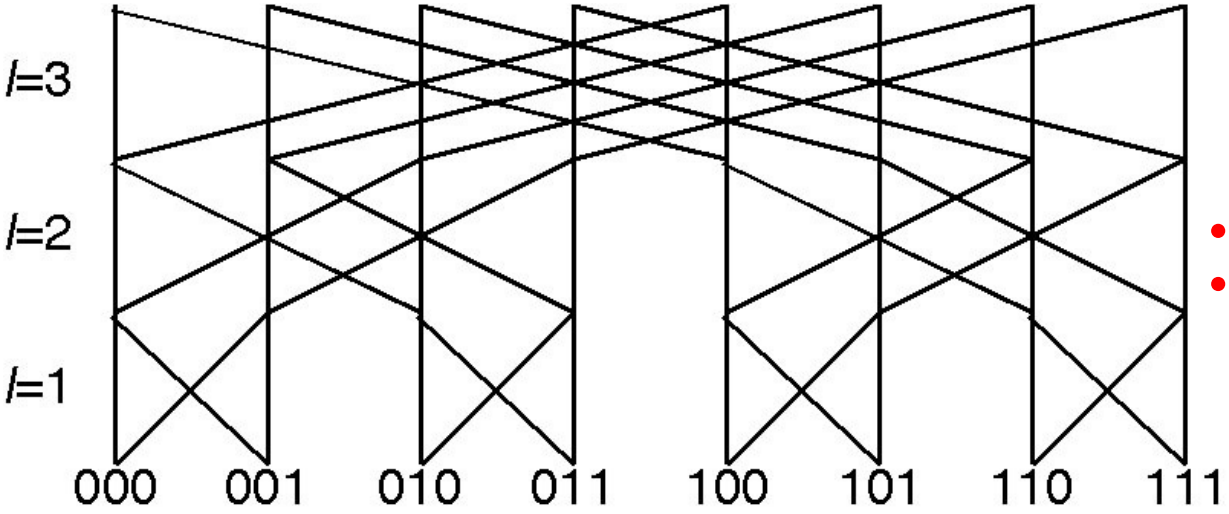
$$S_{P^2} = \frac{N^2P^2T(N^2,1)}{N^2T(N^2,P^2)} = \frac{P^2\left(cN^2\right)}{a\log NP + bN + cN^2} = \frac{P^2}{1 + \frac{b}{cN} + \frac{a}{cN}\log NP}$$

$$E_{P^2} = \frac{S_{P^2}}{P^2} = \frac{1}{1 + \frac{b}{cN} + \frac{a}{cN}\log NP}$$

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

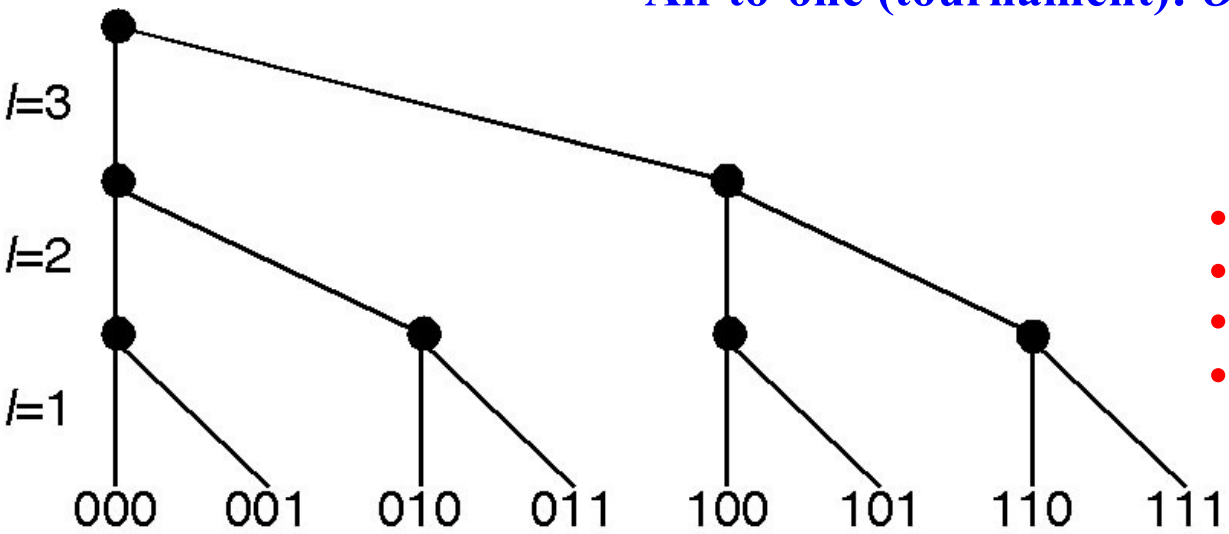
Global Communications

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



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

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



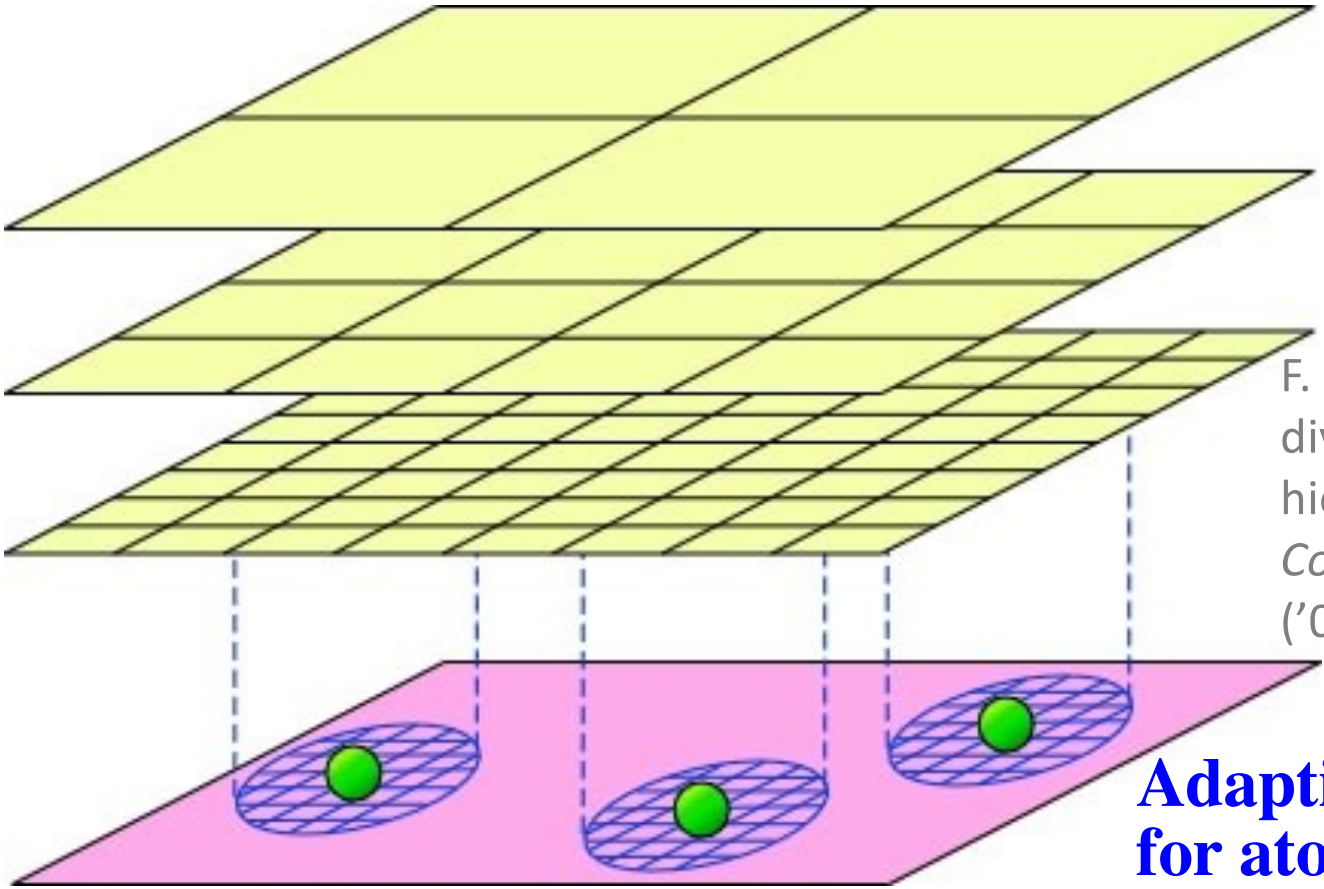
- **Global reduction**
- **Fast multipole method**
- **Multigrid method**
- **Wavelets**

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**



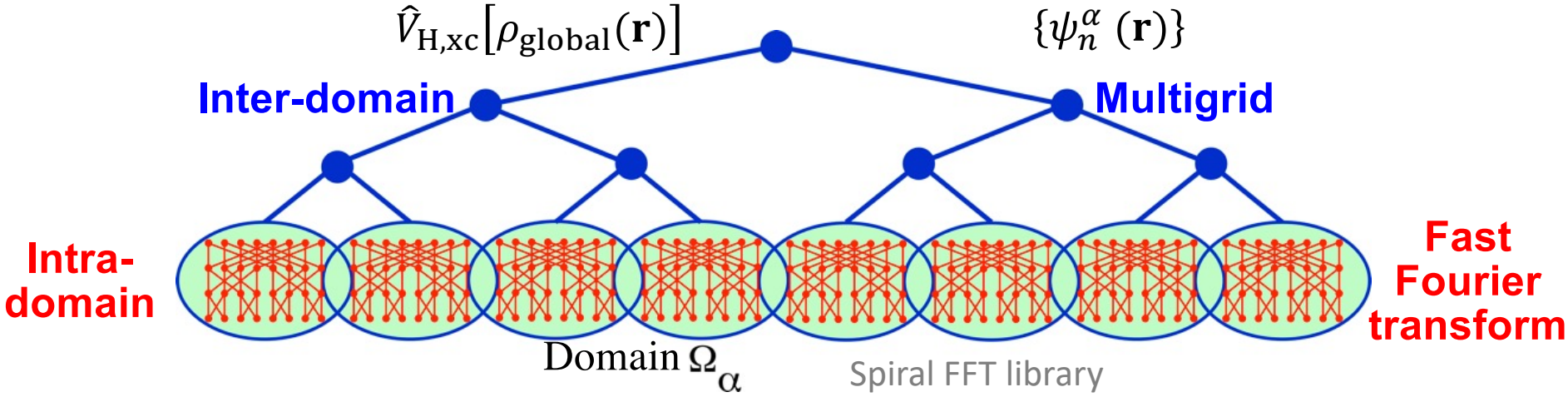
Multigrid acceleration of preconditioned conjugate gradient

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

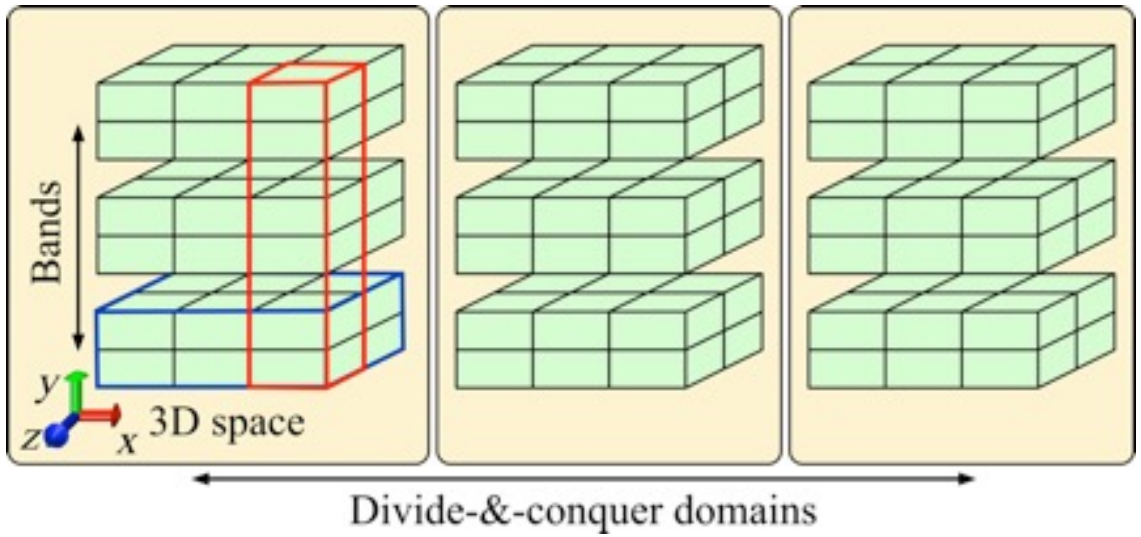
- **Globally scalable (real-space multigrid) + locally fast (plane wave) electronic solver**



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**



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)]