

# Linear-Scaling Quantum Molecular Dynamics

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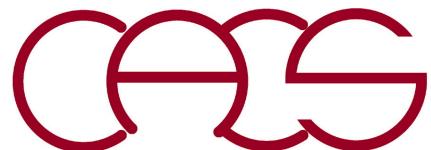
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# Quantum Molecular Dynamics (QMD)

$$M_I \frac{d^2}{dt^2} \mathbf{R}_I = -\frac{\partial}{\partial \mathbf{R}_I} E[\{\mathbf{R}_I\}, \psi(\mathbf{r}_1, \dots, \mathbf{r}_N)] \quad (I = 1, \dots, N_{\text{atom}})$$

First molecular dynamics using an empirical interatomic interaction

A. Rahman, *Phys. Rev.* **136**, A405 ('64)



$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \leftarrow \operatorname{argmin} E[\{\mathbf{R}_I\}, \psi(\mathbf{r}_1, \dots, \mathbf{r}_N)]$$

Density functional theory (DFT)

Hohenberg & Kohn, *Phys. Rev.* **136**, B864 ('64)

W. Kohn, *Nobel chemistry prize*, '98

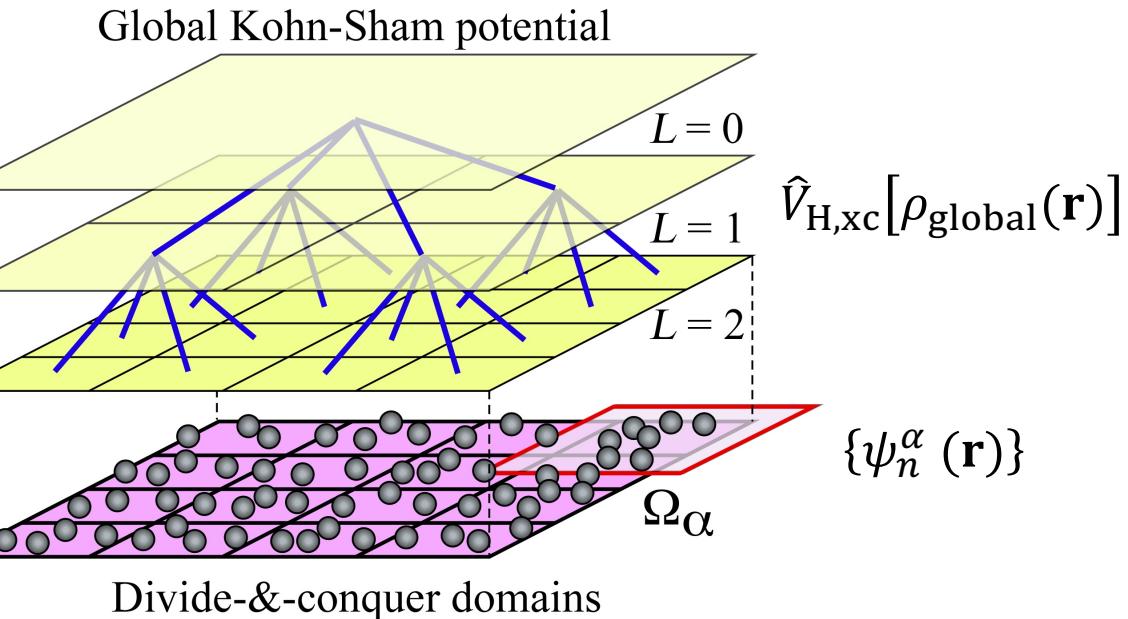
$$\begin{array}{ccc} O(C^N) & \rightarrow & O(N^3) \\ \text{1 } N\text{-electron problem} & & N \text{ 1-electron problems} \\ \text{intractable} & & \text{tractable} \end{array}$$

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad \{\psi_i(\mathbf{r}) | i = 1, \dots, N\}$$

## $O(N)$ DFT algorithms

- **Divide-&-conquer DFT** [W. Yang, *Phys. Rev. Lett.* **66**, 1438 ('91); F. Shimojo *et al.*, *Comput. Phys. Commun.* **167**, 151 ('05); *Phys Rev. B* **77**, 085103 ('08); *Appl. Phys. Lett.* **95**, 043114 ('09); *J. Chem. Phys.* **140**, 18A529 ('14)]
- **Quantum nearsightedness principle** [W. Kohn, *Phys. Rev. Lett.* **76**, 3168 ('96); E. Prodan & W. Kohn, *P. Nat. Acad. Sci.* **102**, 11635 ('05)]
- **A recent review** [Bowler & Miyazaki, *Rep. Prog. Phys.* **75**, 036503 ('12)]

# Divide-&-Conquer Density Functional Theory



- Overlapping spatial domains:  $\Omega = \bigcup_\alpha \Omega_\alpha$
- Domain Kohn-Sham equations

$$\left( -\frac{1}{2} \nabla^2 + \hat{V}_{\text{ion}} + \hat{V}_{\text{H,xc}}[\rho_{\text{global}}(\mathbf{r})] \right) \psi_n^\alpha(\mathbf{r}) = \epsilon_n^\alpha \psi_n^\alpha(\mathbf{r})$$

Global-local  
self-consistent  
field (SCF)  
iteration

- Global & domain electron densities

$$\rho_{\text{global}}(\mathbf{r}) = \sum_\alpha p_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}) \quad \rho_\alpha(\mathbf{r}) = \sum_n [\psi_n^\alpha]^2 \Theta(\mu - \epsilon_n^\alpha)$$

Domain support function

$$\sum_\alpha p_\alpha(\mathbf{r}) = 1$$

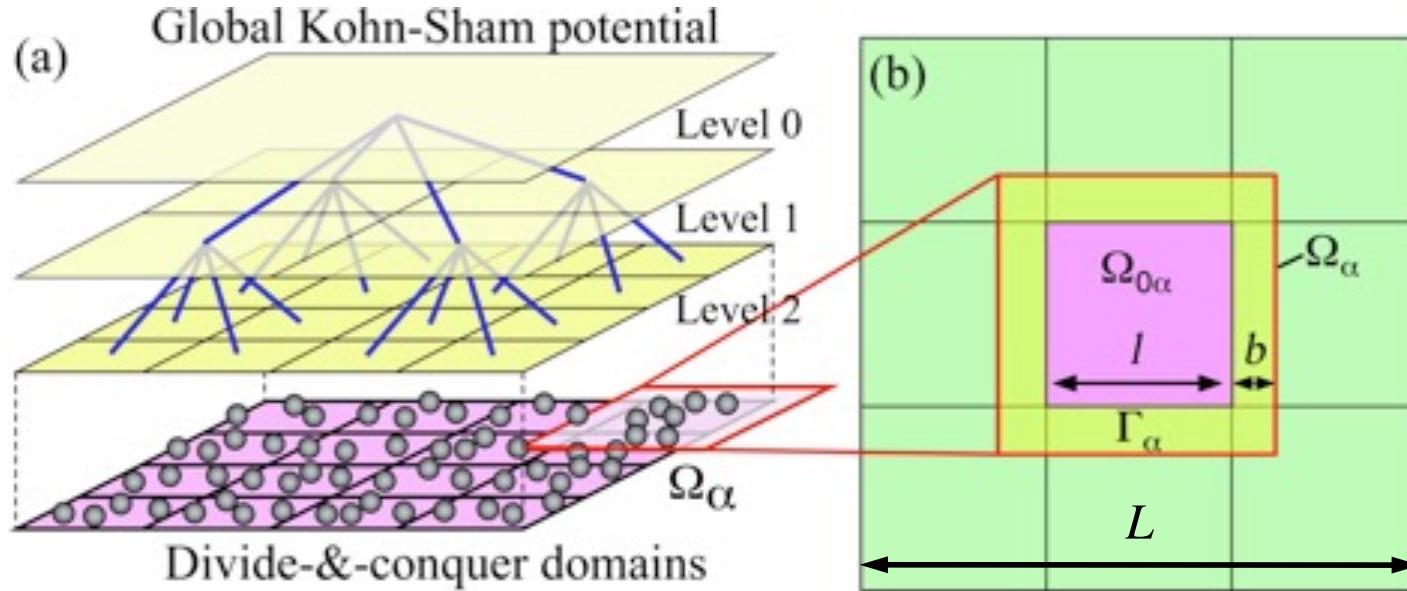
Global chemical potential

$$N = \int d\mathbf{r} \rho_{\text{global}}(\mathbf{r})$$

cf. subsystem DFT [W. Mi et al., *Comput. Phys. Commun.* **269**, 108122 ('21)]

# Optimization of Divide-&-Conquer DFT

- Computational parameters of DC-DFT = domain size ( $l$ ) + buffer thickness ( $b$ )



- Complexity analysis to optimize the domain size  $l$

$$l_* = \operatorname{argmin}(T_{\text{comp}}(l)) = \operatorname{argmin} \left( \left(\frac{L}{l}\right)^3 (l + 2b)^{3\nu} \right) = \frac{2b}{\nu - 1}$$

Per-domain computational complexity of DFT =  $O(n^\nu)$ :  $\nu = 2$  or  $3$  ( $n <$  or  $> 10^3$ )

- Error analysis: Buffer thickness  $b$  is dictated by the accuracy requirement

$$b = \lambda \ln (\max \{ |\Delta \rho_\alpha(\mathbf{r})| \mid \mathbf{r} \in \partial \Omega_\alpha \}) / \varepsilon \langle \rho_\alpha(\mathbf{r}) \rangle \quad |\Delta \rho| e^{-b/\lambda} = \varepsilon \langle \rho \rangle$$

Decay length

$\rho_\alpha(\mathbf{r}) - \rho_{\text{global}}(\mathbf{r})$

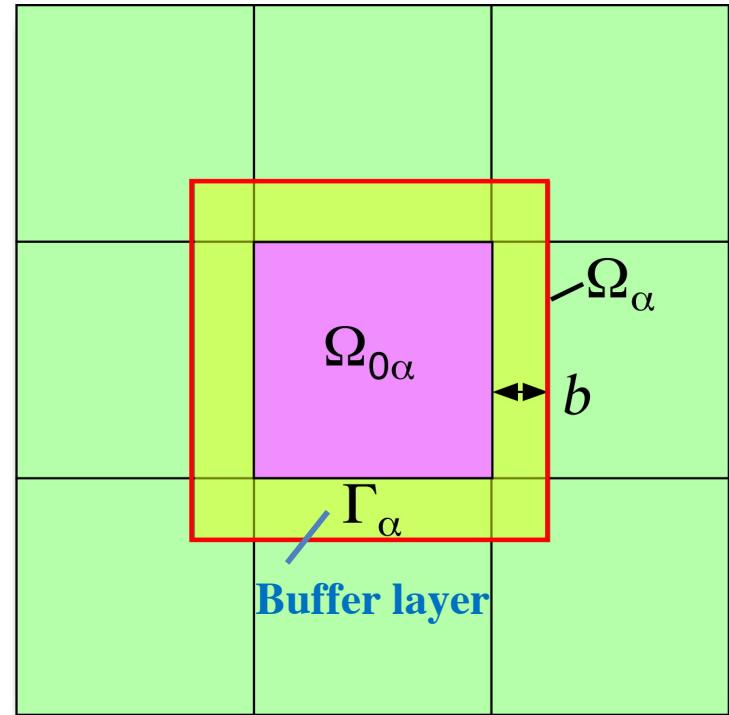
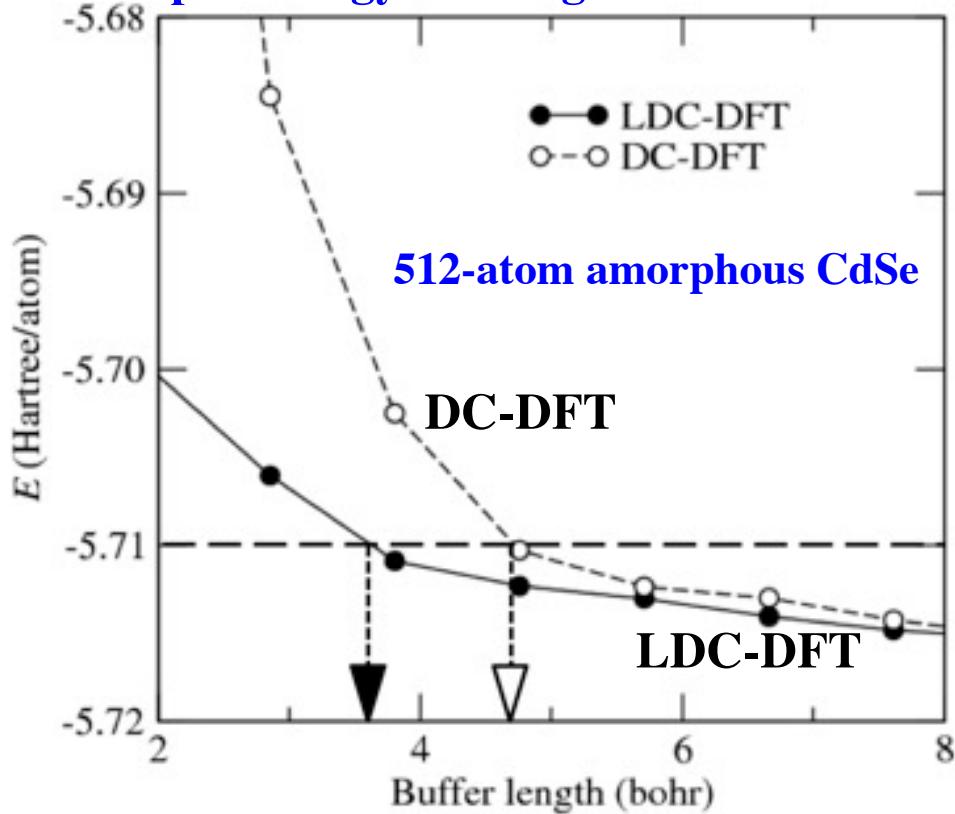
cf. quantum nearsightedness [Kohn, Phys. Rev. Lett. 76, 3168 ('96); Prodan & Kohn, P. Nat. Acad. Sci. 102, 11635 ('05)]

# Lean Divide-&-Conquer (LDC) DFT

- Density-adaptive boundary potential to reduce the  $O(N)$  prefactor local approximation

$$v_{\alpha}^{\text{bc}}(\mathbf{r}) = \int d\mathbf{r}' \frac{\partial v(\mathbf{r})}{\partial \rho(\mathbf{r}')} \left( \rho_{\alpha}(\mathbf{r}') - \rho_{\text{global}}(\mathbf{r}') \right) \cong \frac{\rho_{\alpha}(\mathbf{r}) - \rho_{\text{global}}(\mathbf{r})}{\xi}$$

- More rapid energy convergence of LDC-DFT compared with nonadaptive DC-DFT

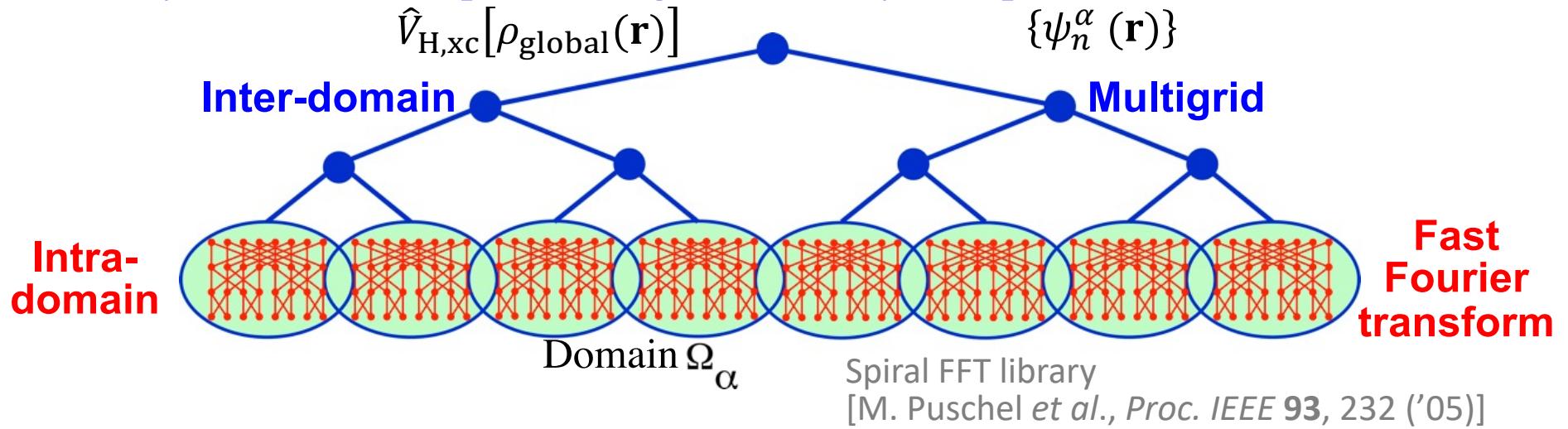


- Factor 2.03 (for  $\nu = 2$ )  $\sim 2.89$  (for  $\nu = 3$ ) reduction of the computational cost with an error tolerance of  $5 \times 10^{-3}$  a.u. (per-domain complexity:  $n^{\nu}$ )

F. Shimojo et al., *J. Chem. Phys.* **140**, 18A529 ('14);  
*Phys. Rev. B* **77**, 085103 ('08); *Comput. Phys. Commun.* **167**, 151 ('05)

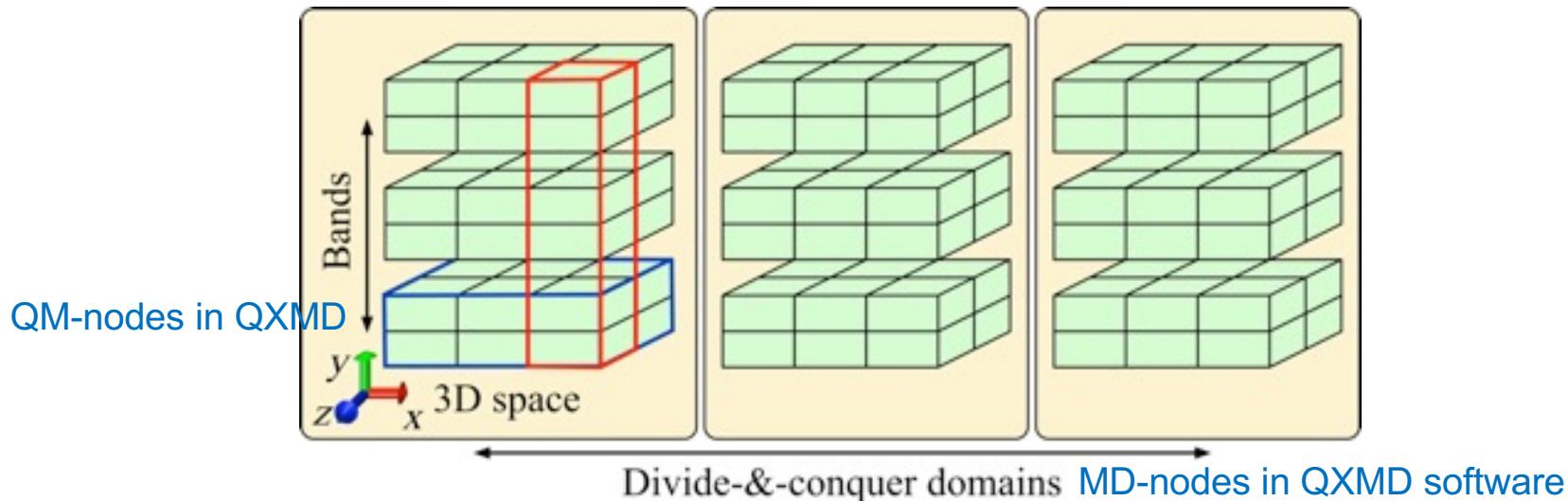
# Hierarchical Computing

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



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

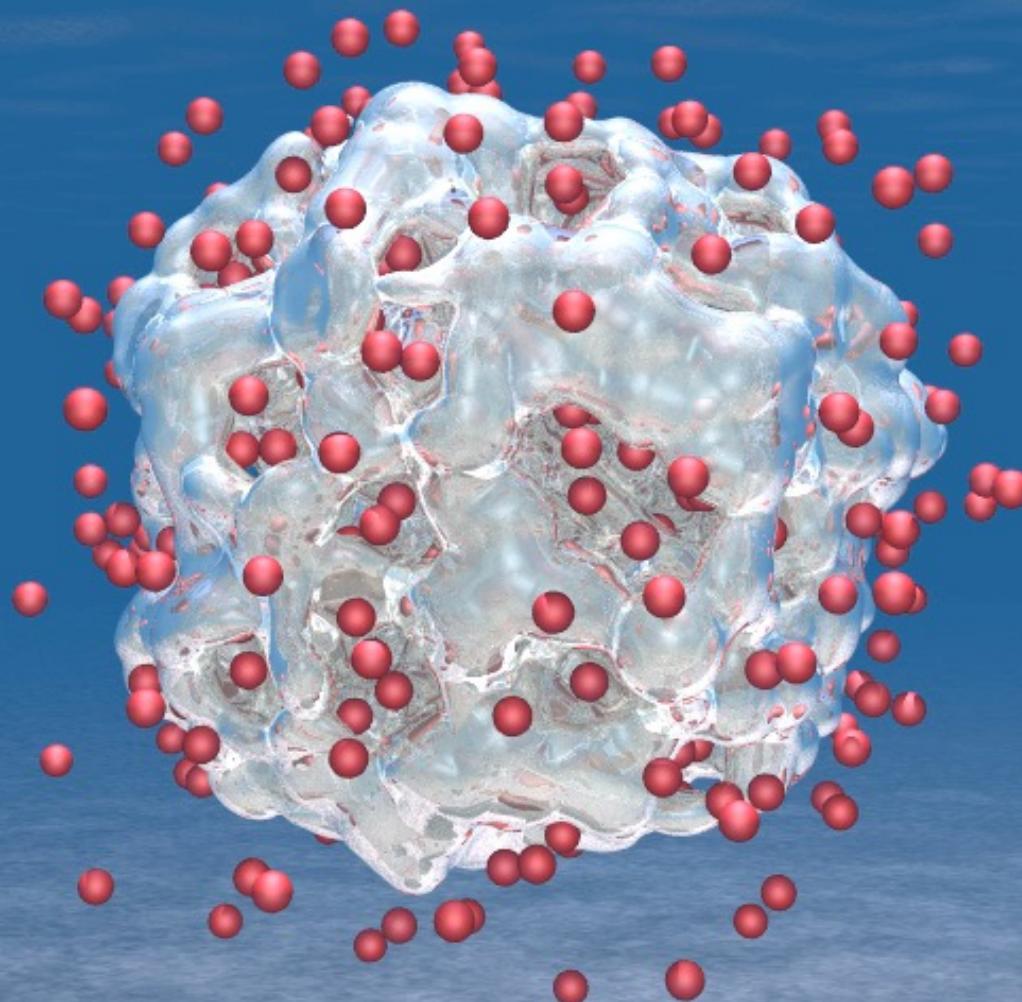
- Hierarchical band (*i.e.*, Kohn-Sham orbital) + space + domain (BSD) decomposition



# H<sub>2</sub> Production from Water Using LiAl Particles

16,661-atom QMD simulation of Li<sub>441</sub>Al<sub>441</sub> in water  
on 786,432 IBM Blue Gene/Q cores

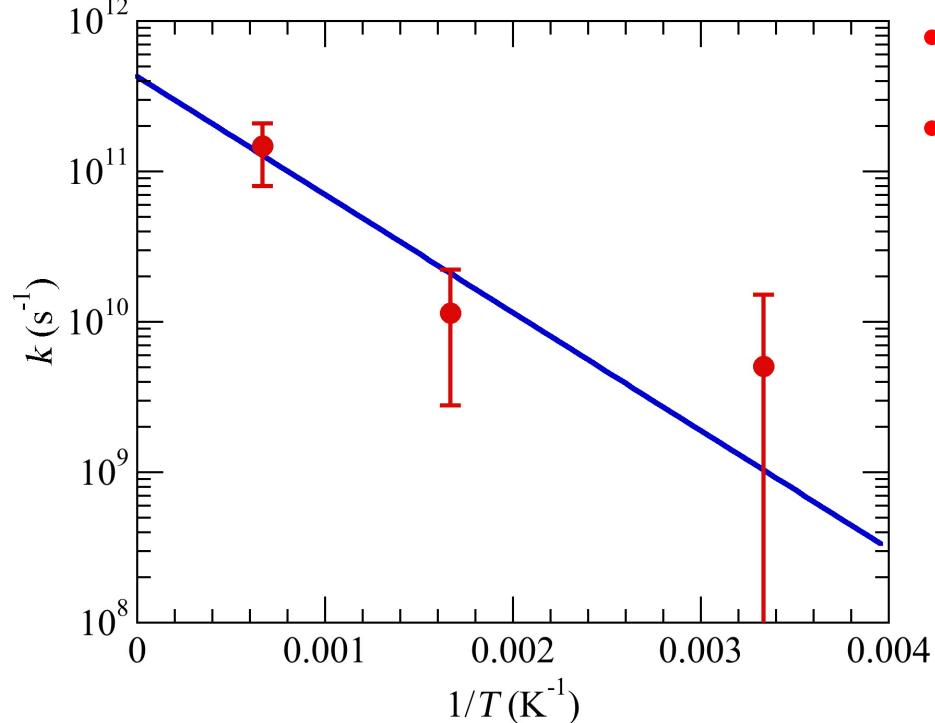
K. Shimamura *et al.*,  
*Nano Lett.* **14**, 4090 ('14)



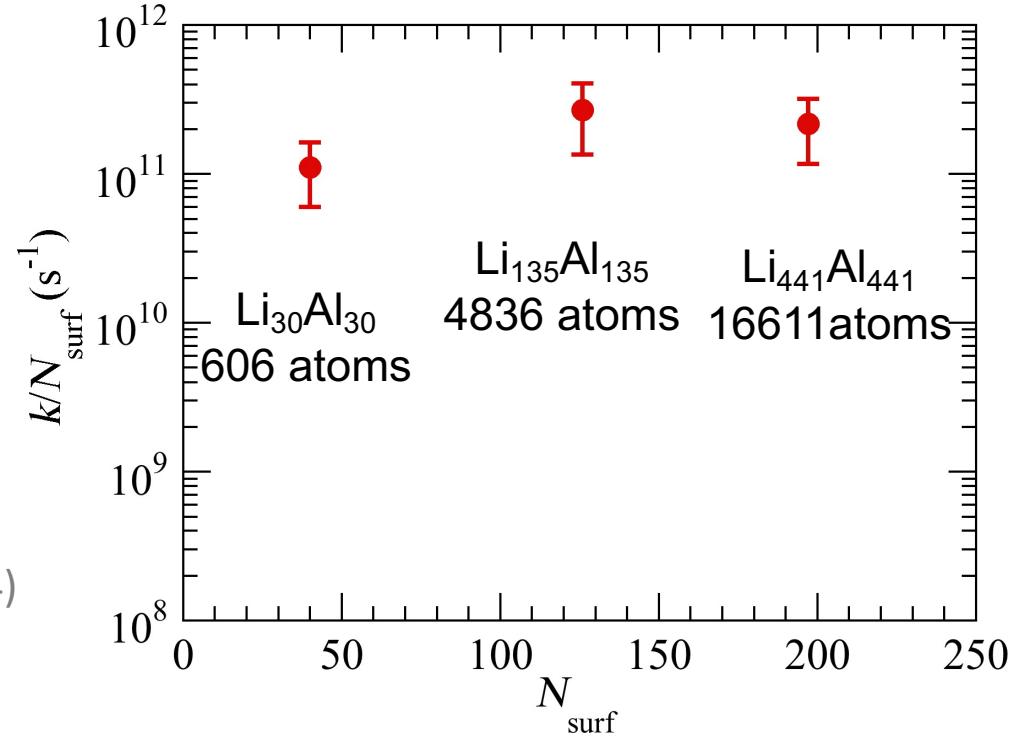
21,140 time steps (129,208 self-consistent-field iterations)

# Rapid & Scalable H<sub>2</sub> Production

- Orders-of-magnitude faster H<sub>2</sub> production from water than with pure Al



- Activation barrier = 0.068 eV
- Reaction rate =  $1.04 \times 10^9 (\text{s}^{-1})$  per LiAl pair at 300 K



K. Shimamura *et al.*, *Nano Lett.* **14**, 4090 ('14)

K. Nomura *et al.*, *IEEE/ACM SC14* ('14)

- Reaction rate does not decrease for larger particles → industrial scalability  
*cf. discontinuous Galerkin DFT* [Lin *et al.*, *J. Comput. Phys.* **231**, 2140 ('12)]

See notes on (1) origin of DCDFT, (2) parallel DCDFT, (3) DCDFT data structures, (4) DCDFT algorithm, (5) DC forces, & (6) lean DCDFT

# Fermi Operator

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- Fermi operator

$$F(\hat{H}) = \frac{2}{\exp\left(\frac{\hat{H} - \mu}{k_B T}\right) + 1}$$

- Projection to the occupied subspace

$$|\psi_{\text{proj}}\rangle = F(\hat{H})|\psi\rangle$$

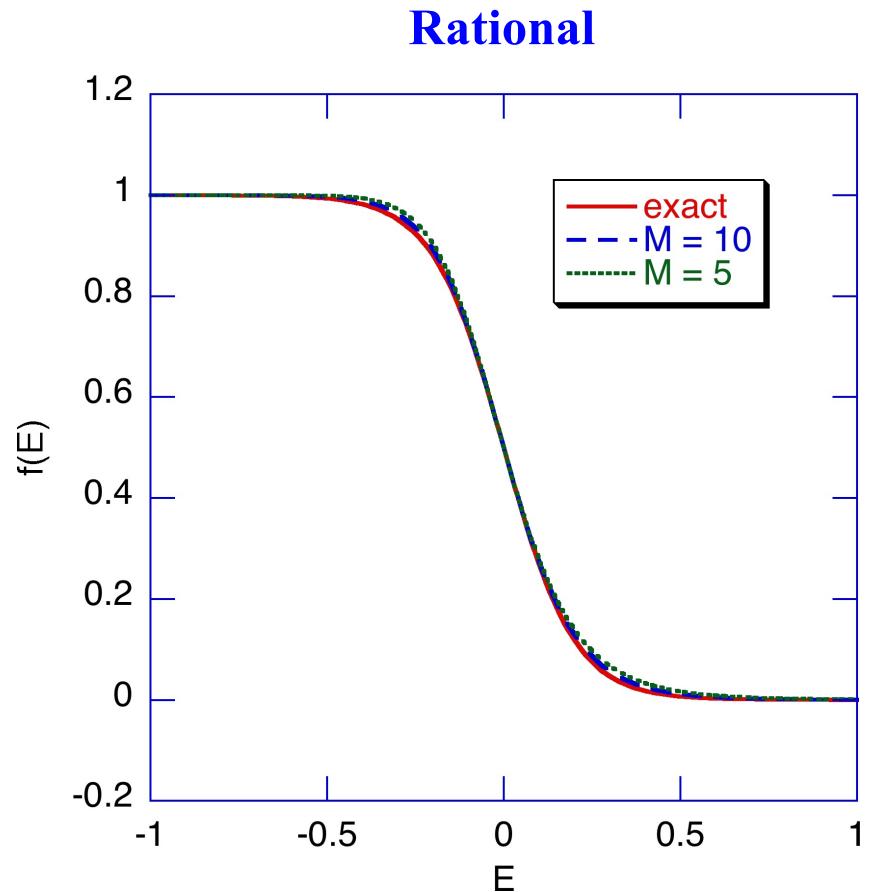
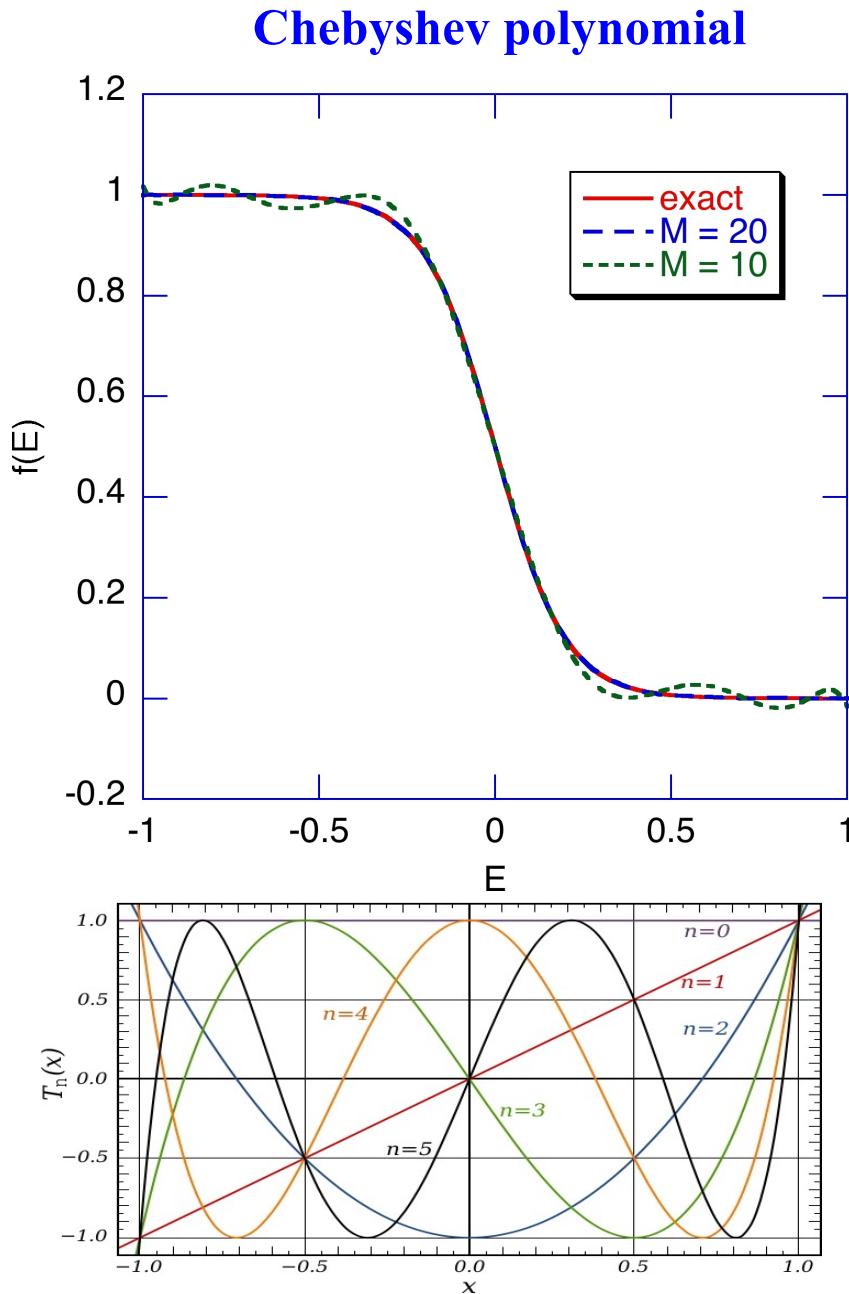
- The expectation value of any operator  $A$  is obtained by

$$\langle \hat{A} \rangle = \text{tr}[\hat{A}\hat{F}]$$

- Widely used in  $O(N)$  electronic structure calculations ( $N$  = number of electrons) through its sparse representation

S. Goedecker, *Rev. Mod. Phys.* **71**, 1085 ('99);  
K. Tsuruta *et al.*, *Phil. Mag. Lett.* **81**, 357 ('01)

# Fermi-Operator Approximations



$$F(\hat{H}) \cong \sum_{\nu=1}^M \frac{R_\nu}{\hat{H} - z_\nu}$$

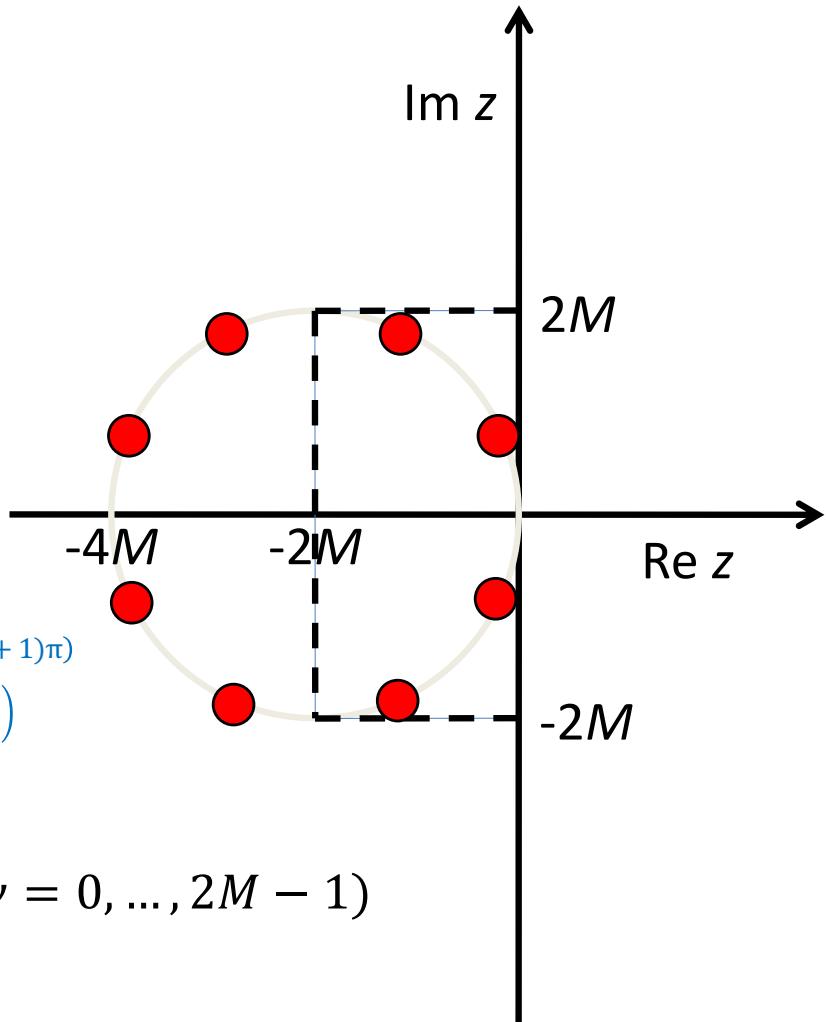
$$(\hat{H} - z_\nu) |\psi_{\text{out}}^\nu\rangle = R_\nu |\psi_{\text{in}}\rangle$$

# Rational Fermi-Operator Expansion

$$\begin{aligned}
 f(z) &= \frac{1}{\exp(z) + 1} \quad \left(1 + \frac{z}{n}\right)^n \xrightarrow{n \rightarrow \infty} \exp(z) \\
 &\approx \frac{1}{\left(1 + \frac{z}{2M}\right)^{2M} + 1} \\
 &\approx \sum_{\nu=0}^{2M-1} \frac{R_\nu}{z - z_\nu} \\
 &\quad \left(1 + \frac{z_\nu}{2M}\right)^{2M} = -1 = \exp(i(2\nu+1)\pi) \\
 &\quad \therefore 1 + \frac{z_\nu}{2M} = \exp\left(i\pi\frac{2\nu+1}{2M}\right)
 \end{aligned}$$

$$\begin{cases}
 \textbf{Poles} & z_\nu = 2M \left( \exp\left(i\frac{(2\nu+1)\pi}{2M}\right) - 1 \right) \quad (\nu = 0, \dots, 2M-1) \\
 \textbf{Residues} & R_\nu = -\exp\left(i\frac{(2\nu+1)\pi}{2M}\right)
 \end{cases}$$

Expand the denominator in  $\Delta = z - z^\nu$  & keep the linear term



- D. M. C. Nicholson *et al.*, *Phys. Rev. B* **50**, 14686 ('94);  
A. P. Horsfield *et al.*, *Phys. Rev. B* **53**, 12694 ('96);  
L. Lin *et al.*, *J. Phys. Condens. Matter* **25**, 1295501 ('13)

# $O(N)$ Fermi Operator Expansion

- Truncated expansion of Fermi-operator by Chebyshev polynomial  $\{T_p\}$

$$F(\hat{H}) \cong \sum_{p=0}^P c_p T_p(\hat{H})$$

- $O(N)$  algorithm

prepare a basis set of size  $O(N)$

(let the size be  $N$  for simplicity)

for  $l = 1, N$

let an  $N$ -dimensional unit vector be  $|e_l\rangle = \begin{bmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{bmatrix}_l$

recursively construct the  $l^{\text{th}}$  column of  
matrix  $T_p$ ,  $|t_l^p\rangle$ , keeping only  $O(1)$   
off-diagonal elements (*cf.* quantum nearsightedness)

$$\begin{cases} |t_l^0\rangle = |e_l\rangle \\ |t_l^1\rangle = \hat{H}|e_l\rangle \\ |t_l^{p+1}\rangle = 2\hat{H}|t_l^p\rangle - |t_l^{p-1}\rangle \end{cases}$$

build a sparse representation of the  $l^{\text{th}}$  column of  $F$  as

$$|f_l\rangle \cong \sum_{p=0}^P c_p |t_l^p\rangle$$

See [note on Fermi-operator expansion](#)

# Local Orbital Minimization

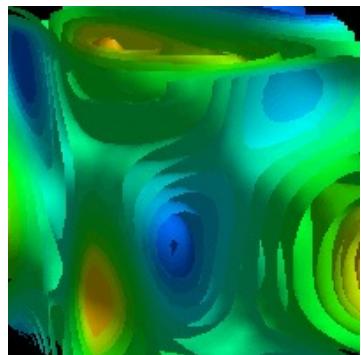
**$O(N)$  DFT algorithm**

- Asymptotic decay of density matrix:

- Localized functions:

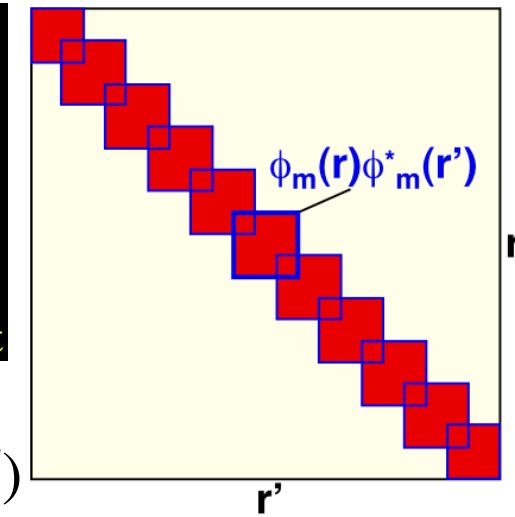
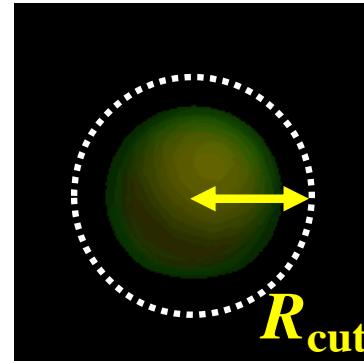
$$\rho(\mathbf{r}, \mathbf{r}') \equiv \sum_{n=1}^{N_{\text{el}}} \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')$$

Nearsightedness!  $\propto \exp(-C |\mathbf{r} - \mathbf{r}'|)$



$$\psi_n(\mathbf{r}) \quad \phi_m(\mathbf{r})$$

$$\phi_m(\mathbf{r}) = \sum_n \psi_n(\mathbf{r}) U_{nm}$$



- Unconstrained minimization:

$$\tilde{E}[\{\phi_n\}] = \sum_{m=1}^{N_{\text{wf}}} \sum_{n=1}^{N_{\text{wf}}} \int d^3r \phi_m^*(\mathbf{r})(H - \eta I)\phi_n(\mathbf{r}) \left( 2\delta_{nm} - \int d^3r \phi_n^*(\mathbf{r})\phi_m(\mathbf{r}) \right) + \eta N_{\text{el}}$$

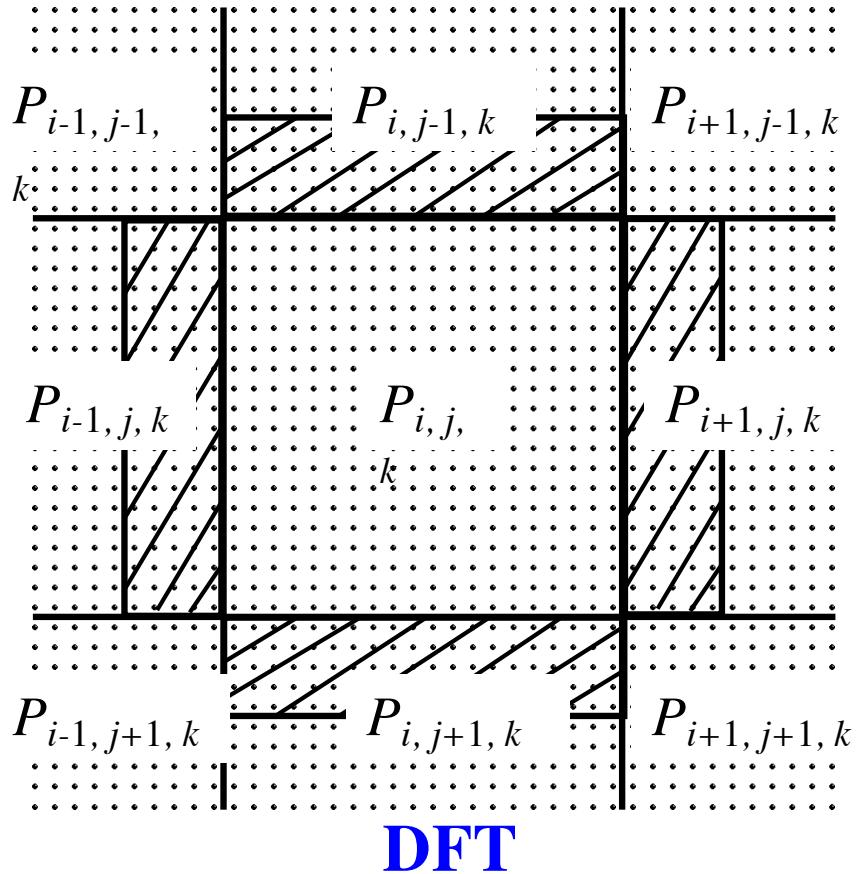
cf.  $O(N^3)$  QR or Cholesky decomposition for orthogonalization

See notes on (1) nonorthogonal orbitals & (2) local orbital minimization

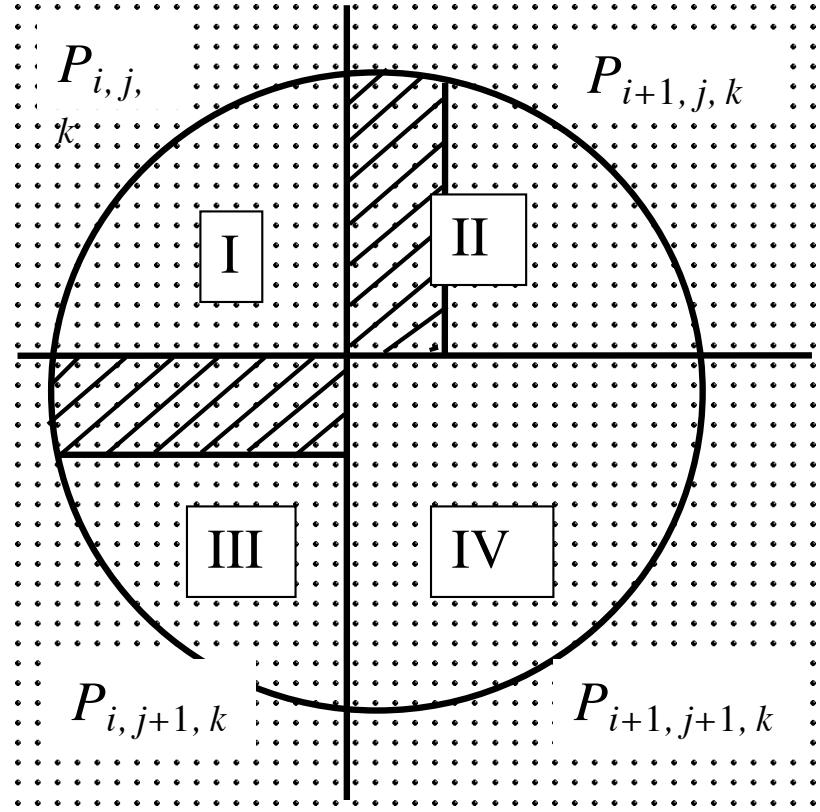
Kim, Mauri & Galli, *Phys. Rev. B* **52**, 1640 ('95); Ordejon *et al.*, *ibid.* **51**, 1456 ('95)  
Shimojo *et al.*, *Comput. Phys. Commun.* **140**, 303 ('01)

# Analysis of Parallel DFT Algorithms

## Spatial decomposition



DFT



Linear-scaling (LS) DFT

## Computation

DFT

$$O(N^3/P)$$

DC-DFT

$$O(N/P)$$

## Communication

$$O(N(N/P)^{2/3} + N^2 \log P)$$

$$O((N/P)^{2/3})$$

# Zoo of $O(N)$ DFT Algorithms (Small Subset)

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- **Density-matrix minimization (DMM)** [Li *et al.*, *Phys Rev. B* **47**, 10891 ('93); Nunes & Vanderbilt, *ibid.* **50**, 17611 ('94); Hernandez *et al.*, *ibid.* **53**, 7147 ('96)]  
See notes on (1) idempotency, (2) orthogonal DMM, (3) nonorthogonal DMM & (4) real-space DMM
- **Filter diagonalization** [Wall & Neuhauser, *J. Chem. Phys.* **102**, 8011 ('95)]  
See note on filter diagonalization *cf.* Koshiba's "egg of dream": 小柴昌俊-夢の卵を孵す
- **Green's function (GF) approaches** [Horsfield *et al.*, *Phys. Rev. B* **53**, 12694 ('96); Hoshi *et al.*, *Proc. SCALA16* ('16)]  
See (1) slide & notes 1 & 2 on Lanczos tridiagonalization, and (2) note on Pade via Lanczos *cf.* Bethe lattice & Laughlin *et al.*, *Phys. Rev. B* **20**, 5228 ('79)
- **Block tridiagonal divide-&-conquer (DC)** [Gansterer *et al.*, *ACM T. Math. Software* **28**, 45 ('02)]  
See note on block tridiagonal DC
- **Embedded-cluster boundary condition (BC): Reduce  $O(N)$  prefactor of DCDFT?**  
See notes on (1) embedded-cluster BC, (2) orbital BC, (3) multiple scattering & (4) surface GF  
*cf.* **Dynamical mean-field theory (DMFT)** [Georges *et al.*, *Rev. Mod. Phys.* **68**, 13 ('96); Kotliar *et al.*, *ibid.* **78**, 865 ('06)]

# Stochastic DFT

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- Project onto a vector space spanned by a set of  $I$  stochastic wave functions  $\kappa(r)$

$$\hat{I} = \sum_{\kappa=1}^I |\kappa\rangle\langle\kappa|$$

- Electron density is obtained by projecting onto the occupied subspace spanned by

$$|\xi\rangle = \theta(\mu - \hat{H})|\kappa\rangle$$

where the step function  $\theta$  is approximated by Chebyshev polynomials with  $\mu$  &  $\hat{H}$  being the chemical potential & Kohn-Sham Hamiltonian

- With sparse representation of  $\hat{H}$ , the algorithmic complexity can be sublinear, since the order of Chebyshev expansion to achieve a prescribed accuracy decreases as a function of the number of electrons (self-averaging)

Baer et al., *Phys. Rev. Lett.* **111**, 106402 ('13); *Annu. Rev. Phys. Chem.* **73**, 255 ('22)

- Sublinear stochastic algorithm also applies to TDDFT

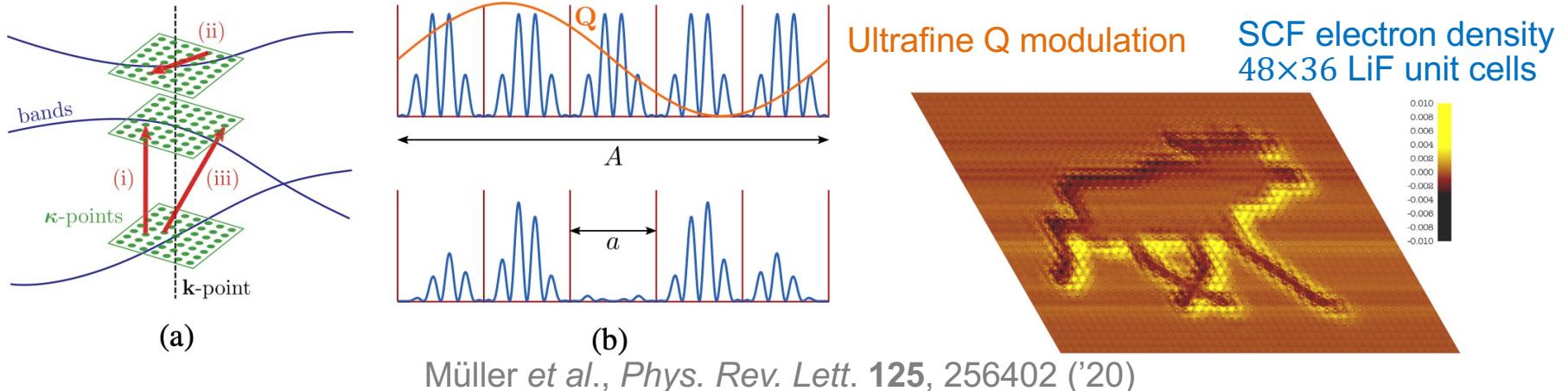
Vlcek et al., *J. Chem. Phys.* **150**, 184118 ('19)

- Key idea: Projection onto randomized vector space

cf. randomized linear algebra [Murray et al., arXiv: 2302.11474 ('23)]

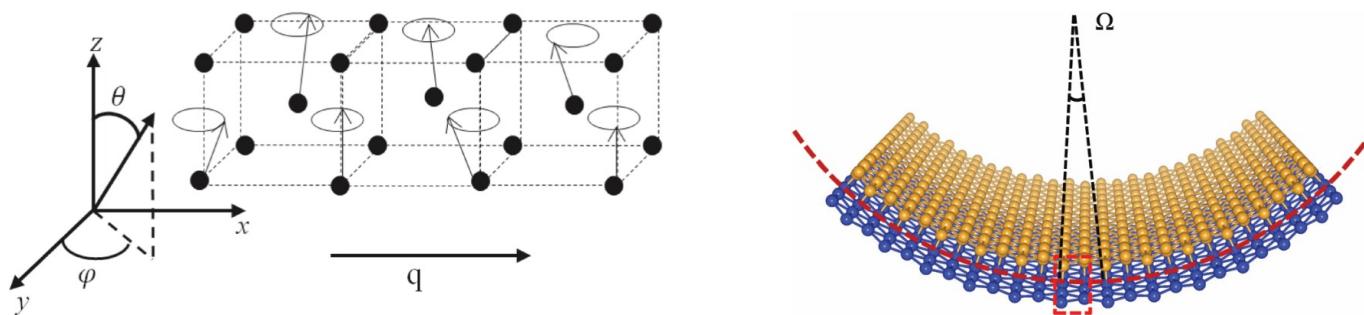
# UltraQ DFT: Recombine in Reciprocal Space

- Additional sum over a finer grid around each  $k$ -point in the reciprocal space describes physics at ultra-long length scales (generalized Block theorem)



- Generalized Block theorem constrains the Hamiltonian invariant under slow spatial modulation (e.g., spiral magnet & bended 2D sheet) via Block-like  $k$ -point sampling

Prayitno et al., JPSJ 87, 114709 ('18); Shi et al., PCCP 22, 11567 ('20)



- Wannier interpolation: Sparse  $k$ -point sampling → construct smooth Wannier functions in real space (cf. tight-binding Hamiltonian) → transform back to dense reciprocal space [Wannier-Berry code: Tsirkin, npjCM 7, 33 ('21)]

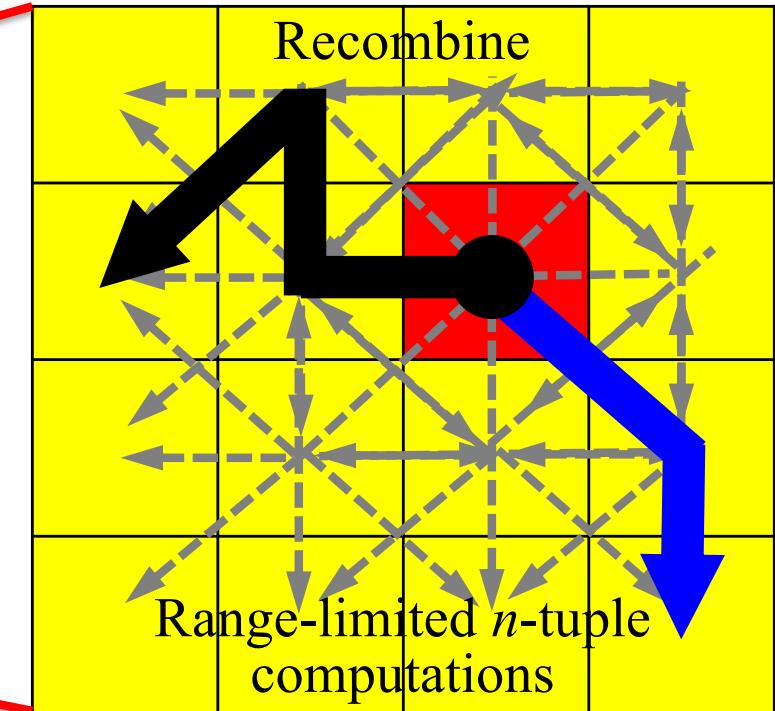
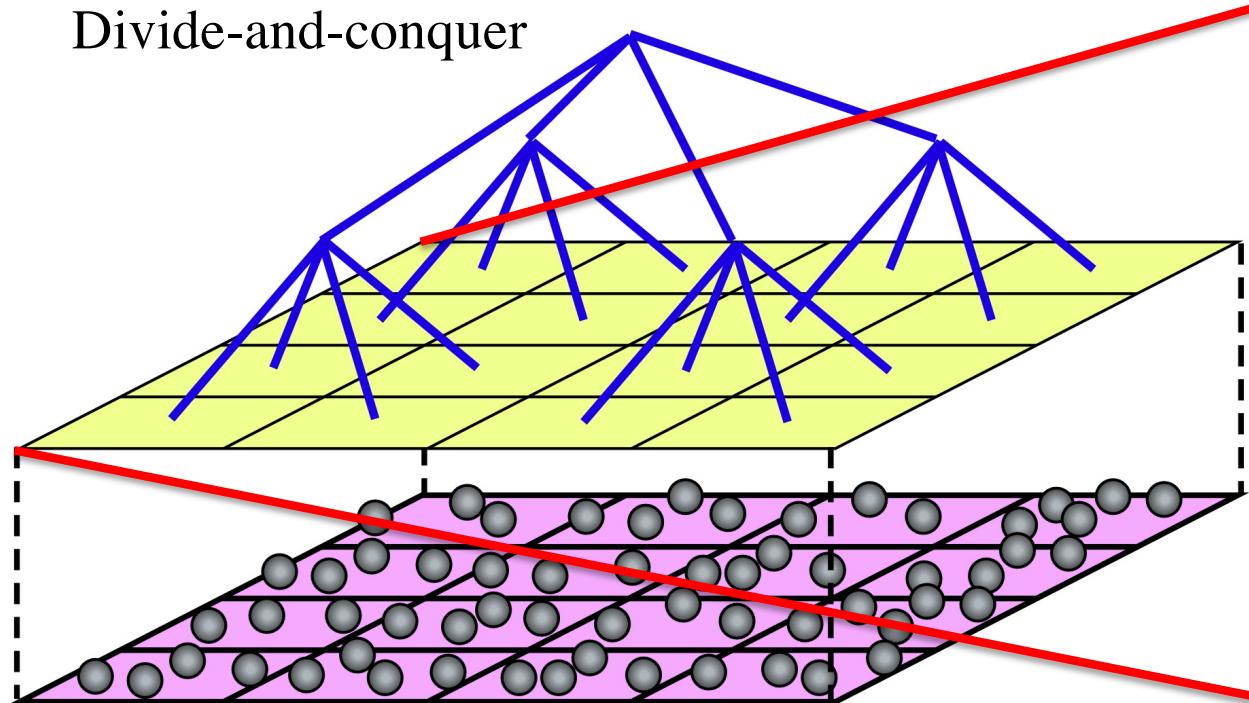
# Related Topics: Research = Directed Random Walk

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- **Fragment molecular orbital (FMO) method: fragment dimer & beyond**  
Kitaura et al., Chem. Phys. Lett. 312, 319 ('99); Tanaka et al., ibid. 556, 272 ('13)
- **Linearly scaling 3D fragment (LS3DF) method ~ real-space FMO**  
Wang et al., Proc. Supercomputing, SC08 ('08)
- **Density matrix renormalization group (DMRG)**  
White, *Phys. Rev. B* 48, 10345 ('93)  
See notes on (1) singular value decomposition (SVD) & (2) DMRG
- **Tensor networks: modern DMRG — combine with message passing (belief propagation or Bethe lattice) in 3D?**  
Chan & Sharma, Annu. Rev. Phys. Chem. 62, 465 ('11)

# Next: Divide-Conquer-Recombine (DCR)

Divide-and-conquer



M. Kunaseth *et al.*, ACM/IEEE SC13 ('13)

Globally-informed local DC solutions are used in the recombine phase as compact bases to synthesize global properties in broad applications

F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14)

K. Nomura *et al.*, *IEEE/ACM SC14* ('14)

T. Razakh *et al.*, *IEEE PDESC* ('24)

# Divide-Conquer-Recombine Applications

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- **High-order inter-molecular-fragment correlation**

Tanaka *et al.*, *Chem. Phys. Lett.* **556**, 272 ('13)

- **Global frontier orbitals (HOMO & LUMO) via linear combination of domain orbitals (LCDO)**

Yamada *et al.*, *Phys. Rev. B* **95**, 045106 ('17)

**Note the projection ( $P$  &  $Q = 1-P$ ) — generalized Langevin approach?**

Mori, *Prog. Theor. Phys.* **33**, 423 ('65); Kinjo & Hyodo, *Mol. Sim.* **33**, 417 ('07)

- **Dielectric response:** Simplified inter-layer coupling in layered materials; equation-of-motion decoupling for density response function, *cf.* linear-response time-dependent DFT in nonadiabatic QMD lecture

Andersen *et al.*, *Nano Lett.* **15**, 4616 ('15)

- **Electron dynamics:** Local plane-wave time-dependent KS equations glued together by Maxwell's equations

Sato & Yabana *et al.*, *J. Adv. Sim. Sci. Eng.* **1**, 98 ('14)

- **Exciton dynamics:** Local nonadiabatic QMD simulations recombined into a global exciton-kinetics graph

Mou *et al.*, *Appl. Phys. Lett.* **102**, 173301 ('13)

# Divide-Conquer-Recombine Approach (1)

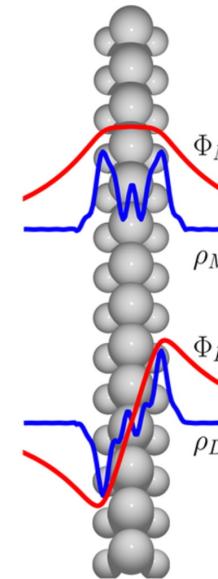
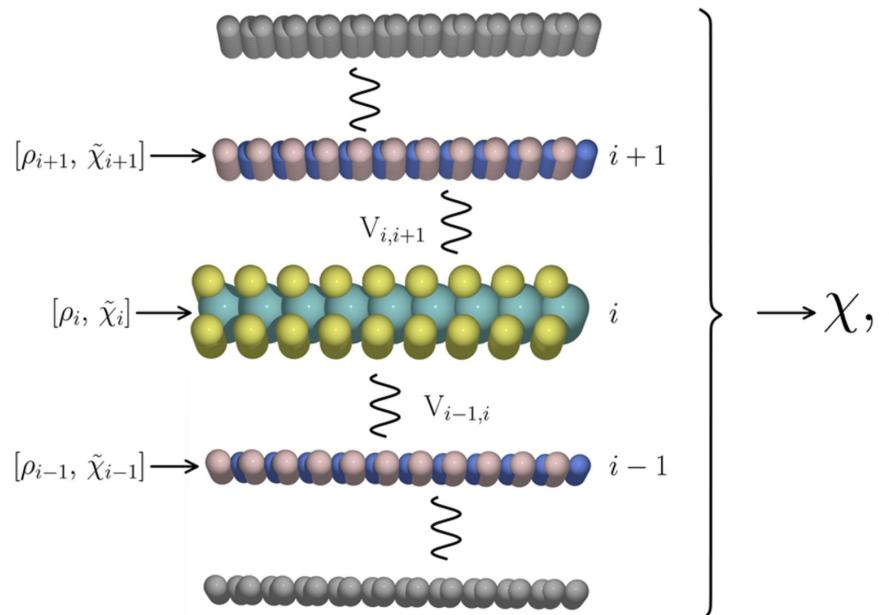
- **Dielectric response:** Simplified inter-layer coupling in layered materials; equation-of-motion decoupling for density response function, *cf.* linear-response time-dependent DFT in [nonadiabatic QMD lecture](#)
- **Density response function**

$$n_{\text{ind}}(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega)$$

- **Multiscale Dyson equations**

$$\tilde{\chi} = \chi^0 + \chi^0 \tilde{\mathbf{V}} \tilde{\chi} \quad \text{Intra-layer (accurate)}$$

$$\chi = \tilde{\chi} + \tilde{\chi} \mathbf{V}^I \chi \quad \text{Inter-layer (simplified, 2 DOF)}$$

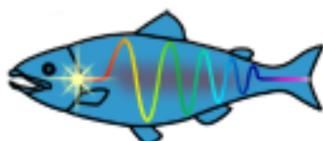
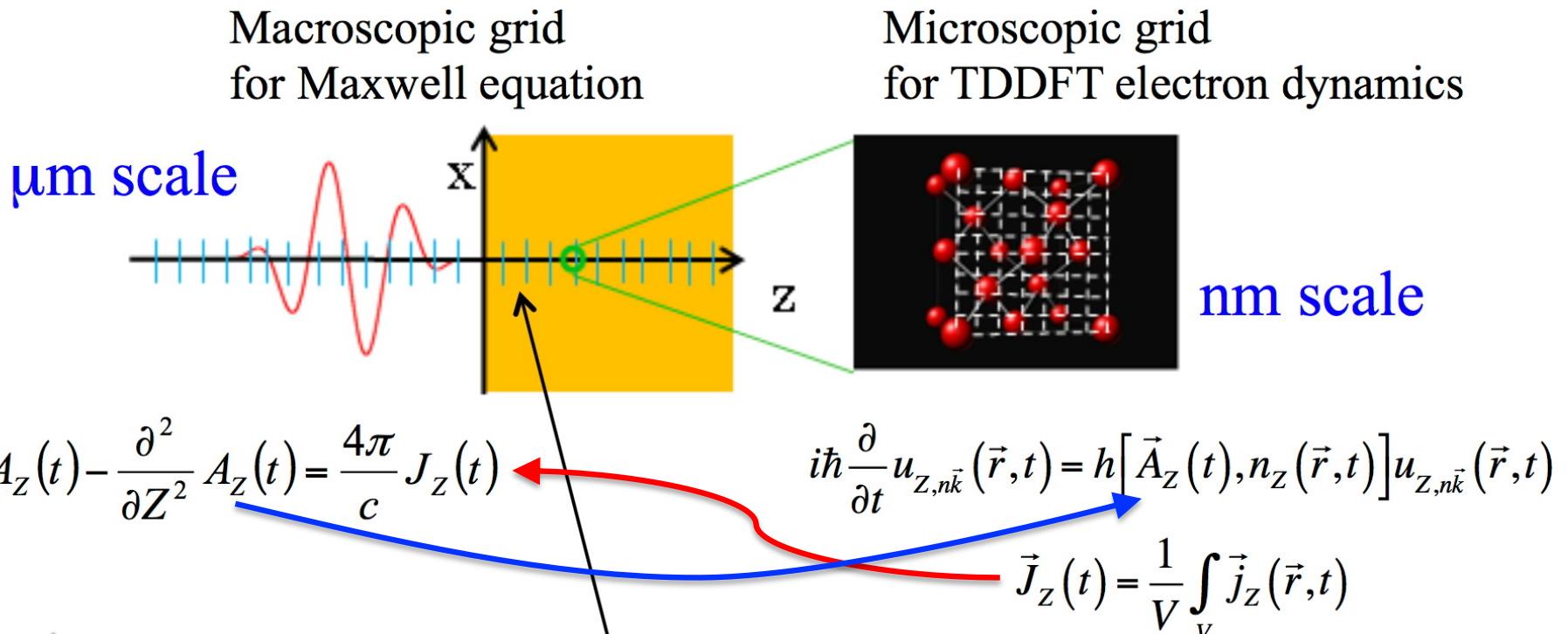


[Andersen et al.,  
Nano Lett. 15,  
4616 \('15\)](#)

[See Dyson equations in a nutshell](#)

# Divide-Conquer-Recombine Approach (2)

- Electron dynamics — Maxwell + TDDFT: Local plane-wave time-dependent KS equations glued together by global Maxwell's equations



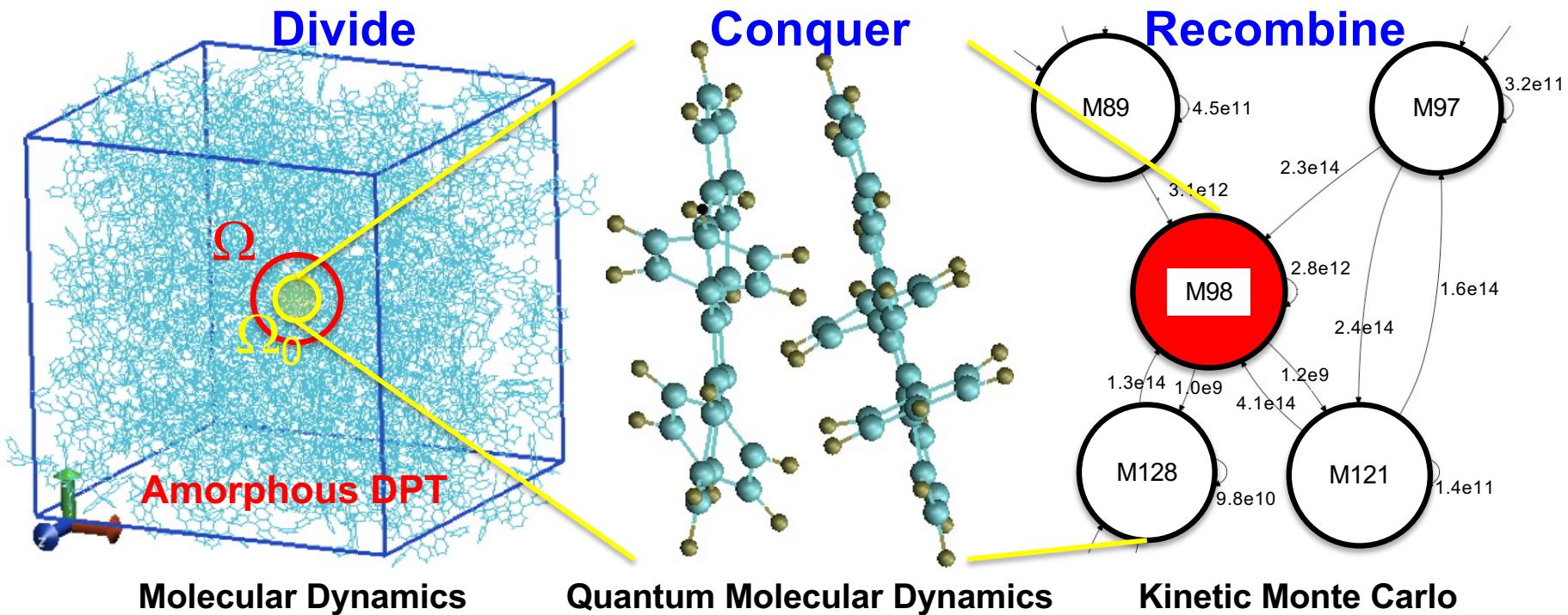
**SALMON**  
<http://salmon-tddft.jp>

Taken from Prof. Kazuhiro Yabana's presentation

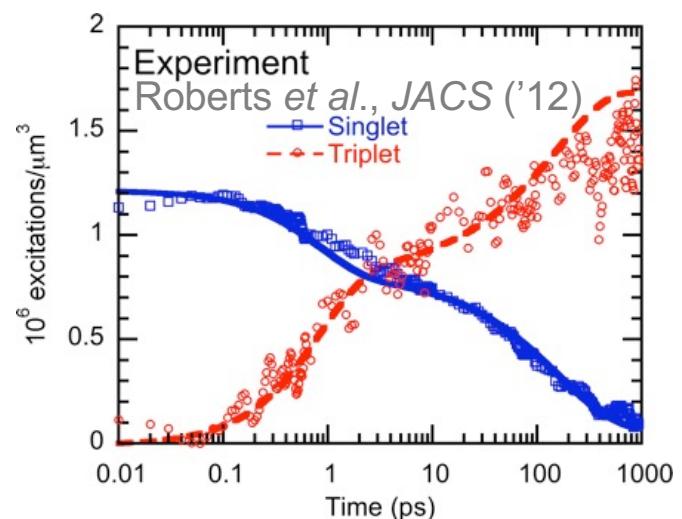
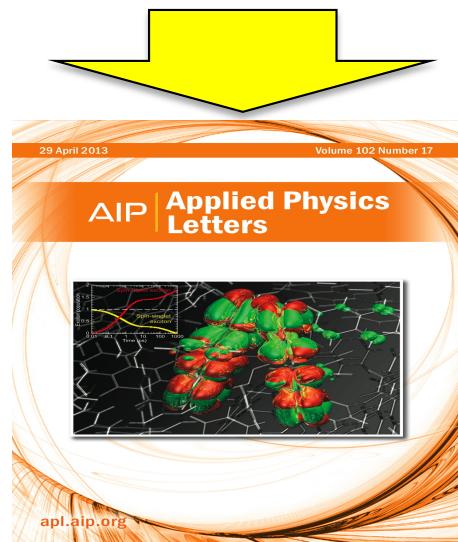
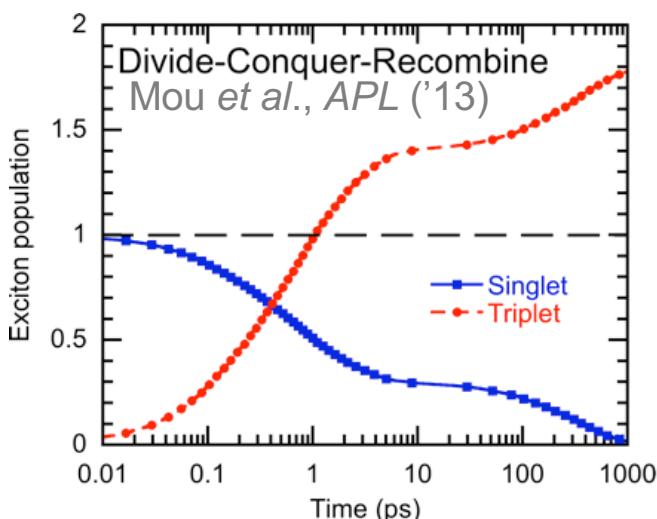
At each macroscopic grid point,  
we solve real-time electron dynamics in parallel

Sato & Yabana et al., J. Adv. Sim. Sci. Eng. 1, 98 ('14)

# Divide-Conquer-Recombine Approach (3)

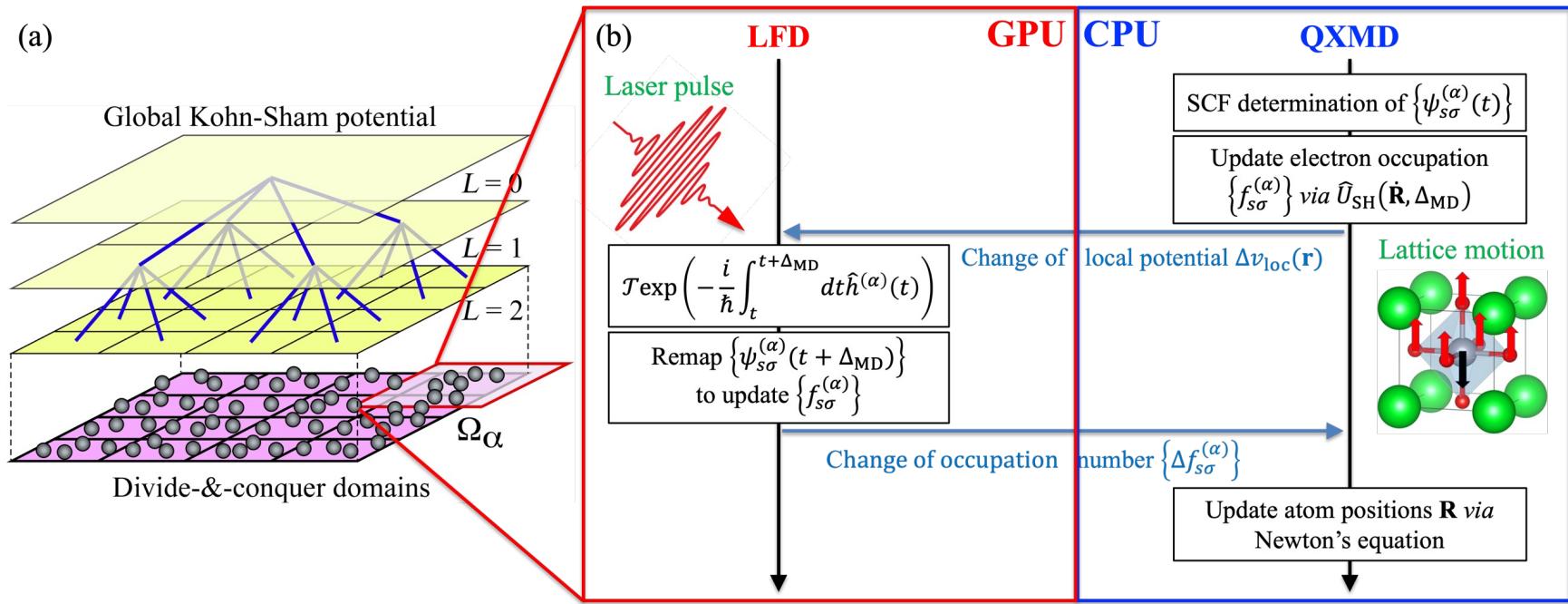


## Global kinetic graph: Experimental Length & Time Scales



# Divide-Conquer-Recombine Approach (4)

## Divide-&-conquer Maxwell-Ehrenfest-surface hopping (DC-MESH) method



- Incorporate multi-physics at appropriate scales & levels of approximation: (1) long-range Hartree coupling of divide-&-conquer (DC) domains; (2) short-range exchange-correlation (e.g., nonlocal xc functional) & light-matter interaction within each domain
- See [DC-MESH lecture](#) [Linker et al., *Science Adv.* **8**, eabk2625 (2022); Razakh et al., *PDSEC* (IEEE, '24)]