State of FHI-aims

Volker Blum

Objective: Electronic structure theory today

Enormous successes:

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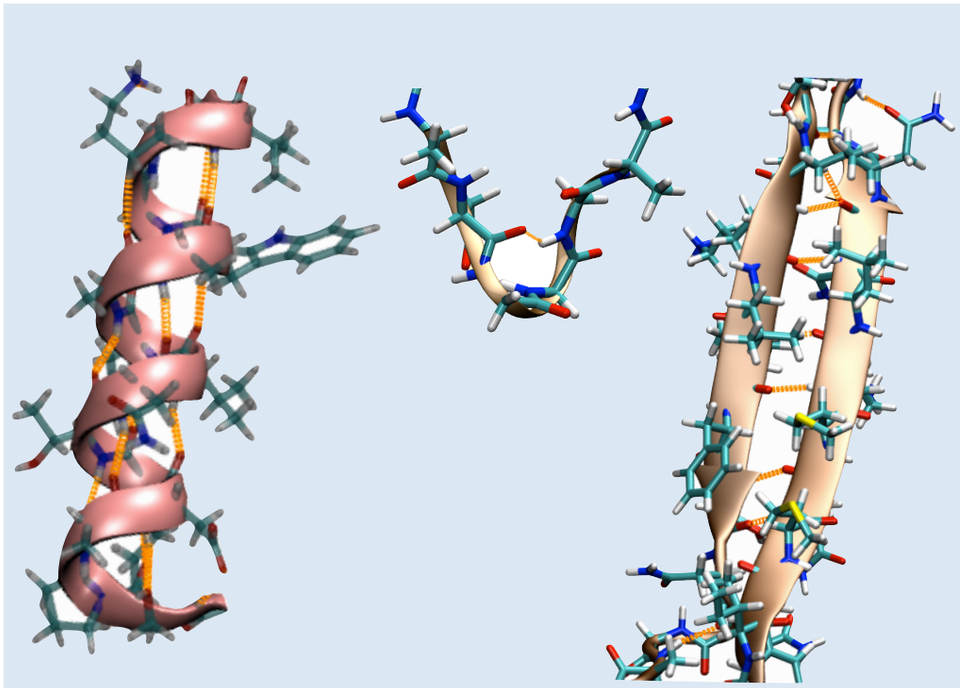

(Bio)molecular matter

- Structural complexity
- statistical averages & dynamics
- “weak” interactions critical

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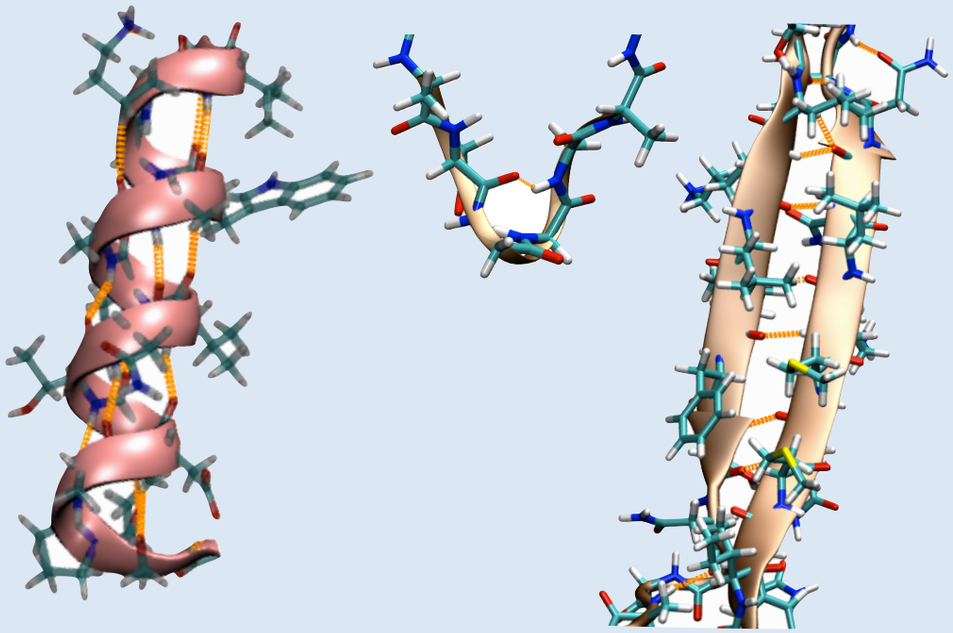

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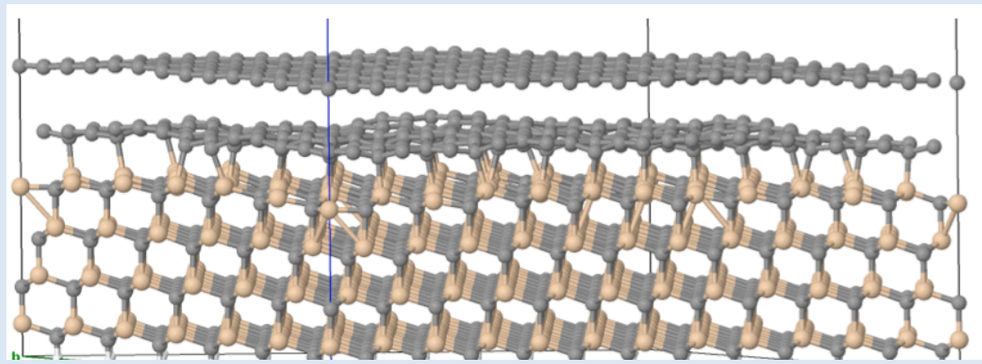
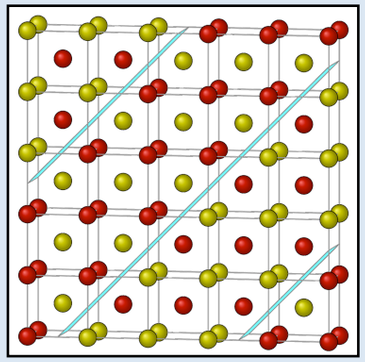
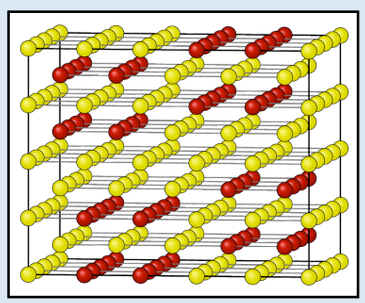


Graphene / SiC



Ta_3W_3



Ta_4W_9

Condensed phases

(solids, surfaces, ...)

- Structure!
- Stability, free energies
- electronic, mechanical, optical, ... properties

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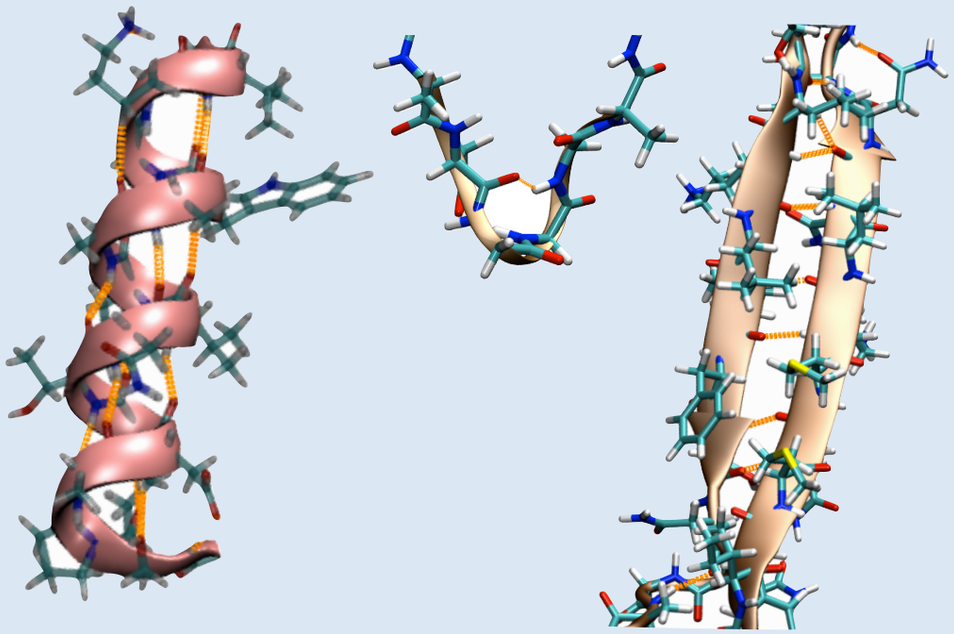

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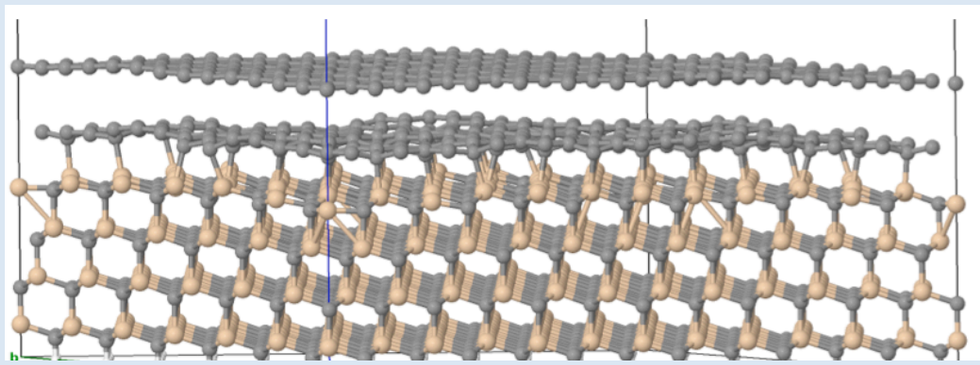

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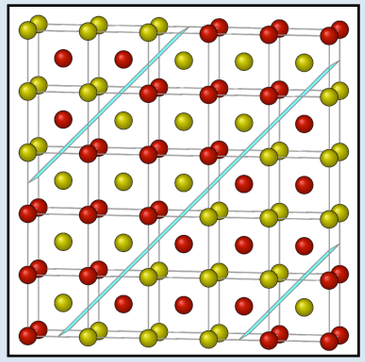

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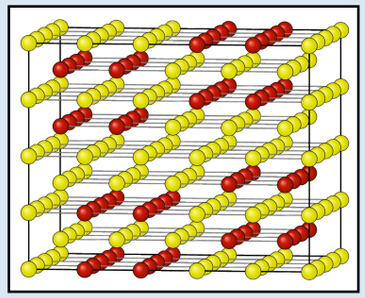

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Matter at extreme conditions

- “electron gas + protons”; high-pressure compounds, transitions
- (Born-Oppenheimer) molecular dynamics, classical nuclei
- Quantum nuclei? (PIMD)

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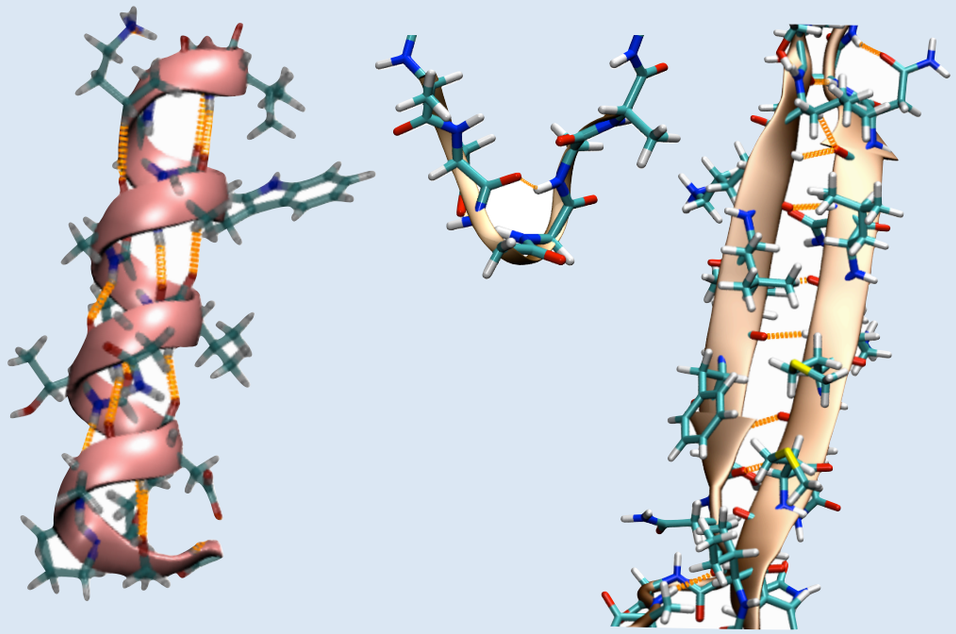

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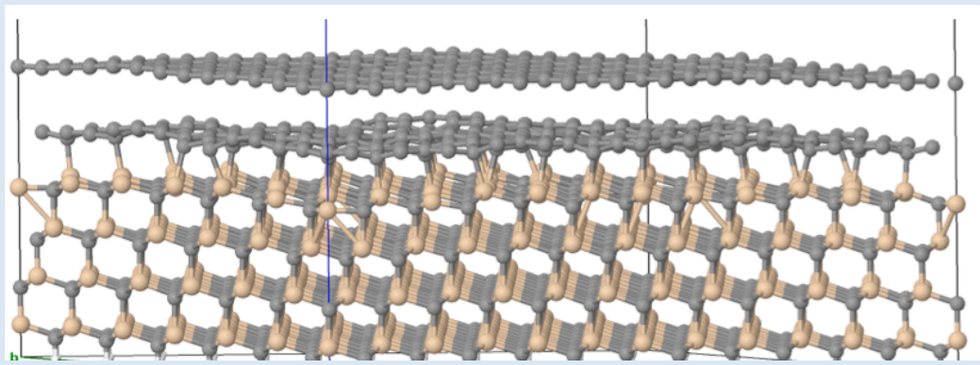

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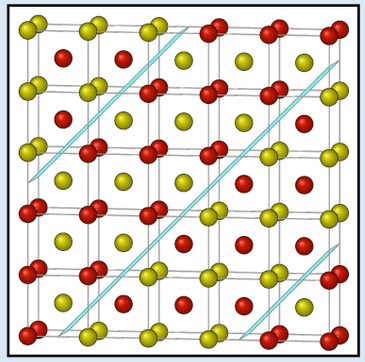

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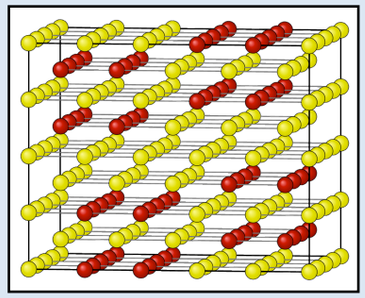

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Condensed phases

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Today: "Mostly density-functional theory", plenty of flavors

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Electronic structure theory for real materials

... but also some significant challenges:

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- Are we computing the right thing?
  - Current DFT (LDA/GGA *and beyond*) may qualitatively fail with *or without* warning for much of the interesting space, even for "structure"
  - Other numerical approximations? (grids, cutoffs, core vs. valence, ...)
  - "Classical" vs. "quantum" nuclei? Born-Oppenheimer?

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- Can we compute the right thing?
  - Realistically sized systems to capture "reality"
  - Statistical averages, dynamics, combinatorial complexity of "structure"?
  - Simply, hardware vs. software - utilize *available* hardware effectively

Outline

- FHI-aims: Some (very) few basics

- Significant new developments:

  Periodic Hartree-Fock and hybrid functionals

  Unit cell relaxation & analytical stress tensor

  Many-body perturbation theory: sc*GW* and rPT2

  "Quantum nuclei"

  ... many others! (transport, visualization, ...)

- and how far can we push? Large-scale surface reconstruction

- "What would be good to have" (future?)

People

Fritz Haber Institute, Berlin [Richard-Willstätter-Haus]

People

Matthias Scheffler

Fritz Haber Institute, Berlin [Richard-Willstätter-Haus]

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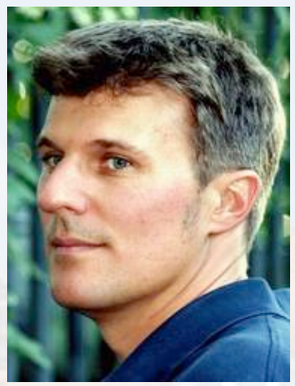

Karsten Reuter (now Munich)

Fritz Haber Institute, Berlin [Richard-Willstätter-Haus]

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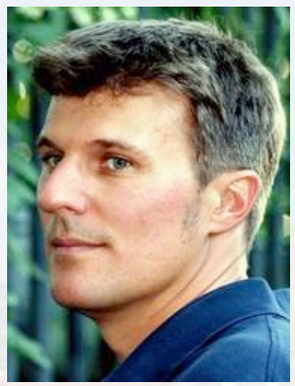

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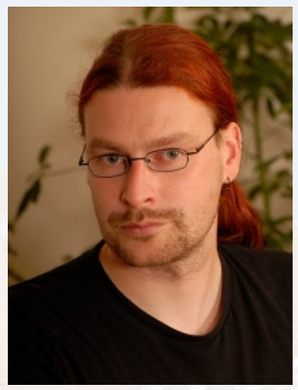

Patrick Rinke

Fritz Haber Institute, Berlin [Richard-Willstätter-Haus]

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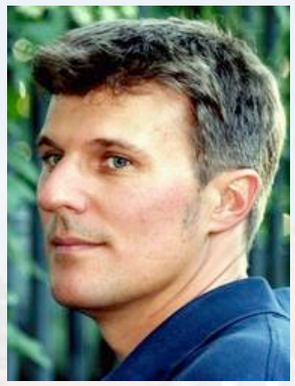

Karsten Reuter (now Munich)

Patrick Rinke

... FHI-aims - MANY contributors:

Xinguo Ren, Ville Havu, Paula Havu, Ralf Gehrke, Rainer Johanni, Andreas Dolfen, Felix Hanke, Stefan Gutzeit, Andrea Sanfilippo, Luca Ghiringhelli, Mariana Rossi, Alex Tkatchenko, Sergey Levchenko, Matthias Gramzow, Benedikt Biedermann, Aloysius Soon, Mina Yoon, Jörg Meyer, Christian Carbogno, Norbert Nemec, Fabio Caruso, Sucismita Chutia, Franziska Schubert, Jürgen Wieferink, Simiam Ghan, Viktor Atalla, Matti Ropo, Ferdinand Evers, Alexej Bagrets, Fabio Della Sala, Eduardo Fabiano, Heiko Appel, Daniel Berger, Oliver Hofmann, Yong Xu, Marco Casadei, Klaus Reuter, Andreas Marek, Werner Jürgens, Igor Ying Zhang, Jan Kloppenburg, Franz Knuth, Xin-Zheng Li, ...

Fritz Haber Institute, Berlin

[Richard-Willstätter-Haus]

Dr. Rainer Johanni (1959-2012)

Dr. Rainer Johanni

* 20. 6. 1959 † 5. 6. 2012

Reminder - what did we want from a new code

Cover essentially the entirety of materials / chemistry

- Light main-group elements (H, C, N, O, ...)
- 3*d* transition metals & compounds
- 4*d* / 5*d* transition metals
- *f* elements
- ...

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Periodic and non-periodic systems on equal footing

All-electron method

Reliable production methods (DFT-LDA, -GGA, hybrids)

Validation "beyond DFT" (RPA, *GW*, Hartree-Fock+MP2, ...)

Scalable from laptop to massively parallel platforms

Efficient (1000s of atoms), but do not sacrifice accuracy!

Key choice: Numeric atom-centered basis functions

$$\varphi_{i[lm]}(\boldsymbol{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega)$$

- $u_i(r)$: Flexible choice - "Anything you like."

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig *et al.*), PLATO (Horsfield *et al.*), PAOs (Siesta, Conquest, OpenMX[2], Fireball, ...)

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- free ions, harm. osc. (Gaussians), ...

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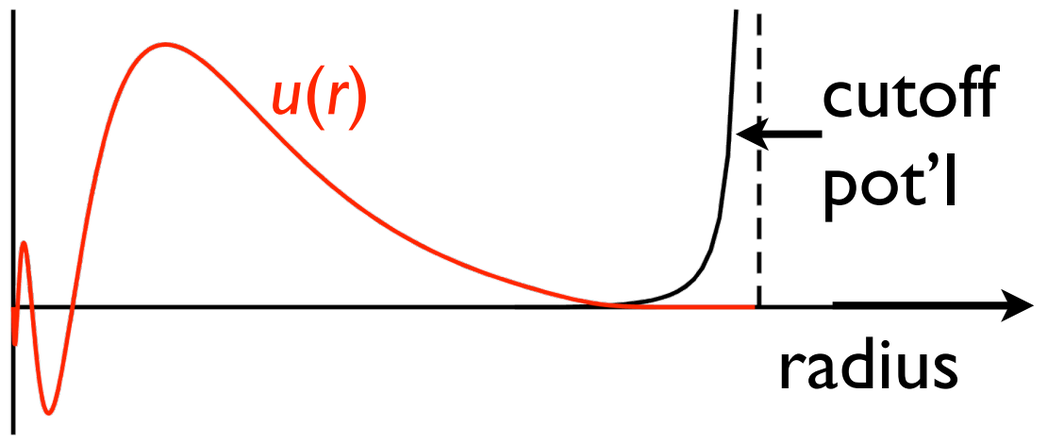

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- $u_i(r)$: Flexible choice - "Anything you like."

→ Localized; "naturally" all-electron

→ The choice of efficient and of enough radial functions is obviously important

→ We have a basis set library for all elements (1-102), from fast qualitative to meV-converged (total energy, LDA/GGA) calculations - efficient and accurate approach

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler,
"Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals",
Computer Physics Communications ***180****, 2175-2196 (2009)*

Basis set "language" in FHI-aims

	H	C	O	Au
minimal	$1s$	[He]+$2s2p$	[He]+$2s2p$	[Xe]+$6s5d4f$
Tier 1	H($2s$,2.1)	H($2p$,1.7)	H($2p$,1.8)	Au^{2+}(6p)
	H($2p$,3.5)	H($3d$,6.0)	H($3d$,7.6)	H($4f$,7.4)
		H($2s$,4.9)	H($3s$,6.4)	Au^{2+}(6s)
				H($5g$,10)
				H($6h$,12.8)
				H($3d$,2.5)
Tier 2	H($1s$,0.85)	H($4f$,9.8)	H($4f$,11.6)	H($5f$,14.8)
	H($2p$,3.7)	H($3p$,5.2)	H($3p$,6.2)	H($4d$,3.9)
	H($2s$,1.2)	H($3s$,4.3)	H($3d$,5.6)	H($3p$,3.3)
	H($3d$,7.0)	H($5g$,14.4)	H($5g$,17.6)	H($1s$,0.45)
		H($3d$,6.2)	H($1s$,0.75)	H($5g$,16.4)
				H($6h$,13.6)
Tier 3	H($4f$,11.2)	H($2p$,5.6)	O^{2+}($2p$)	H($4f$,5.2)*
	H($3p$,4.8)	H($2s$,1.4)	H($4f$,10.8)	H($4d$,5.0)
	...	...	...	...

Systematic hierarchy of basis (sub)sets, iterative *automated* construction based on *dimers*

"First tier"

"Second tier"

"Third tier"

...

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	...	...	...	...

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"First tier"

"Second tier"

... bundled together in "light", "tight", really_tight" standard settings with grids, Hartree potential, etc. - but every piece verifyable "by hand."

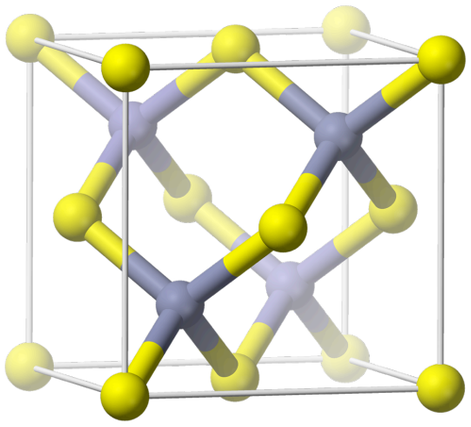
"Third tier"

...

Accuracy: Periodic hybrid functionals

Cohesive properties, bulk semiconductors

	a [Å]	B_0 [Mbar]	E_{coh} [eV]
Si			
PBE0			
FHI-aims, *tight*	5.439	0.99	4.553
Ref. [1]	5.433	1.00	4.555
HSE06			
FHI-aims, *tight*	5.446	0.98	4.527
Ref. [2]	5.435	0.98	4.582
GaAs			
HSE06			
FHI-aims, *tight*	5.695	0.71	3.150
Ref. [2]	5.687	0.71	3.149
Ge			
HSE06			
FHI-aims, *tight*	5.700	0.71	3.761
Ref. [3]	5.703	0.73	n/a



Zincblende GaAs

Essentially linear scaling exchange operator:

Levchenko, Ren, Wieferink, Johanni, Blum, Rinke, Scheffler 2012

[1] J. Paier *et al.*, J. Chem. Phys. **124**, 154709 (2006).

[2] J. Paier *et al.*, J. Chem. Phys. **125**, 249901 (2006).

[3] A. Stroppa *et al.*, PRB **83**, 085201 (2011).

State of periodic hybrid functionals in FHI-aims

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$$E_{\mathrm{xc}}[n] = (1-\alpha)E_{\mathrm{x}}^{\mathrm{loc}}[n] + \alpha E_{\mathrm{x}}^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{loc}}[n]$$

Becke, Burke, Perdew, Ernzerhoff, others

- Long-standing "most wanted" feature in the code
- Now stable (single-point geometries) in an effective *O*(*N*) implementation

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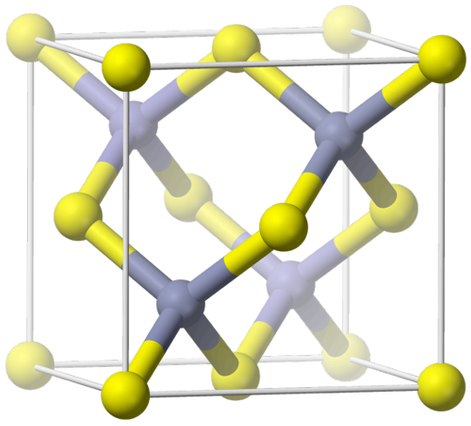

Zincblende GaAs

HSE06 - GaAs, tight, 48 CPUs, no symmetry use yet(!)

	Time for K_{ij}:
2 atom cell, k-grid 8x8x8	63 s

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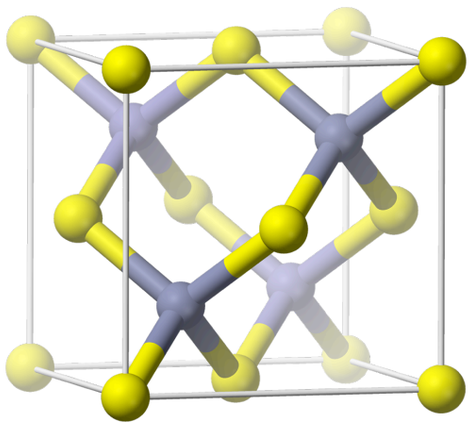

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16 atom cell, k-grid 4x4x4	311 s	0.77
128 atom cell, k-grid 2x2x2	3629 s	1.18

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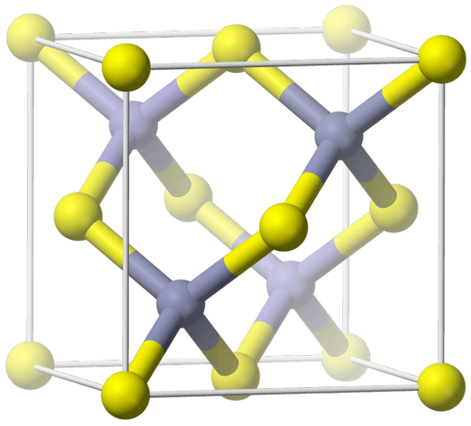

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128 atom cell, k-grid 2x2x2	3629 s	1.18

- Forces, relaxation: "Experimental" - first implementation, small basis sets at present!

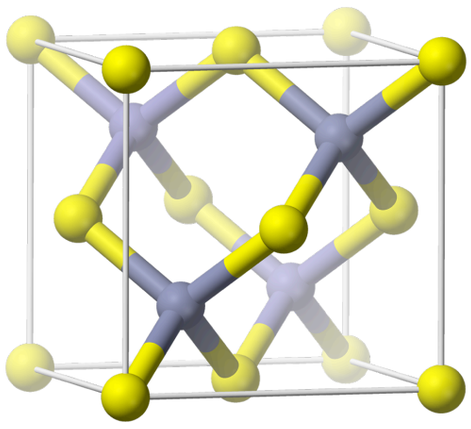
State of periodic hybrid functionals in FHI-aims

See Sergey Levchenko, Tue 11:50!

Levchenko, Ren, Wieferink, Johanni, Blum, Rinke, Scheffler 2012

$$E_{\mathrm{xc}}[n] = (1-\alpha)E_{\mathrm{x}}^{\mathrm{loc}}[n] + \alpha E_{\mathrm{x}}^{\mathrm{HF}} + E_{\mathrm{c}}^{\mathrm{loc}}[n]$$

- Long-standing "most wanted" feature in the code
- Now stable (single-point geometries) in an effective *O*(*N*) implementation



Zincblende GaAs

HSE06 - GaAs, tight, 48 CPUs, no symmetry use yet(!)

	Time for K_{ij}:	Scaling exponent
2 atom cell, k-grid 8x8x8	63 s	
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128 atom cell, k-grid 2x2x2	3629 s	1.18

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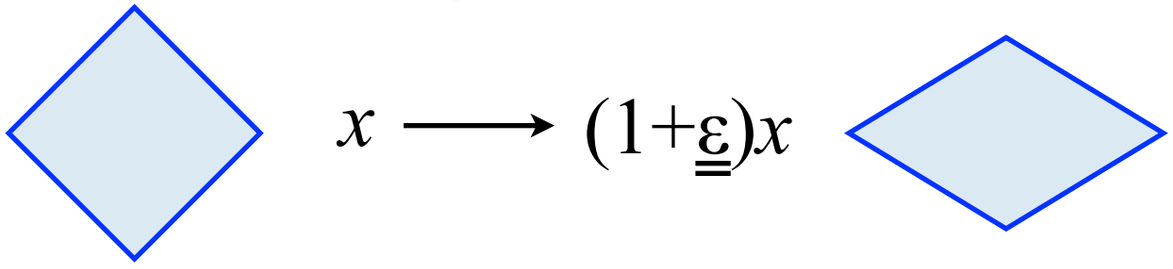
Another "most wanted" feature: Analytical stress tensor

Global spatial distortion:

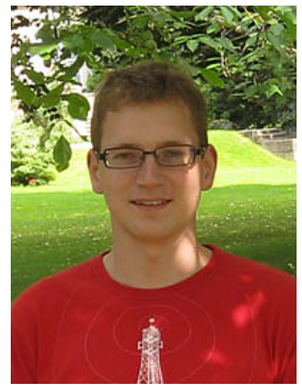


→Strain derivative (stress tensor):

$$\sigma^{\mu\nu} = \frac{1}{V} \frac{\partial E}{\partial \varepsilon_{\mu\nu}}\bigg|_{\varepsilon_{\mu\nu}=0}$$

Christian Carbogno

Viktor Atalla

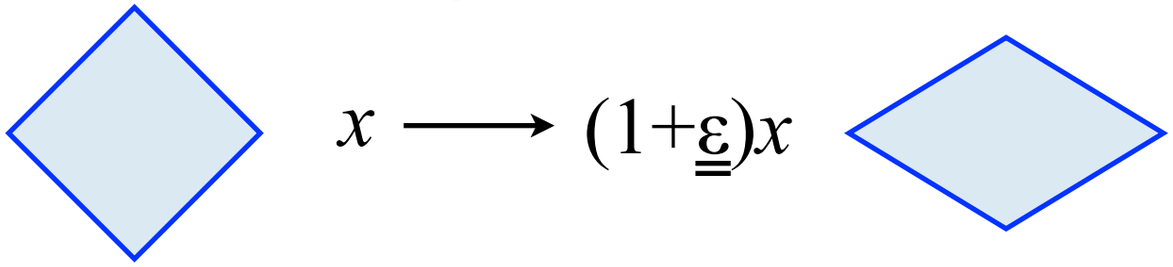


Franz Knuth

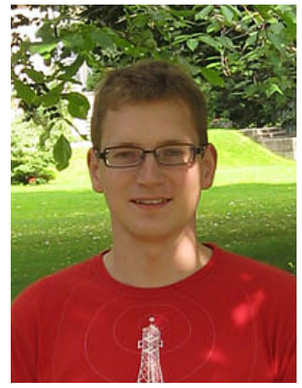
- Standard energy derivative for unit cell shape optimization, pressure
- Finite-difference implementation, cell shape optimization exist but costly
- Analytical implementation: (Somewhat) faster, but unfortunately a lot of terms

Another "most wanted" feature: Analytical stress tensor

Global spatial distortion:







→Strain derivative (stress

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- Standard energy derivative f
  shape optimization, pressure
- Finite-difference implementa
  shape optimization exist but
- Analytical implementation: (S
  faster, but unfortunately a lo

Formulas for analytical stress

$$\sigma_{ij} = \sigma_{ij}^{\mathrm{HF}} + \sigma_{ij}^{\mathrm{MP}} + \sigma_{ij}^{\mathrm{Pulay}} + \sigma_{ij}^{\mathrm{kin}} + \sigma_{ij}^{\mathrm{Jac}}.$$

$$\sigma_{ij}^{\mathrm{HF}} = \frac{1}{2V}\sum_{\alpha,\beta\neq\alpha}\frac{\partial v_{\beta}^{\mathrm{es,tot}}(|\mathbf{R}_\alpha-\mathbf{R}_\beta|)}{\partial R_i^\alpha}(\mathbf{R}_\alpha-\mathbf{R}_\beta)_j$$

$$\sigma_{ij}^{\mathrm{MP}} = \frac{1}{V}\sum_{\alpha}\int_{\mathrm{UC}}\mathrm{d}\mathbf{r}\left[n(\mathbf{r})-\frac{1}{2}n_{\mathrm{MP}}(\mathbf{r})\right]\frac{\partial v_{\alpha}^{\mathrm{es,tot}}(|\mathbf{r}-\mathbf{R}_\alpha|)}{\partial r_i}(\mathbf{r}-\mathbf{R}_\alpha)_j$$

$$-\frac{1}{2V}\sum_{\alpha}\int_{\mathrm{UC}}\mathrm{d}\mathbf{r}\,\frac{\partial n_{\alpha}^{\mathrm{MP}}(\mathbf{r}-\mathbf{R}_\alpha)}{\partial r_i}(\mathbf{r}-\mathbf{R}_\alpha)_j v_{\mathrm{es,tot}}(\mathbf{r})$$

$$\sigma_{ij}^{\mathrm{Pulay}} = \frac{2}{V}\sum_{k}\sum_{\alpha,l(\alpha)}\sum_{\beta,m(\beta)} f_k c_{kl} c_{km}\int_{\mathrm{UC}}\mathrm{d}\mathbf{r}\,\frac{\partial\varphi_l(\mathbf{r}-\mathbf{R}_\alpha)}{\partial r_i}(\mathbf{r}-\mathbf{R}_\alpha)_j\left[\hat{h}_{\mathrm{KS}}-\varepsilon_k\right]\varphi_m(\mathbf{r}-\mathbf{R}_\beta)$$

$$\sigma_{ij}^{\mathrm{kin}} = \frac{1}{V}\sum_{k}\sum_{\alpha,l(\alpha)}\sum_{\beta,m(\beta)} f_k c_{kl} c_{km}\int_{\mathrm{UC}}\mathrm{d}\mathbf{r}\,\varphi_l(\mathbf{r}-\mathbf{R}_\alpha)(\mathbf{r}-\mathbf{R}_\alpha)_j\left[\frac{\partial}{\partial r_i}\frac{\partial}{\partial r_j}\varphi_m(\mathbf{r}-\mathbf{R}_\beta)\right]$$

$$\sigma_{ij}^{\mathrm{Jac}} = \frac{1}{V}\delta_{ij}\left[E_{\mathrm{xc}}[n]-\int\mathrm{d}\mathbf{r}\,n(\mathbf{r})v_{\mathrm{xc}}(\mathbf{r})-\frac{1}{2}\int\mathrm{d}\mathbf{r}\,n_{\mathrm{MP}}(\mathbf{r})v_{\mathrm{es,tot}}(\mathbf{r})\right]$$

Another "most wanted" feature: Analytical stress tensor

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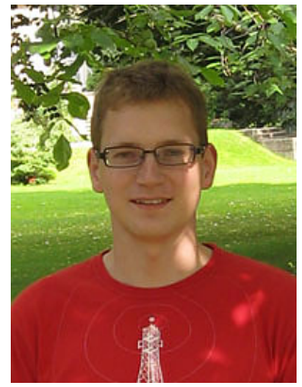
Christian Carbogno

Viktor Atalla



Franz Knuth

The analytical stress tensor is now here ...

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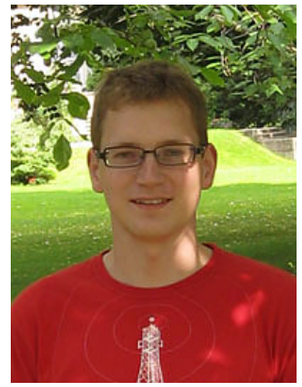

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…istian Bogno

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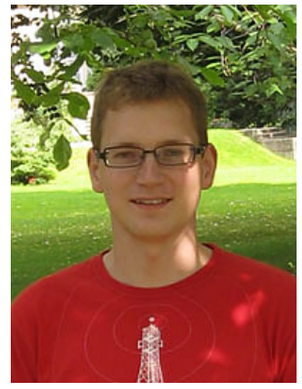
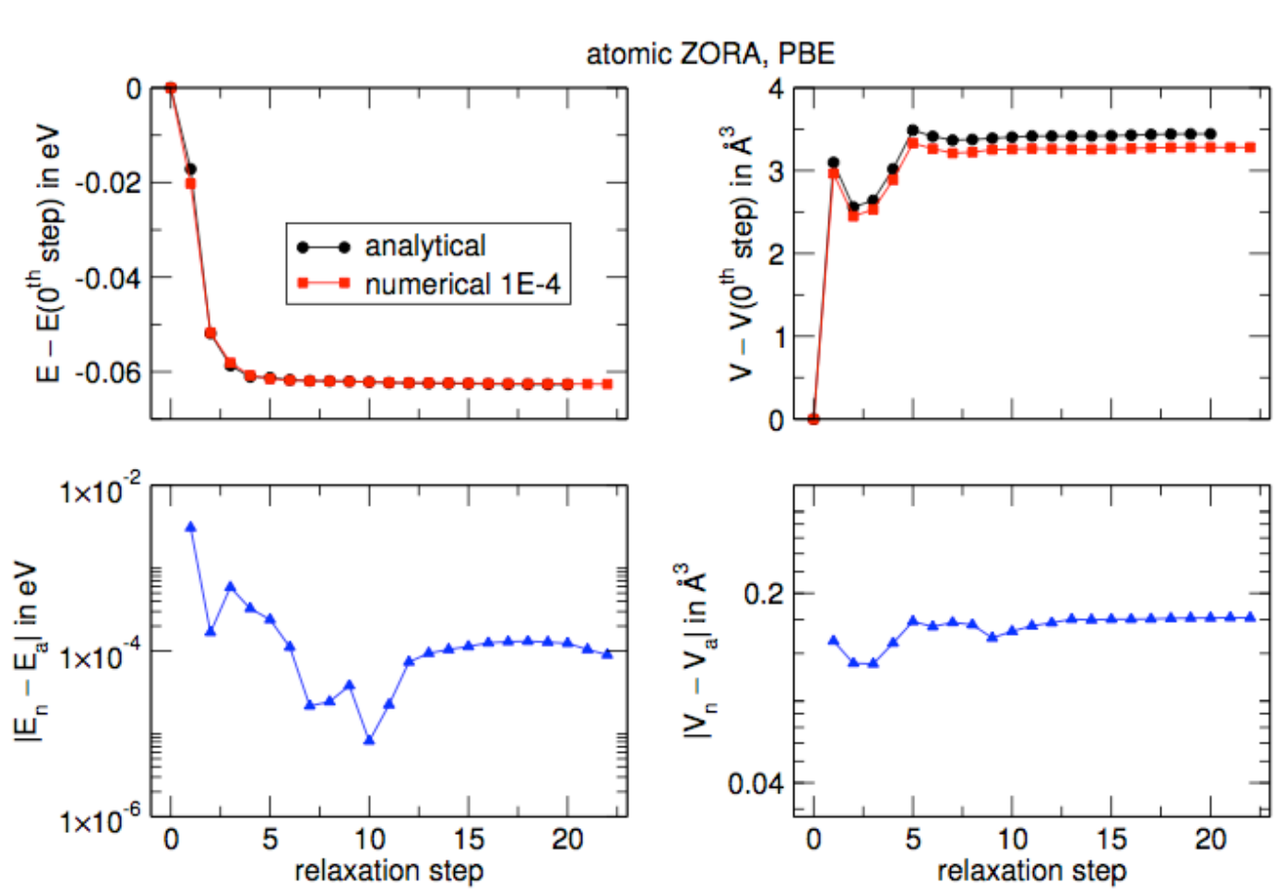
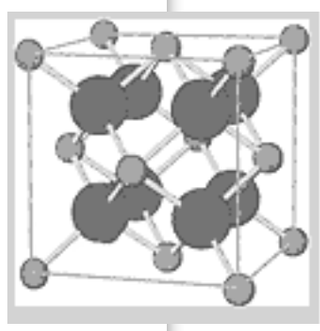


Franz Knuth

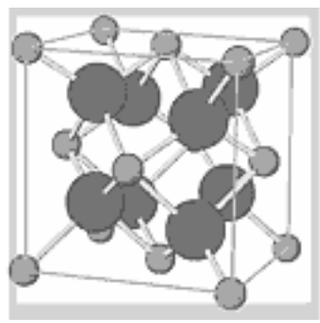
2) Relaxation of ZrO_2 monoclinic – 12 atoms

Starting geometry is near equilibrium

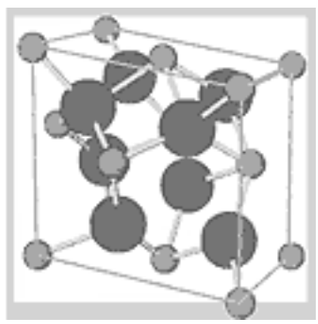




ZrO_2 cubic



ZrO_2 tetragonal



ZrO_2 monoclinic

http://www.keramverband.de

... and next?

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Christian Carbogno

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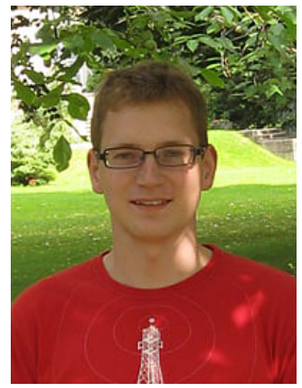


Franz Knuth

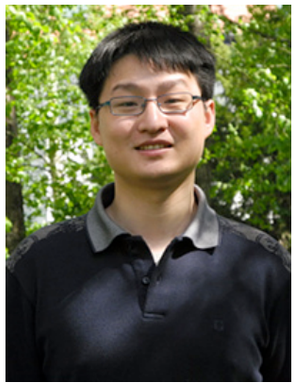
- ... works for LDA, GGA[+vdW]
- Unit cell shape relaxation, constant pressure thermostats?
- Next: Hybrid functionals (so far, stress by finite differences)
- Numerical improvements? (speed?)
- ... in general, second energy derivatives are needed.

“Beyond LDA / GGA / mGGA / hybrids”

Current DFT may fail with or without warning,
even qualitatively (for structure).
How to go beyond?

Xinguo Ren

Fabio Caruso



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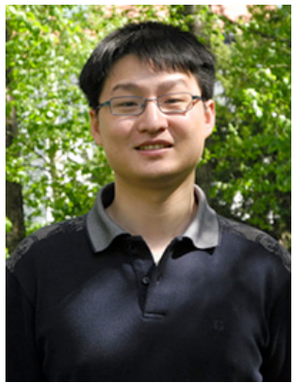
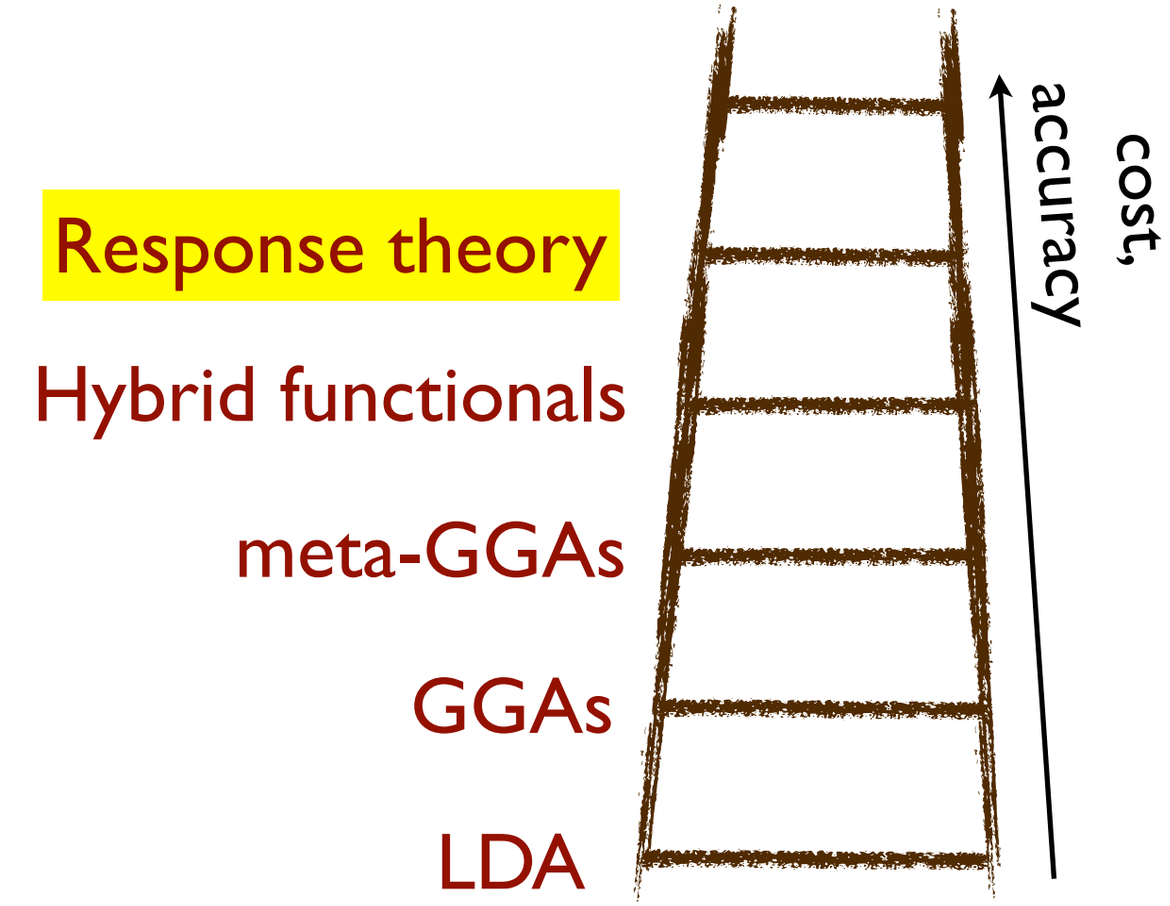


Igor Zhang

“Perdew’s ladder”
to exact solution



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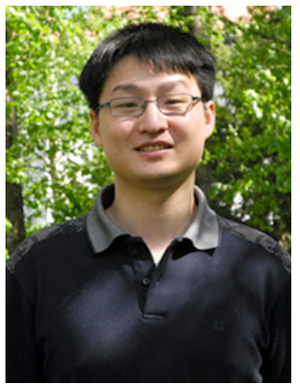

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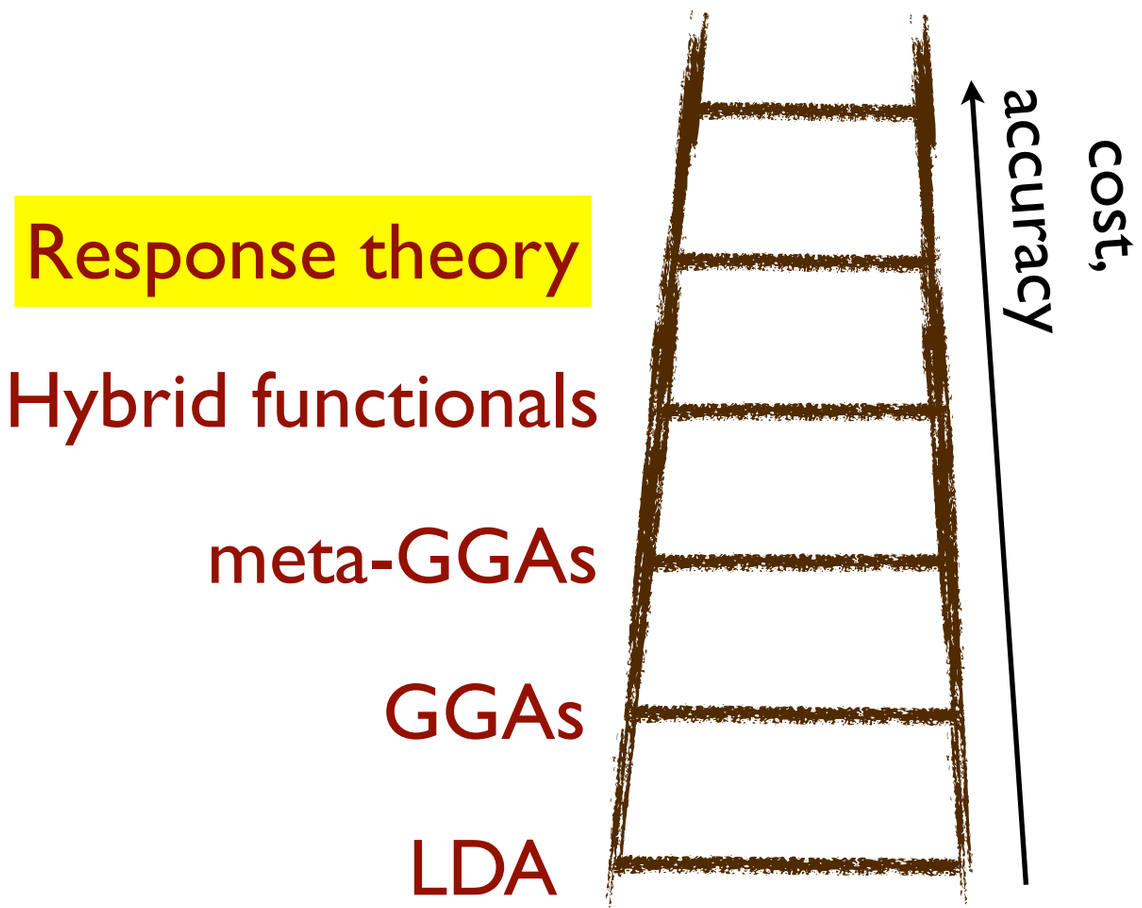


- Renormalized second-order perturbation theory ("rPT2"): RPA+rSE+SOSEX

  Xinguo Ren, Wed. 11:15 h

- Self-consistent *GW*

  Fabio Caruso, Wed. 11:50 h

- Doubly-hybrid functionals

  Igor Zhang, Fri. 09:35 h

Where MBPT makes a difference: Ce

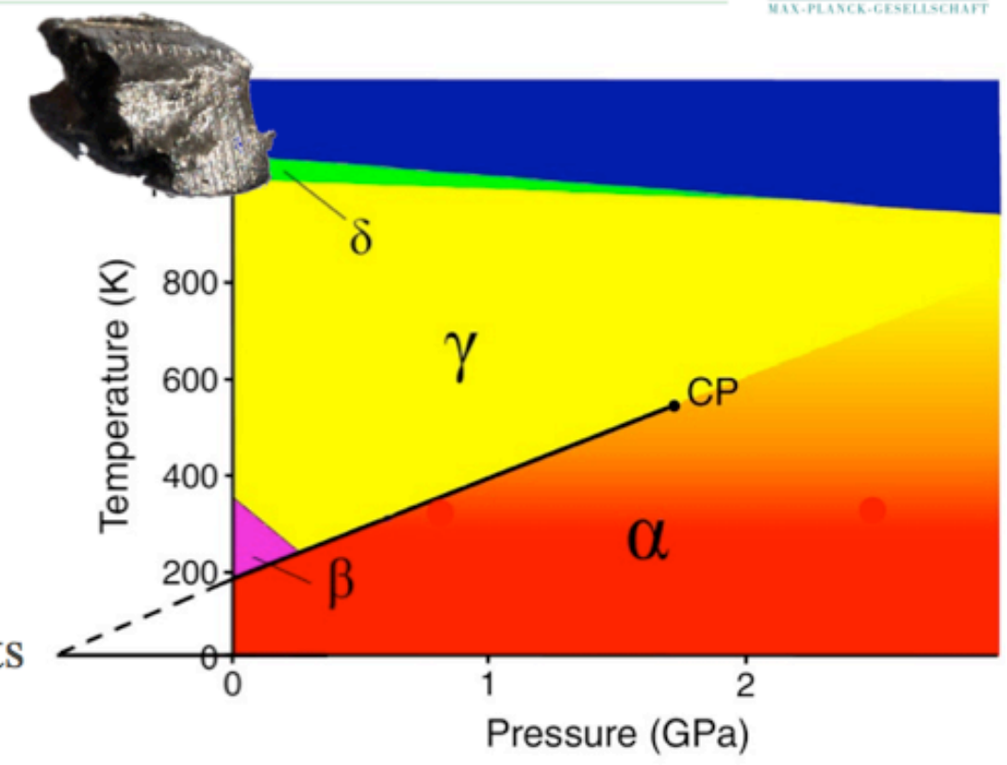
Casadei, Ren, Rinke, Rubio, Scheffler, PRL 2012

Marco Casadei

Cerium

- First of the lanthanide elements
- 58 electrons, one electron in the *4f* states
- Very abundant in the earth crust
- Growing interest for application

- Isostructural (fcc→fcc) α-γ phase transition
- Accompanied by volume collapse of 15-17% at room temperature
  - High volume γ phase → magnetic moments
  - Low volume α phase → paramagnetic



* Krisch M. et al., Proc. Natl. Acad. Sci. USA. 108, 9342 (2011)

- LDA, GGA → capable of describing only the α-phase, *4f* electrons are always at the Fermi level (self-interaction problem)
- SIC-LSD, LDA+U → add non local potential to localized electrons, capable of describing only the γ-phase
- LDA+DMFT → results for high temperature

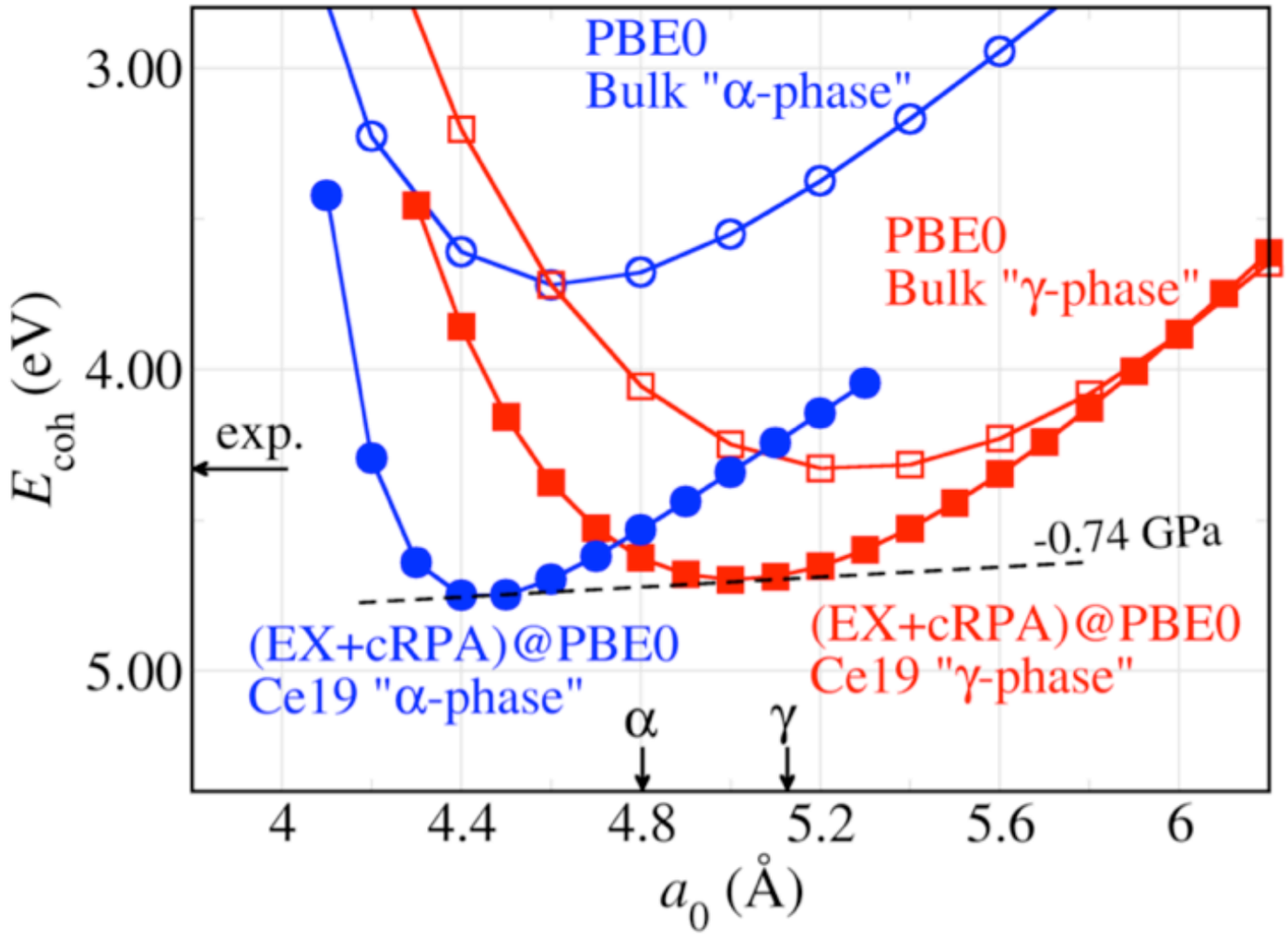
Where MBPT makes a difference: Ce

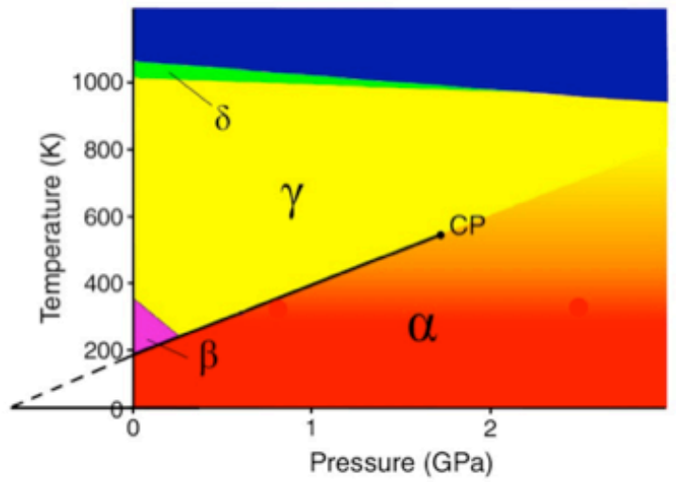
Casadei, Ren, Rinke, Rubio, Scheffler, PRL 2012

EX+cRPA@PBE0

Marco Casadei

- Correct phase ordering





... and "beyond electronic structure"?

25 ps Born-Oppenheimer molecular dynamics, "tight"(!), DFT-PBE+vdW

<u>Here:</u>

Infrared multiphoton dissociation spectroscopy, FELIX free electron laser

Room temperature

$$I(\omega) \propto \omega^2 \int_{\infty}^{\infty} dt \, \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{} \, e^{iwt}$$

dipole-dipole time correlation function

see, e.g., M.-P. Gaigeot, others

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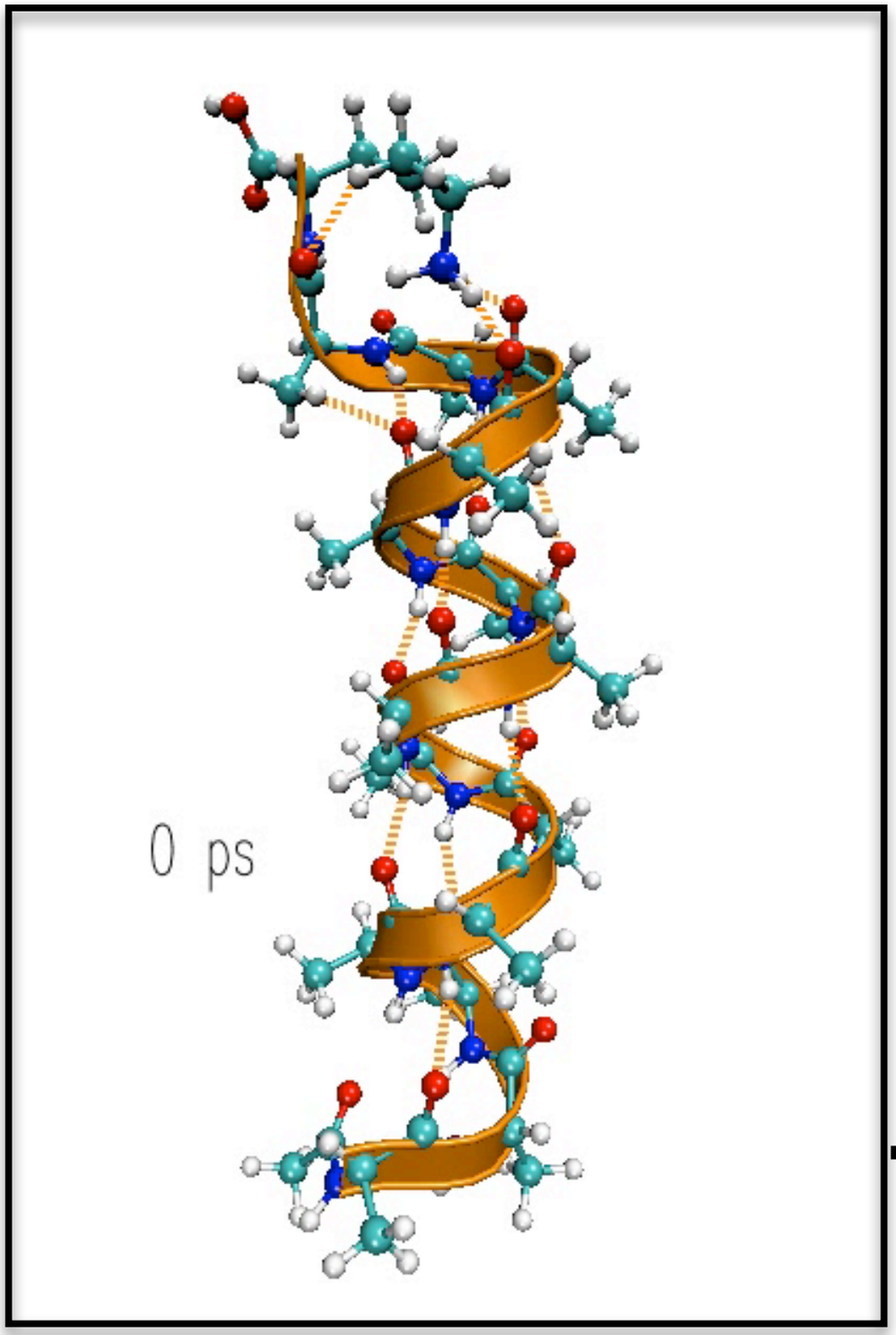

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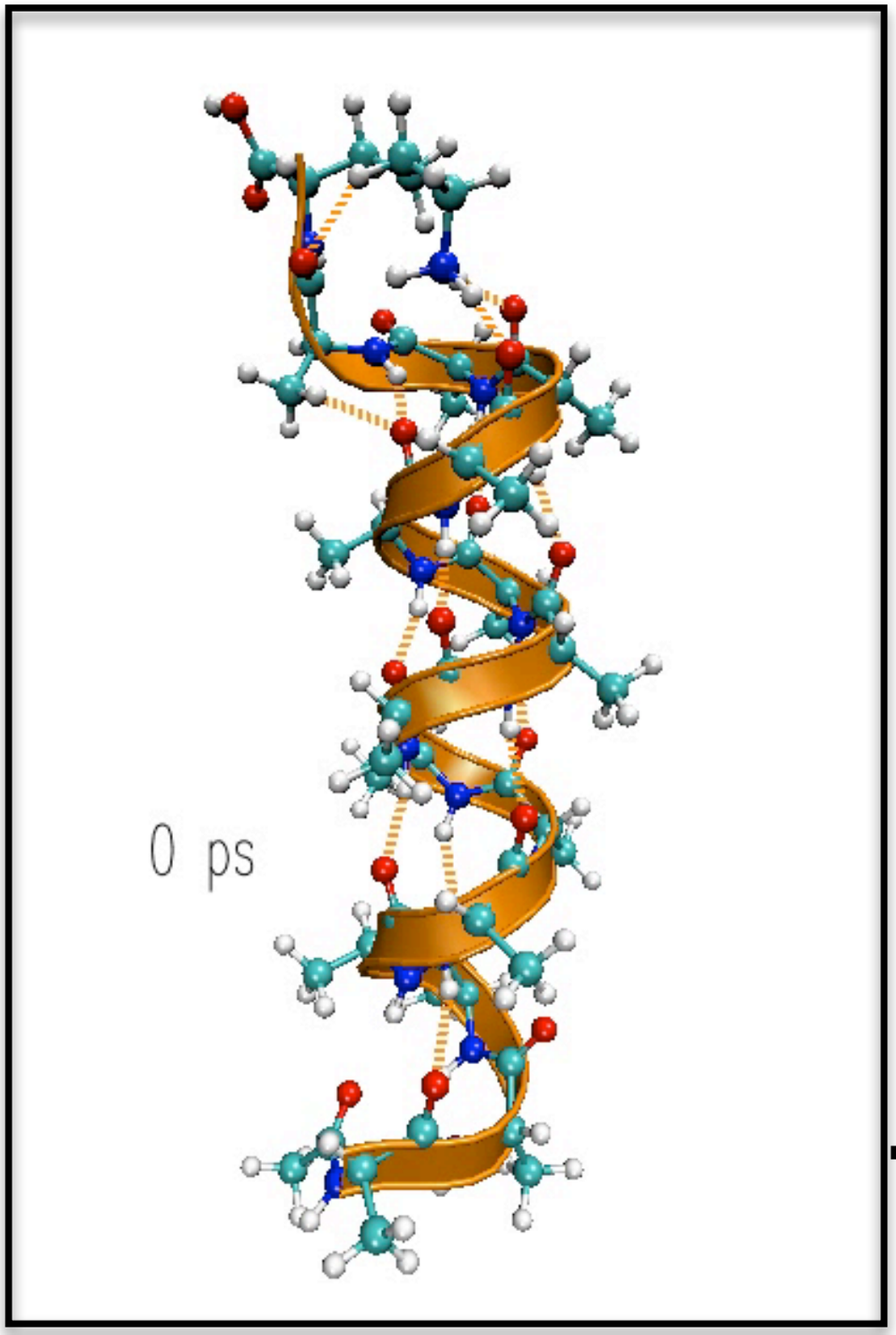

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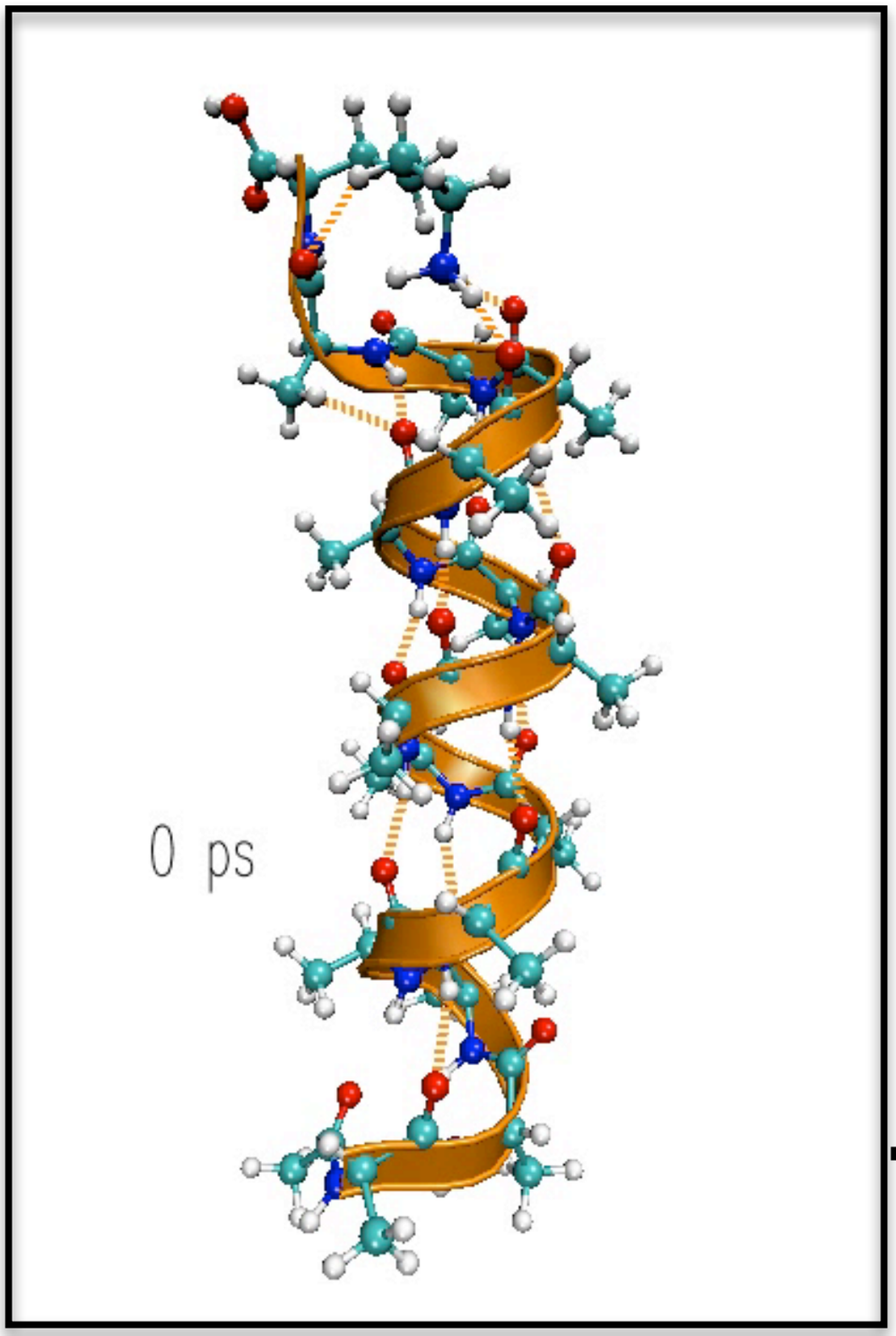

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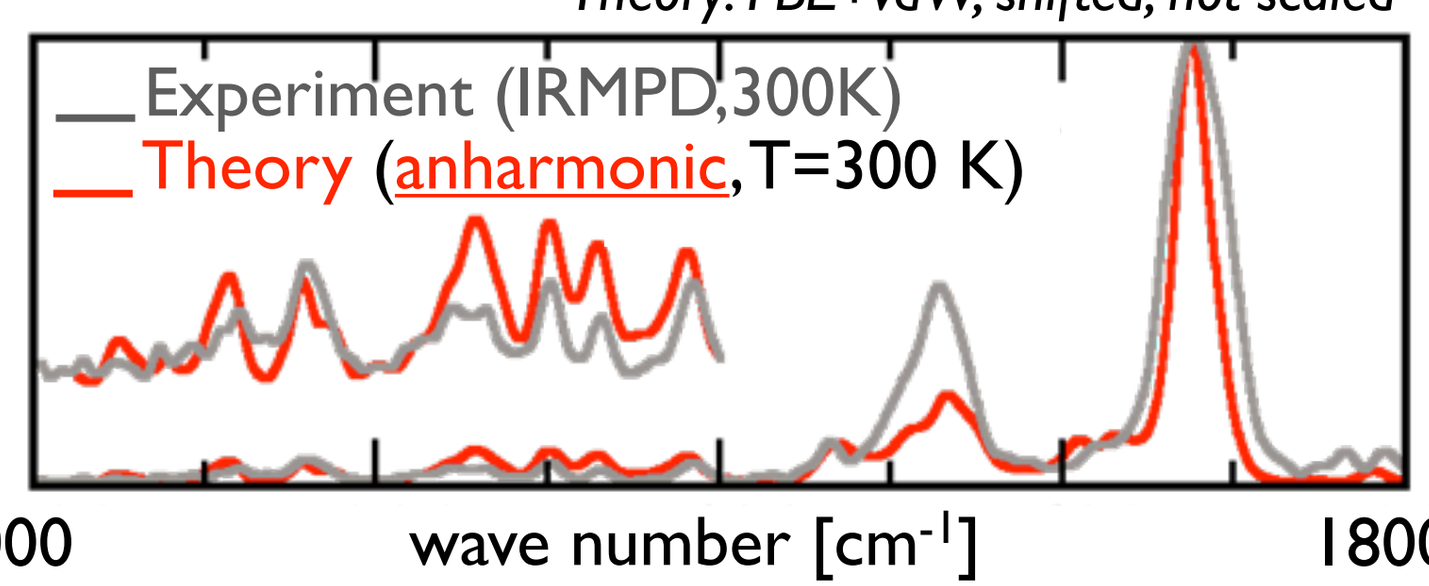
Theory: PBE+vdW, shifted, not scaled



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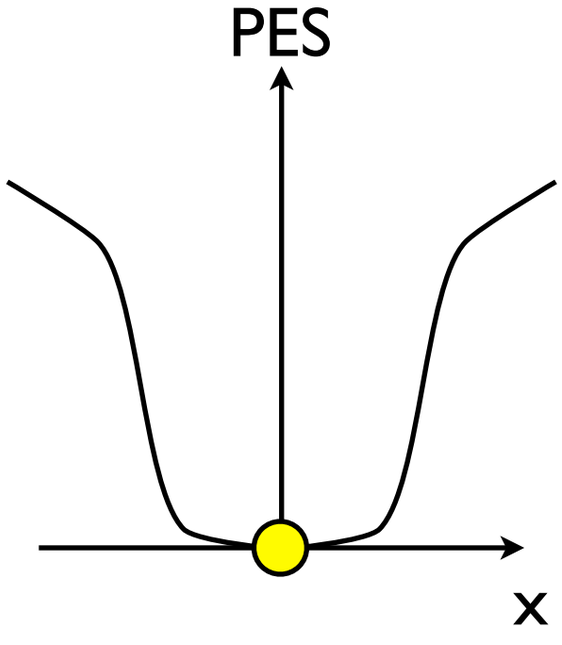
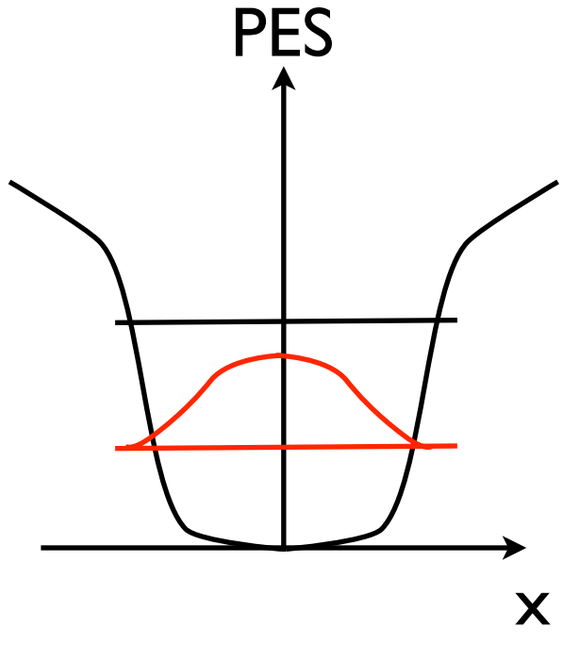
But nuclei are not classical particles!





Mariana Rossi

Xin-Zheng Li

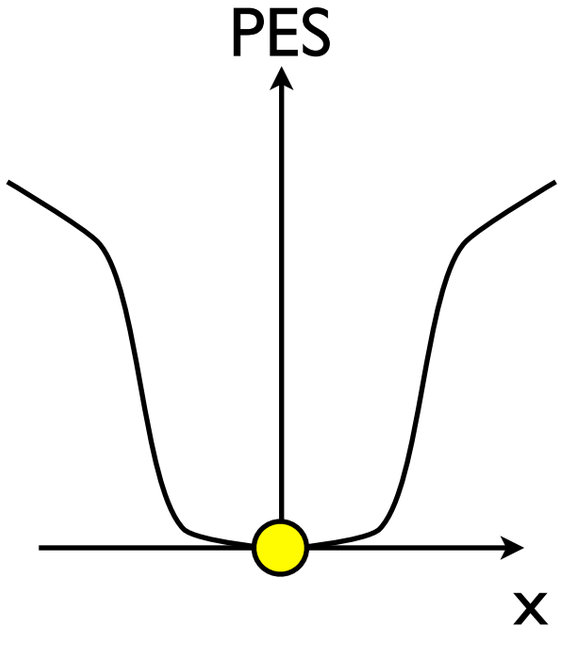
Classical system, T=0:
$\Delta x=0, \Delta p=0$

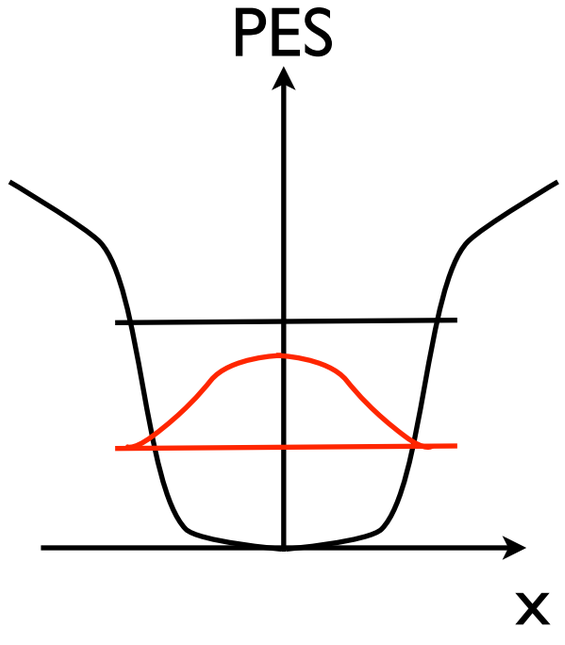
Quantum system, T=0:
$\Delta x\neq 0, \Delta p\neq 0$

<u>Especially affected: Hydrogen-bonded systems (protons!)</u>

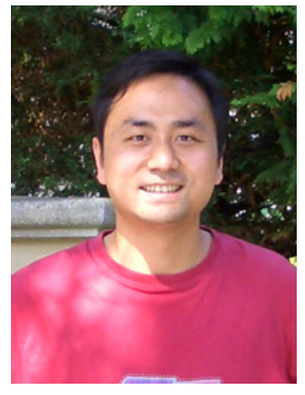
- Finite-temperature effects?
- Statistical averages? (free energy?)
- Dynamical quantities?

But nuclei are not classical particles!





Mariana Rossi



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<u>Two recent additions (any T≠0):</u>

1) Colored-noise thermostat, keep quantum nuclear momentum distribution
(Parrinnello, Ceriotti, Bussi)

Mariana Rossi, Thu. 09:35 h

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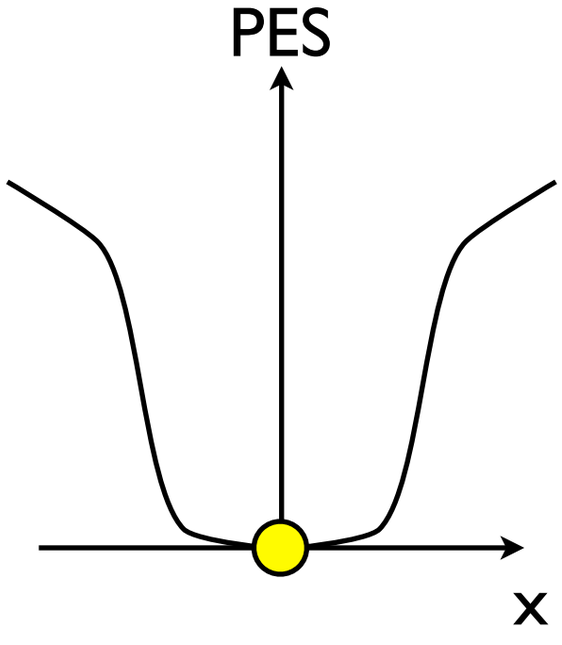

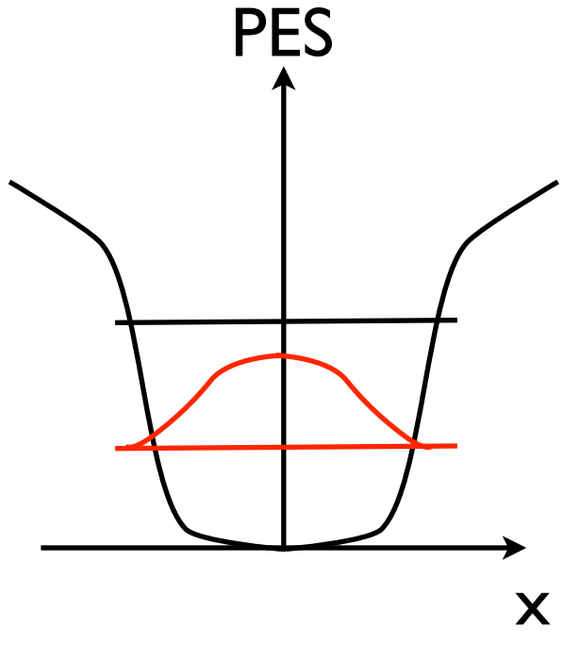

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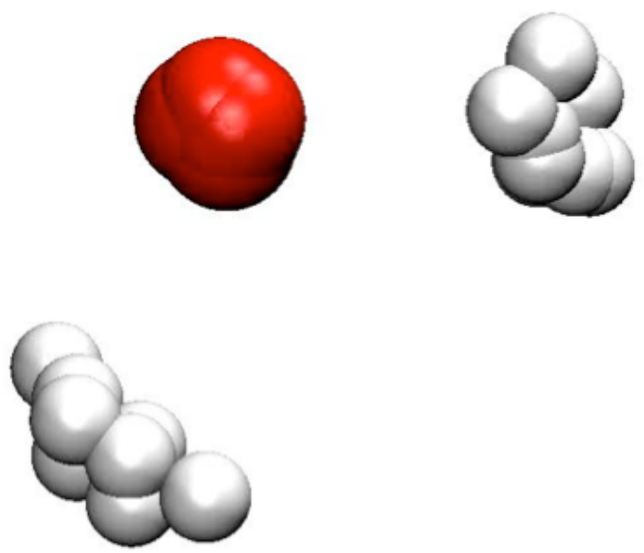
Mariana Rossi, Thu. 09:35 h

2) Path-integral molecular dynamics

Xin-Zheng Li, Poster



Large-scale surface reconstruction: Graphene on SiC

Even for conceptually simple materials or molecules, the *relevant* structures can be uncomfortably large.

Lydia Nemec

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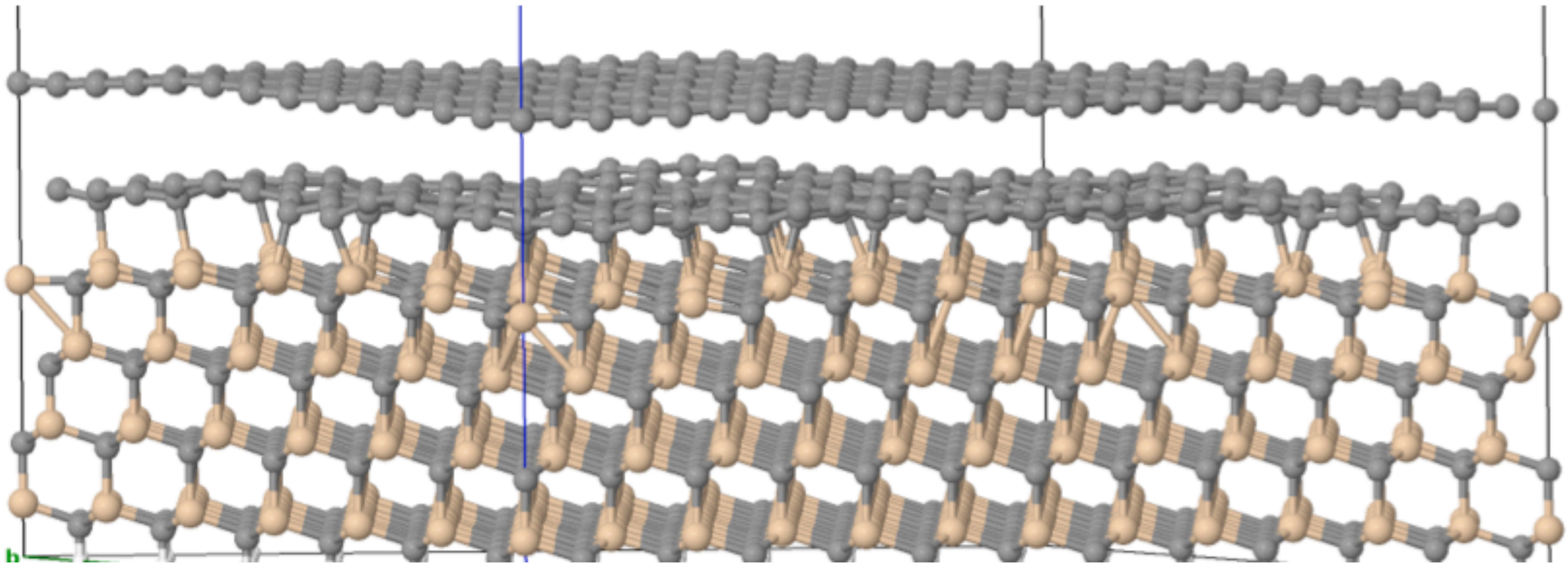

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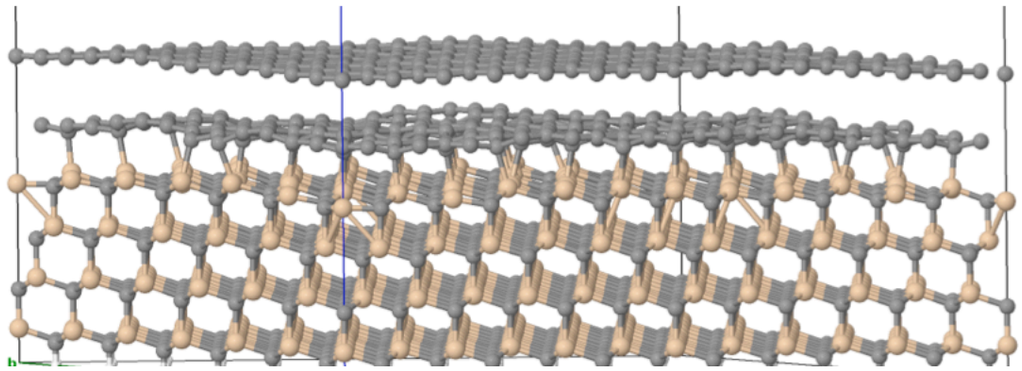

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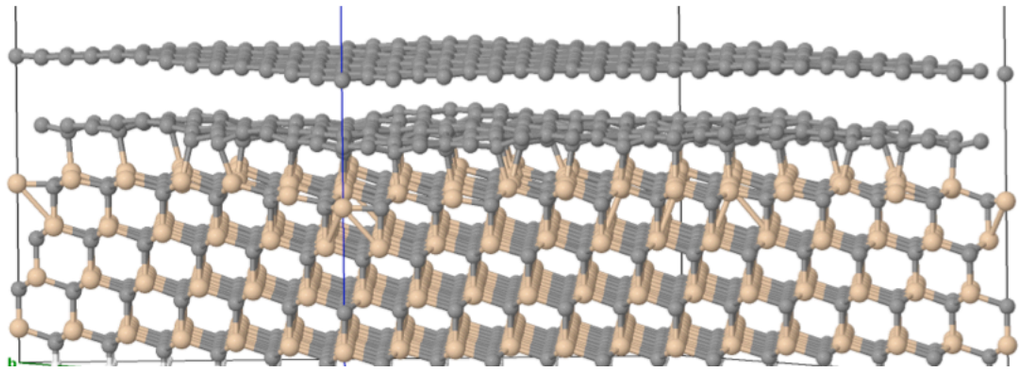

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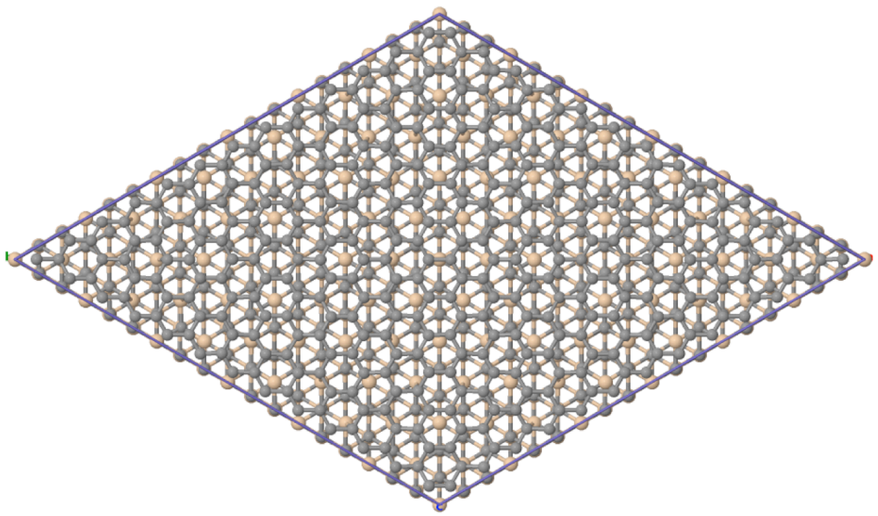

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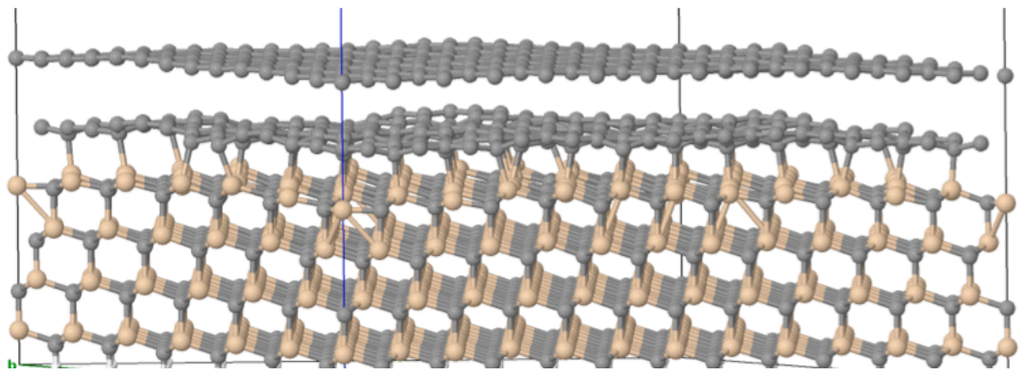

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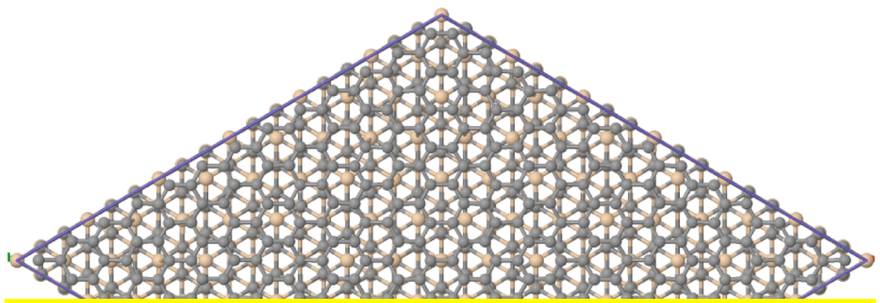

Surface energy? Strain?
Electronic effect of interface?
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Epitaxial graphene on a semiconducting substrate: SiC

Many ways to grow graphene: Exfoliation, growth on metals ...

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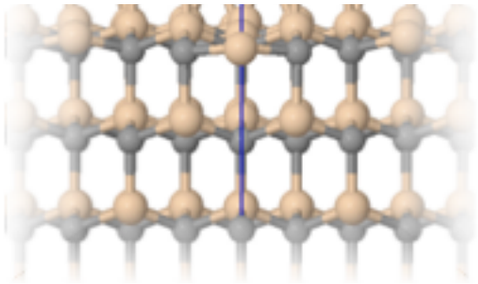

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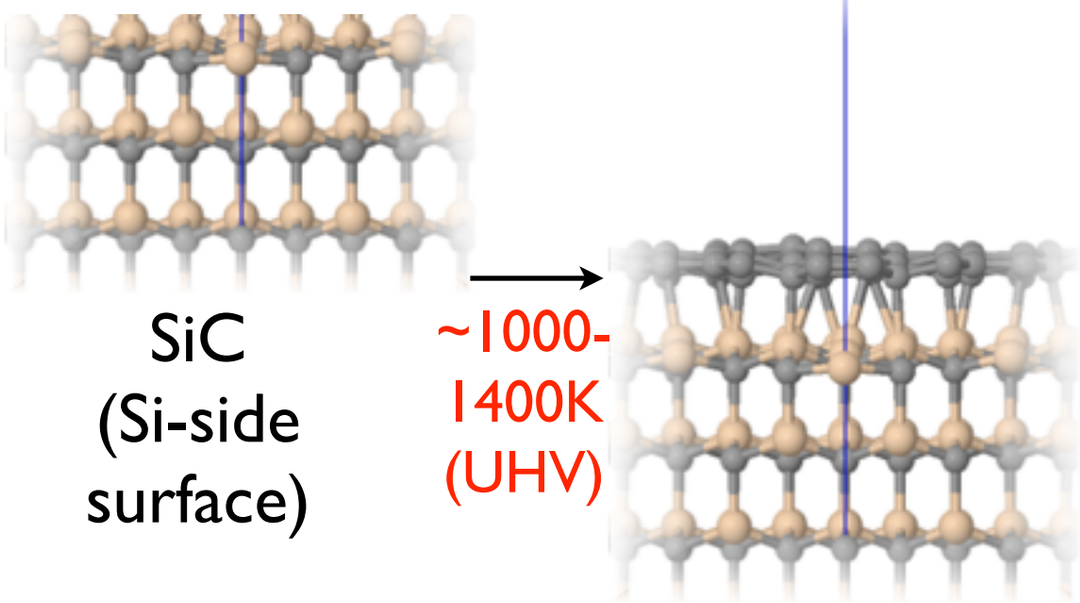

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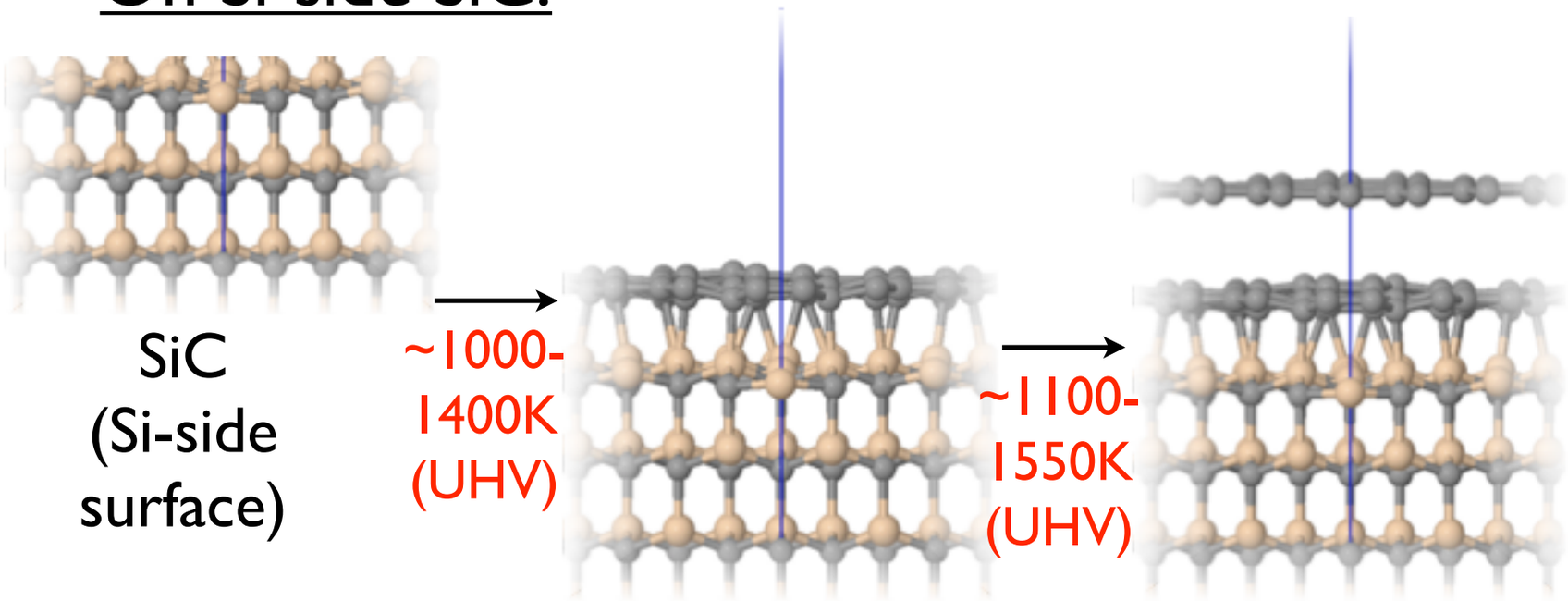

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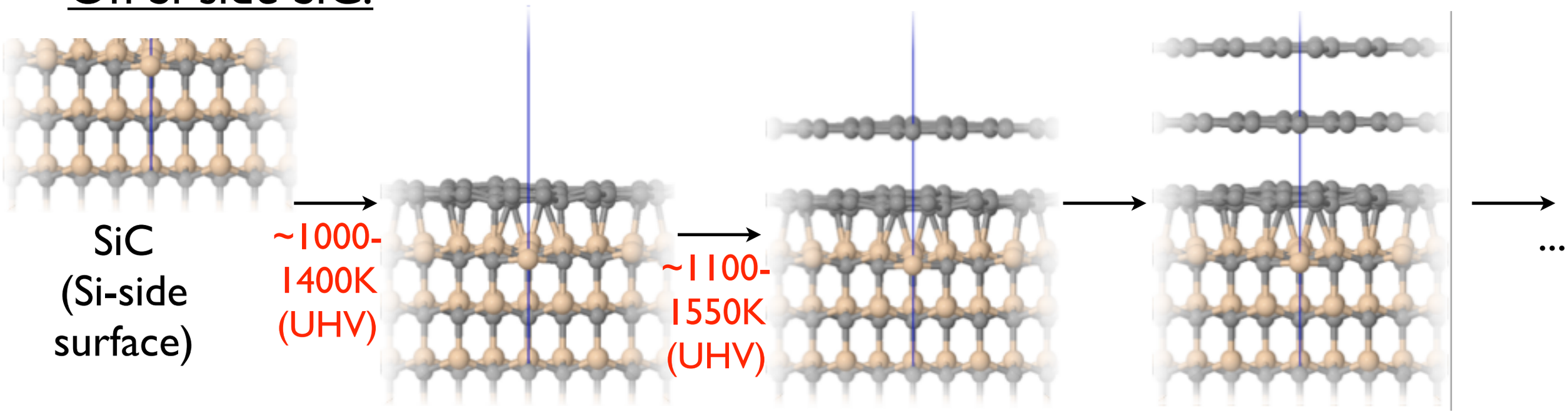

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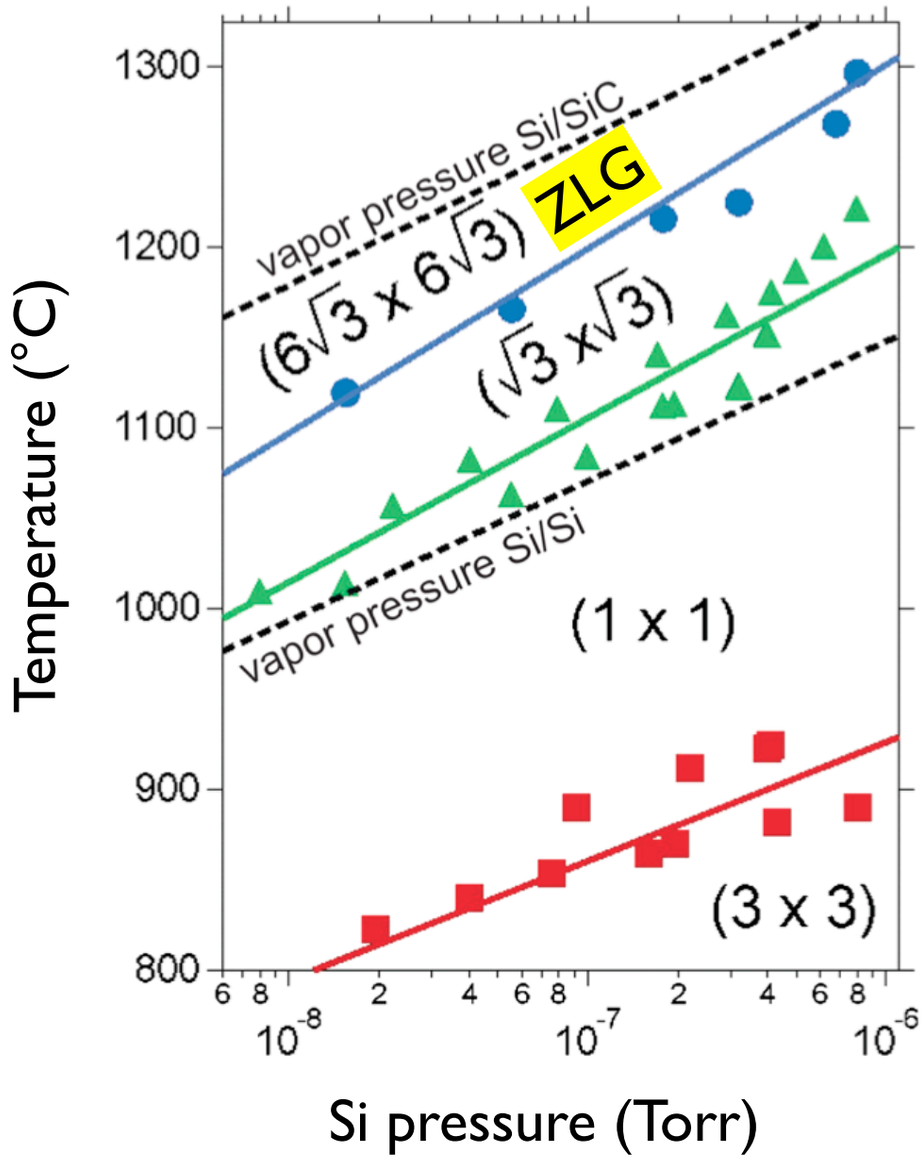

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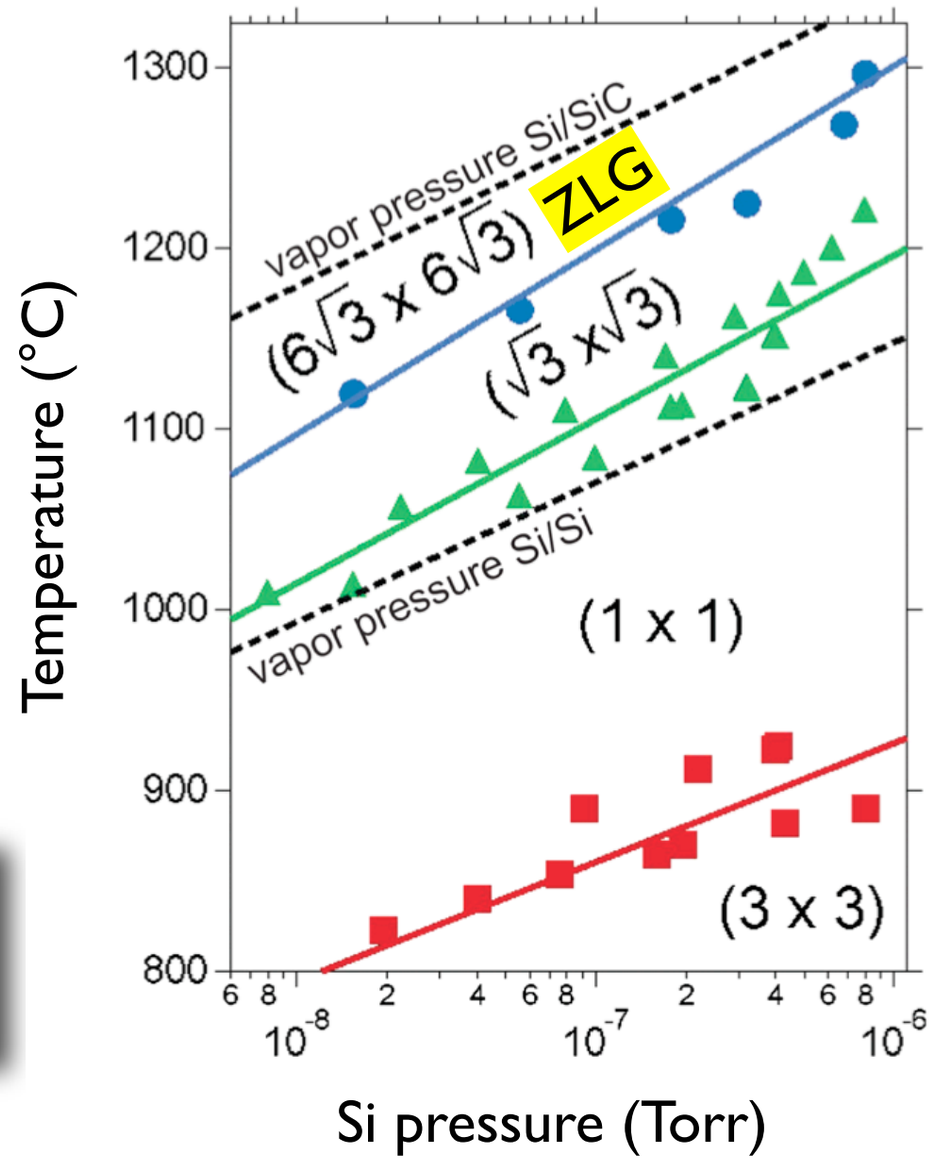
How close are MLG and BLG on SiC(111) to equilibrium phase growth?



Ab initio thermodynamics for Si-side graphene/SiC

Thermodynamic stability criterion for competing surface phases:

$$E_{\mathrm{surf}} = \frac{1}{A}\left[E_{\mathrm{slab}} - N_{\mathrm{Si}}\mu_{\mathrm{Si}} - N_{\mathrm{C}}\mu_{\mathrm{C}}\right]; \quad E_{\mathrm{SiC}} = \mu_{\mathrm{Si}} + \mu_{\mathrm{C}}$$

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- full relaxation, "tight" numerical settings (C: tier 2, Si: tier1+*gd*)
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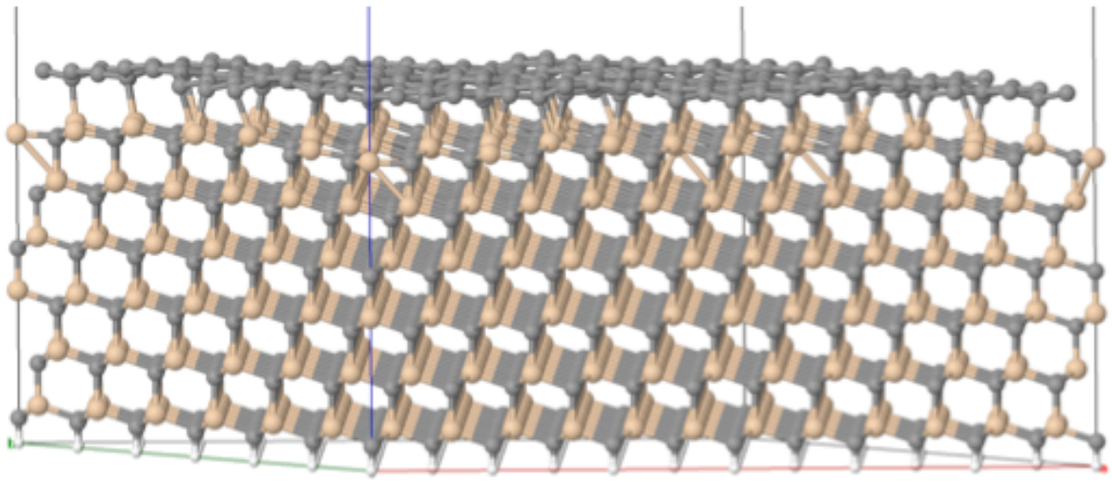
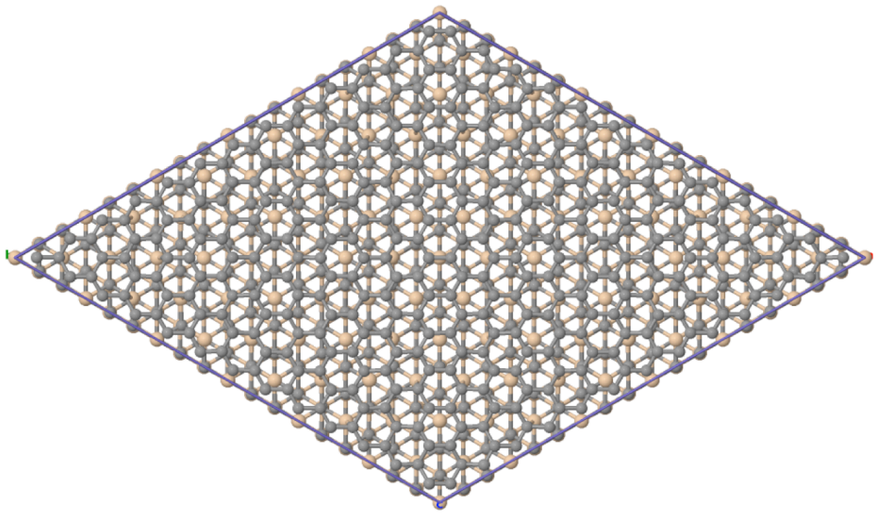


ZLG, side view



Commensurate growth -
nearly strain-free (0.2%), but large:
1742 atoms (ZLG) - 2756 atoms (3LG)

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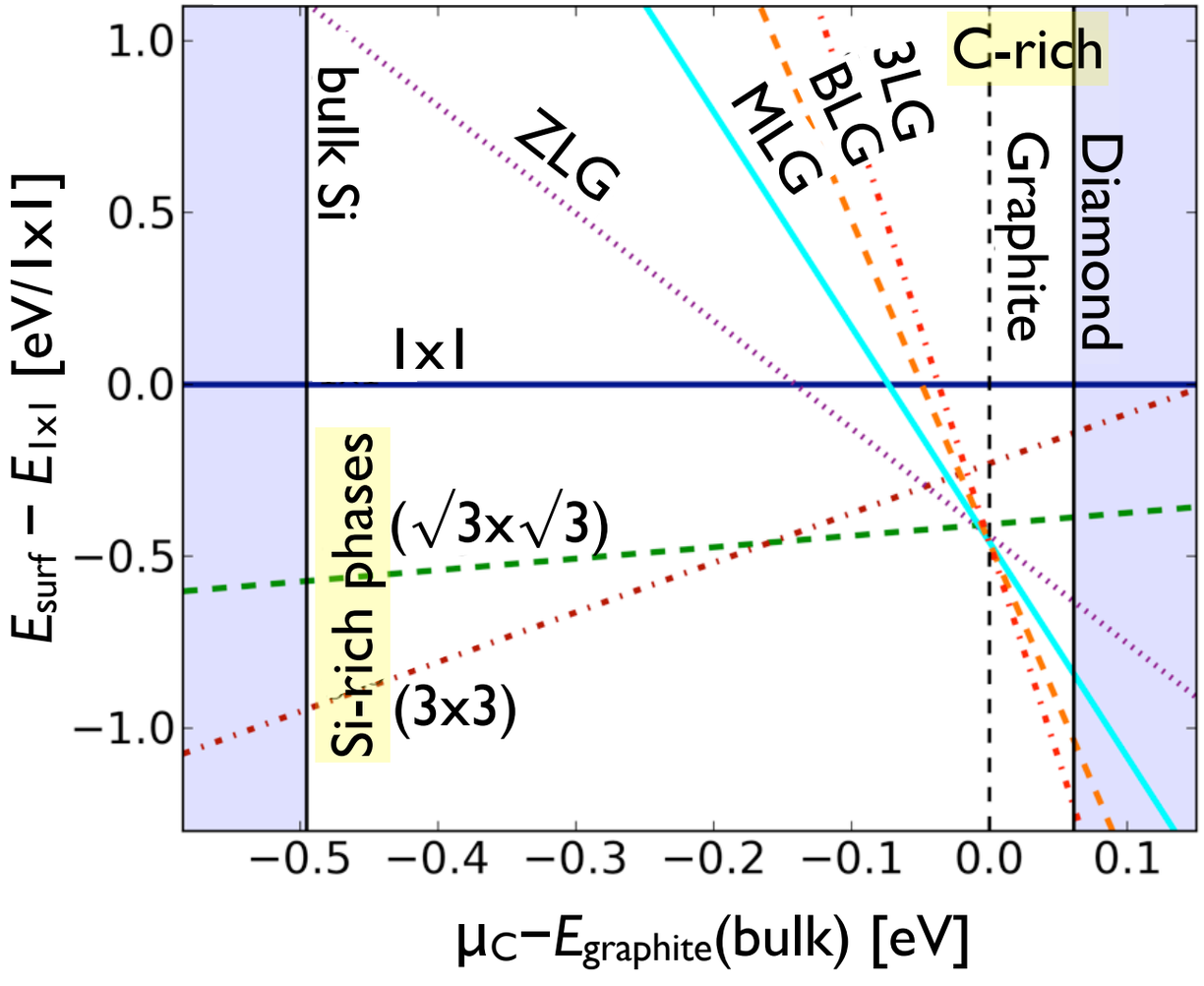
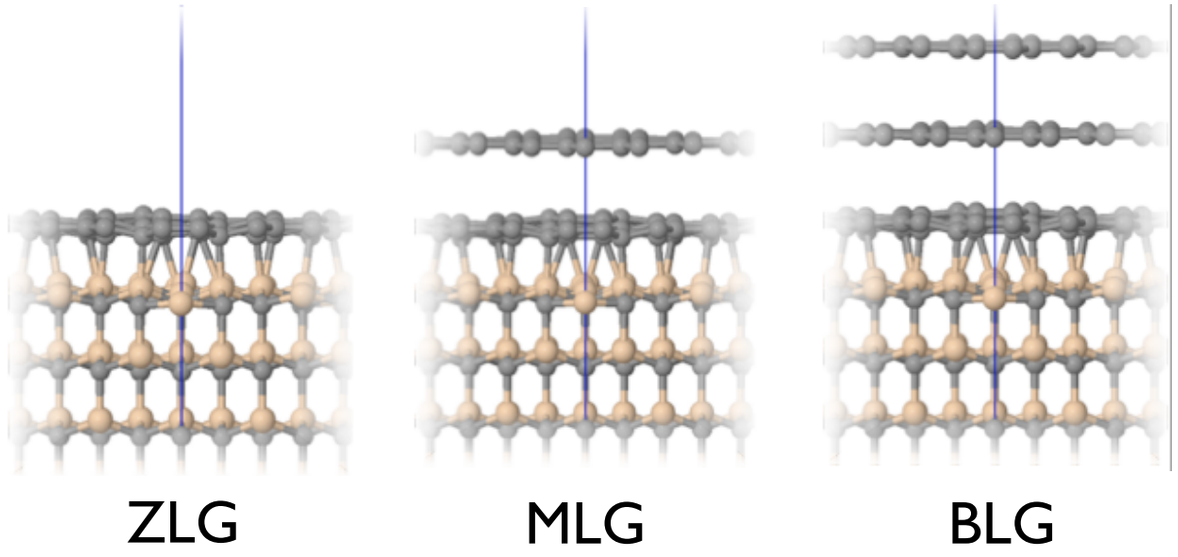
Surface energy hierarchy: 3C-SiC(111)

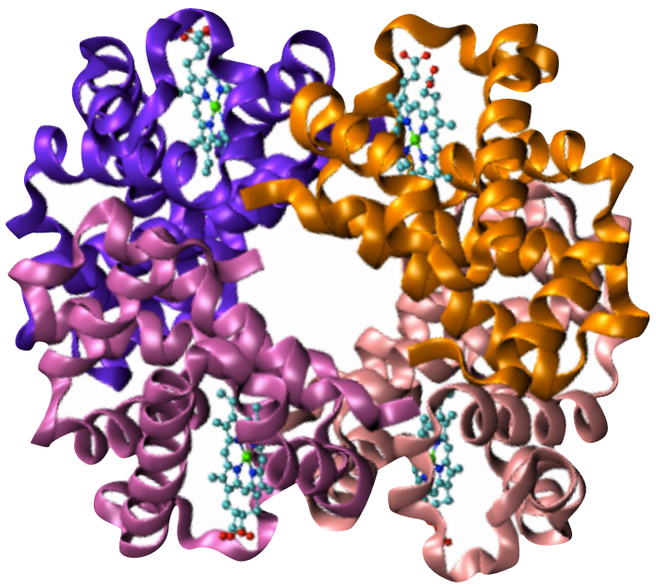




ZLG MLG BLG

So which (computational) challenges are next?

Molecular world



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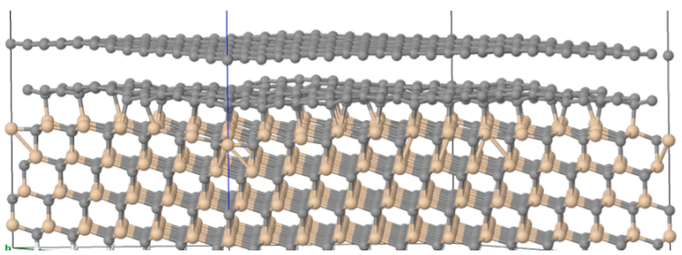

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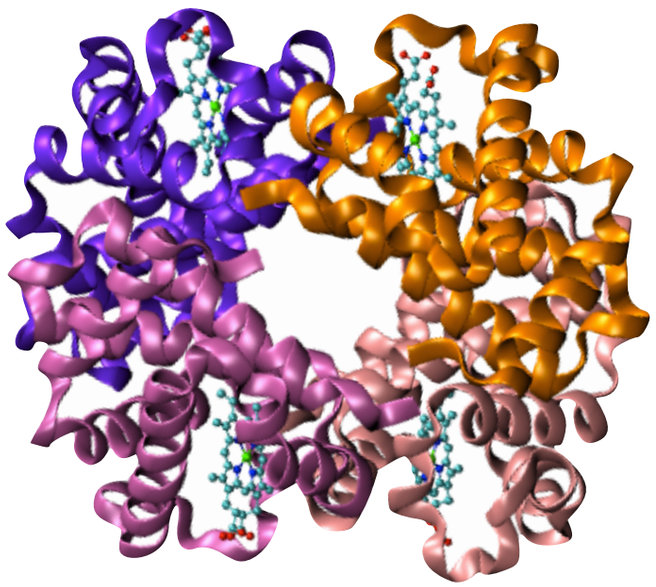

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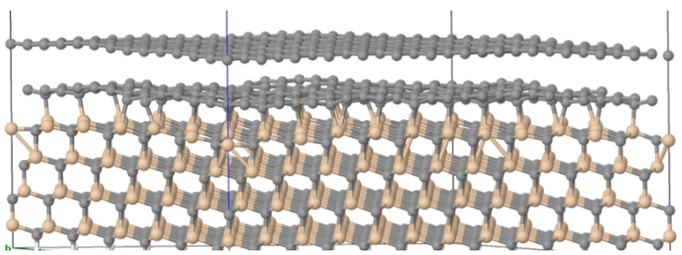

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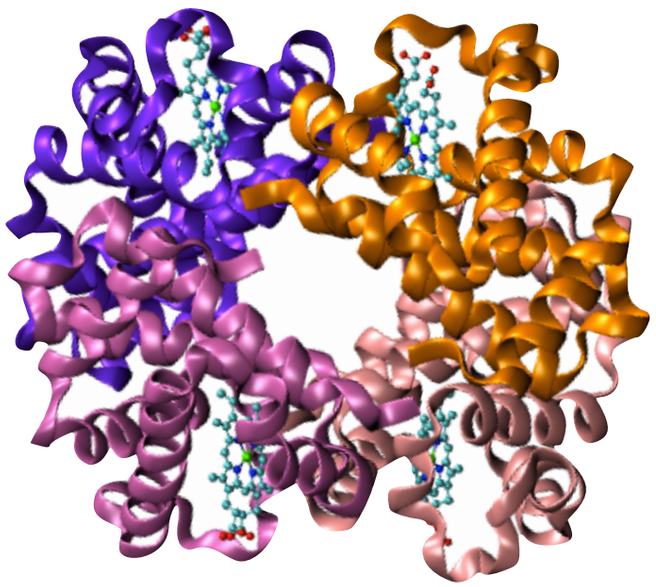

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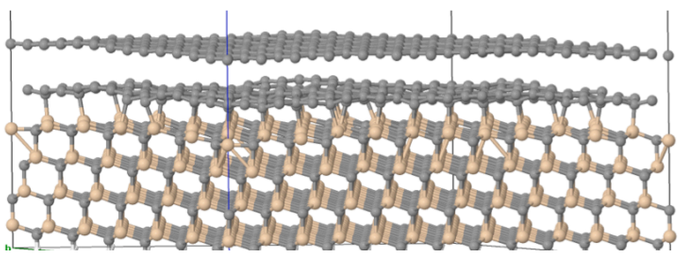

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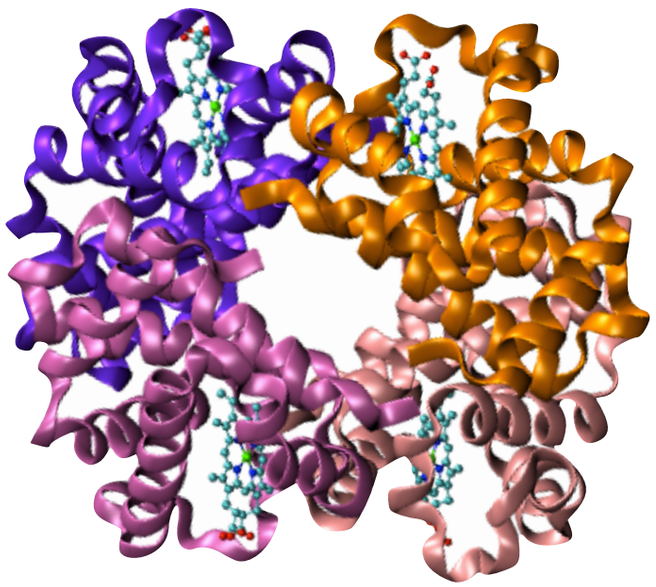

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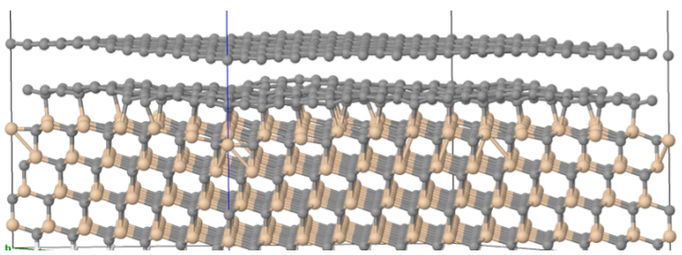

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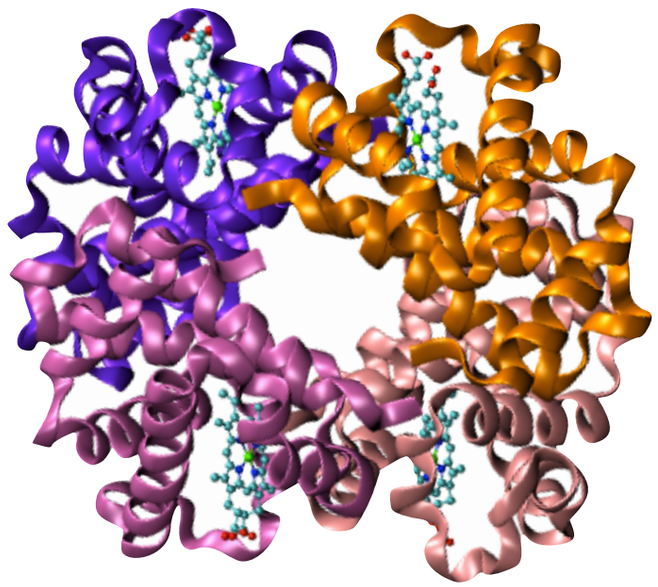

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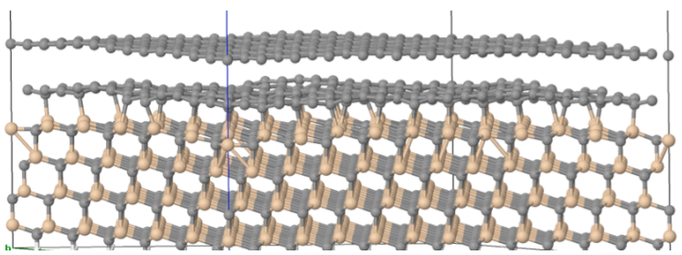

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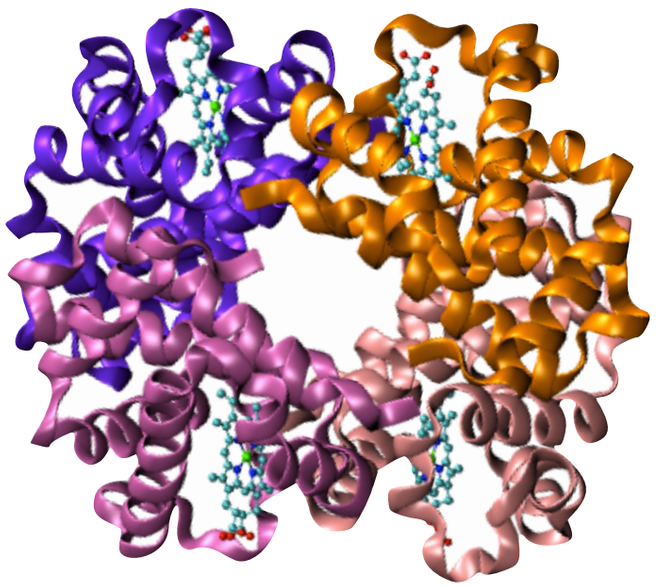

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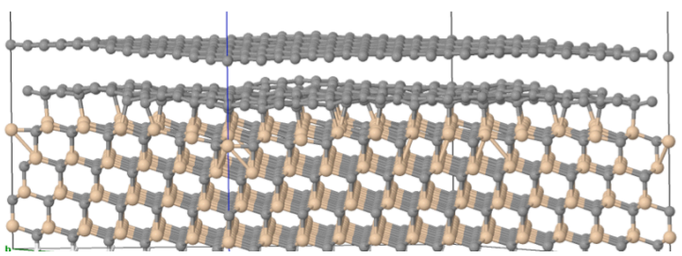

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- Standard and non-standard functionals: LDA, GGA, hybrid functionals, van der Waals, many-body perturbation theory (RPA, MP2, *GW*)
- Non-periodic and periodic systems (molecules and solids) on equal footing
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- "Properties and function":

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Computer Physics Communications ***180****, 2175-2196 (2009)* - *http://aims.fhi-berlin.mpg.de/*

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