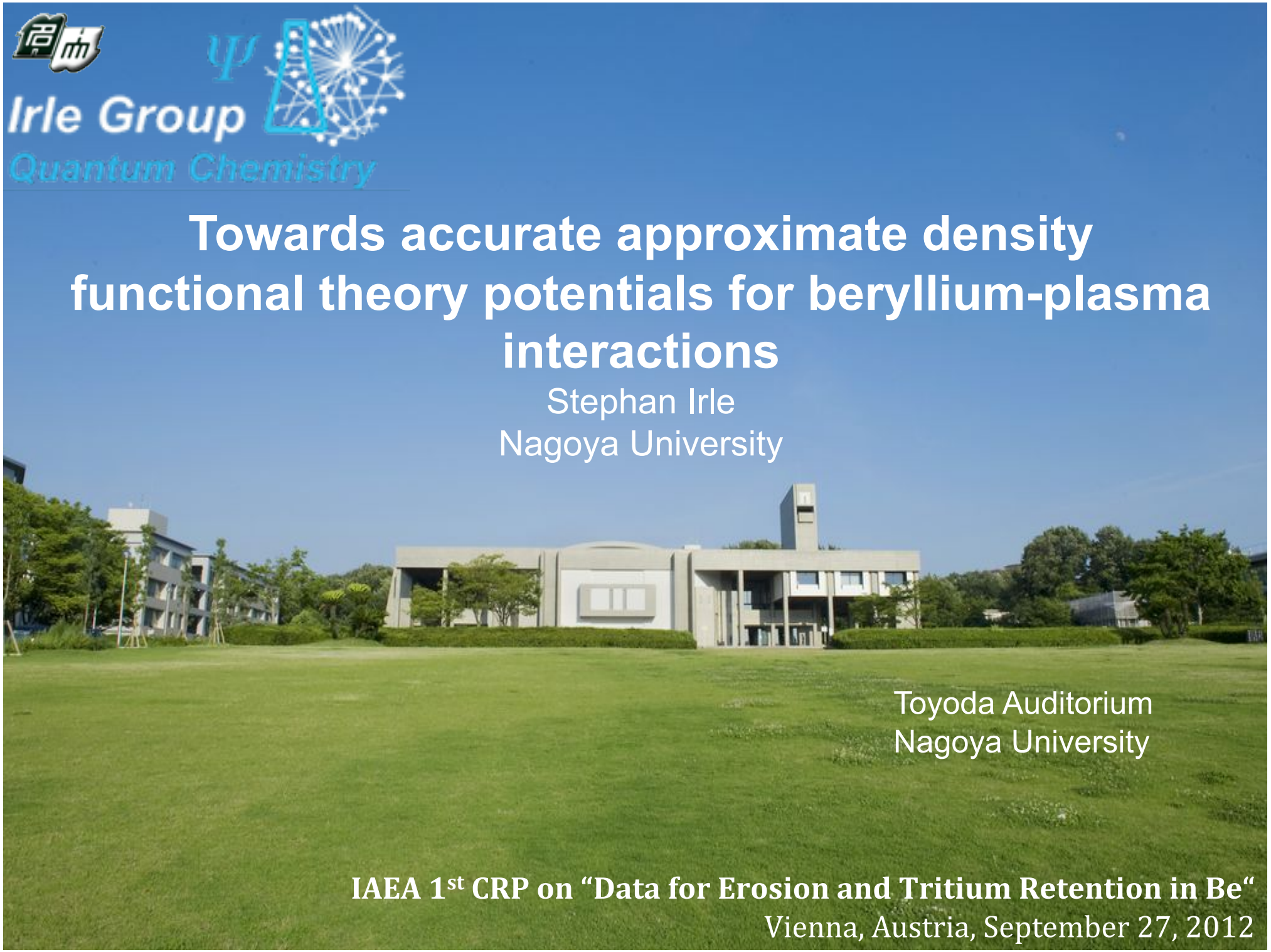


Towards accurate approximate density functional theory potentials for beryllium-plasma interactions

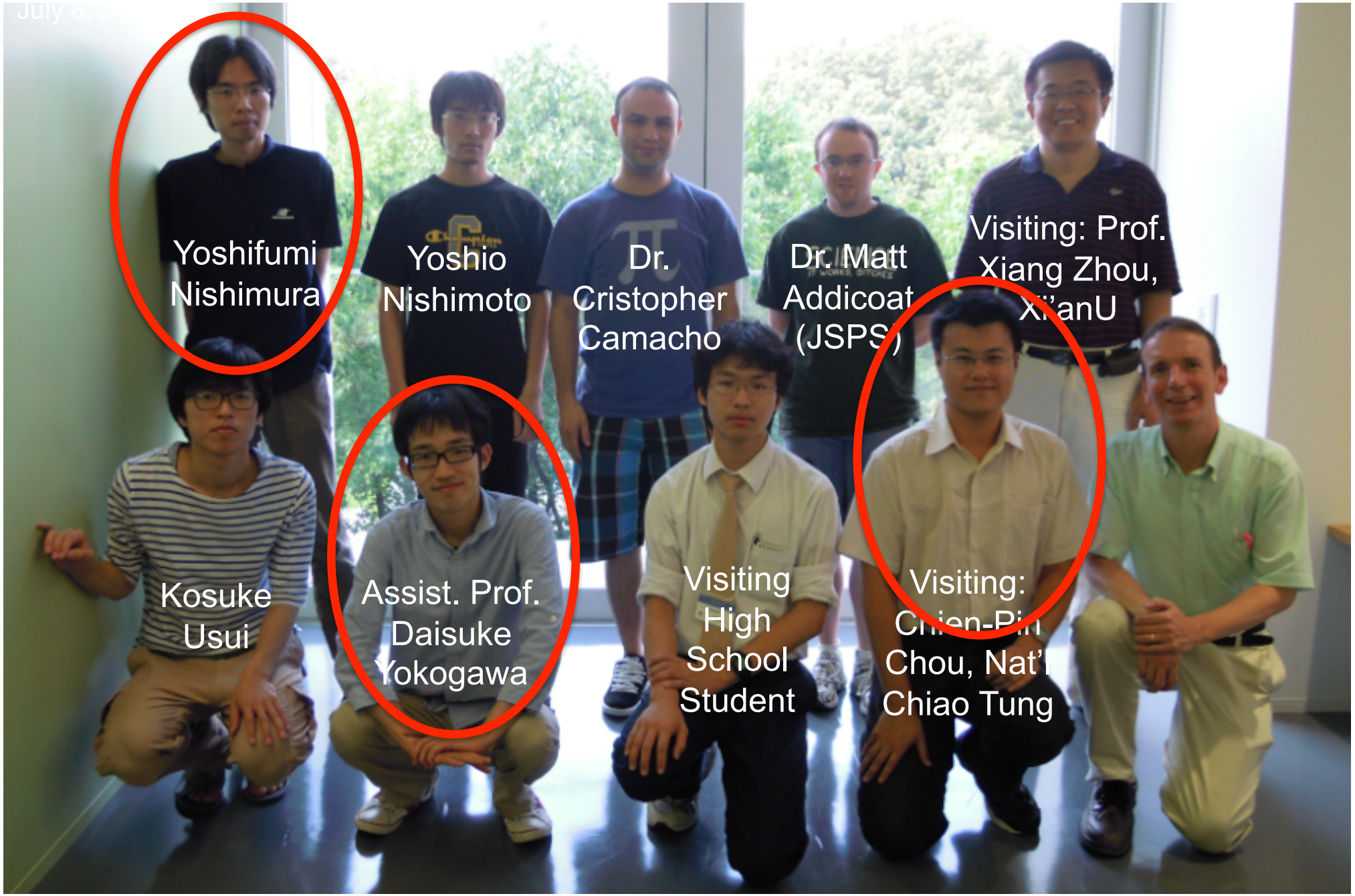
Stephan Irle
Nagoya University

Toyoda Auditorium
Nagoya University

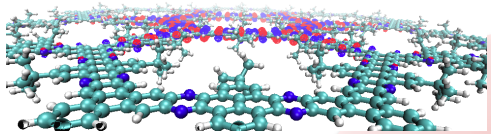
IAEA 1st CRP on "Data for Erosion and Tritium Retention in Be"
Vienna, Austria, September 27, 2012

August 9, 2012

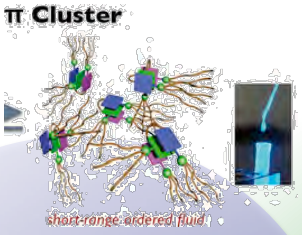
The Group



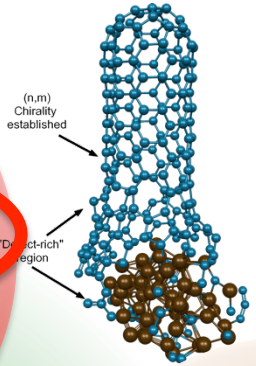
Quantum Chemistry of Complex Systems in Nagoya



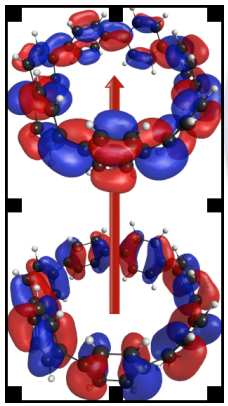
Collaborator:
Yamaguchi (expt)
Itami (expt)
Others (expt)



QM/MD of nanostructure self-assembly and erosion
Structure, properties, reactivity



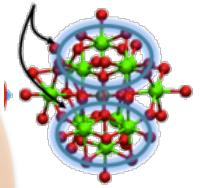
Collaborator:
Shinohara (expt)
Kusunoki (expt)
Jiang (IMS, expt)
Many others (expt)



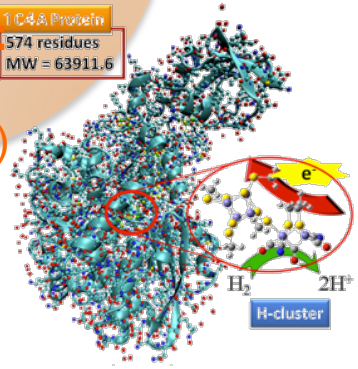
Excited states of large organic molecules and ensembles

Approximate DFT & *ab initio* methods

Transition metal cluster chemistry: Materials and quantum proteins



Collaborator:
Awaga (expt)
Tatsumi (expt)
Endo (expt)

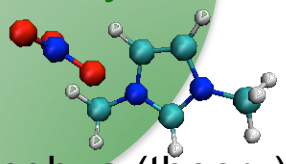


$$ih\frac{dP(t)}{dt} = [P(t), F(t)]$$

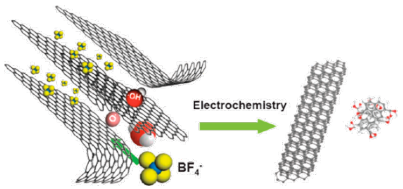
Method Development: DFTB parameter, LVNMD, GA algorithms

Collaborator:
Witek (theory)
Jakowski, Niehaus (theory)

Simulation of ionic liquids: dynamics and catalytic activity



Collaborator:
Ouchi (expt)
Parasuk/Hannongbua (theory)



Overview

Motivation

DFTB Method

DFTB/MD Applications

DFTB Parameterization

Summary

Overview

Motivation

DFTB Method

DFTB/MD Applications

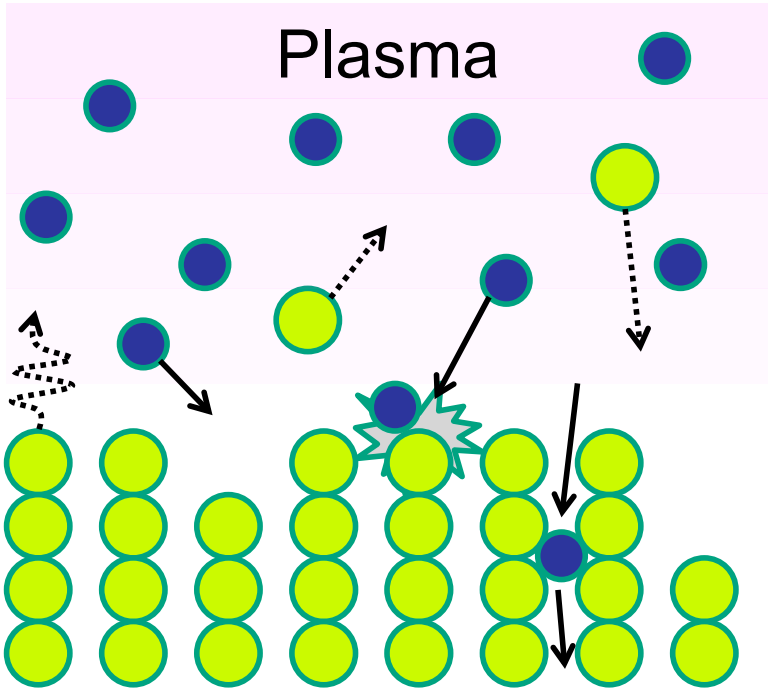
DFTB Parameterization

Summary

Chemical Sputtering on Be

- Little is known about the plasma wall processes on Be surface
- Performing accurate molecular dynamics (MD) simulations is important to extend our knowledge at the atomistic level

Temperature ~ 600 ºC



(pure/mixed) Be surfaces

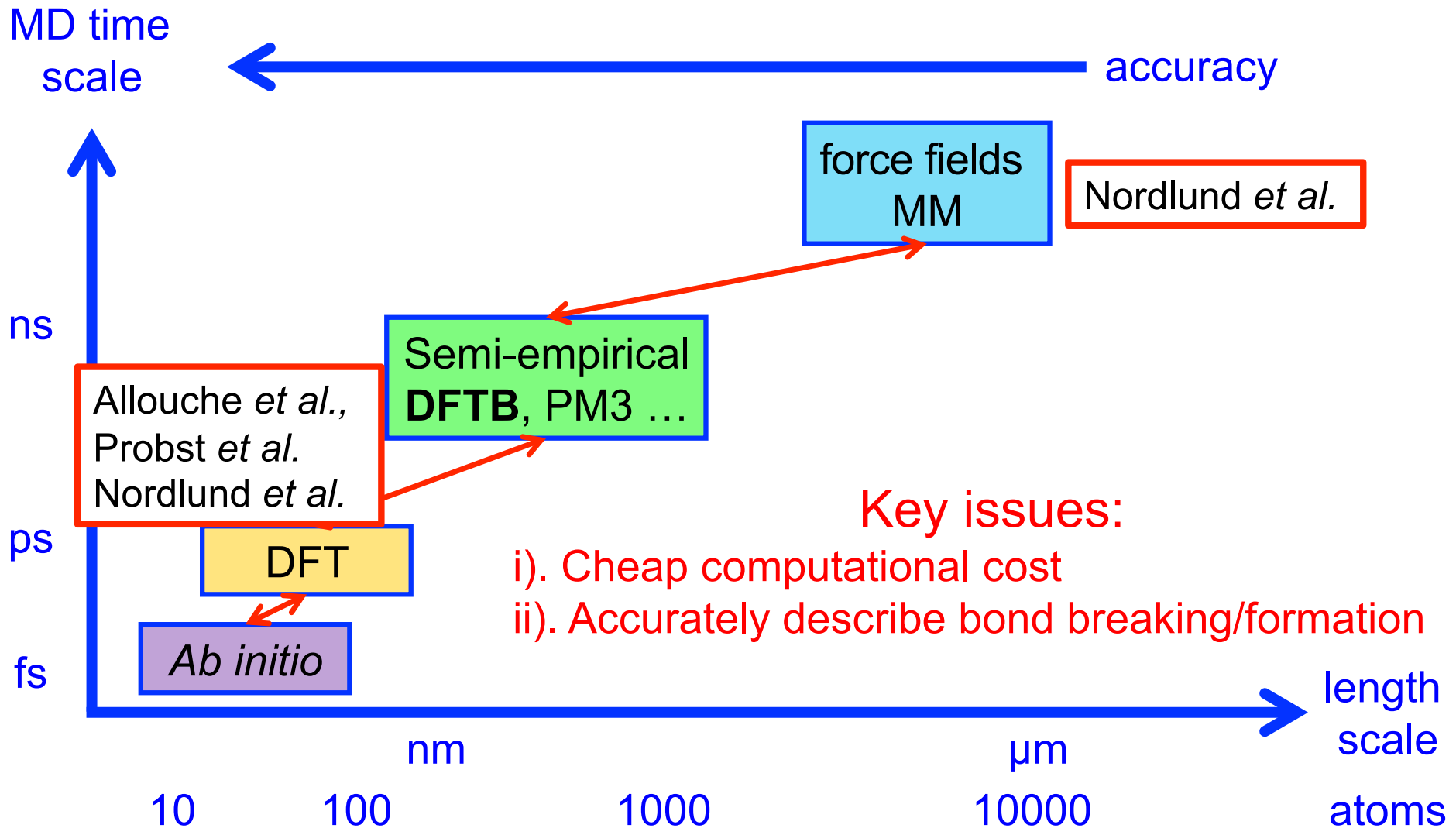
= Be

= H/D/T, He, H_2O, CH_4, N_2, W,

Getting insights into plasma wall interactions;
- Incident energy dependence (adsorption, reflection, penetration)
- Temperature dependence
- Conditions of surface structures (how erosion, retention processes proceed)
- Comparison with experimental data and previous theoretical works (classical MD simulations* and static DFT calculations**)

*Bjorkas, C. *et al.*, *New. J. Phys.*, **11**, 123017, (2009).; Ueda, S. *et al.*, *J. Nucl. Mater.*, **258-263**, 713, (1998).; Ueda, S. *et al.*, *J. Nucl. Mater.*, **283-287**, 1100, (2000).
Allouche, A. *et al.*, *J. Phys. Chem. C*, **114, 3588, (2010).

Method Multiscale Hierarchy



➢DFTB (density-functional tight-binding) is a well established **approximate DFT method** but there are *no available Be-X parameters*. Therefore, we started to develop Be-Be and Be-H parameters at first.

Overview

Motivation

DFTB Method

DFTB/MD Applications

DFTB Parameterization

Summary

Alternative to DFT: Approximate DFT

Density-Functional Tight-Binding: Method using atomic parameters from DFT (PBE, GGA-type), diatomic repulsive potentials from B3LYP

- Seifert, Eschrig (1980-86): minimum STO-LCAO; 2-center approximation
- Porezag, Frauenheim, *et al.* (1995): efficient parameterization scheme: ***NCC-DFTB***


Gotthard Seifert


Thomas Frauenheim


Helmut Eschrig

- Elstner *et al.* (1998): charge self-consistency: ***SCC-DFTB***
- Köhler *et al.* (2001): spin-polarized DFTB: ***SDFTB***

$$E^{(NCC-)DFTB} = \sum_{i}^{\substack{valence\\orbitals}} n_i \varepsilon_i + \frac{1}{2} \sum_{A \neq B}^{atoms} E_{AB}^{rep}$$

$$E^{(SCC-)DFTB} = E^{(NCC-)DFTB} + \frac{1}{2} \sum_{A \neq B}^{atoms} \gamma_{AB} \Delta q_A \Delta q_B$$

$$E^{S(pin-polarized)DFTB} = E^{(SCC-)DFTB} + \frac{1}{2} \sum_{A}^{atoms} \sum_{l \in A} \sum_{l' \in A} p_{Al} p_{Al'} W_{All'}$$

Linear response: TD-DFTB


Thomas Niehaus


Marcus Elstner


Christof Köhler

Taken from Oliviera, Seifert, Heine, Duarte, *J. Braz. Chem. Soc. 20*, 1193-1205 (2009)

Thomas Heine

Helio Duarte

J. Braz. Chem. Soc., Vol. 20, No. 7, 1193-1205, 2009.
Printed in Brazil - ©2009 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Review

Density-Functional Based Tight-Binding: an Approximate DFT Method

Augusto F. Oliveira,[*,a,b] Gotthard Seifert,*[b] Thomas Heine*[c] and Hélio A. Duarte*[*,a]

[a]*Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, 31270-901 Belo Horizonte-MG, Brazil*

[b]*Physikalische Chemie, Technische Universität Dresden, Mommsenstr, 13, D-01062 Dresden, Germany*

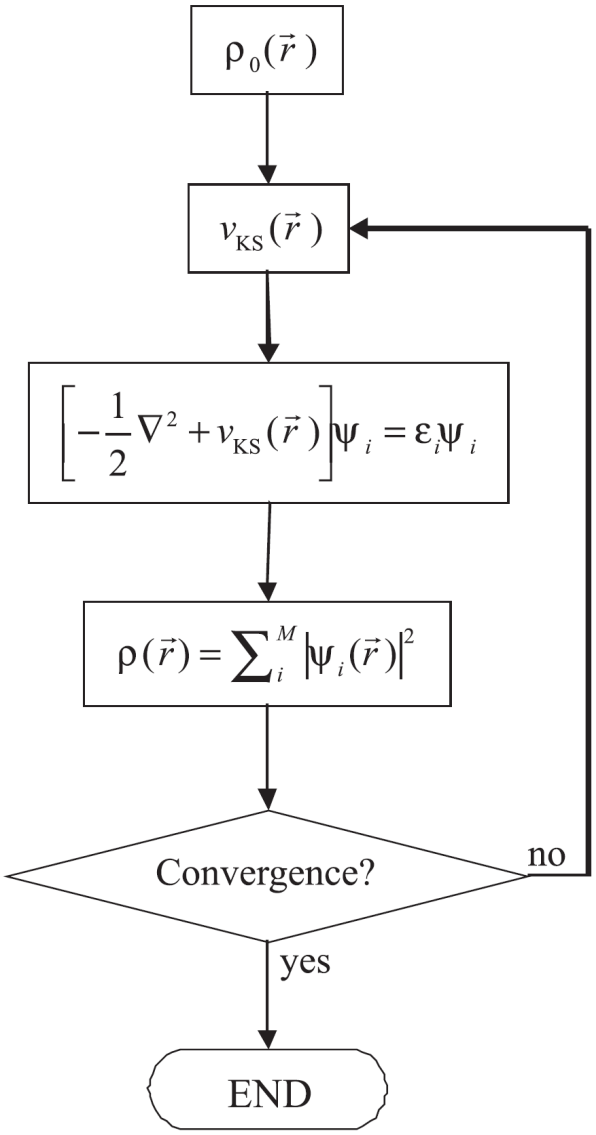
[c]*School of Engineering and Sciences, Jacobs University, P.O. Box 750 561, 28725 Bremen, Germany*

...open access

Quick review II

Density Functional Theory (DFT)

Walter Kohn/John A. Pople 1998



at convergence:

$$E[\rho] = \sum_{i=1}^{M} n_i \langle \psi_i | -\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3r' | \psi_i \rangle$$

$$+ E_{xc}[\rho] - \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3r d^3r' + \frac{1}{2}\sum_{\substack{\alpha,\beta=1 \\ \alpha \neq \beta}}^{N} \frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

$$= \sum_{i=1}^{M} n_i \varepsilon_i + E_{rep}$$

Various criteria for convergence possible:

- Electron density
- Potential
- Orbitals
- Energy
- Combinations of above quantities

Foulkes + Haydock Ansatz

Phys. Rev. B, 39, 12520 (1989)

$$\rho(\vec{r}) = \rho_0(\vec{r}) + \delta\rho(\vec{r})$$

$$E[\rho_0 + \delta\rho] = \sum_i^M n_i \left\langle \psi_i \left| -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho_0'}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{\text{xc}}[\rho_0] \right| \psi_i \right\rangle$$

$$-\frac{1}{2}\iint \frac{\rho_0'(\rho_0 + \delta\rho)}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' - \int v_{\text{xc}}[\rho_0](\rho_0 + \delta\rho) d\vec{r}$$

$$+\frac{1}{2}\iint \frac{\delta\rho'(\rho_0 + \delta\rho)}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{\text{xc}}[\rho_0 + \delta\rho] + E_{\text{nn}}$$

Second-Order Taylor Expansion

Elstner et al. *Phys. Rev. B: 58*, 7260 (1998)

$$E_{xc}[\rho_0 + \delta\rho] = E_{xc}[\rho_0] + \int \left.\frac{\delta E_{xc}}{\delta\rho}\right|_{\rho_0} \delta\rho\, d\vec{r} + \frac{1}{2}\iint \left.\frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho'}\right|_{\rho_0} \delta\rho\,\delta\rho'\, d\vec{r}\, d\vec{r}' \qquad (17)$$

Note that $\delta E_{xc}/\delta\rho)_{\rho 0} = \nu_{xc}[\rho_0]$

DFT 2nd Order Energy Expression

Elstner et al. *Phys. Rev. B: 58*, 7260 (1998)

$$E = \sum_i^M n_i \left\langle \psi_i \left| -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho_0'}{|\vec{r}-\vec{r}'|} d\vec{r}' + v_{\text{xc}}[\rho_0] \right| \psi_i \right\rangle$$

$$-\frac{1}{2}\iint \frac{\rho_0'\rho_0}{|\vec{r}-\vec{r}'|} d\vec{r}d\vec{r}' + E_{\text{xc}}[\rho_0] - \int v_{\text{xc}}[\rho_0]\rho_0 d\vec{r} + E_{\text{nn}}$$

$$+\frac{1}{2}\iint \left(\frac{\delta\rho\delta\rho'}{|\vec{r}-\vec{r}'|} + \left.\frac{\delta^2 E_{\text{xc}}}{\delta\rho\delta\rho'}\right|_{\rho_0} \right) d\vec{r}d\vec{r}'$$

$$E[\rho_0, \delta\rho] = \sum_{i=1}^M n_i \langle \psi_i | \hat{H}_0 | \psi_i \rangle + E_{rep} + E_{2nd}$$

Approximations

- Get the best possible ρ_0 – atomic densities, new ideas possible, e.g. fragment densities etc.…
- Reduce number of basis functions as much as possible – minimum valence basis set (atomic orbitals, optimized local orbitals)
- Ignore (DFTB) or approximate (e.g. as in SCC-DFTB) 2^{nd} order terms, (add 3^{rd} order terms, DFTB3)
- Introduce further approximations in the Hamiltonian

Approximations

Traditional DFTB concept: Hamiltonian matrix elements are approximated to two-center terms. The same types of approximations are done to E_{rep}.

$$H^0_{\mu\nu} = \begin{cases} \varepsilon_\mu^{\text{neutral free atom}} & \text{if } \mu = \nu \\ \langle \varphi_\mu^\alpha | \hat{T} + V_0^\alpha + V_0^\beta | \varphi_\nu^\beta \rangle & \text{if } \alpha \neq \beta \\ 0 & \text{otherwise.} \end{cases}$$

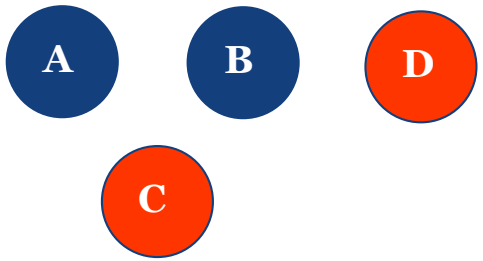
From Elstner et al., PRB 1998

$$V_{eff}[\rho_0] \approx V_{eff}[\rho_A + \rho_B] \qquad \text{(Density superposition)}$$

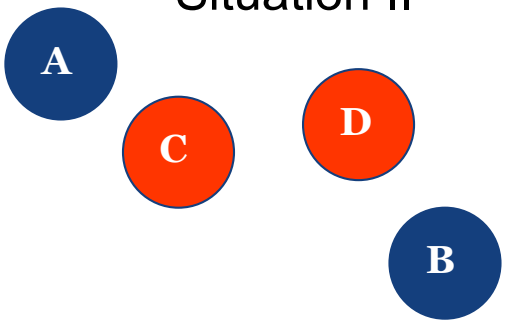
$$V_{eff}[\rho_0] \approx V_{eff}[\rho_A] + V_{eff}[\rho_B] \qquad \text{(Potential superposition)}$$

Both approximations are justified by the screening argument: Far away, neutral atoms have no Coulomb contribution.

Situation I



Situation II



Approximations

Approximations in SCC-DFTB (2nd order expansion only) potential:

$$\delta\rho = \sum_{\alpha}^{N} \delta\rho_{\alpha} \qquad \delta\rho_{\alpha} \approx \Delta q_{\alpha} F_{00}^{\alpha} Y_{00}$$

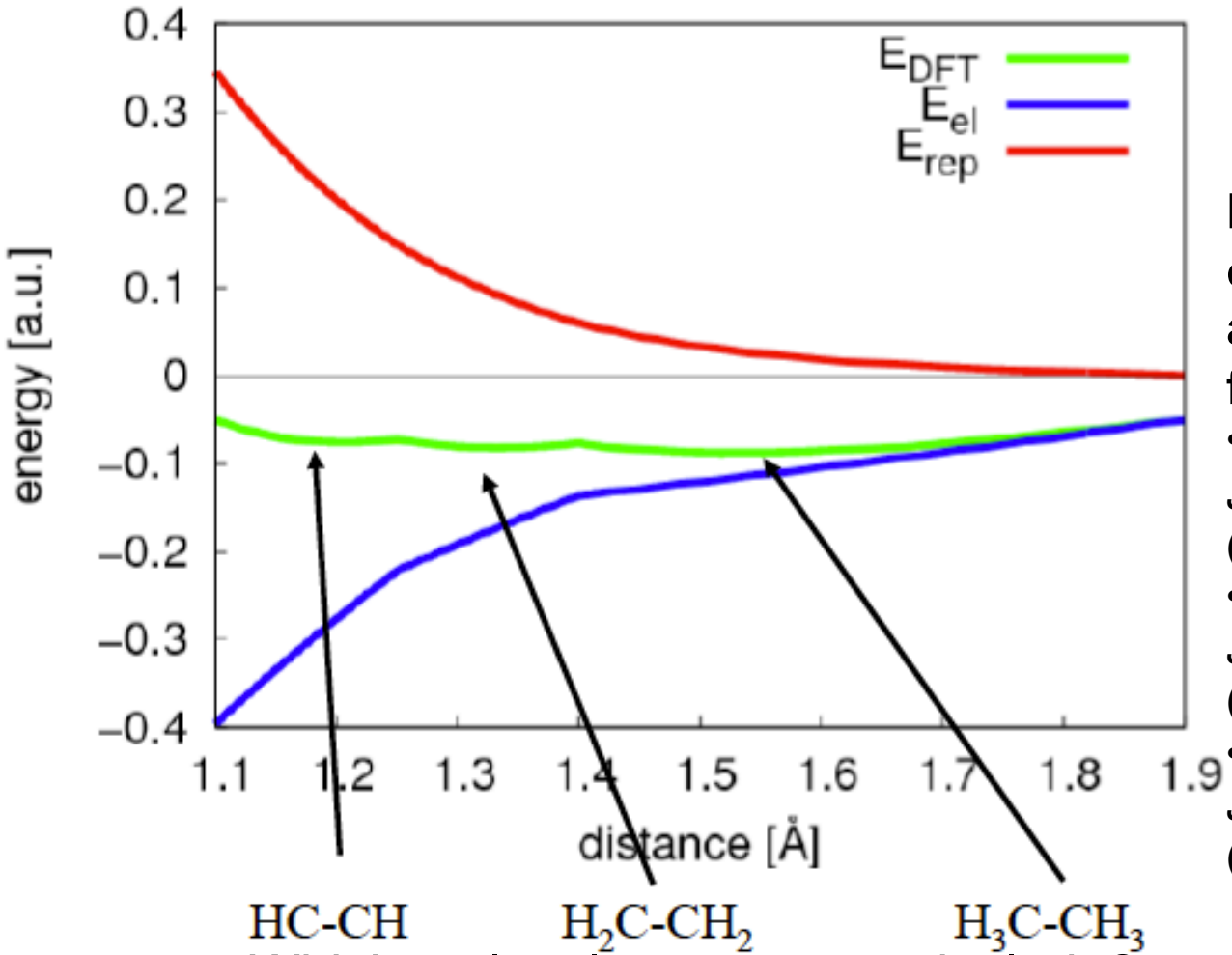
$$E_{2nd} \approx \frac{1}{2} \sum_{\alpha,\beta}^{N} \Delta q_{\alpha} \Delta q_{\beta} \underbrace{\iint \left(\frac{1}{|\vec{r} - \vec{r}'|} + \left. \frac{\delta^2 E_{xc}}{\delta\rho \delta\rho'} \right|_{\rho_0} \right)}_{\gamma_{\alpha\beta}} F_{00}^{\alpha} F_{00}^{\beta} Y_{00}^{2} \, d\vec{r} \, d\vec{r}'$$

$$U_{Ai} = \frac{\partial^2 E_{DFT}^{total}}{\partial n_i^2} = \frac{\partial \varepsilon_i}{\partial n_i}$$

Note that directional changes of the density are not covered with this approximation.

DFTB repulsive potential E_{rep}

$$E[\rho] = \sum_{i}^{occ} \epsilon_i^H + \sum_{\alpha\beta} U_{\alpha\beta} \quad \rightarrow \quad U_{\alpha\beta} = E^{DFT}[\rho](R_{\alpha\beta}) - \sum_{i}^{occ} \epsilon_i^H(R_{\alpha\beta})$$



Which molecular systems to include?

Development of (semi-) automatic fitting:

- Knaup, J. *et al.*, *JPCA,* **111**, 5637, (2007)
- Gaus, M. *et al.*, *JPCA*, **113**, 11866, (2009)
- Bodrog Z. *et al.*, *JCTC*, **7**, 2654, (2011)

SCC-DFTB

1. All contributions to Hamiltonian and Overlap matrices are pre-computed. At runtime, values have to be interpolated (negligible time for computing matrix elements)
2. Total energy is simply computed using KS orbital energies (eigenvalues of the Hamiltonian matrix) and repulsive potential (simple short-range two-body force field)
3. Energy gradients are easily calculated (analytical derivative of total energy expression)
4. Aiming at large systems, Hamiltonian and Overlap matrices are very sparse. Sparsity can be transferred to energy and energy gradient calculations, as density / energy weighted density matrices are required only where other matrices are non-zero (identical sparsity pattern)
5. Typically 1000 times faster than conventional DFT

Overview

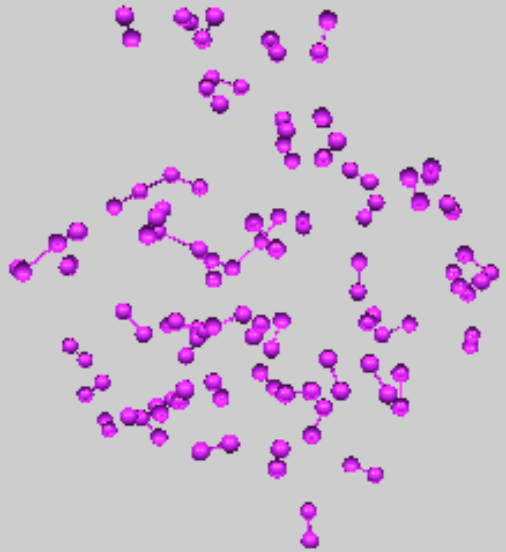
Motivation

DFTB Method

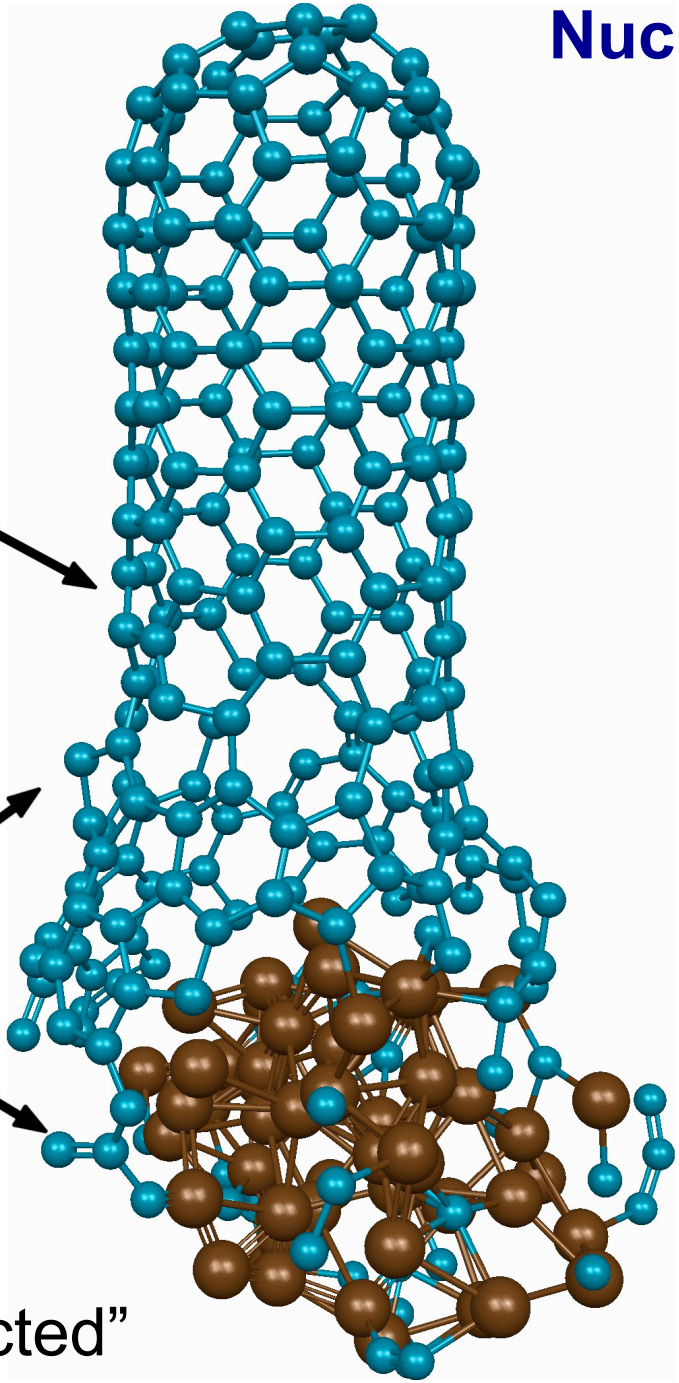
DFTB/MD Applications

DFTB Parameterization

Summary



Carbon nanotube growth



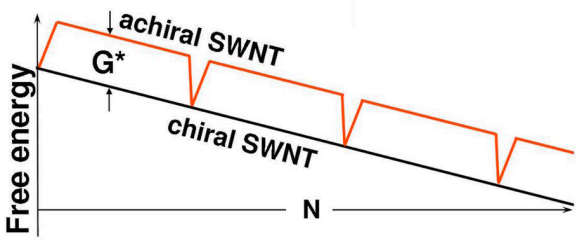
"constructed"

Nucleation and growth hypothesis:

A. J. Page, Y. Ohta, S. Irle, and K. Morokuma,

In sharp contrast to:

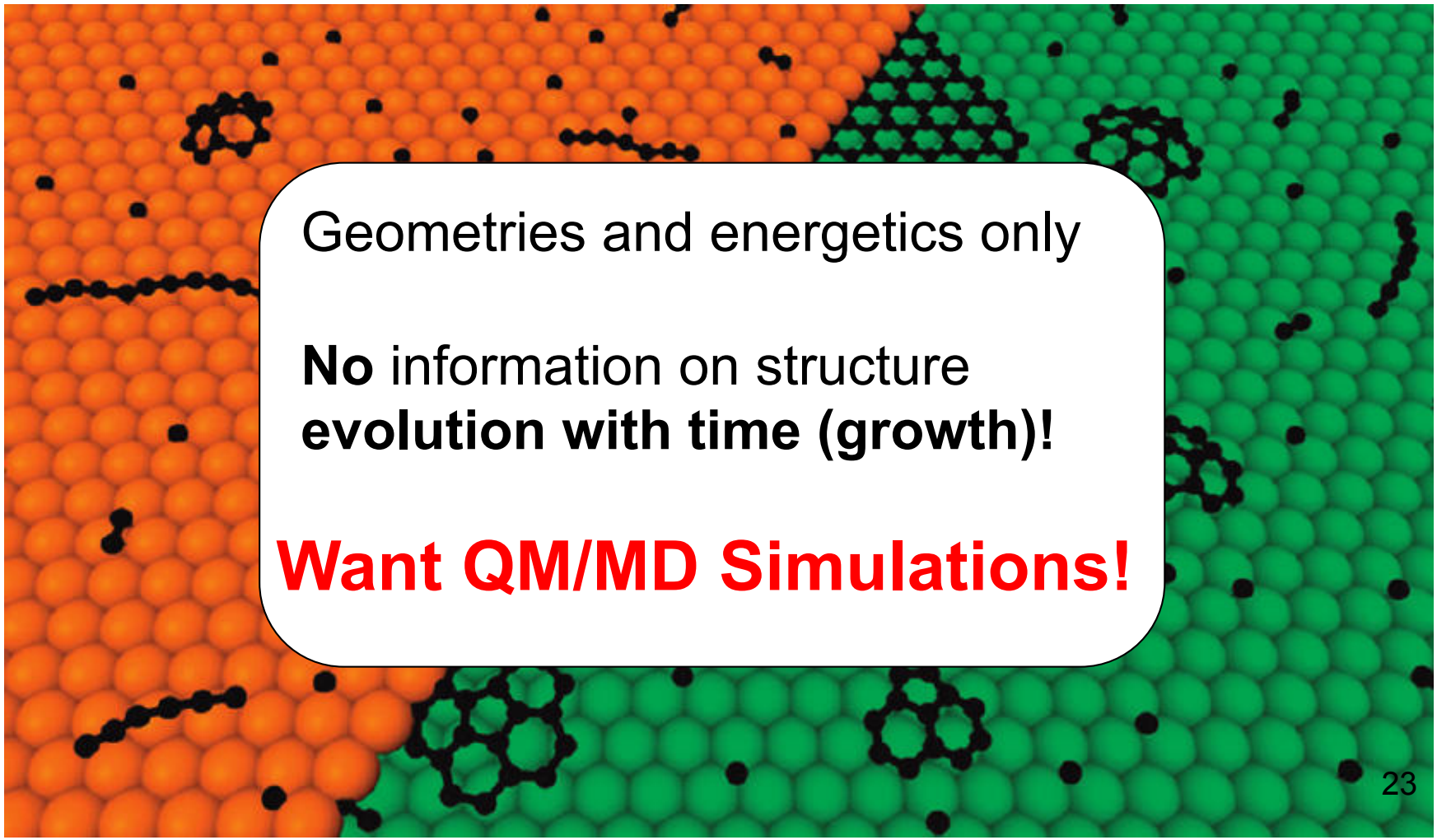
F. Ding, A. Harutyunyan, B. I. Yakobson,
Proc. Natl. Acad. Sci. **106**, 2506 (2009)



How Does Graphene Form on Ni(111)?

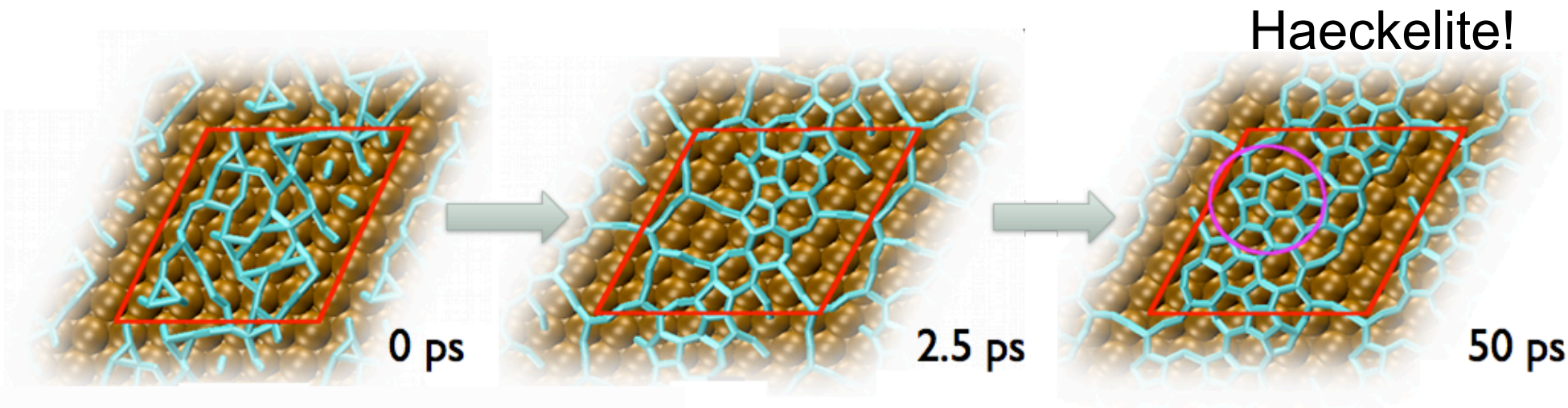
Gao *et al.* J. Am. Chem. Soc. **133**, 5009 (2011)

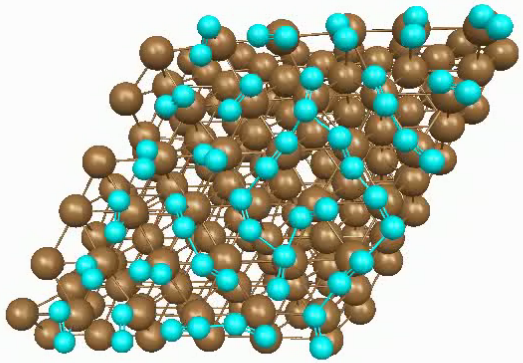
- GGA PW91/UPP-PW (VASP) geometry optimizations
- individual clusters on Ni(111) C1-C24

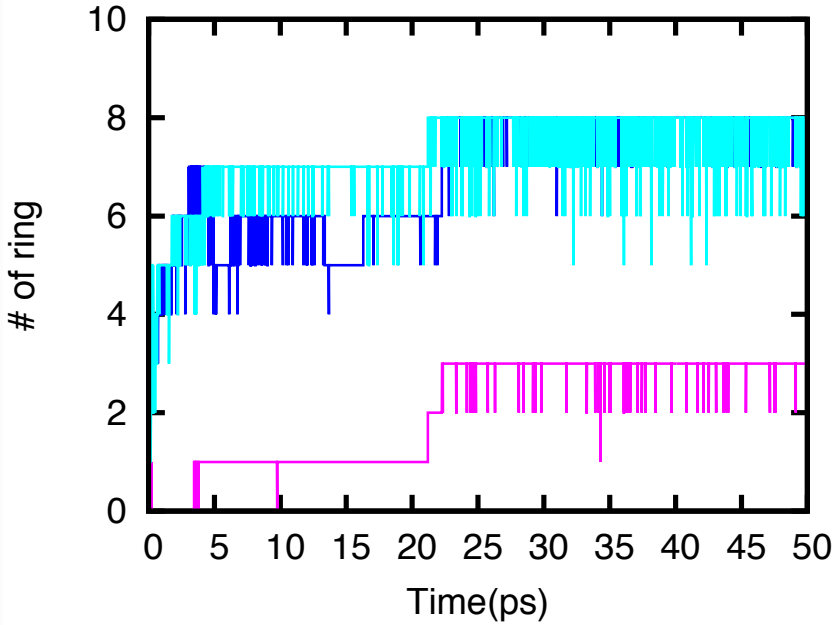


QM/MD of 30 C_2 on Ni(111), 1180 K

Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, K. Morokuma, SI, JACS (2011)

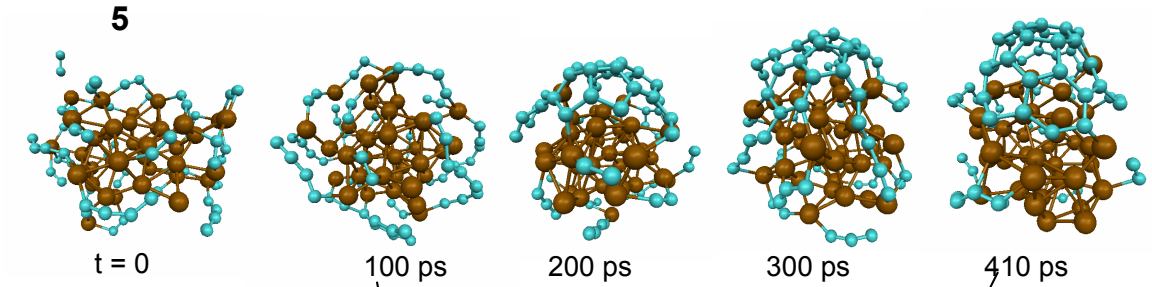


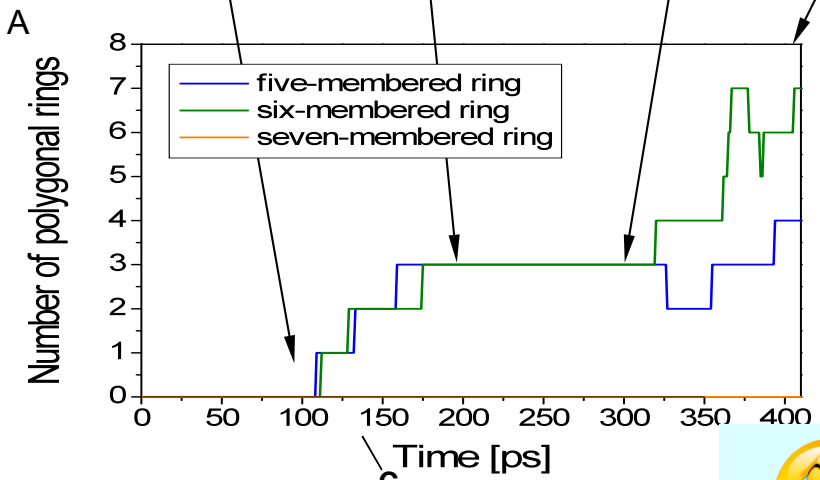




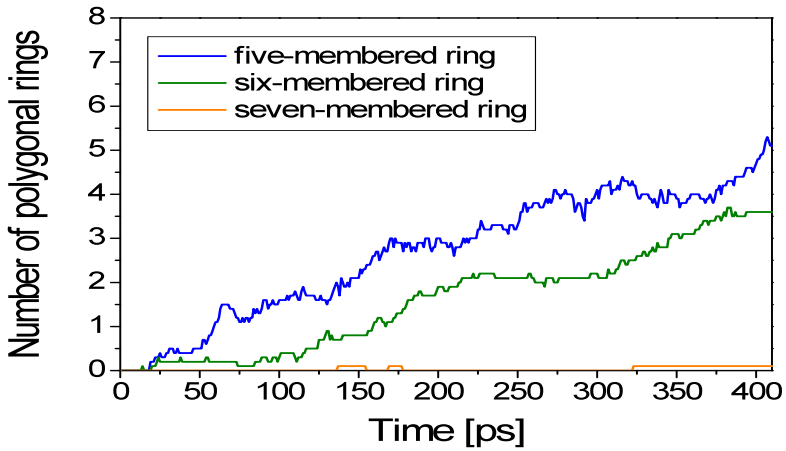
Graphene growth

Y. Ohta, Y. Okamoto, A. J. Page, SI, K. Morokuma, ACS Nano **3**, 3413 (2009)



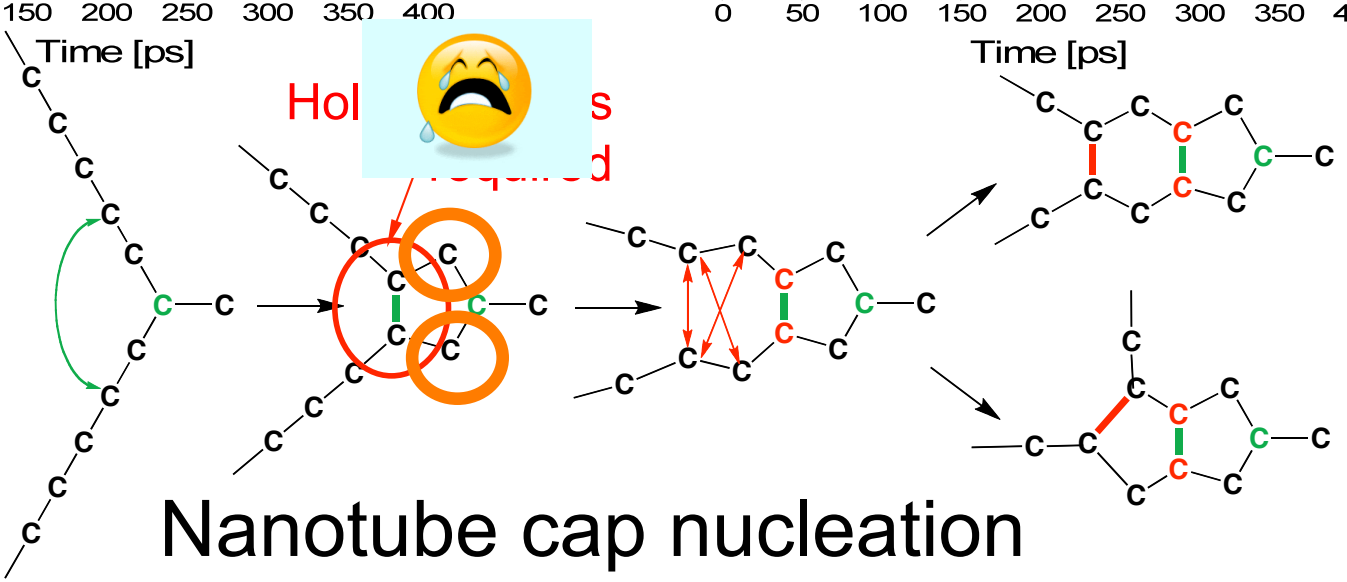


Average 5- and 6-ring counts over 10 annealing trajectories



Formation of first condensed 2-ring system (5/5 or 5/6)

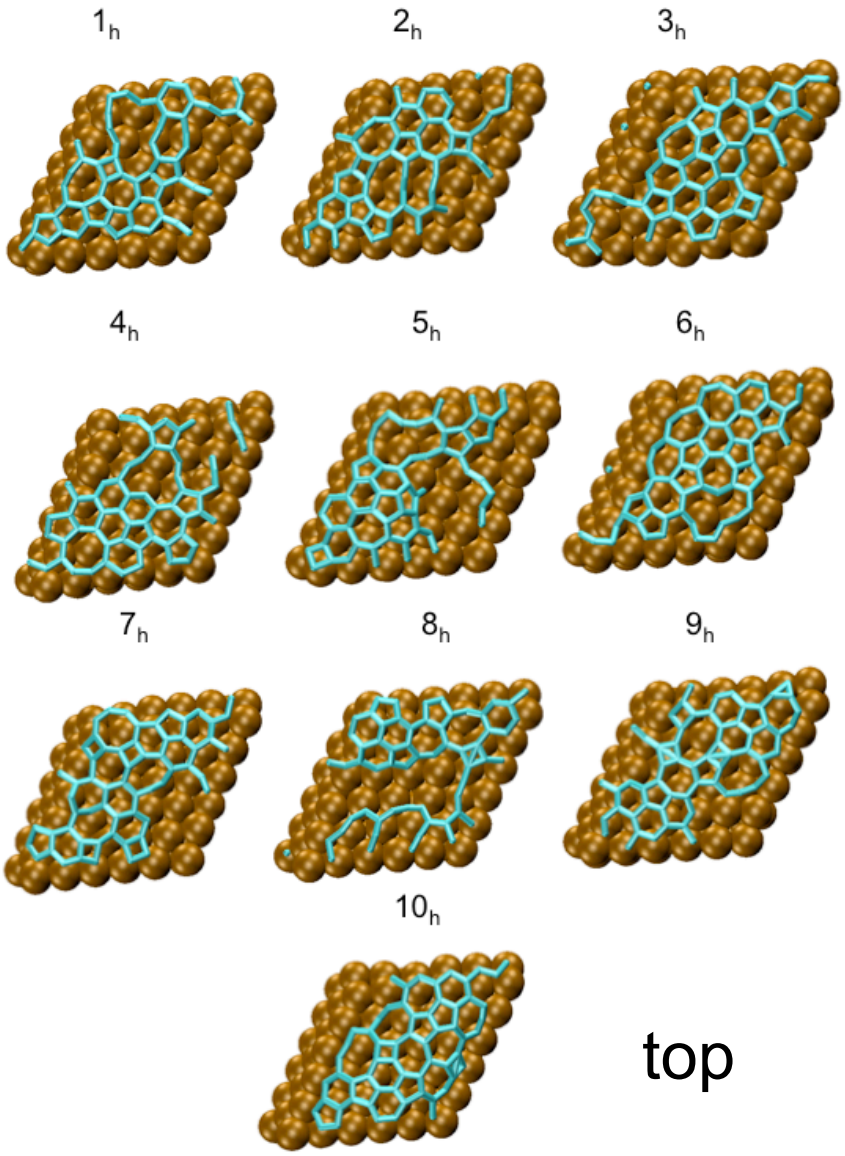
Always pentagon first!

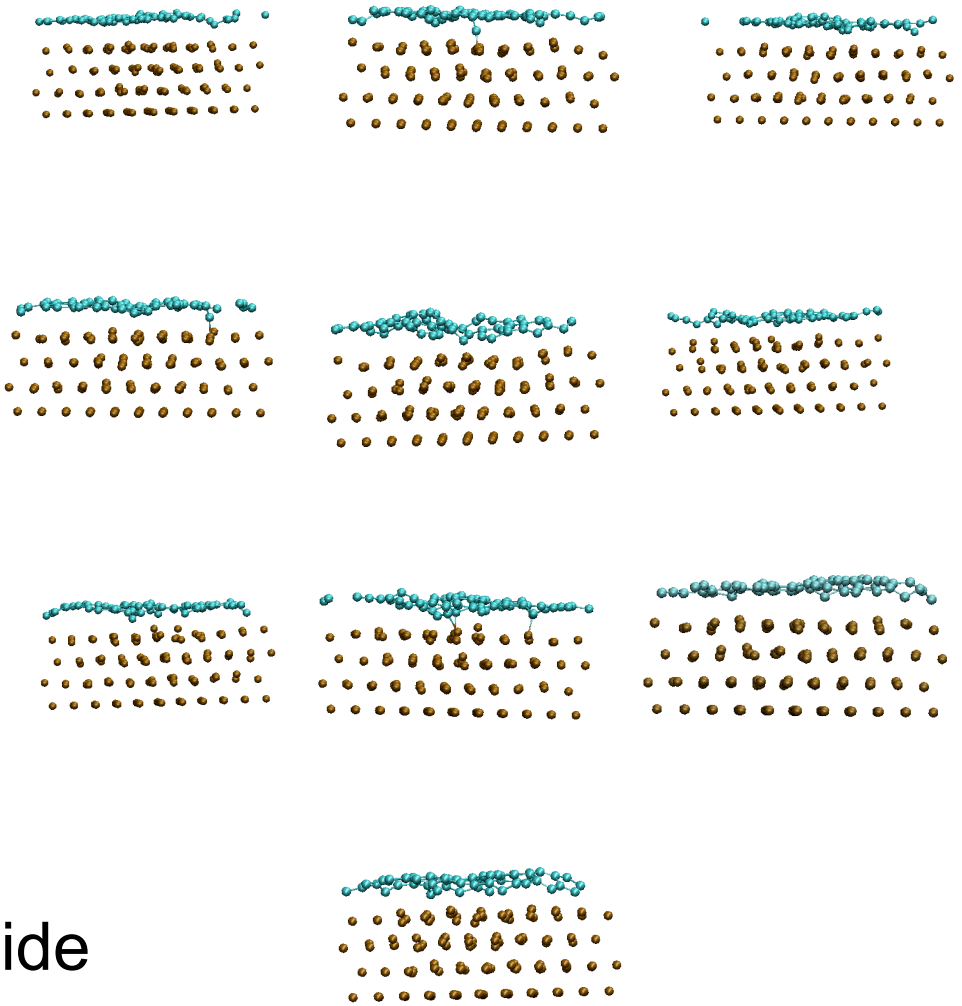


Nanotube cap nucleation

QM/MD of 30 C_2 on Ni(111), 1180 K

Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, K. Morokuma, SI, JACS (2011)

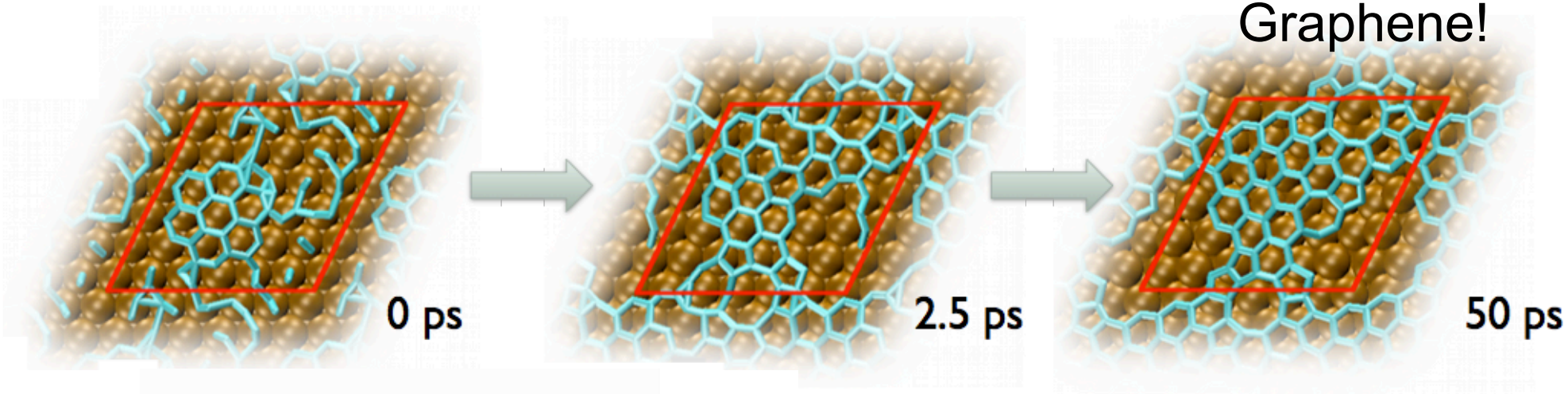


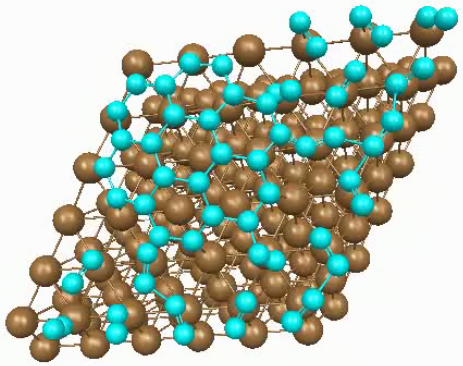


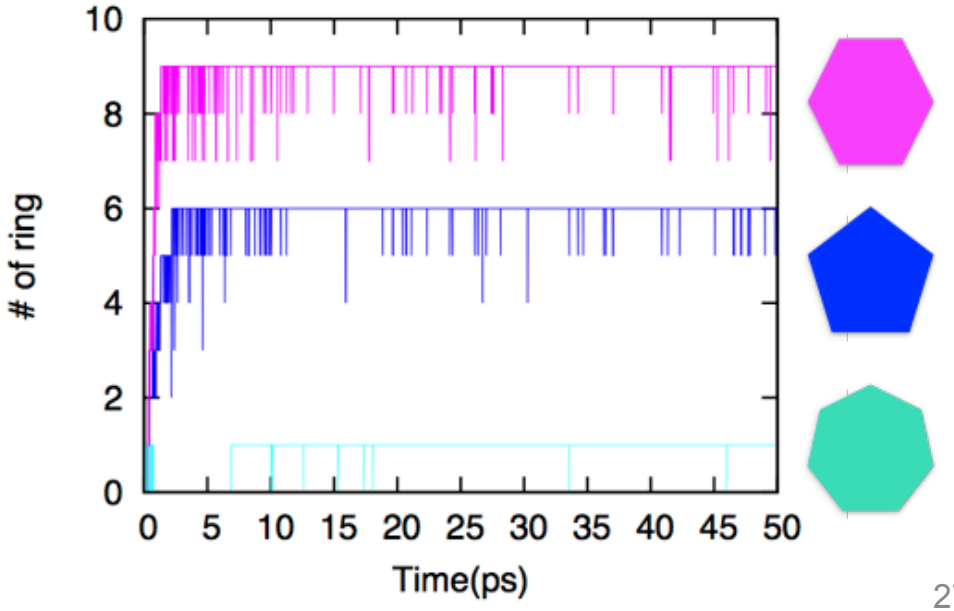
top side

QM/MD of 18 C_2 + C_{24} on Ni(111), 1180 K

Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, K. Morokuma, SI, JACS (2011)

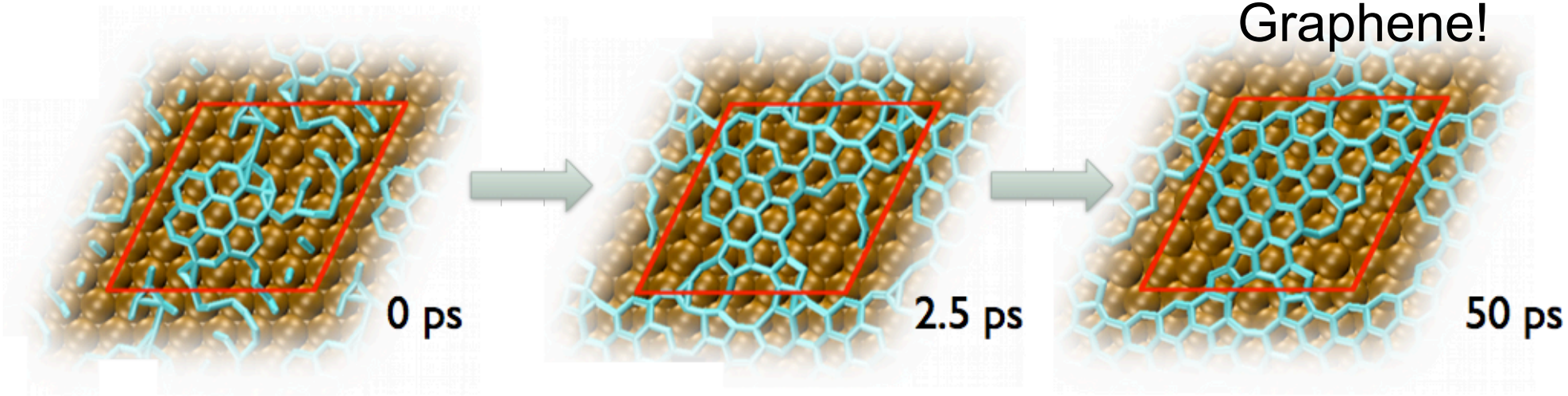




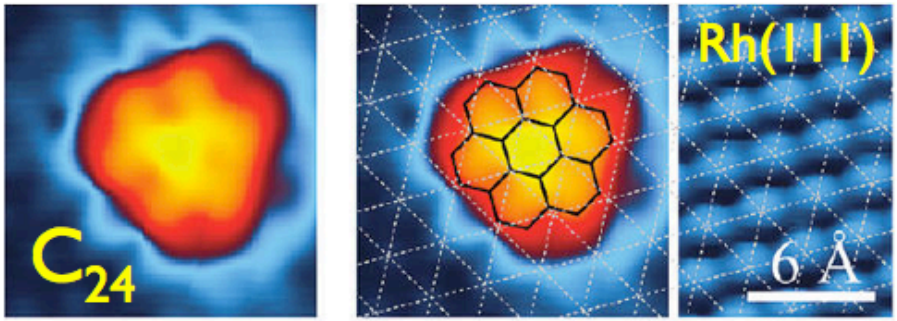


QM/MD of 18 C_2 + C_{24} on Ni(111), 1180 K

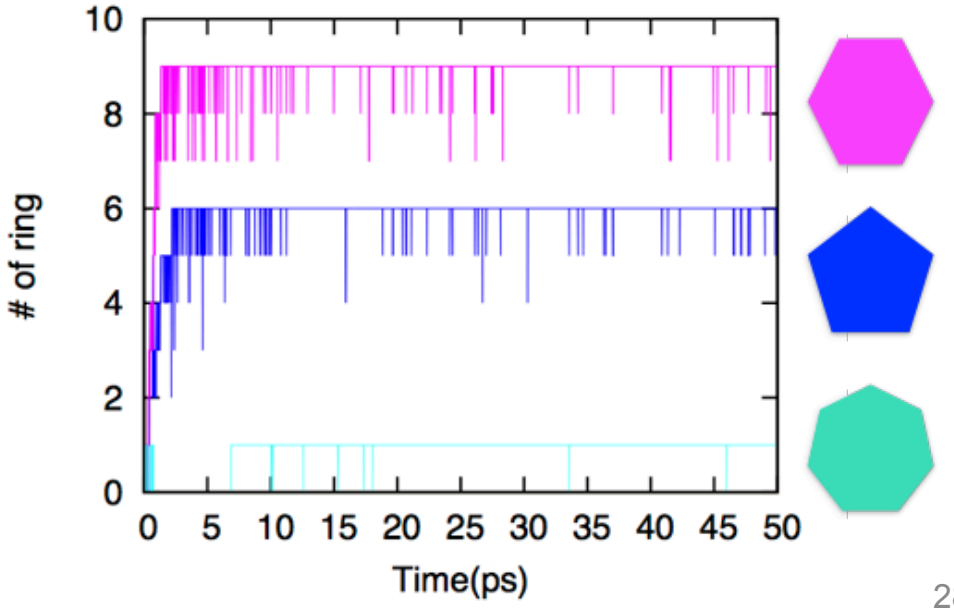
Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, K. Morokuma, SI, JACS (2011)



- Pentagon-first vs. **template effect**.
- Suppression of heptagons and pentagons

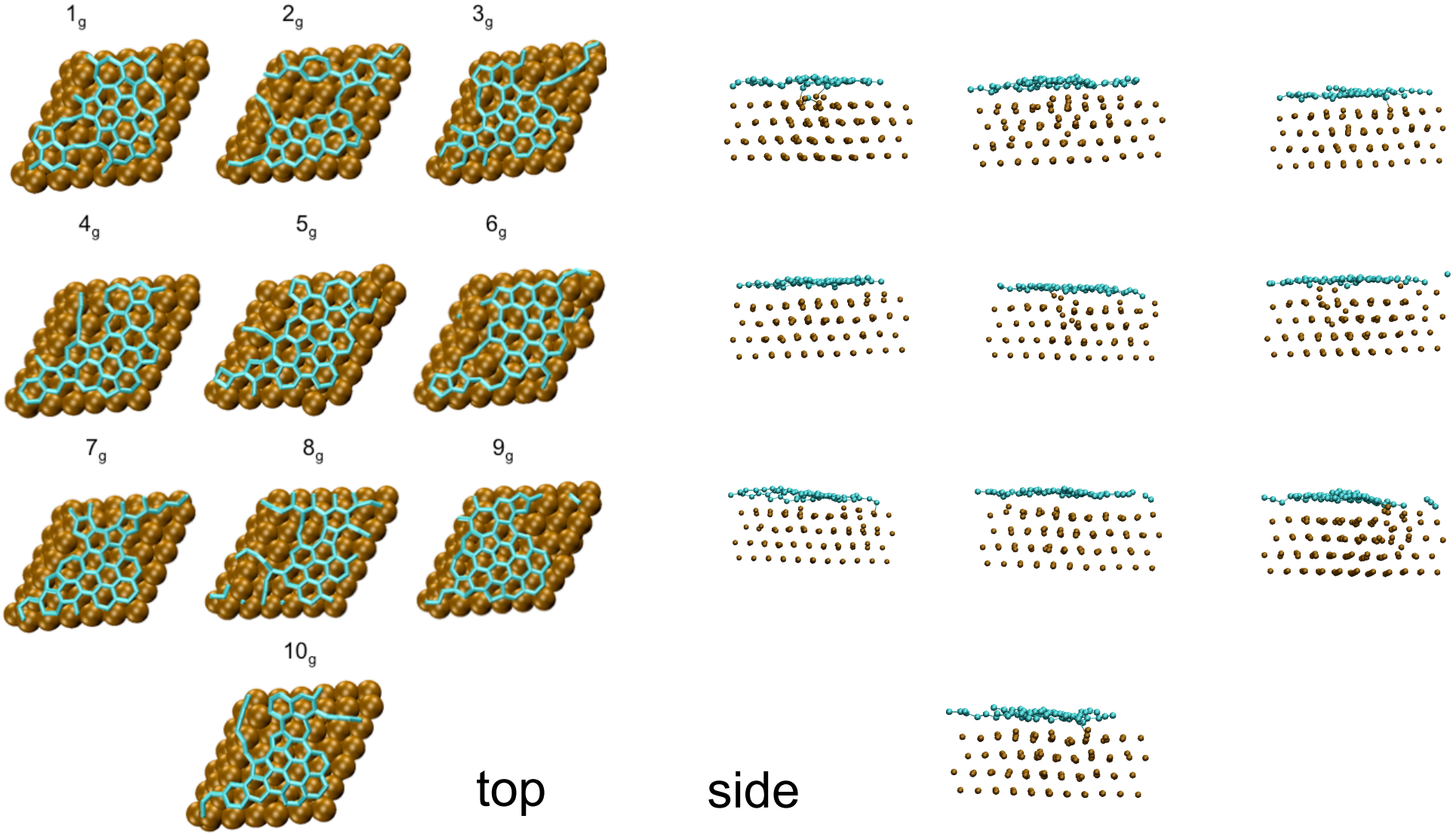


Wang *et al., Nano Lett., (2011)*

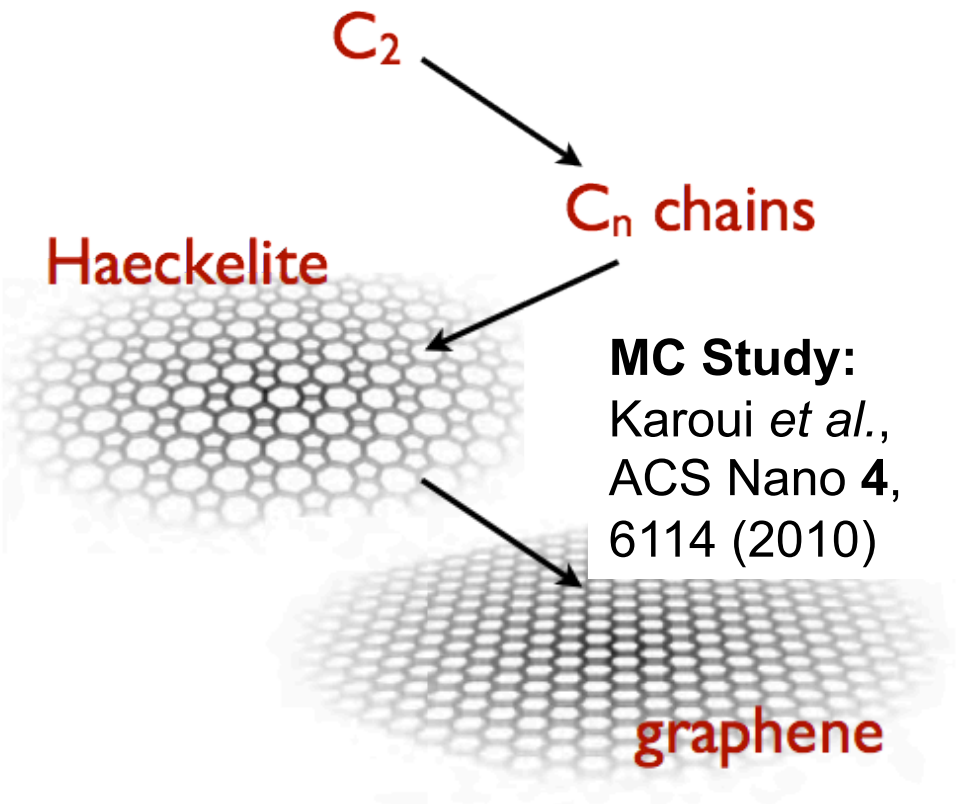


QM/MD of 18 C_2 + C_{24} on Ni(111), 1180 K

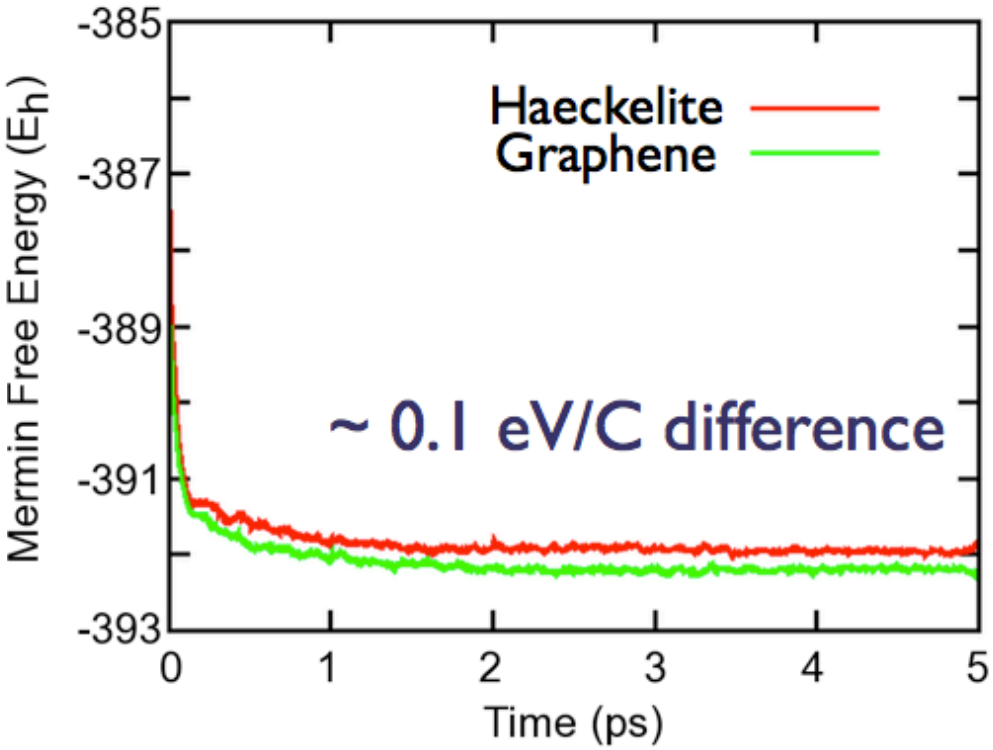
Y. Wang, A. J. Page, Y. Nishimoto, H.-J. Qian, K. Morokuma, SI, JACS (2011)



Haeckelite is a Metastable Phase

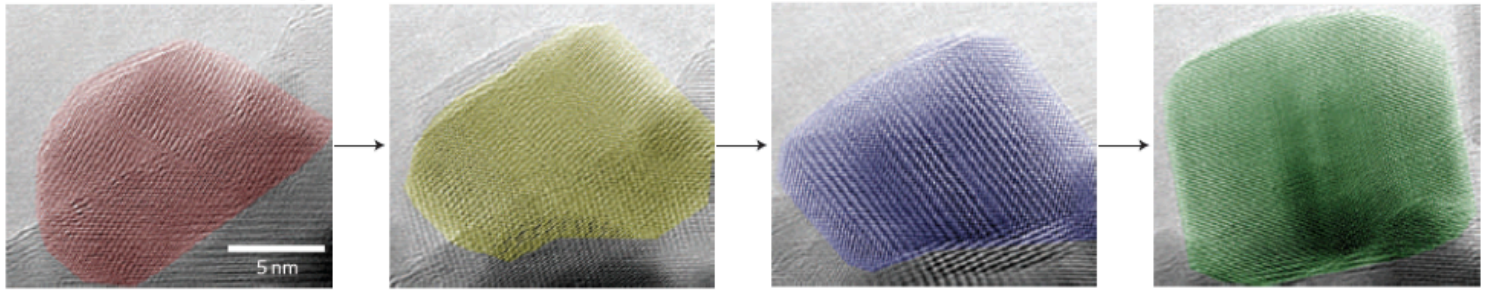


MC Study:
Karoui *et al.*,
ACS Nano **4**,
6114 (2010)



LiFePO4 nanocrystal, 450 °C

Ostwald's 'rule of stages'



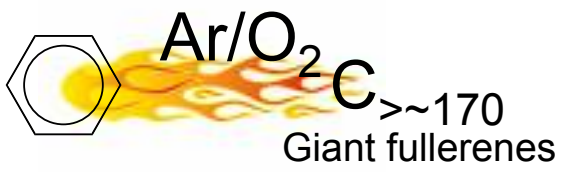
Chung *et al.*, Nature Phys. (2008)

F. W. Ostwald,
Z. Phys. Chem.
22, 289 (1897)

Other simulations

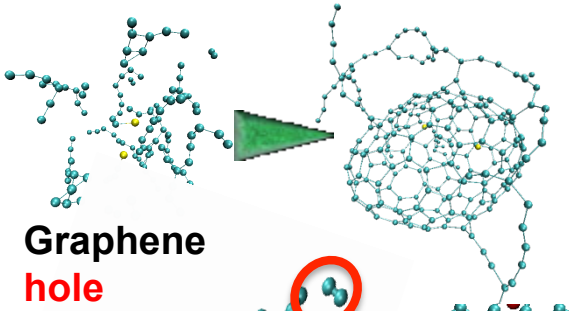
Saha *et al.*, *ACS Nano* **3**, 2241 (2009)

Fullerenes in benzene combustion

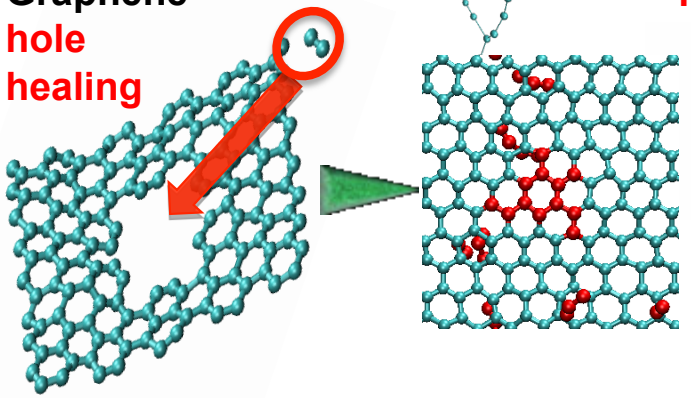


Sc & Ti

metallofullerene formation

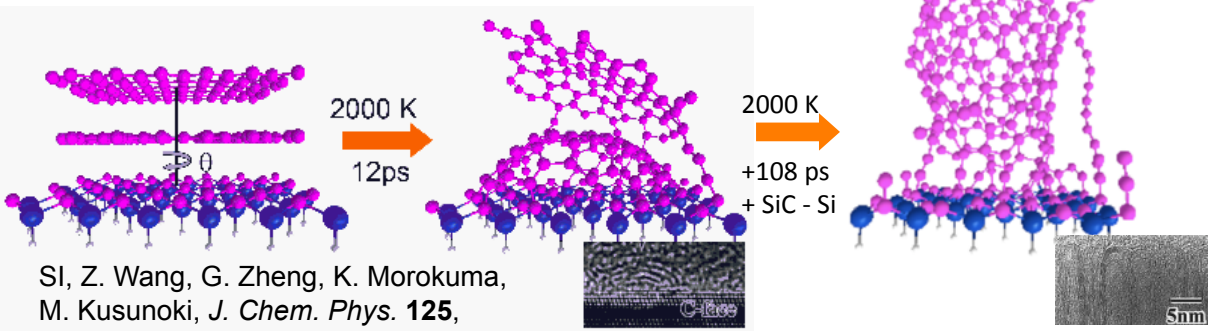


Graphene hole healing



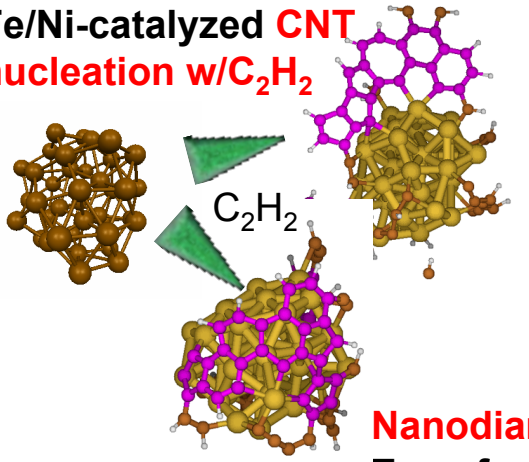
CNT growth on SiC(000-1)

Z. Wang, SI, G. Zheng, M. Kusunok, K. Morokuma, *J. Phys. Chem. C* **111**, 12960 (2007)

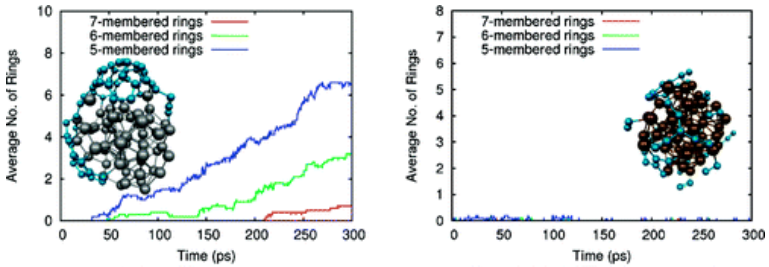


SI, Z. Wang, G. Zheng, K. Morokuma, M. Kusunoki, *J. Chem. Phys.* **125**, 044702 (2006)

Fe/Ni-catalyzed CNT nucleation w/C_2H_2



CNT nucleation from metal carbide

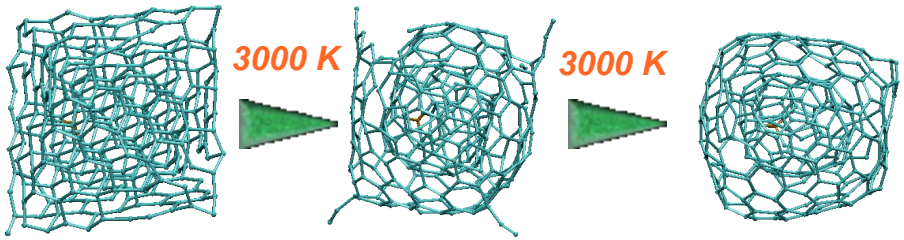


Ni_xC_y: SWNT Nucleation enhanced

Fe_xC_y: SWNT Nucleation impeded

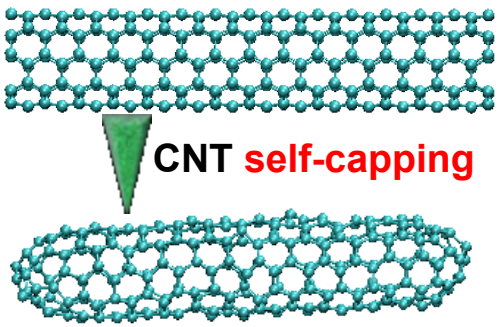
Page *et al. J. Am. Chem. Soc.* **132**, 15699 (2010)

Nanodiamond to Spiroid to Onion Transformation upon Heating

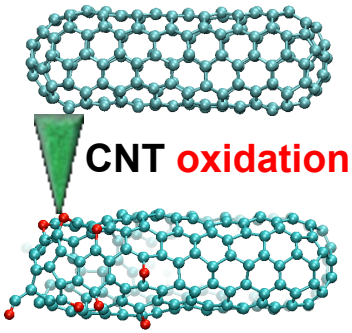


0.1 ps **25.0 ps** **64.2 ps**

CNT self-capping



CNT oxidation

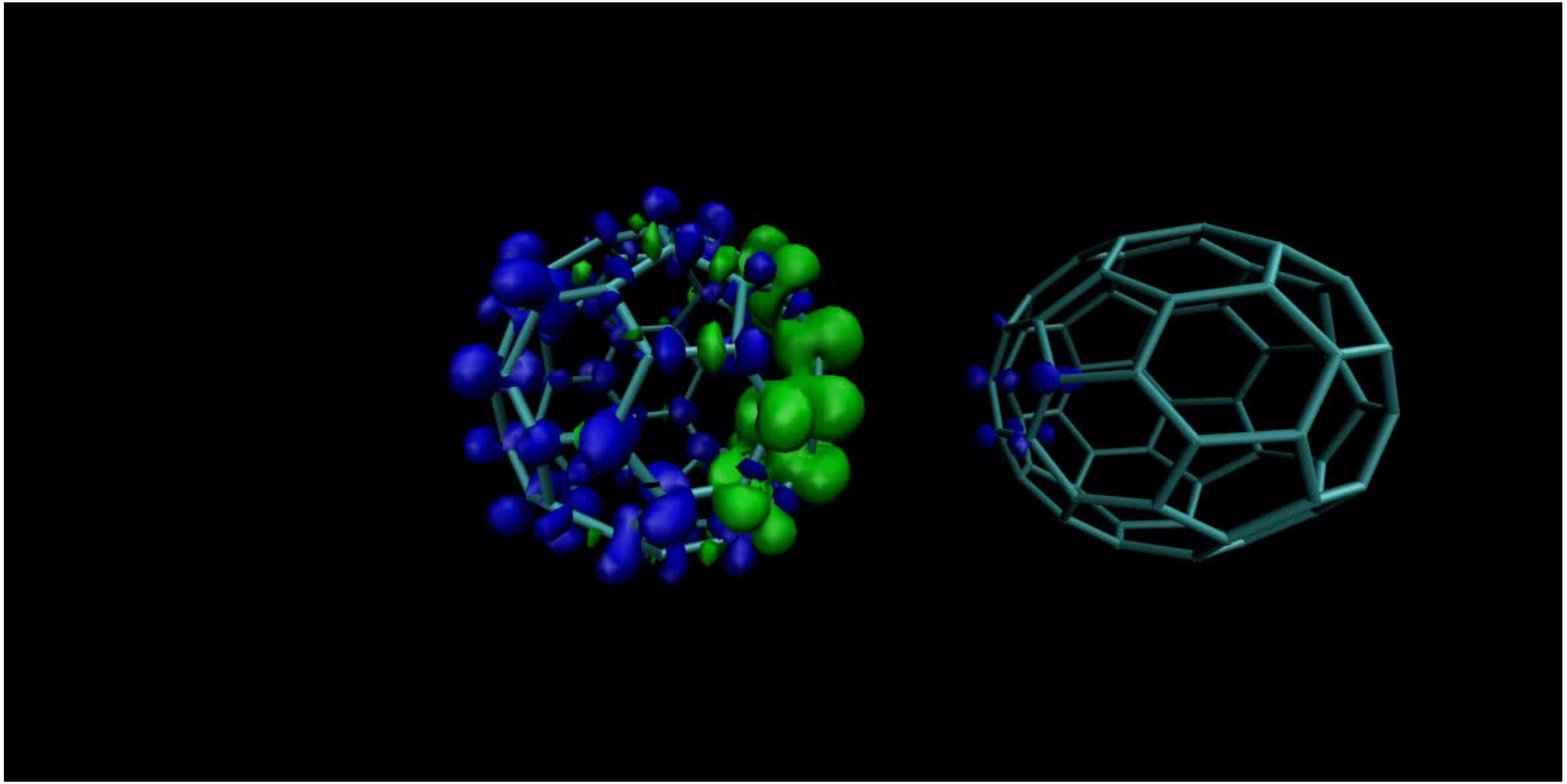


Methods to propagate molecular systems on a single potential energy surface (PES)

Reactive force fields	Born-Oppen-heimer MD	Extended Lagrangian MD	**Liouville-von Neumann MD**
			Jakowski, Morokuma, JCP **130**, 224106 (2009)
Energy and forces on molecules from exp parameters	Solve electronic Schrödinger Eq. (convergence) at nuclear configuration	Electronic structure *propagated classically*: *not converged* *integer occ. numbers: metals difficult*	Electronic structure: *Quantum dynamics: mixed states possible* $i\hbar\frac{\partial}{\partial t}\psi(r;t)=\hat{H}\psi(r;t)$
Nuclei moved: Newton's laws	Nuclei propagated from gradients (classically)	"Simultaneous" classical propagation of electrons and nuclei	Nuclei propagated from gradients (classically)
(MM)	(BOMD)	(CPMD)	(LvNMD)

Fullerene Collisions

Collision energy: 1.4 eV C_{60}^{+} C_{60}^{+}



$\Delta\rho = \rho_{total} - \rho_{C60}$

Green: $-\Delta\rho$
Blue: $+\Delta\rho$

$\Delta\rho = \rho_{total} - \rho_{C60}^{2+}$

Jakowski, SI, Morokuma, J. Phys. Chem. Lett **3**, 1536 (2012)

Overview

Motivation

DFTB Method

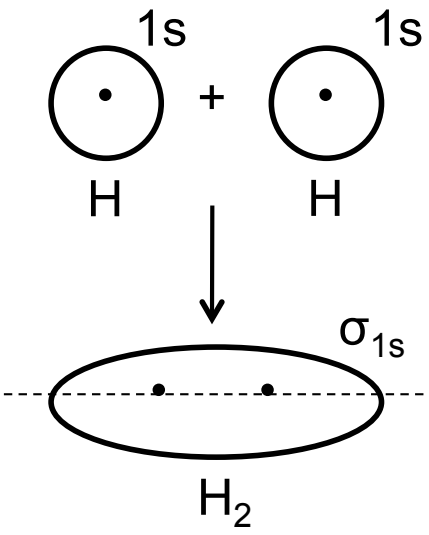
DFTB/MD Applications

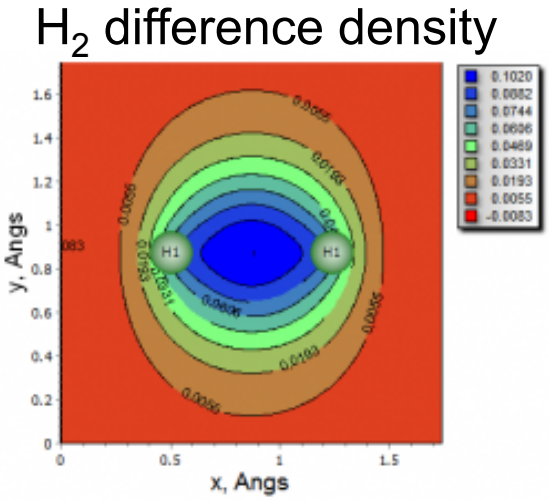
DFTB Parameterization

Summary

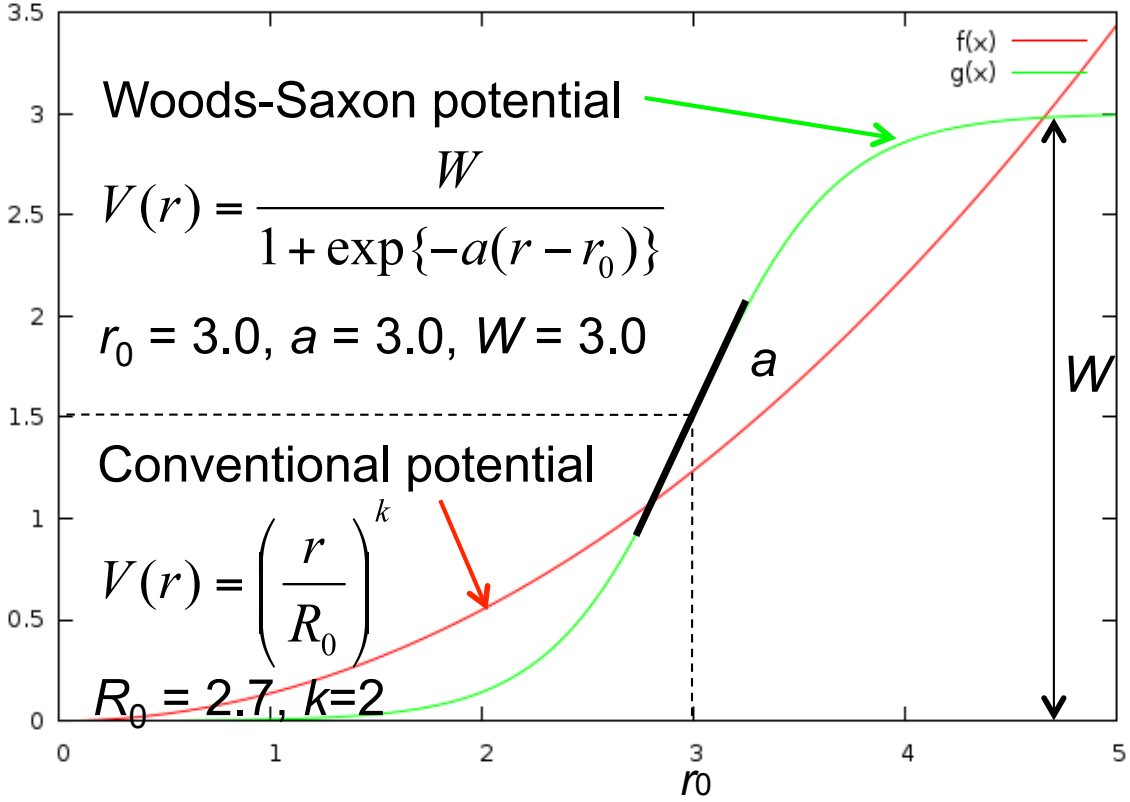
New Confining Potentials

- Typically, electron density contracts under covalent bond formation.
- In standard *ab initio* methods, this problem can be remedied by including more basis functions.
- DFTB uses minimal valence basis set: the confining potential is adopted to mimic contraction





$\Delta\rho = \rho - \Sigma_a \rho_a$



Henryk Witek

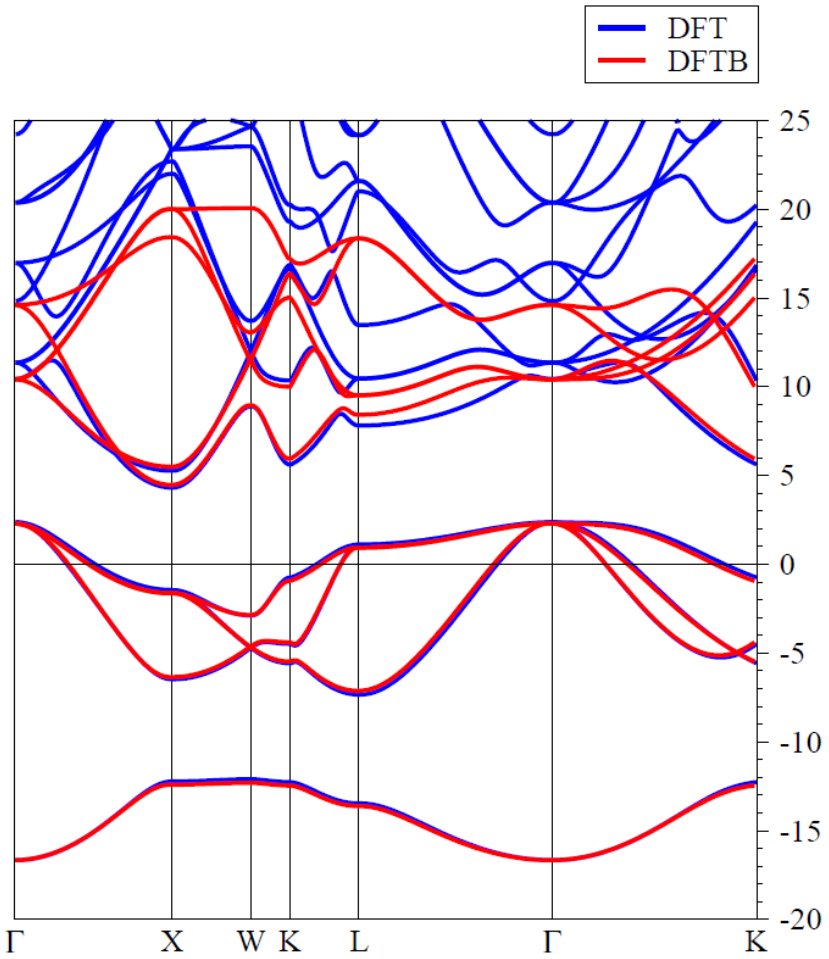
1). DFT band structure calculations

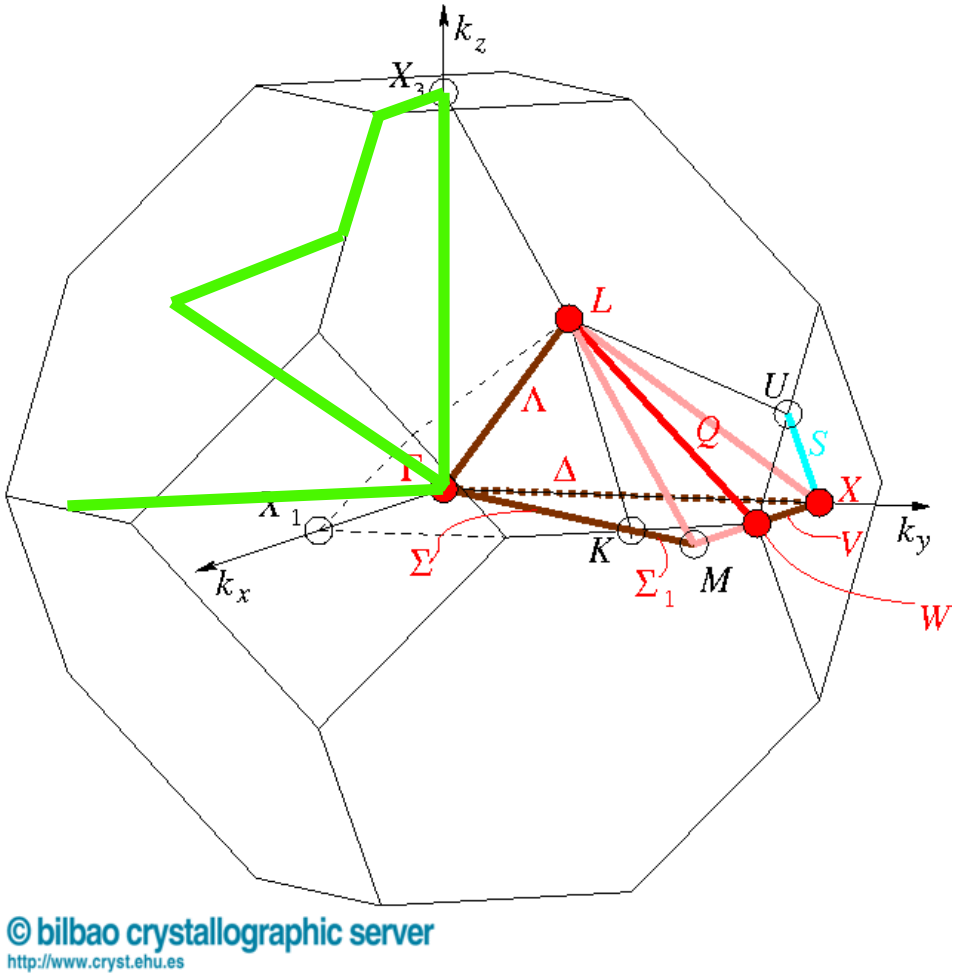
- VASP 4.6
- One atom per unit cell
- PAW (projector augmented wave) method
- 32 x 32 x 32 Monkhorst-Pack *k*-point sampling
- cutoff = 400 eV
- Fermi level is shifted to 0 eV

2). DFTB band structure fitting

- Optimization of parameter sets for Woods-Saxon confining potential (orbital and density) and unoccupied orbital energies
- Fixed orbital energies for electron occupied orbitals
- Valence orbitals : [1*s*] for 1st row
  [2*s*, 2*p*] for 2nd row
  [n*s*, n*p*, m*d*] for 3rd – 6th row
  (n ≥ 3, m = n-1 for group 1-12, m = n for group 13-18)
- Fitting points : valence bands + conduction bands (depending on the system, at least including up to ~+5 eV with respect to Fermi level)

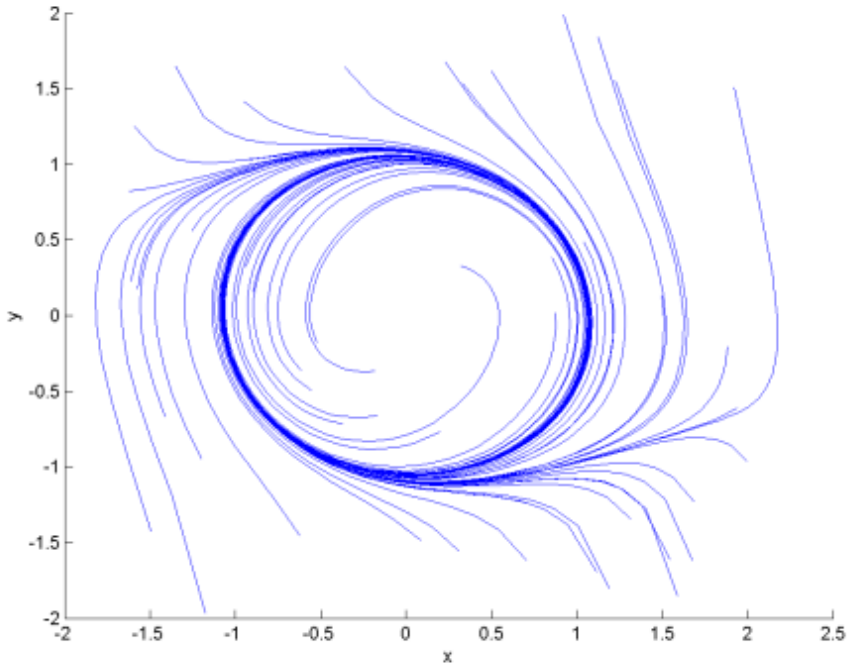
Band structure for Se (FCC)



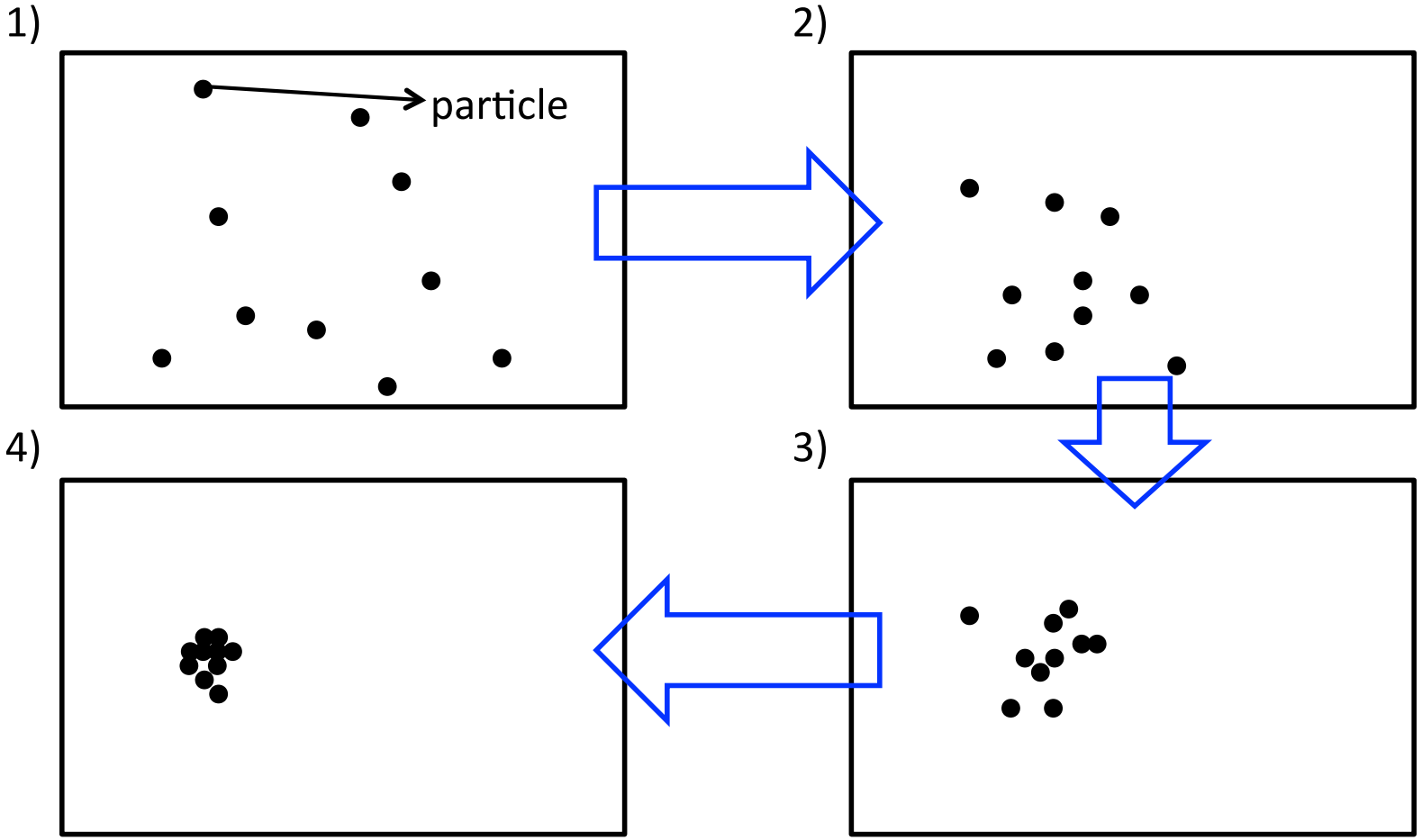


Brillouin zone

Particle swarm optimization (PSO)

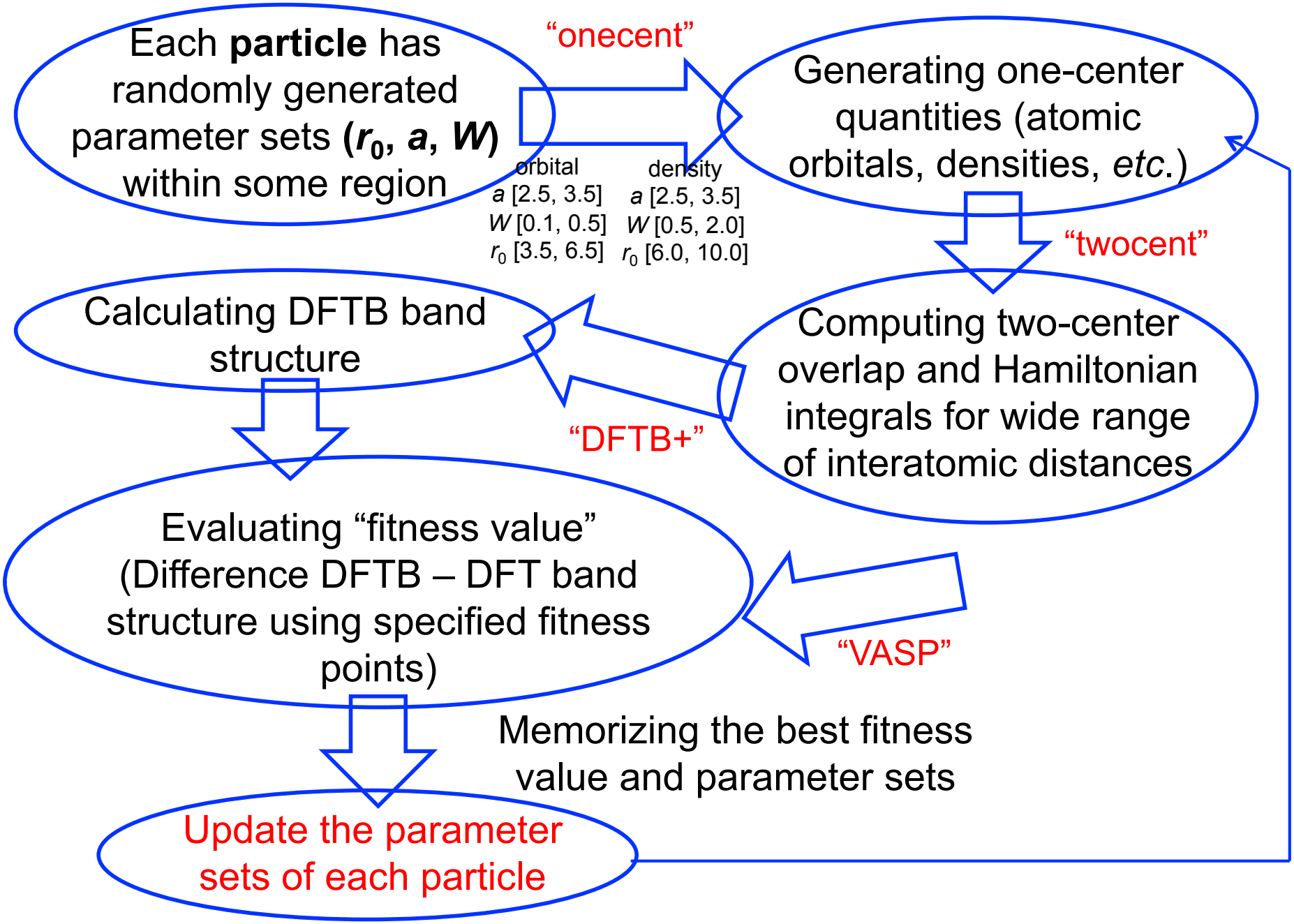


Particle Swarm Optimization



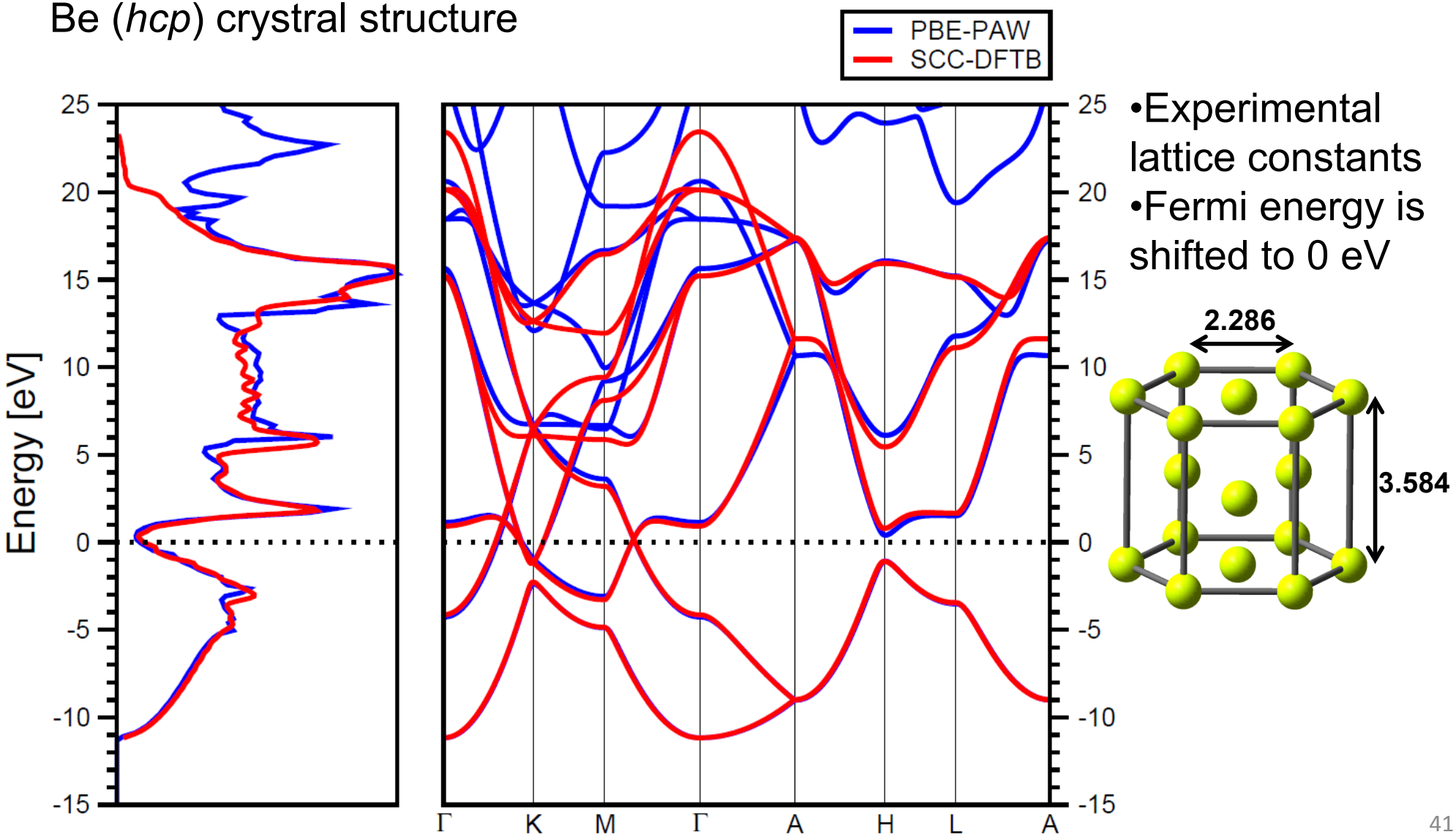
1) Particles (=candidate of a solution) are randomly placed initially in a target space.
2) – 3) Position and velocity of particles are updated based on the exchange of information between particles and particles try to find the best solution.
4) Particles converges to the place which gives the best solution after a number of iterations.

Particle Swarm Optimization



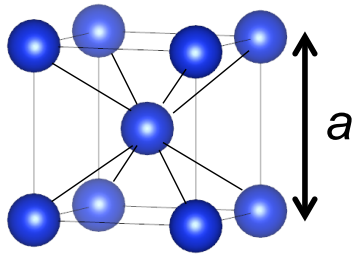
Example: Be, HCP crystal structure

Total density of states (left) and band structure (right) of Be (*hcp*) crystral structure



- Experimental lattice constants
- Fermi energy is shifted to 0 eV

Band structure fitting for BCC crystal structures



- space group No. 229
- 1 lattice constant (*a*)

➢No POTCAR file for $Z \geq 84$ in VASP

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

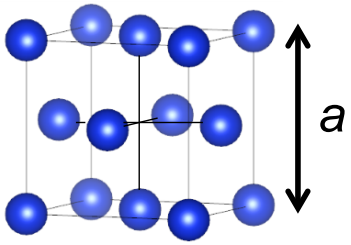
Transferability checked (single point calculation)

Reference system in PSO

Experimental lattice constants available

*Lanthanoids	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinoids	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Band structure fitting for FCC crystal structures



- space group No. 225
- 1 lattice constant (*a*)

Transferability checked (single point calculation)

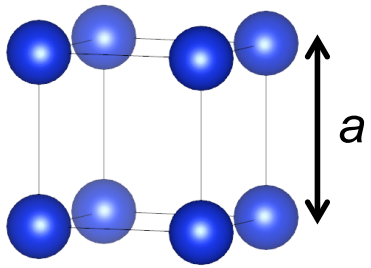
Reference system in PSO

Experimental lattice constants available

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

*Lanthanoids	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinoids	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Band structure fitting for SCL crystal structures



- space group No. 221
- 1 lattice constant (*a*)

Transferability checked (single point calculation)

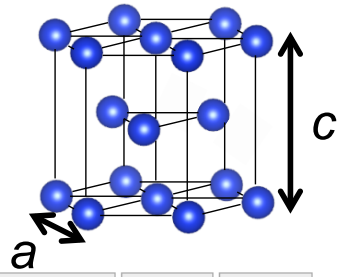
Reference system in PSO

Experimental lattice constants available

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

*Lanthanoids	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinoids	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Band structure fitting for HCP crystal structures



- space group No. 194
- 2 lattice constants (*a*, *c*)

Transferability checked (single point calculation)

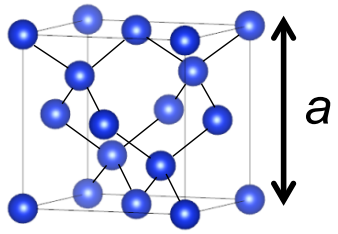
Reference system in PSO

Experimental lattice constants available

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

*Lanthanoids	* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinoids	** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Band structure fitting for Diamond crystal structures



- space group No. 227
- 1 lattice constant (*a*)

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Transferability checked (single point calculation)

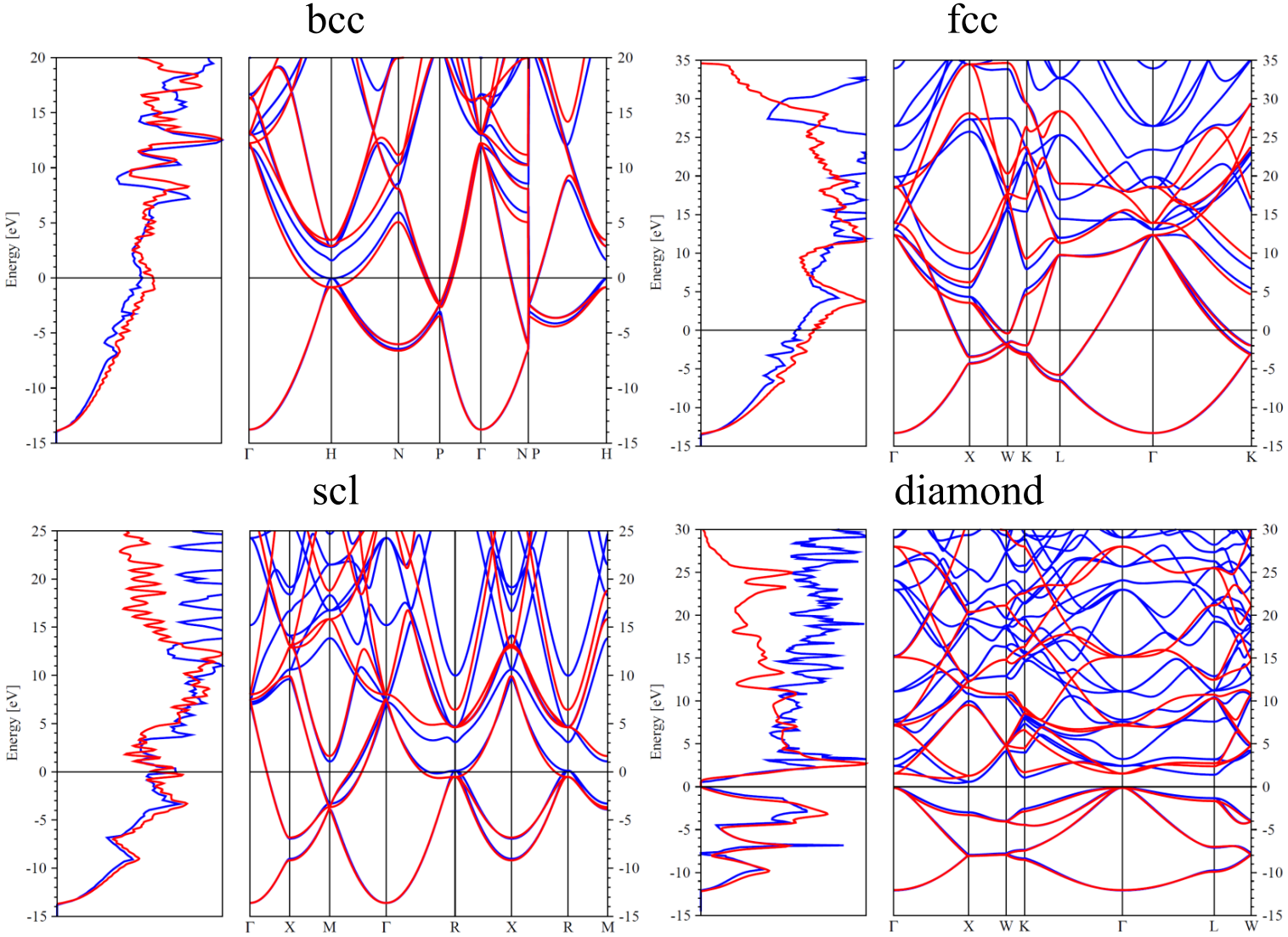
Reference system in PSO

Experimental lattice constants available

*Lanthanoids	*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**Actinoids	**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Transferability of optimum parameter sets for different structures

e.g. : Si, parameters were optimized with bcc only



$3s^2 3p^2 3d^0$

Lattice constants:

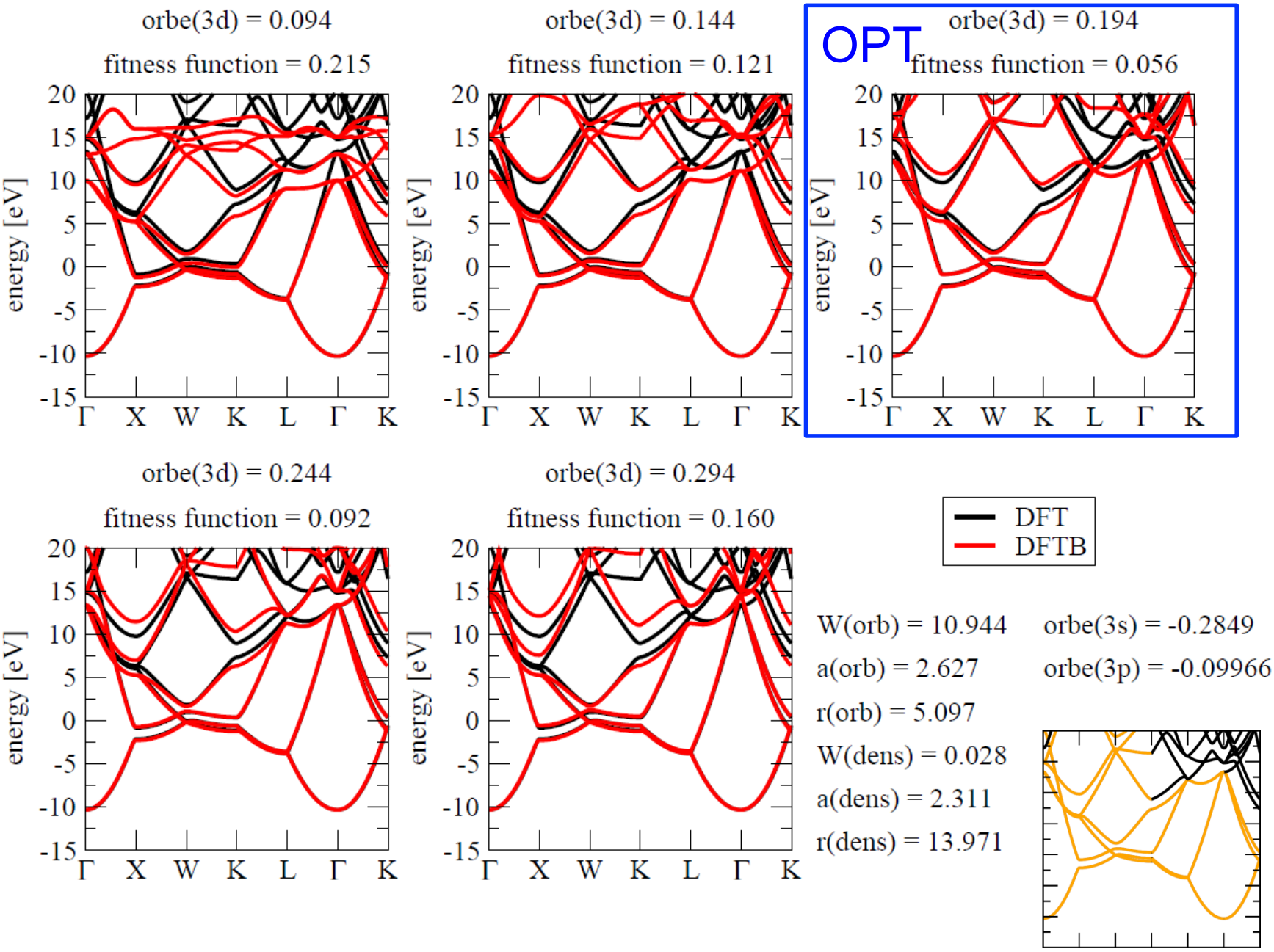
Expt	
· bcc	3.081
fcc	3.868
scl	2.532
diamond	5.431

Parameter sets:

W (orb)	3.33938
a (orb)	4.52314
r (orb)	4.22512
W (dens)	1.68162
a (dens)	2.55174
r (dens)	9.96376
ε_s	-0.39735
ε_p	-0.14998
ε_d	0.21210

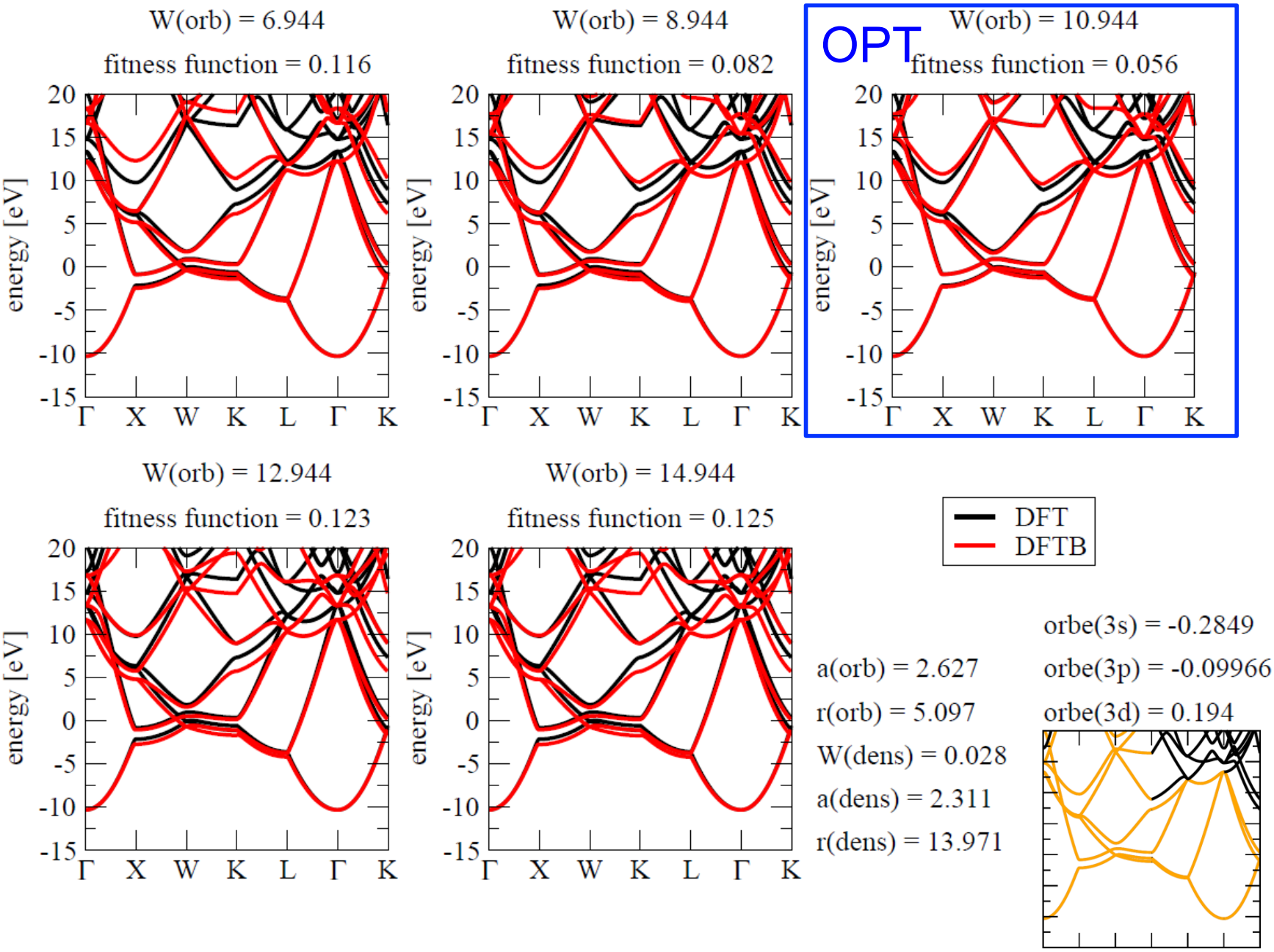
➢Artificial crystal structures can be reproduced well

Influence of virtual orbital energy (3d) to Al (*fcc*) band structure



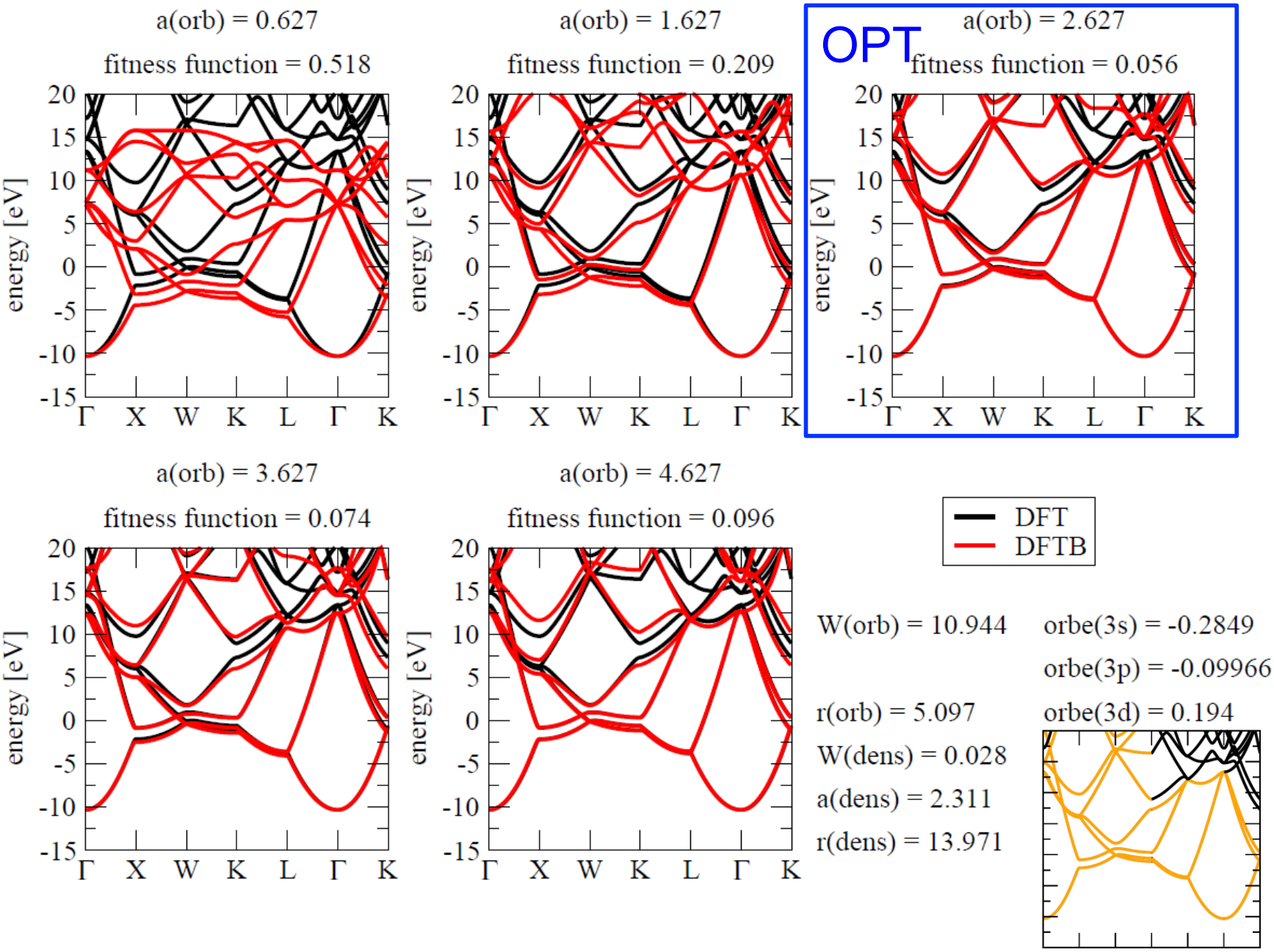
➢The bands of upper part are shifted up constantly as orbε(3d) becomes larger

Influence of *W*(orb) to Al (*fcc*) band structure



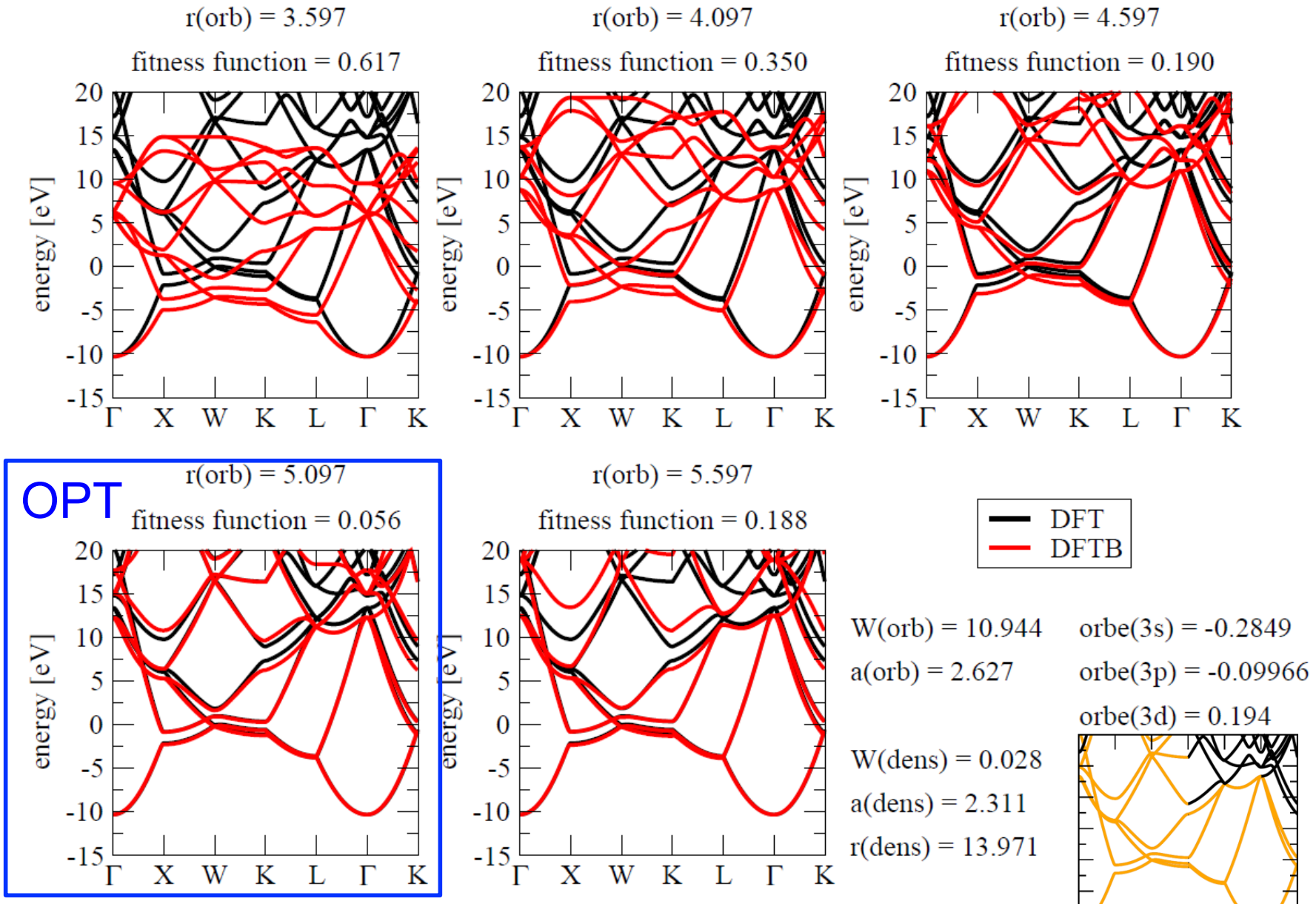
➢The bands of upper part go lower as *W*(orb) becomes larger

Influence of *a*(orb) to Al (*fcc*) band structure



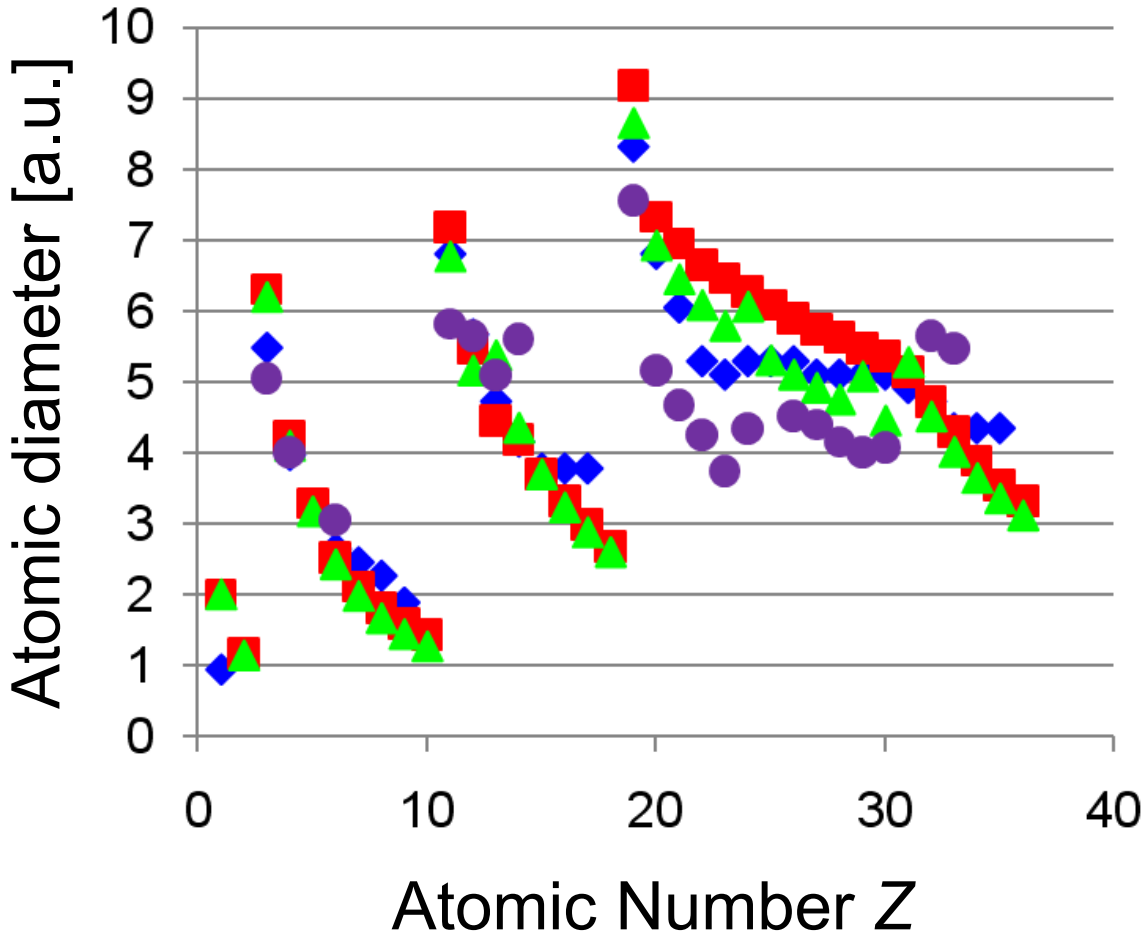
➢Too small *a*(orb) gives the worse band structure

Influence of *r*(orb) to Al (*fcc*) band structure



➢*r*(orb) strongly influences DFTB band structure

Correlation of *r*(orb) vs. atomic diameter

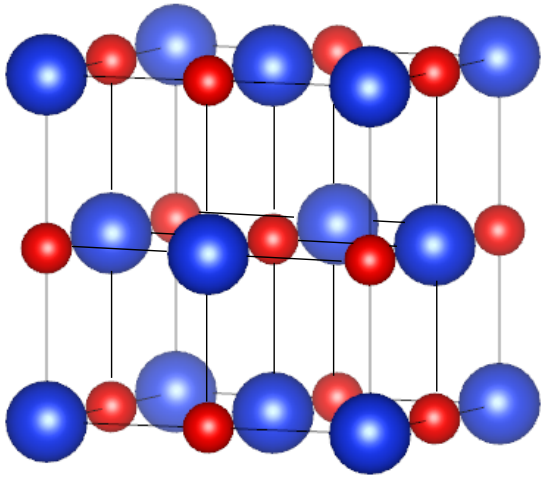


- Empirically measured radii (Slater, J. C., *J. Chem. Phys.*, **41**, 3199-3204, (1964).)
- Calculated radii with minimal-basis set SCF functions (Clementi, E. *et al*., *J. Chem. Phys.*, **47**, 1300-1307, (1967).)
- Expected value using relativistic Dirac-Fock calculations (Desclaux, J. P., *Atomic Data and Nuclear Data Tables*, **12**, 311-406, (1973).)
- This work *r*(orb)

➢In particular for main group elements, there seems to be a correlation between *r*(orb) and atomic diameter.

Straightforward application to binary crystal structures

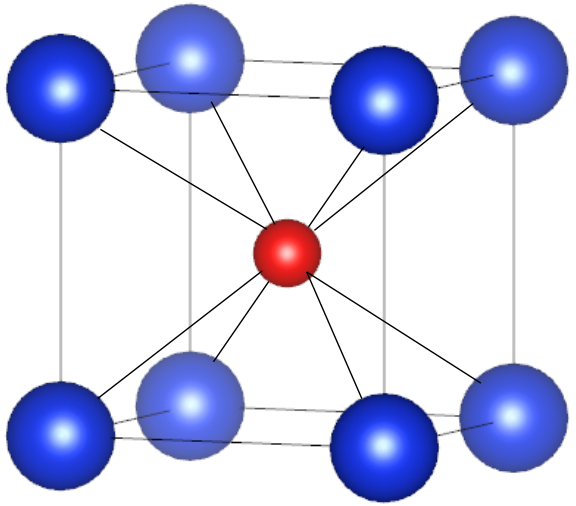
Rocksalt (space group No. 225)



- NaCl
- MgO
- MoC
- AgCl

…

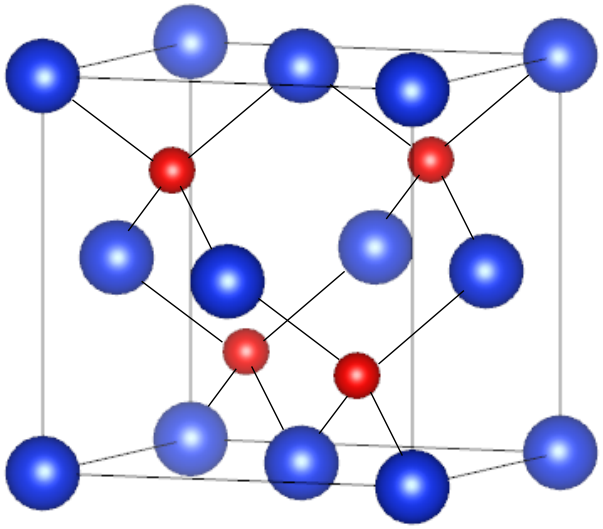
B2 (space group No. 221)



- CsCl
- FeAl

…

Zincblende (space group No. 216)



- SiC
- CuCl
- ZnS
- GaAs

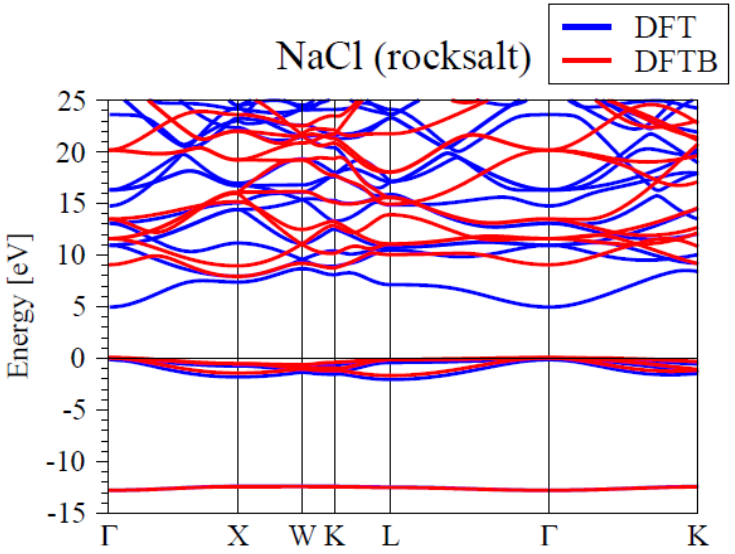
…

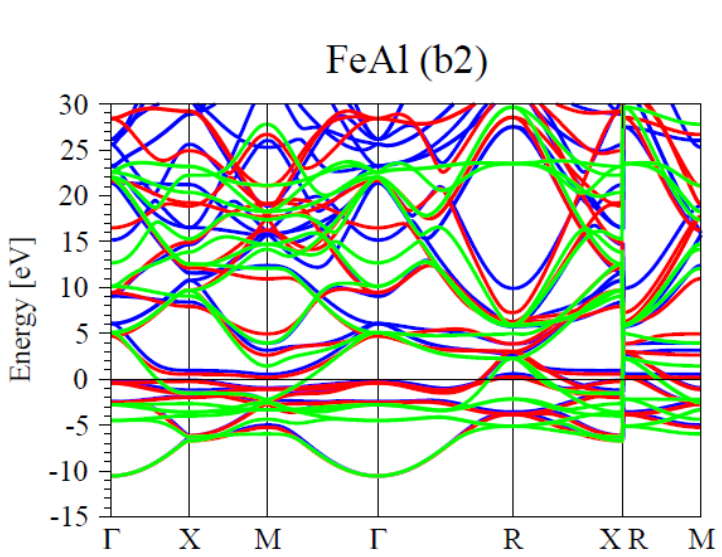
Others

- Wurtzite (BeO, AlO, ZnO, GaN, …)
- Hexagonal (BN, WC)
- Rhombohedral (*ABCABC* stacking sequence, BN)

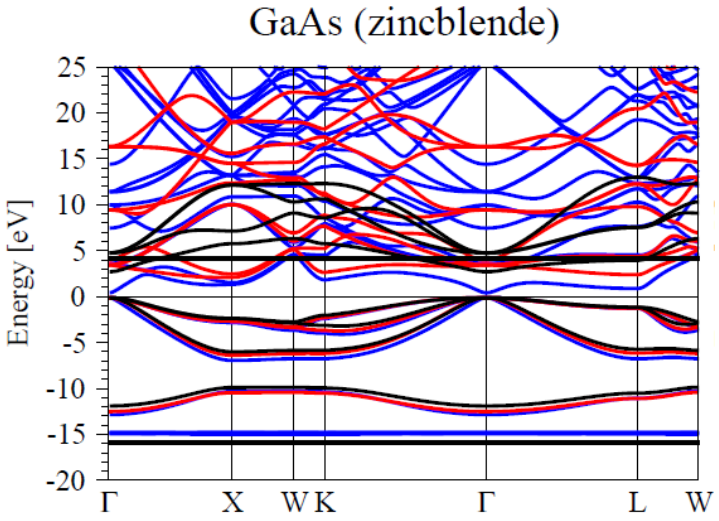
➢ more than 100 pairs tested

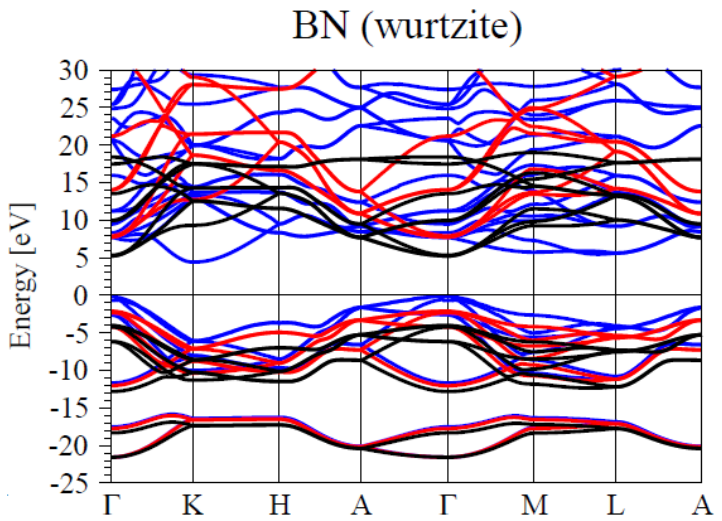
Selected examples for binary crystal structures





- d^7s^1 is used in POTCAR (DFT)



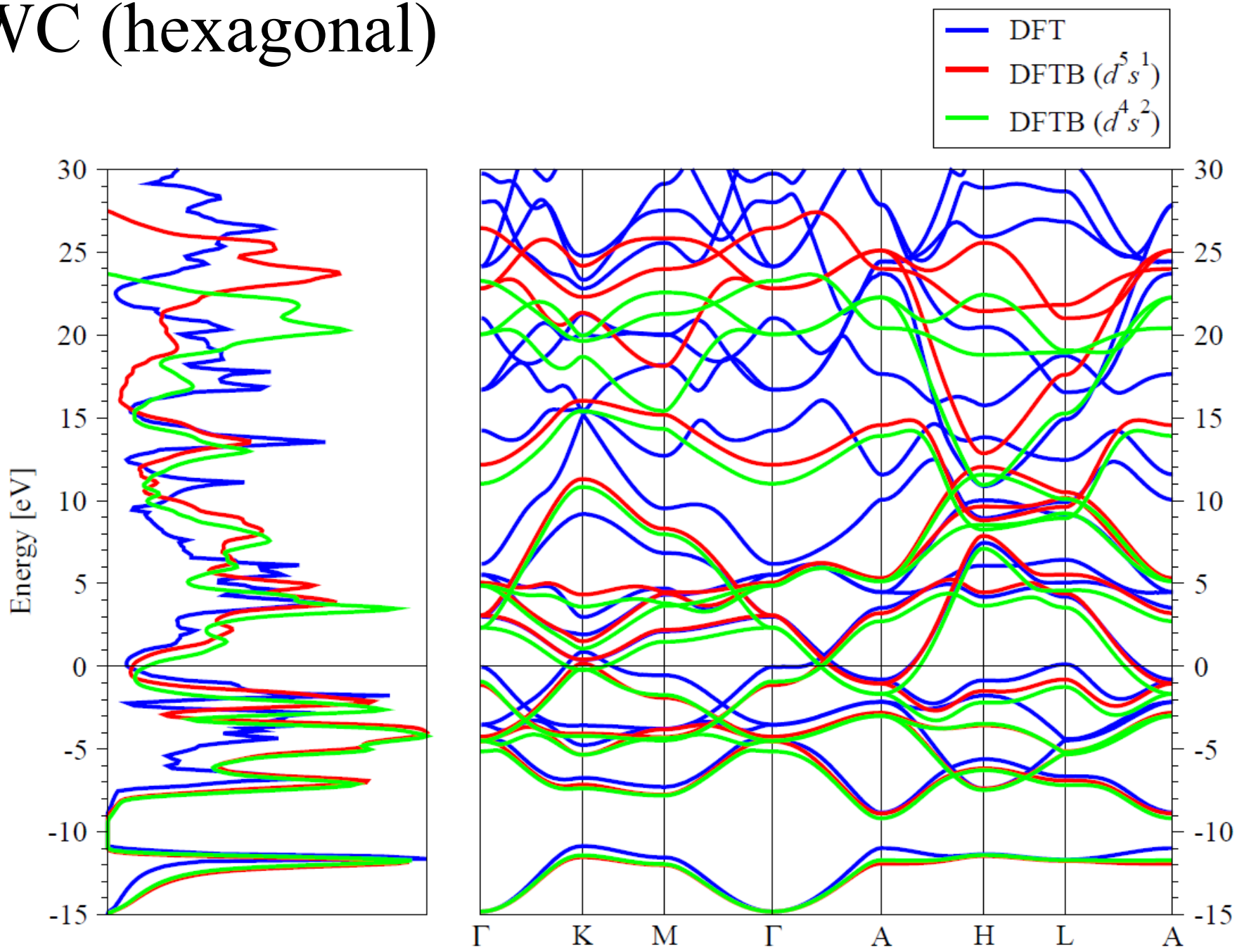


Reference of previous work :

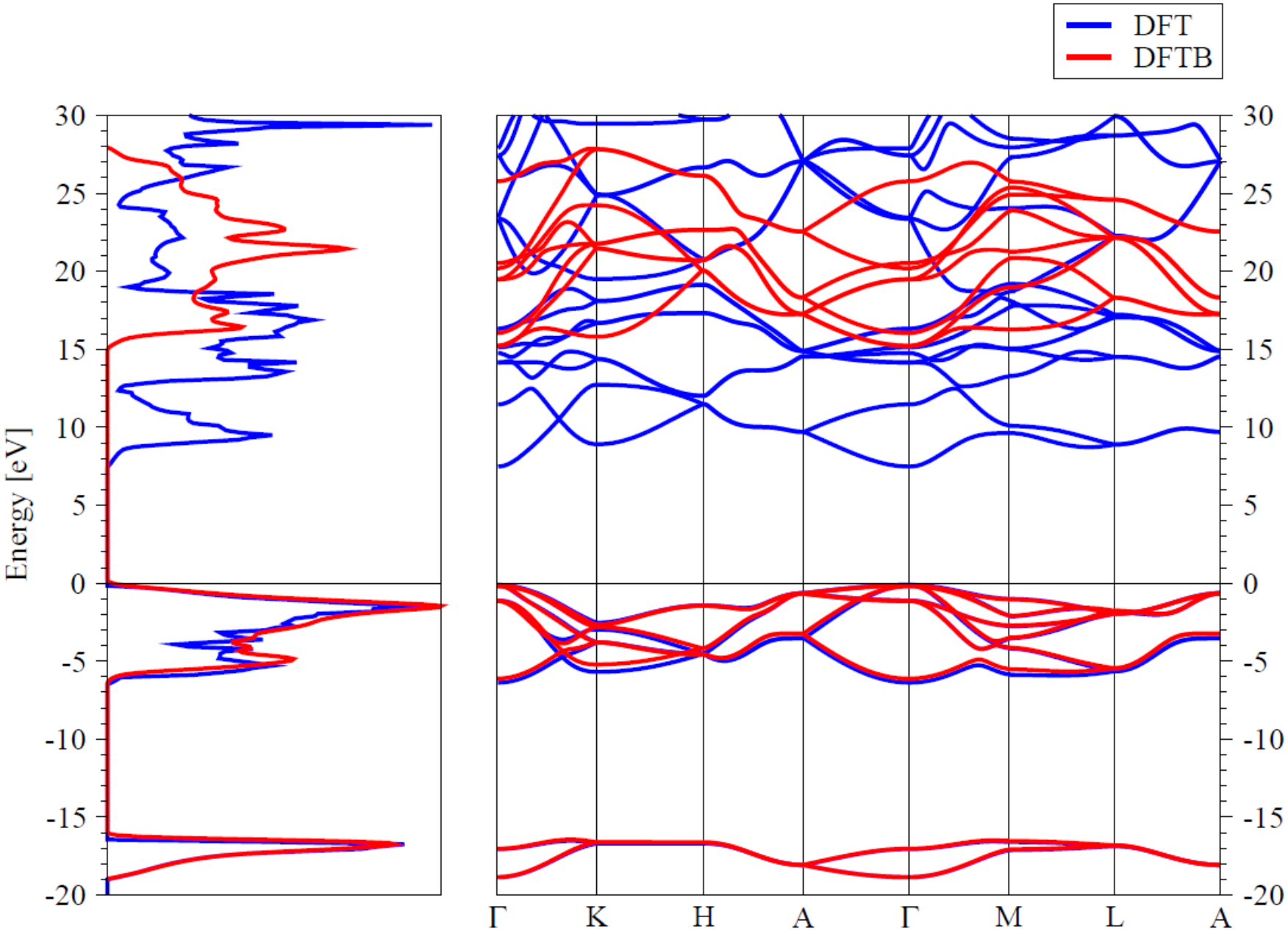
element	name
Ga, As	hyb-0-2
B, N	matsci-0-2

➢Further improvement can be performed for specific purpose but this preliminary sets will work as good starting points

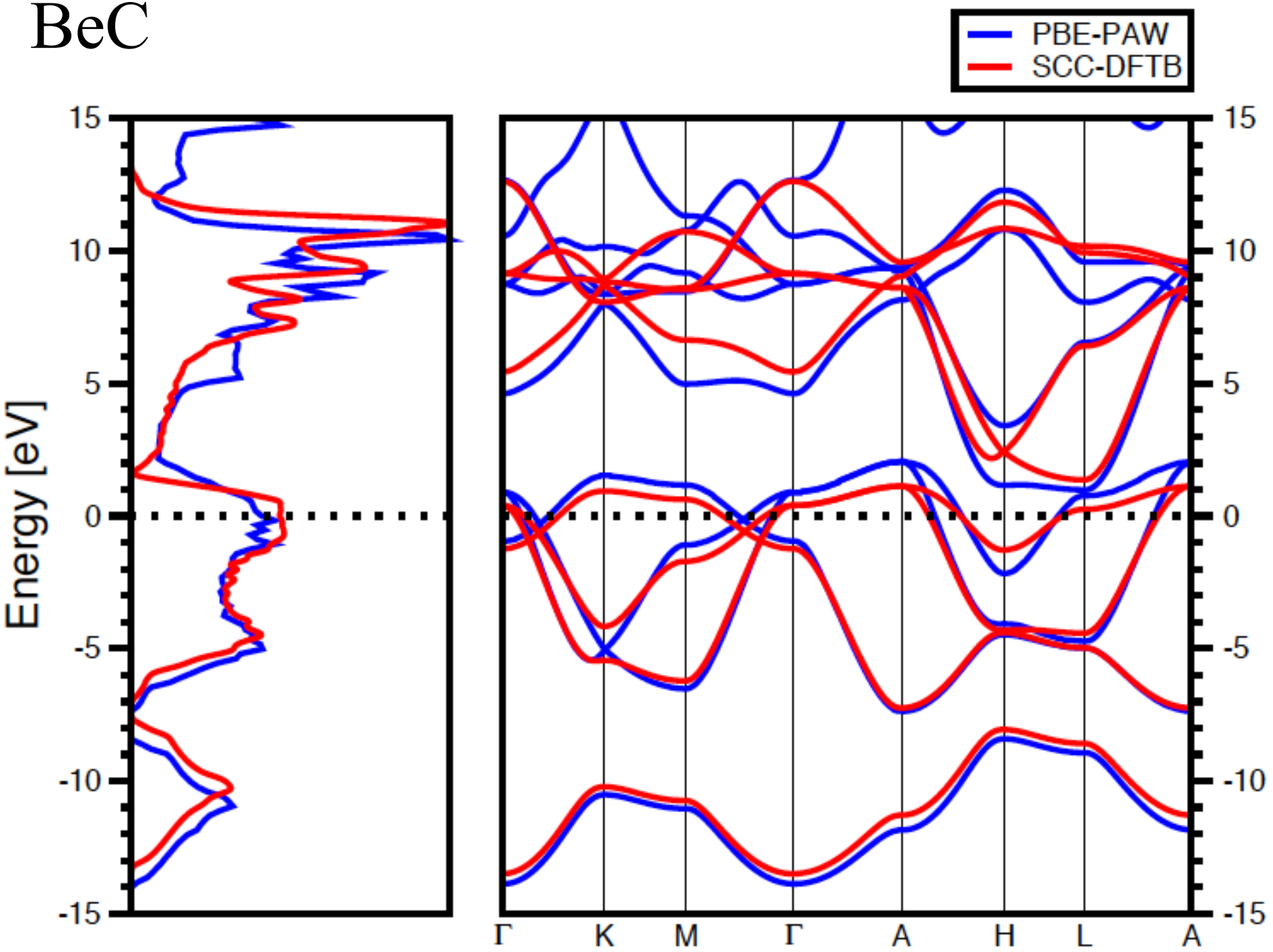
WC (hexagonal)



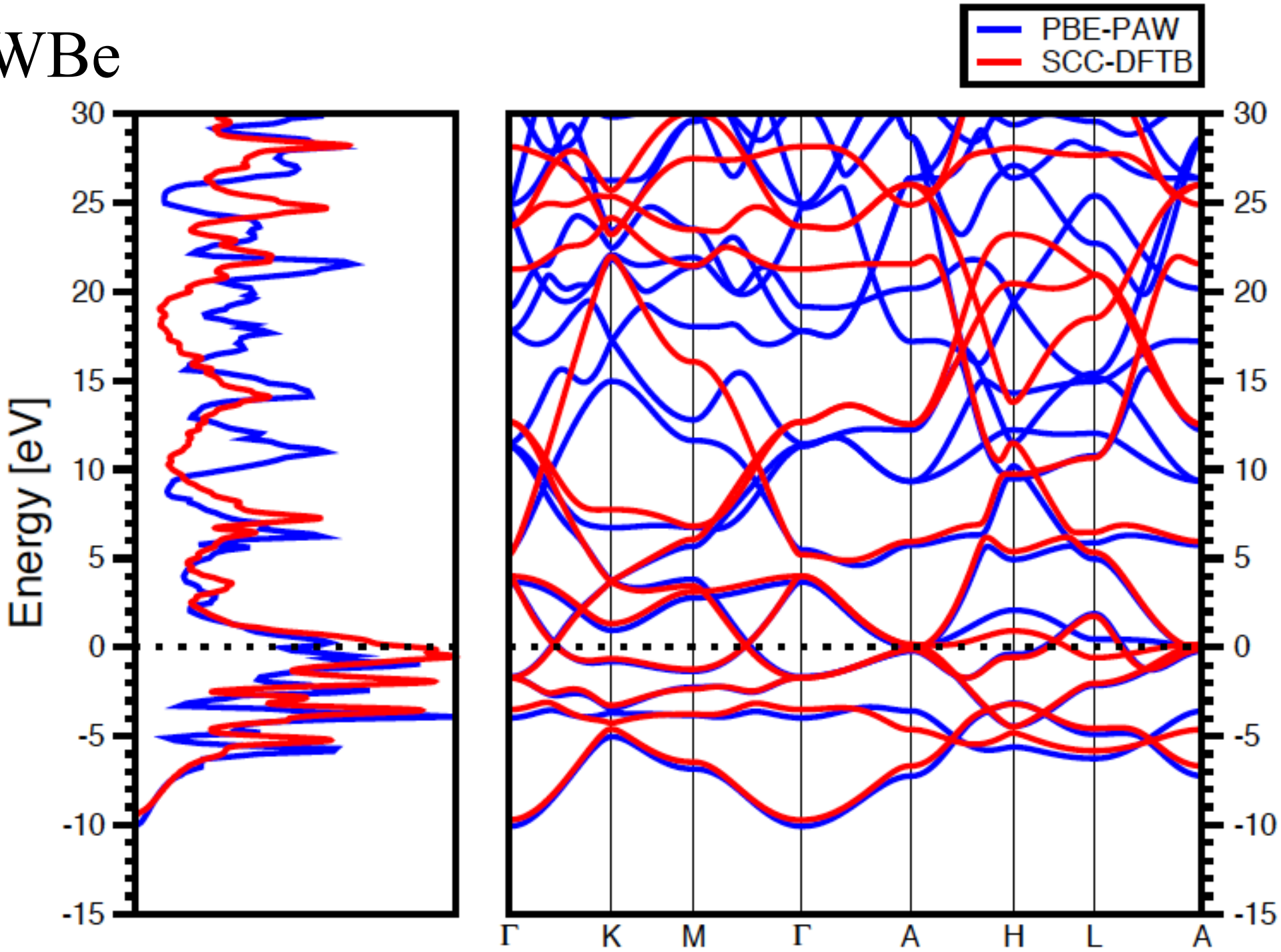
BeO



BeC



WBe



Description of small neutral beryllium clusters

- Distance in [Å]
- Closed shell singlet

B3LYP/cc-pVTZ
SCC-DFTB
PM3

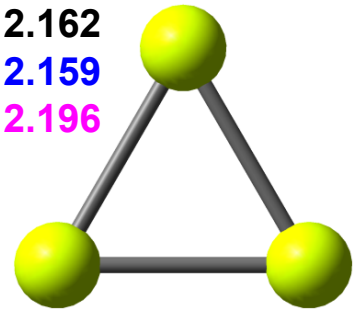
$Be_2\ (D_{\infty h})$

2.483
2.492
2.205

$$\mathrm{BE/atom} = \frac{n * E(\mathrm{Be}) - E(\mathrm{Be}_n)}{n}$$

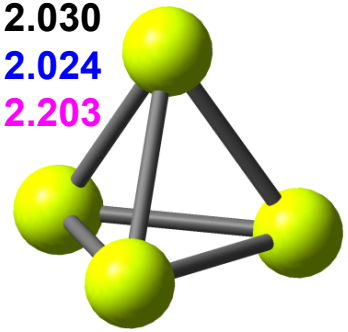
$Be_3\ (D_{3h})$

2.162
2.159
2.196



$Be_4\ (T_d)$

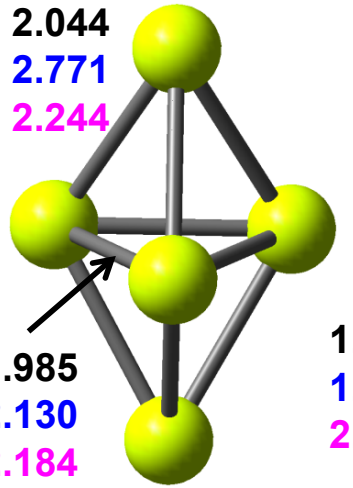
2.030
2.024
2.203



$Be_5\ (D_{3h})$

2.044
2.771
2.244

1.985
2.130
2.184



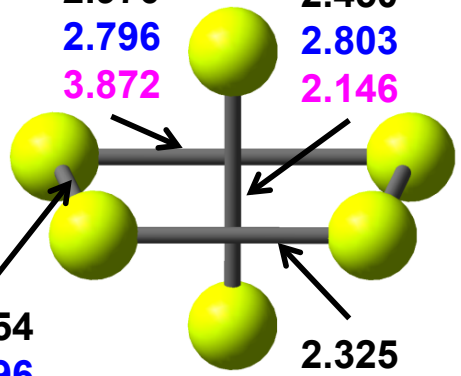
$Be_6\ (C_{2v})$

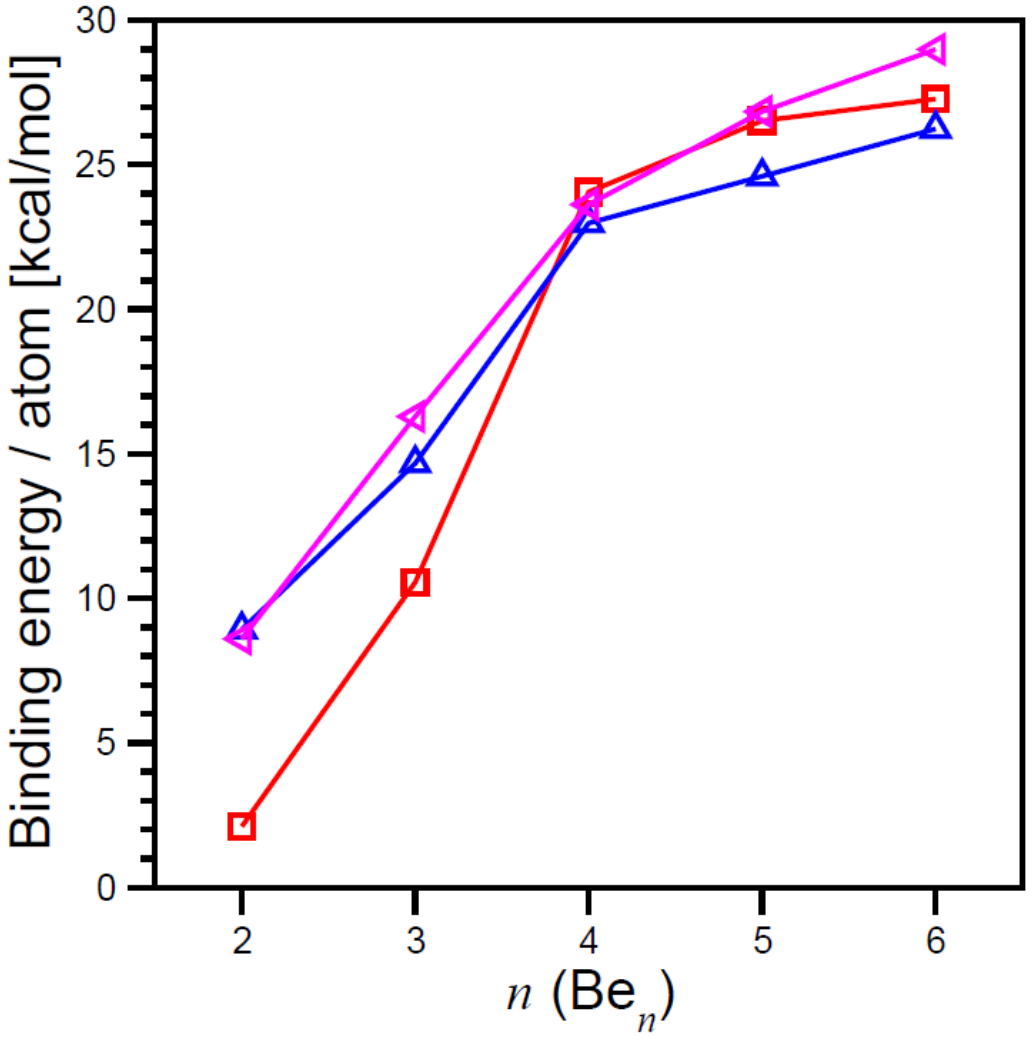
2.970
2.796
3.872

2.450
2.803
2.146

1.854
1.796
2.191

2.325
2.796
2.244

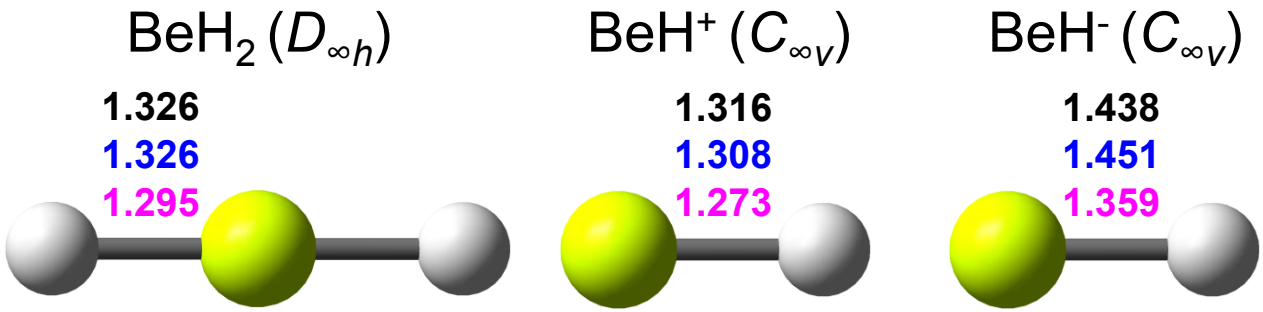


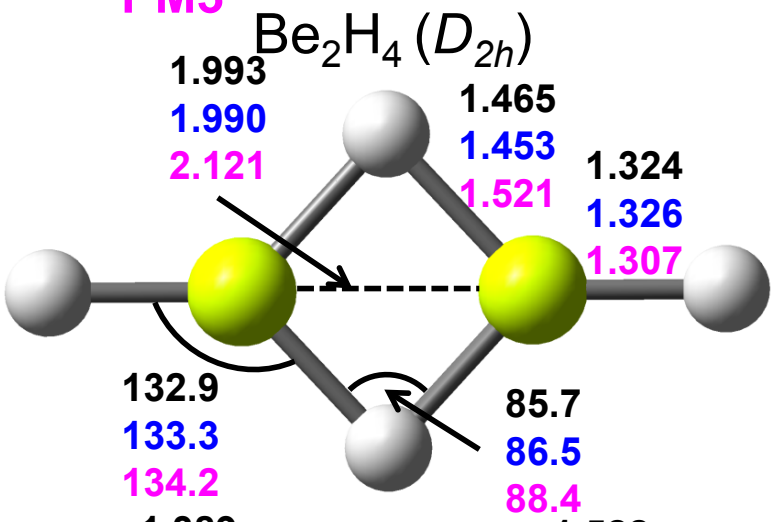


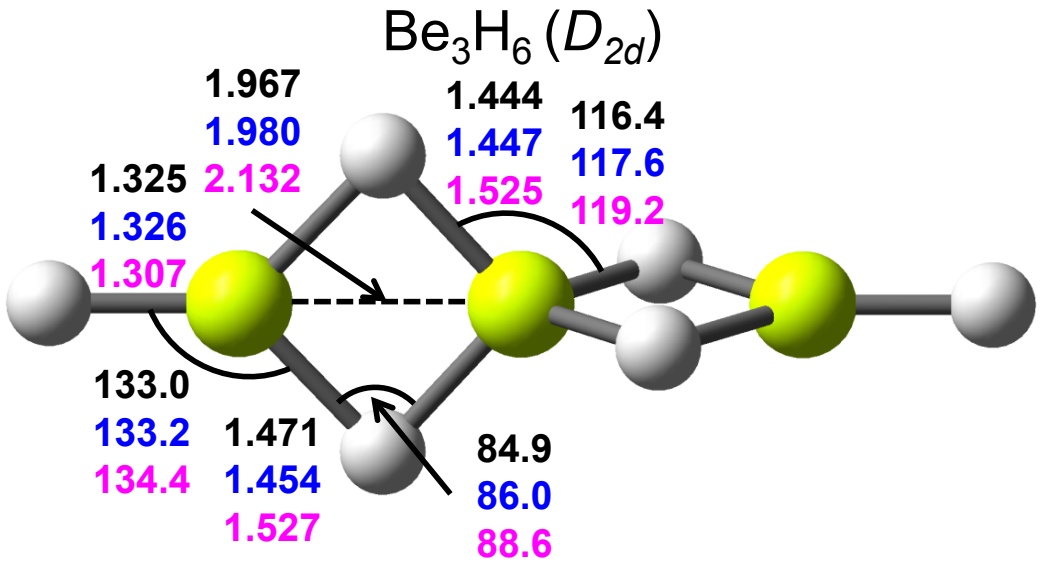
Geometries of beryllium hydride molecules

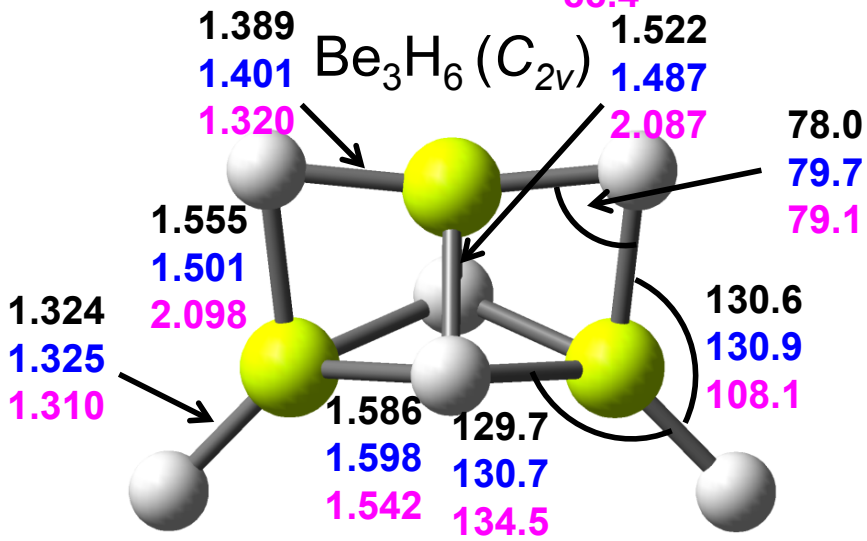
- Distance in [Å]
- Angle in [degree]
- Closed shell singlet

B3LYP/cc-pVTZ
SCC-DFTB
PM3







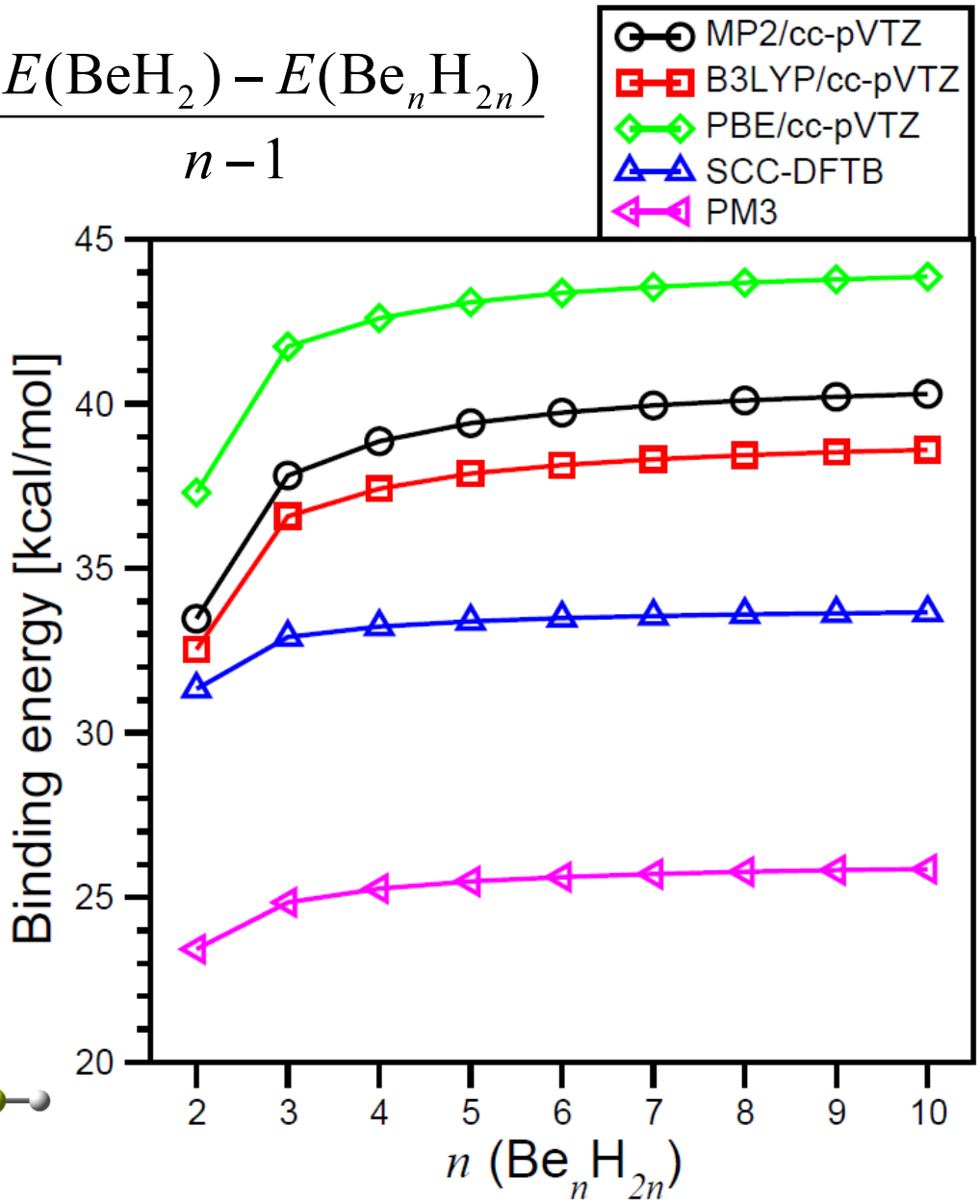


➢DFTB potentially predicts good geometries for small beryllium molecules

Binding energy of beryllium hydride oligomers

BeH_2
Be_2H_4
Be_3H_6
Be_4H_8
Be_5H_{10}
Be_6H_{12}
Be_7H_{14}
Be_8H_{16}
Be_9H_{18}
$Be_{10}H_{20}$

$$BE = \frac{n * E(BeH_2) - E(Be_nH_{2n})}{n-1}$$



➢Discrepancy of DFTB binding energy from DFT or MP2 is reduced compared with other semi-empirical methods (PM3)

- Approximate DFT and DFT methods useful to study quantum chemistry of complex systems
- DFTB Be-X parameters will be used for:
  - A) chemical sputtering simulations for calibration/validation of classical potential simulations
  - B) structure/energy calculations of amorphous systems

Funding:

GLOBAL COE IN CHEMISTRY NAGOYA JAPAN

JST Japan Science and Technology Agency

CREST "Multiscale Physics" (2006-2011)

CREST "Soft π–materials: (2011-2015)

SRPR tenure track program (2006-2011)

JSPS KAKENHI


Thank you for your attention!