Eigenstate-analysis using Sakurai-Sugiura method with O(N)-DFT code CONQUEST

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[3] University College London

2018/8/17 @ ELSI workshop

Today's topics

- Electronic structure analysis of large materials using Sakurai-Sugiura (SS) method and CONQUETS

  Introduction of CONQUEST

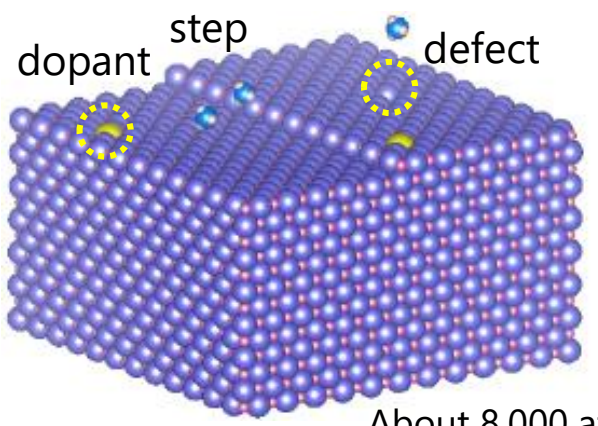
  O(N) DFT

  Multi-site method

  O(N)-DFT + SS

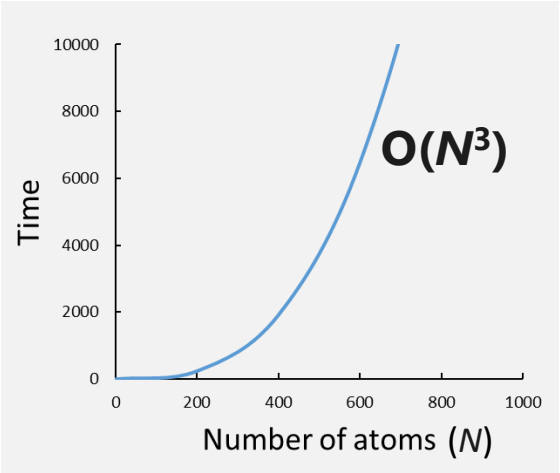
  Multi-site method + SS

Large-scale DFT calculations



About 8,000 atoms

Large-scale model is needed
to represent **specific**
atomic and electronic structures



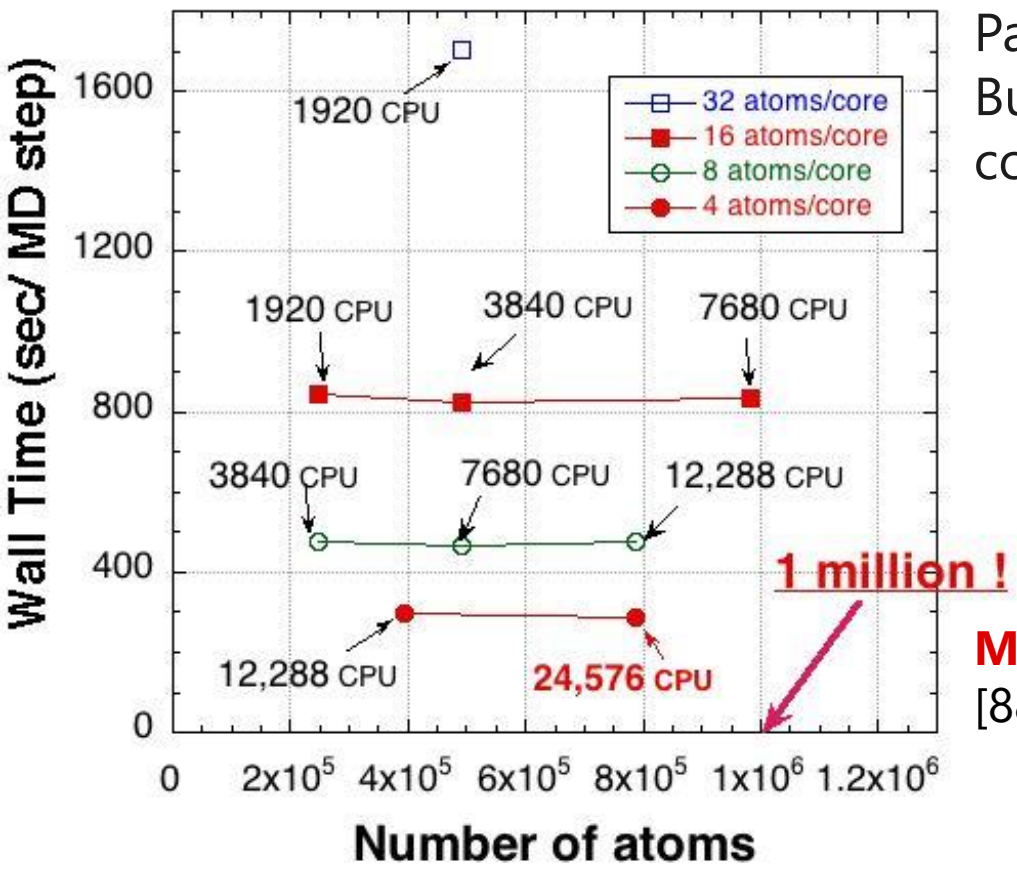
Scales cubically to
system size (# of atoms *N*) [**O(*N*³)**]

Usually **≤ 1,000 atoms**

Large-scale DFT with CONQUEST

Concurrent **O**(**N**) **QU**antum **E**lectronic **S**tructure **T**echnique [1]

DFT code for large-scale systems



Parallel efficiency in K-computer
Bulk Si,
constant # of atoms / node

Million atom systems: 5 min./MD step
[88,128 CPU = 705,024core]

[1] http://www.order-n.org

Large-scale DFT with CONQUEST

Concurrent **O**(**N**) **QU**antum **E**lectronic **S**tructure **T**echnique [1]

DFT code for large-scale systems

- Local orbital functions
- Order-*N* method (Density matrix minimization)
- High parallel efficiency

[1] http://www.order-n.org

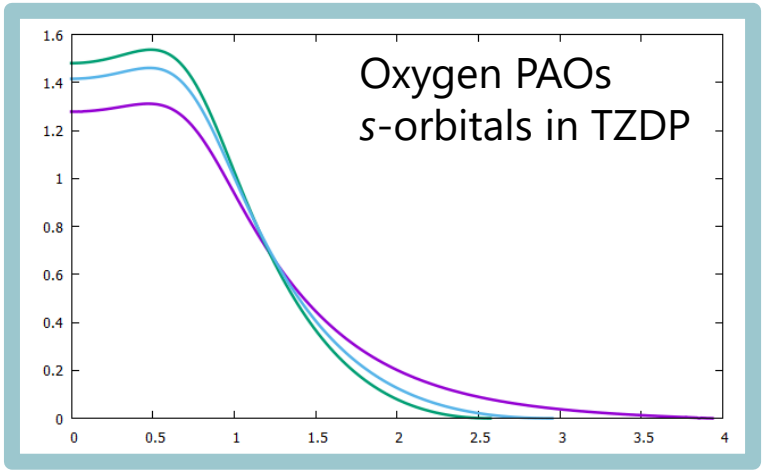
Local orbital functions

Construct from basis functions

$$\phi_\alpha(r) = \sum_\mu c_{\alpha\mu}\chi_\mu(r)$$

Local orbitals (Support function=SF)

Real-space



- Finite-element (B-spline) basis (akin to plane-wave functions)
- **Pseudo atomic orbital (PAO) basis**

$$\chi_\mu(r) = \chi_i^{\zeta lm}(r) = R_i^{l\zeta}(r)Y_i^{lm}(\mathbf{r})$$

ζ ... Radial functions
l ... Angular momentum number
m ... Magnetic quantum number

Radial functions Spherical harmonic functions

A. S. Torralba et al., J. Phys. Cond. Matt. 8, 20, 294206 (2008)

How to optimize electronic density

- Diagonalization **O(N^3)**

$$\mathbf{HC} = \boldsymbol{\varepsilon}\mathbf{SC}$$

$\mathbf{H}$: Electronic Hamiltonian
$\mathbf{S}$: Overlap matrix
$\mathbf{C}$: Eigenvectors (Bands/MOs)
$\boldsymbol{\varepsilon}$: Eigenvalues (Band/MO energies)

by using Scalapack

- Density matrix minimization → **O(N)**

O(*N*) in CONQUEST

- **Density matrix minimization (DMM)**

$$E_{\text{tot}} = E_{\text{T}} + E_{\text{ps}} + E_{\text{H}} + E_{\text{xc}} + E_{\text{M}}$$

$$E_{\text{T}} = -\frac{\hbar^2}{m}\int d\mathbf{r}\left[\nabla^2 \rho(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'}$$

$$E_{\text{ps}} = 2\int d\mathbf{r}d\mathbf{r}' V_{ps}(\mathbf{r}',\mathbf{r})\rho(\mathbf{r},\mathbf{r}')$$

$$E_{\text{H}} = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$$

$$E_{\text{xc}} = \int d\mathbf{r} n(\mathbf{r}) e_{\text{xc}}\left[n(\mathbf{r})\right]$$

$$\rho(\mathbf{r},\mathbf{r}') = \sum_i f_i \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}') = \sum_{\alpha\beta}\phi_\alpha(\mathbf{r})K_{\alpha\beta}\phi_\beta^*(\mathbf{r}')$$

$$n(\mathbf{r}) = 2\rho(\mathbf{r},\mathbf{r})$$

$$\frac{\partial E^{\text{tot}}}{\partial L} = 6\left(SLH + HLS\right)_{\alpha\beta} - 4\left(SLSLH + SLHLS + HLSLS\right)_{\alpha\beta}$$

L = Auxiliary density matrix

[3] E. Hernandez and M. J. Gillan, PRB_51_10157 (1995) [4] E. Hernandez, M. J. Gillan and C. M. Goringe, PRB_53_7147 (1996)

O(*N*) in CONQUEST

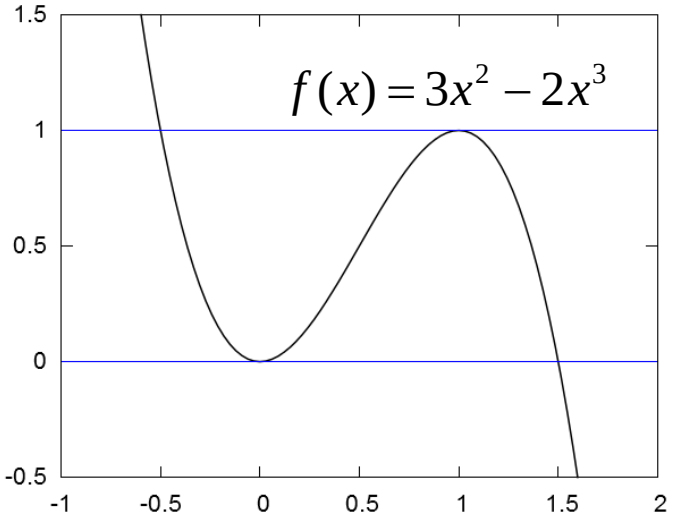
- **Density matrix minimization (DMM)**

$$\frac{\partial E}{\partial L}$$

Energy minimization
keeping idempotency condition (LNV)

$$K = 3LSL - 2LSLSL$$

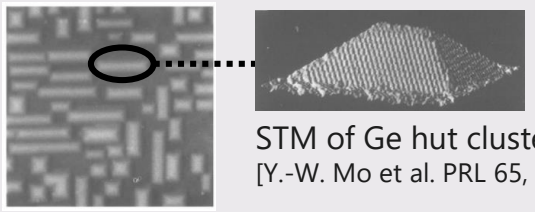
$\boldsymbol{K}$ = Density matrix
$\boldsymbol{L}$ = Auxiliary density matrix
$\boldsymbol{S}$ = Overlap matrix



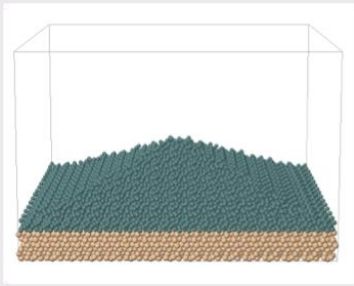
Spacial cutoff for L ⇒ O(*N*)

Capability of CONQUEST

Geometry optimization



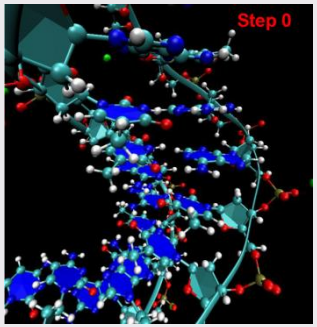
STM of Ge hut cluster on Si surface
[Y.-W. Mo et al. PRL 65, 1020 (1990).]

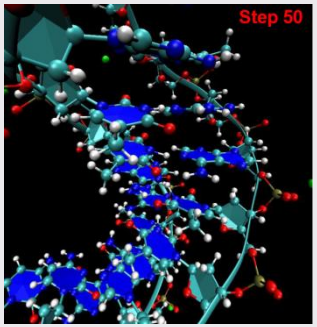


About **200,000 atoms**

Optimized geometry by CONQUEST
[Miyazaki et al., JPSJ, 77, 123706 (2008).]

Ab initio MD





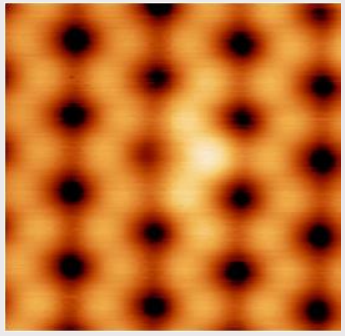
Hydrated DNA (**3,439 atoms**) PBE/SZP
[T. Otsuka et al, in preparation.]

Si (**32,768 atoms**) LDA/DZP
Combination with extended Lagrangian method
[M. Arita et al, JCTC, 10, 5419 (2014).]

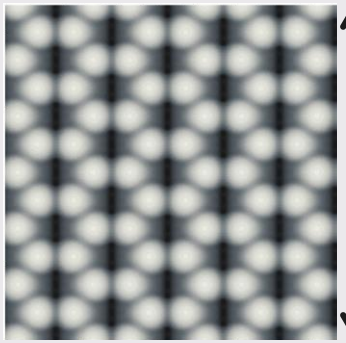
STM, STS

STM picture of Si (100) surface (-1.5eV)

Exptl



CONQUEST



4.6 nm

TDDFT,

Constraint DFT, EXX,

Blue-moon ensemble simulation,

…

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Eigenstates with O(*N*) in CONQUEST

O(*N*) method

☺ Low cost: O(*N*)

☺ Energies and geometries

😐 Metals??

☹ **No 1-e$^-$ wave functions (Bands, MOs)**

Electronic states:
Orbital pictures
Density of states
STM images …
(IPs, EAs, excitation energies)

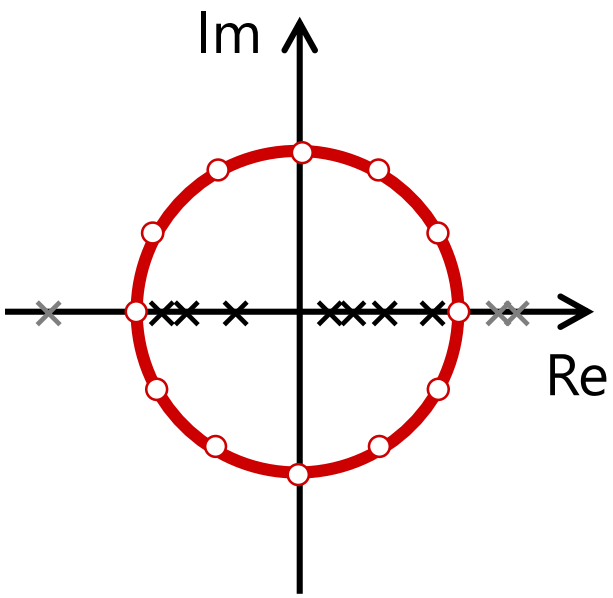
Sakurai-Sugiura method:

Projection method to obtain

eigenstates in a finite range

Sakurai-Sugiura method

Projection method to obtain the eigenstates in a **finite range**



(1) *N* simultaneous linear equations
(number of integration points on the curve)

$$\left(\omega_j \mathbf{B} - \mathbf{A}\right)\mathbf{y}_j = \mathbf{v} \qquad \omega_k = \gamma + R_D \exp\left(\frac{2\pi i}{N}k\right), \quad (k = 0,1,\cdots,N-1)$$

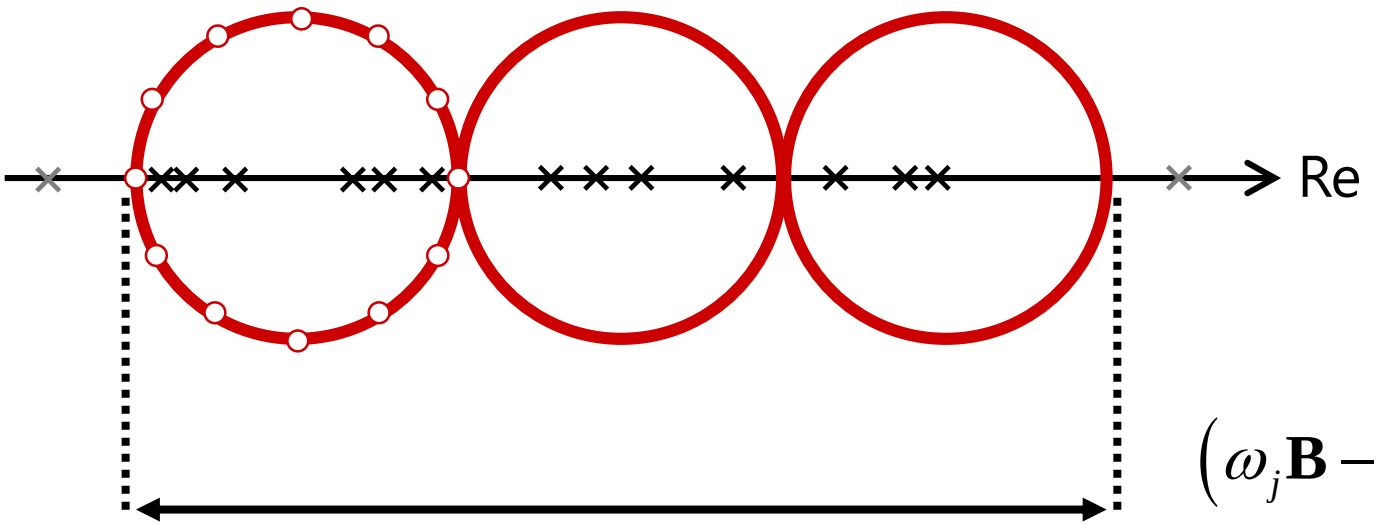
(2) m×m diagonalization
(number of states in the region) $\mathbf{H}_m^{<} - \lambda \mathbf{H}_m$

$$\mathbf{H}_m := \begin{pmatrix} \mu_0 & \mu_1 & \cdots & \mu_{m-1} \\ \mu_1 & \mu_2 & \cdots & \mu_m \\ \vdots & \vdots & \ddots & \vdots \\ \mu_{m-1} & \mu_m & \cdots & \mu_{2m-2} \end{pmatrix} \quad \mathbf{H}_m^{<} := \begin{pmatrix} \mu_1 & \mu_2 & \cdots & \mu_m \\ \mu_2 & \mu_3 & \cdots & \mu_{m+1} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_m & \mu_{m+1} & \cdots & \mu_{2m-1} \end{pmatrix}$$

$$\mu_k = \frac{1}{2\pi i}\int_\Gamma \frac{f(z)}{(z-\gamma)^{k+1}}dz \qquad \mu_k \approx \hat{\mu}_k := \frac{1}{N}\sum_{j=0}^{N-1}(\omega_j - \gamma)^{k+1} f(\omega_j), \quad (k = 0,1,\cdots) \quad f_j \leftarrow \mathbf{u}^{\mathrm{H}} y_j, \quad (j = 0,\cdots,n-1)$$

T. Sakurai, H. Sugiura, J. Comput. Appl. Math. 159, 119 (2003).

Sakurai-Sugiura method



$$\left(\omega_j \mathbf{B} - \mathbf{A}\right)\mathbf{Y}_j = \mathbf{BV}$$

N_{SS} = number of quadrature points

M_{SS} = number of complex moments

L_{SS} = number of columns of the source matrix V ($M_{SS}L_{SS} > m$)

Estimate the number of eigenstates in the region stochastically by using Sylvester' s law of inertia

T. Sakurai et al., Journal of Algorithms & Computational Technology, 7, 249 (2013).

Procedure

Construct Hamiltonian and overlap matrices with **CONQUEST**

↓ (sum over k-points)
(save only lower-triangle elements, larger than threshold)

Eigenstate calculation with Sakurai-Sugiura calculations with **zPares**

↓

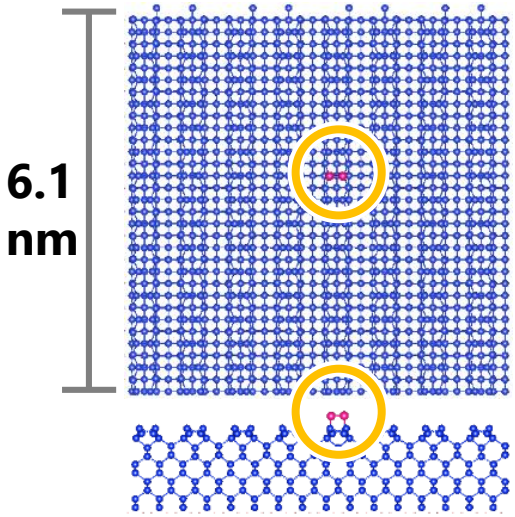
Read eigenvectors and eigenvalues with **CONQUEST**

MO / Band information → Electronic properties
STM pictures

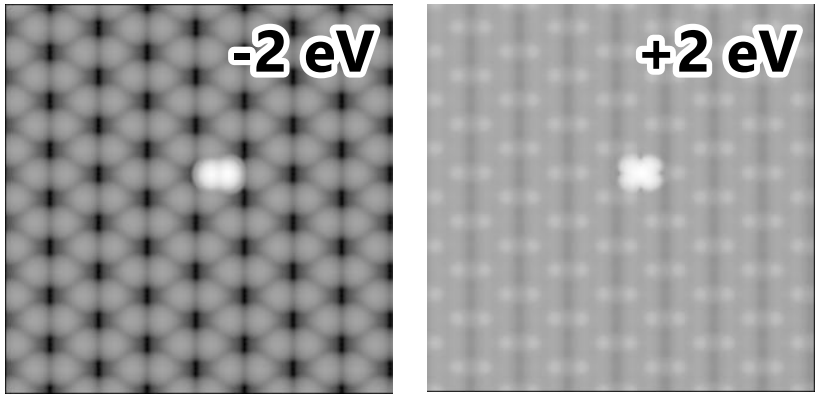
A. Nakata, Y. Futamura, T. Sakurai, D. R. Bowler, T. Miyazaki, J. Chem. Theory. Comput., 13, 4146 (2017)
[CQ] http://www.order-n.org [Z-pares] http://zpares.cs.tsukuba.ac.jp/

STM images

P_2 on Si(100)



(GGA/TDZP)



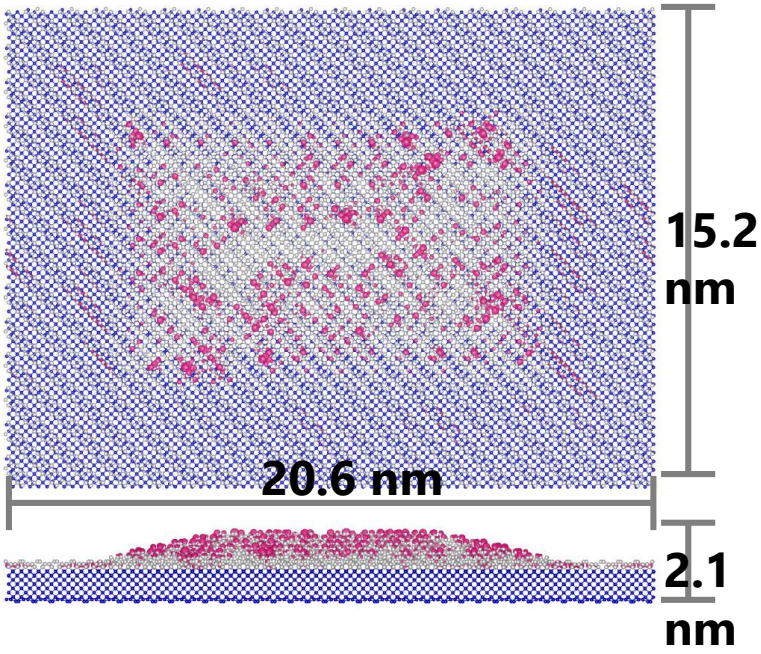
	4 node	64 node
Scalapack (PDSYGVX)	5,064 s	629 s
Sakurai-Sugiura (N_{SS}=16, M_{SS}=8, L_{SS}=100)	924 s	85 s

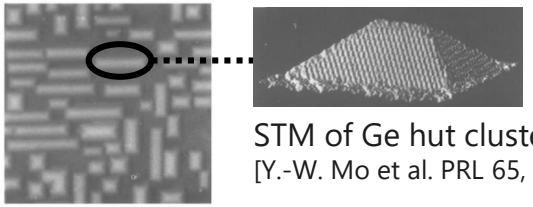
by PACS-IX (Intel Xeon E5-2670v2) in Univ of Tsukuba

Large systems

Ge hut cluster on Si(001)

- Charge distributions





STM of Ge hut cluster on Si surface
[Y.-W. Mo et al. PRL 65, 1020 (1990).]

±0.01eV around Fermi level

213,633 states

43 states (GGA/SZP)

atoms	node	time
23,737	64	146
194,573	6,400	2,399

(N_{SS}=16, M_{SS}=8, L_{SS}=64)

with K computer

S. Arapan, D. R. Bowler, T. Miyazaki, arXiv:1510.00526.

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  - Multi-site method

  O(N)-DFT + SS

  Multi-site method + SS

Large-scale DFT with CONQUEST

Concurrent **O**(**N**) **QU**antum **E**lectronic **S**tructure **T**echnique [1]

DFT program for large scale systems

- High parallel efficiency
- Order-*N* method (Density matrix minimization)
- **Local orbital function (support function)**

  Localized in finite region around each atom → sparse

  Cost scales cubically to the number of functions

Diagonalization	aN^3
Order-*N*	bN

N = number of atoms

Multi-site functions

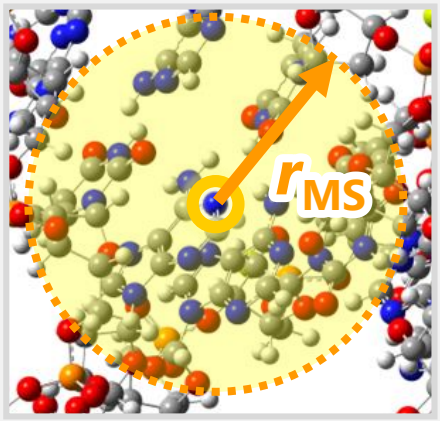
No contraction — Primitive functions

Single-site contraction

$$\phi_{i\alpha}(r) = \sum_{\varsigma \in i} c_{i\alpha}^{\varsigma lm} \chi_i^{\varsigma lm}(r)$$

Linear combination of AOs on each atom

Multi-site contraction



$$\phi_{i\alpha}(r) = \sum_{k}^{neighbors} \sum_{\varsigma lm \in k} C_{i\alpha}^{k\varsigma lm} \chi_k^{\varsigma lm}(r)$$

Linear combination of AOs in cutoff region

Contract to be **minimal size**
keeping primitive AOs' accuracy

A. Nakata, D. R. Bowler, T. Miyazaki, Phys. Chem. Chem. Phys., 17, 31427 (2015)

Gradient wrt coefficients

$$\frac{\partial E}{\partial C_{i\alpha,k\mu}} = \frac{\partial E}{\partial \phi_{i\alpha}} \frac{\partial \phi_{i\alpha}}{\partial C_{i\alpha,k\mu}} = \frac{\partial E}{\partial \phi_{i\alpha}} \chi_{k\mu}$$

$$\frac{\partial E}{\partial \phi_{i\alpha}(\mathbf{r})} = 4 \sum_{\beta} \left[K_{\alpha\beta} \hat{H} + G_{\alpha\beta} \right] \phi_{j\beta}(\mathbf{r})$$

Diag.

$$G_{\alpha\beta} = \sum_{n} f_n \varepsilon_n u_{n\alpha} u^*_{n\beta}$$

$$K_{\alpha\beta} = \sum_{n} f_n u_{n\alpha} u^*_{n\beta}$$

O(*N*)

$$G_{\alpha\beta} = 3(LHL)_{\alpha\beta} - 2(LSLHL + LHLSL)_{\alpha\beta}$$

$$K_{\alpha\beta} = 3(LSL)_{\alpha\beta} - 2(LSLSL)_{\alpha\beta}$$

Advantages of multi-site method

- Applicable to metallic systems

  Cutoff is introduced for support functions
  but not for wave functions

- Improve accuracy as much as we want

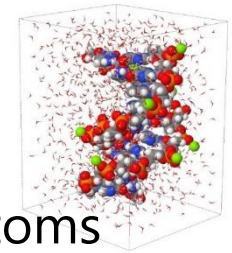
  (ex) Si atom

	Primitive		Multi-site support functions
DZP	13	→	4
TZDP	22	→	4

Always to be minimal size

Computational time

DNA in water



3439 atoms

	Primitive AO (DZP)	Multi-site SFs (8 bohr)	Multi-site SFs (16 bohr)
# of functions	27883	**4744**	**4744**
Time [sec.]			
Matrix construction	28.0	34.5	484.8
Diagonalziation	12317.4	**627.7**	**566.3**
Gradient of coefficients	–	4.3	25.7

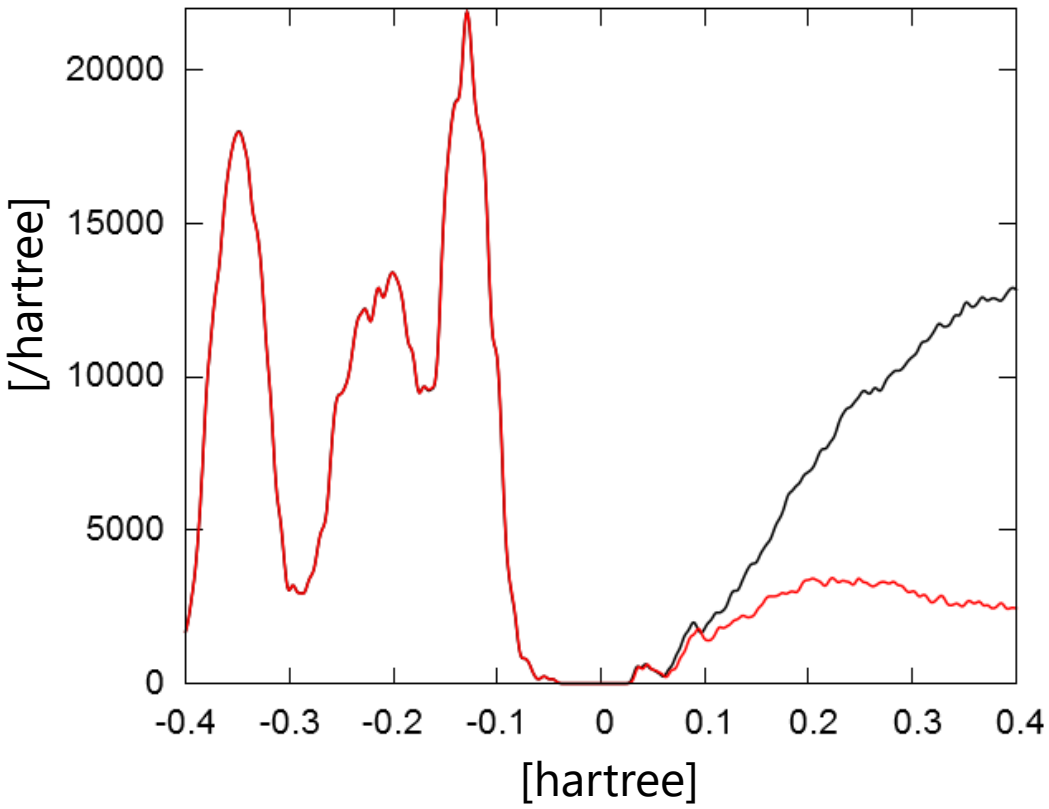
PBE / DZP
HA8000t (Kyushu Univ)
96 cores parallel

Large reduction! (about 1/12)

DOS of DNA in water (8 bohr)

Cutoff r_{MS} = 8.0 bohr

Black: Primitive AO (DZP)
Red : Multi-site SFs



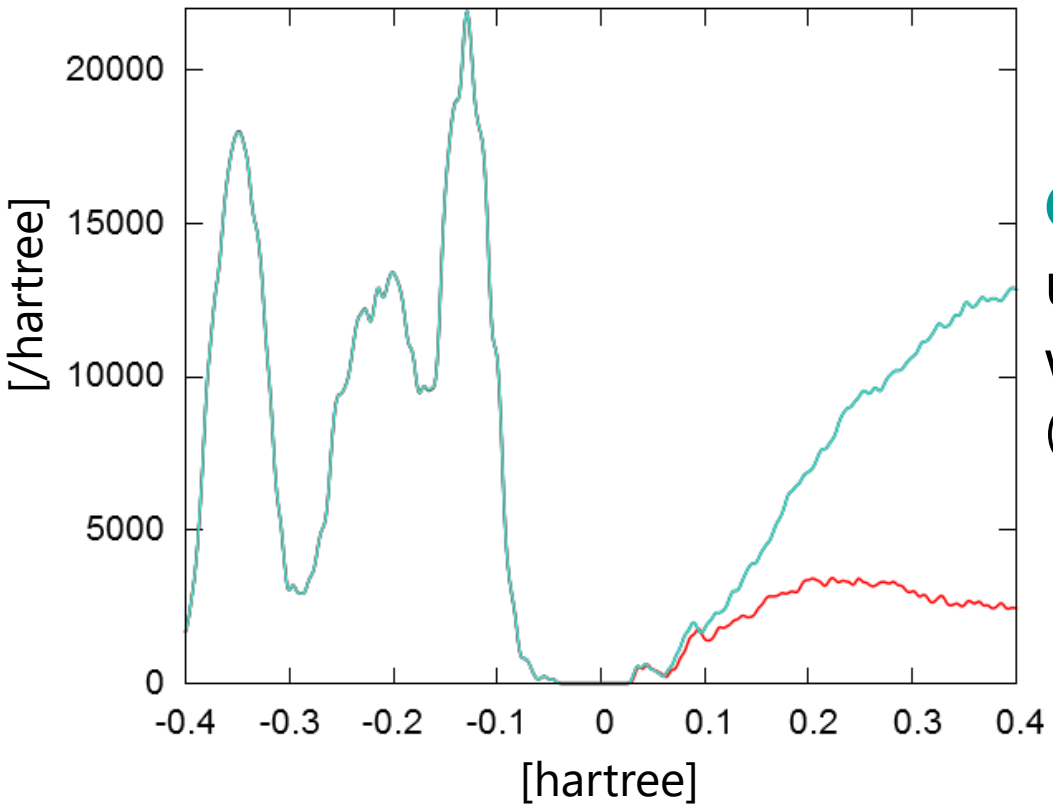
☺ Occupied space

☹ Unoccupied space

DOS of DNA in water (8 bohr)

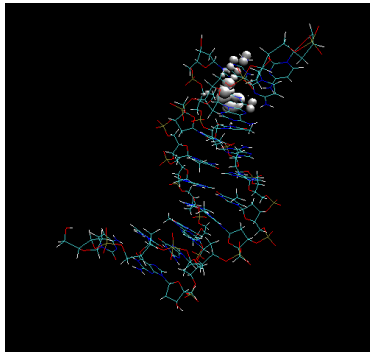
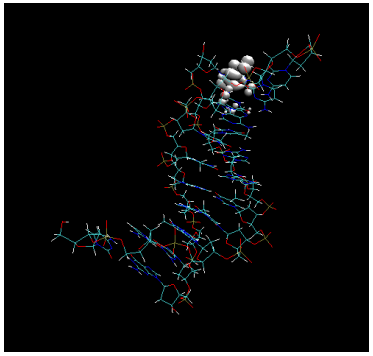
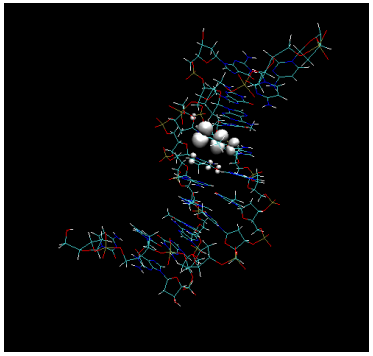
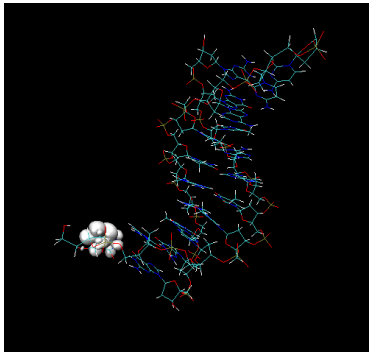
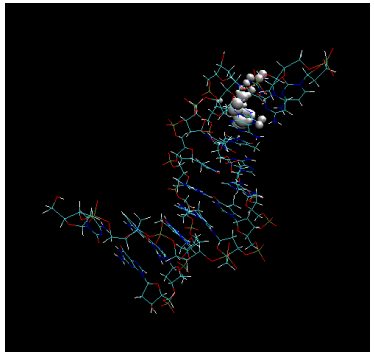
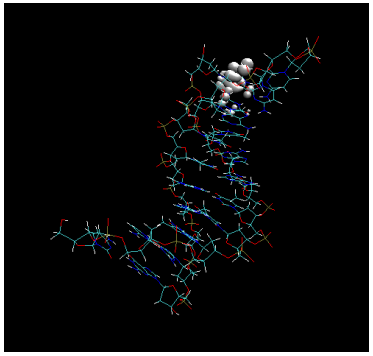
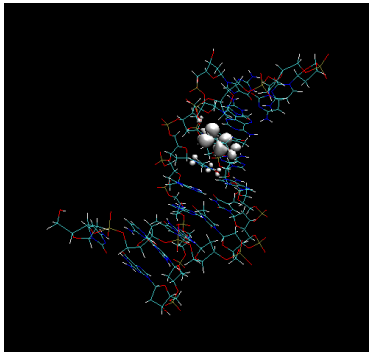
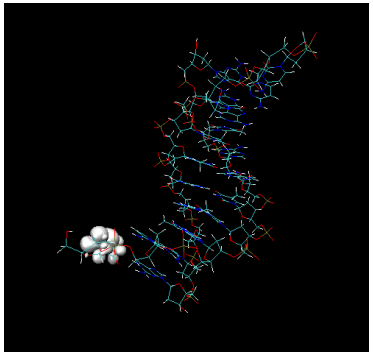
Cutoff r_{MS} = 8.0 bohr

Black: Primitive AO (DZP)
Red : Multi-site SFs
Blue : Primitive AO (DZP) with charge of multi-site SFs



One-shot recalculation using multi-site charge with primitive AOs
(by Sakurai-Sugiura method)

MOs of DNA in water

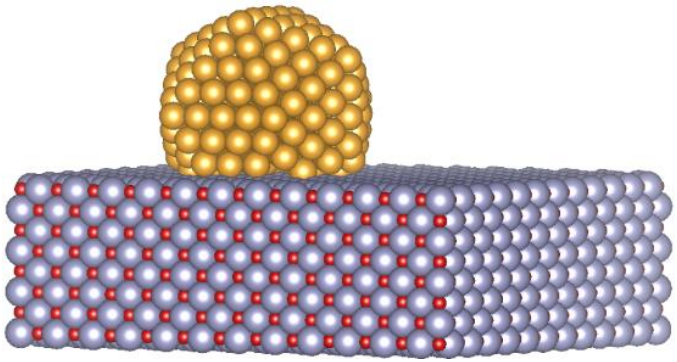
	-1.4458947736	-1.2563299879	0.9071560148	0.9438977188
Exact Diag.				
	HOMO-1	HOMO	LUMO	LUMO+1
SS				
	-1.4458947736	-1.2563299881	0.9071560149	0.9438977187

[eV]

Summary

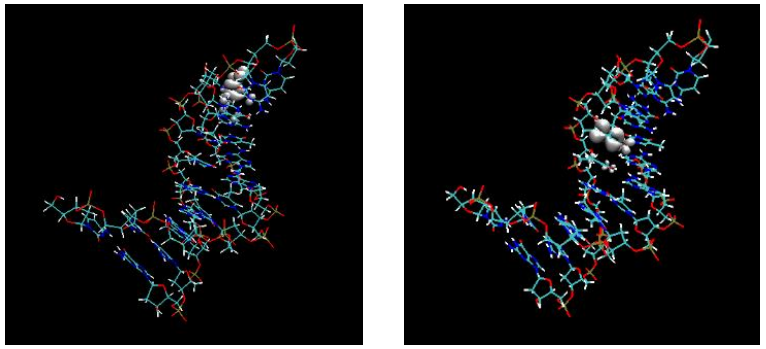
Investigation of eigenstates (1e- wave functions)
becomes available even with O(*N*) method
by using Sakurai-Sugiura method

Multi-site method makes available
accurate calculation with low computational cost
simulation of large metallic systems



Metallic nanoparticles

HOMO LUMO



MO pictures of DNA