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Educational, Scientific and
Cultural Organization

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Spring College on Computational Nanoscience

17 - 28 May 2010

Computational Science as Nanotechnology Pillar

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Spring College in Computational Nanoscience
Trieste, May 17-28, 2010

Aalto University

Computational Science as Nanotechnology Pillar

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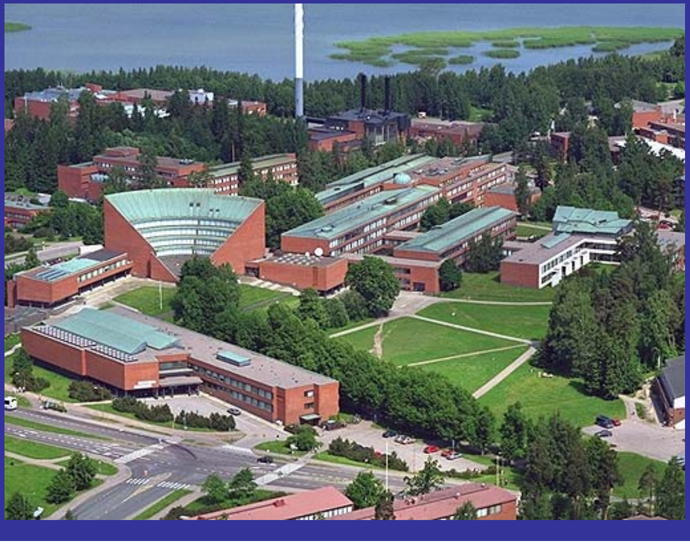


The three pillars of nanoscience and -technology

Manufacture and manipulation

"top-down":
lithography

"bottom-up": self-assembly

Characterisation, imaging and probing

SPM
TEM
PES…

Theory, modelling and simulation

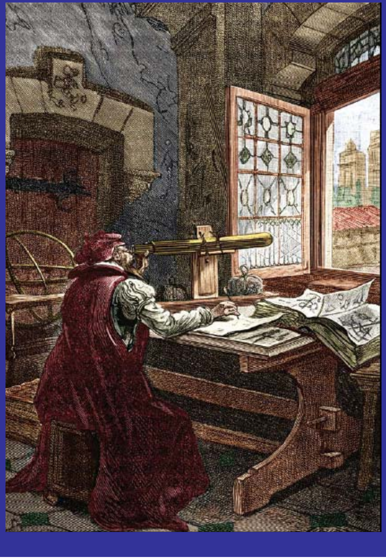
- Predictive computation of physical, chemical and biological functions
- Process design
- Interpretation of probe data

Computational nanoscience

Science Paradigms

- *A thousand years ago….*

Empirical, observational



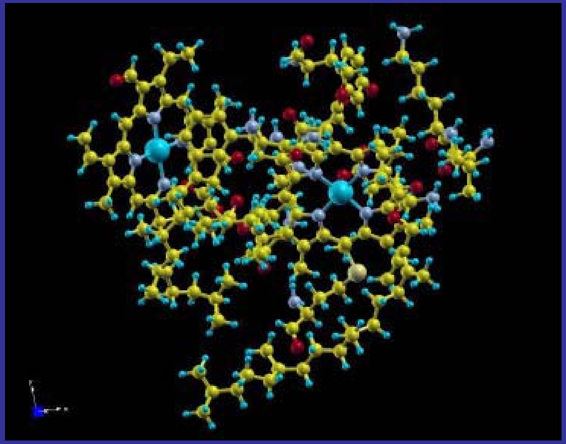
- *A few hundred years ago…*

Theoretical branch emerges

$$i\hbar\frac{\partial}{\partial t}u_{n\vec{k}}(\vec{r},t)=\left\{-\frac{\hbar^2}{2m}\left(\vec{\nabla}+i\vec{k}+\frac{ie}{\hbar c}\vec{A}(t)\right)^2+V(\vec{r},t)\right\}u_{n\vec{k}}(\vec{r},t)$$

- *A few decades ago …*

Computational branch emerges: simulating complex phenomena



- *Today …*

Data-centric branch emerges: unifies experiment, theory and simulation

Data management, mining and curation

Computational science

- Uses the capabilities of computers through the methodologies of scientific computing to solve scientific and engineering problems across all disciplines.

- Draws heavily on the advances in applied mathematics and computer science: numerics, graphics, complex optimisation, data structures, statistics *etc.*

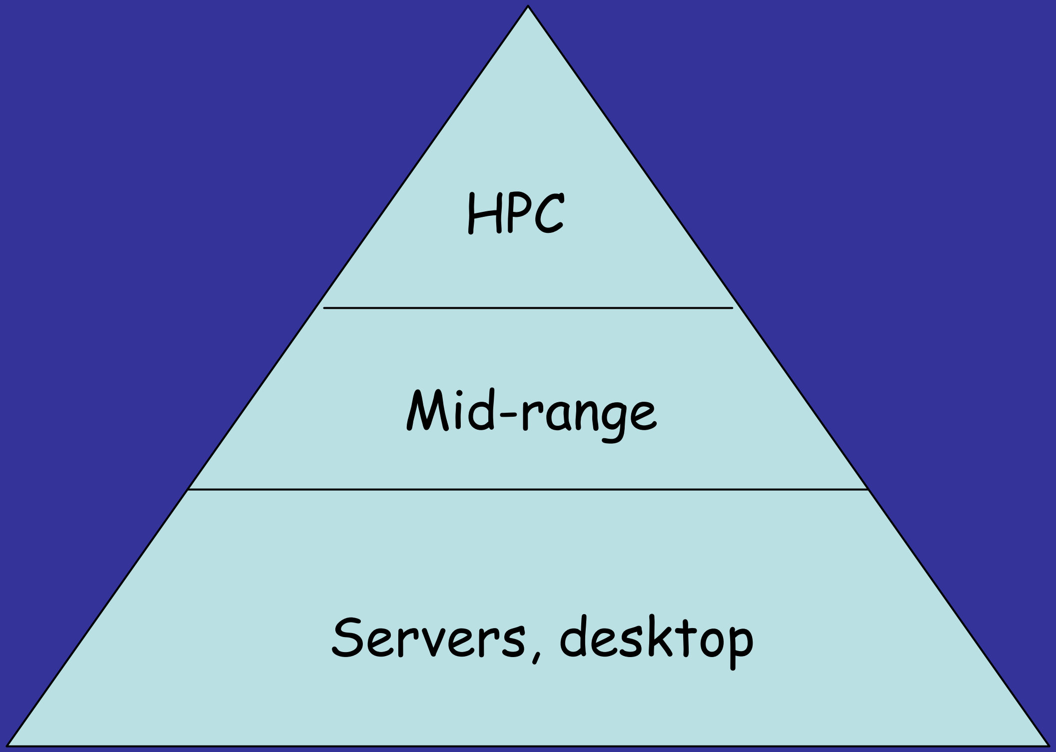
- Contributes to the emergence of data-intensive scientific enquiry.

Computational Science

Towards increasing complexity

- Nonlinearity
- Multi-scale problems
- Multi-disciplinary problems
- Large-scale problems
- Simultaneous deterministic and stochastic phenomena
- Inverse problems

Computational science is technology-driven: the Computational Pyramid



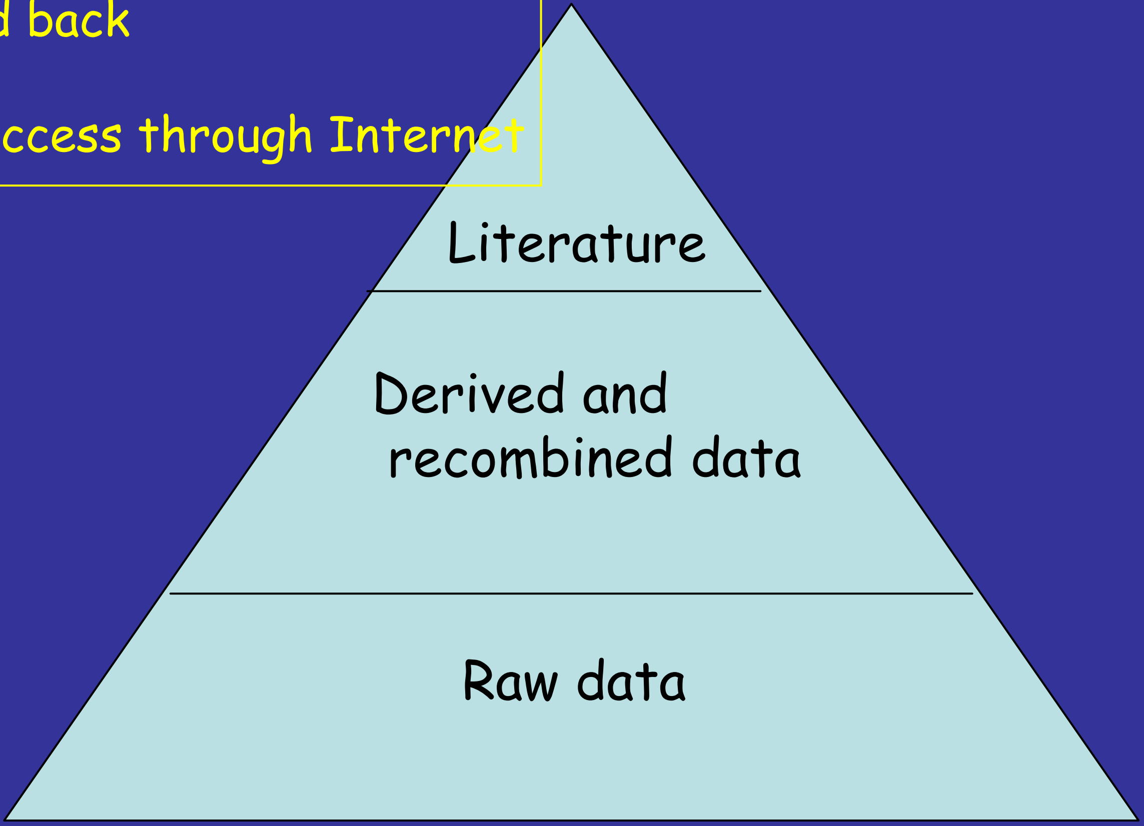
Tip of the iceberg: High Performance Computing

The "Fourth Paradigm": Online Data Pyramid

- Overlapping disciplines share data

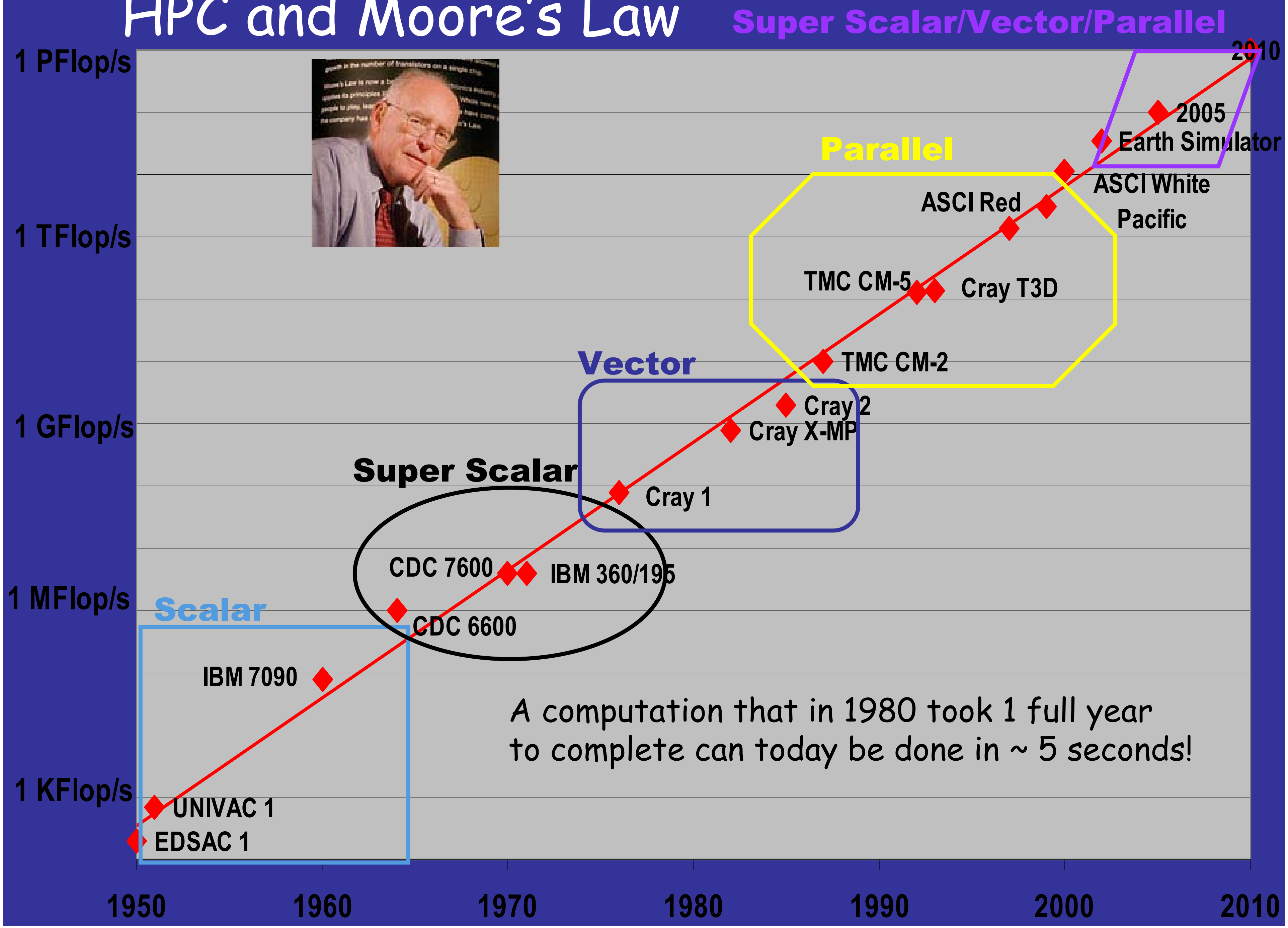
- From literature to computation to data – and back

- Universal access through Internet



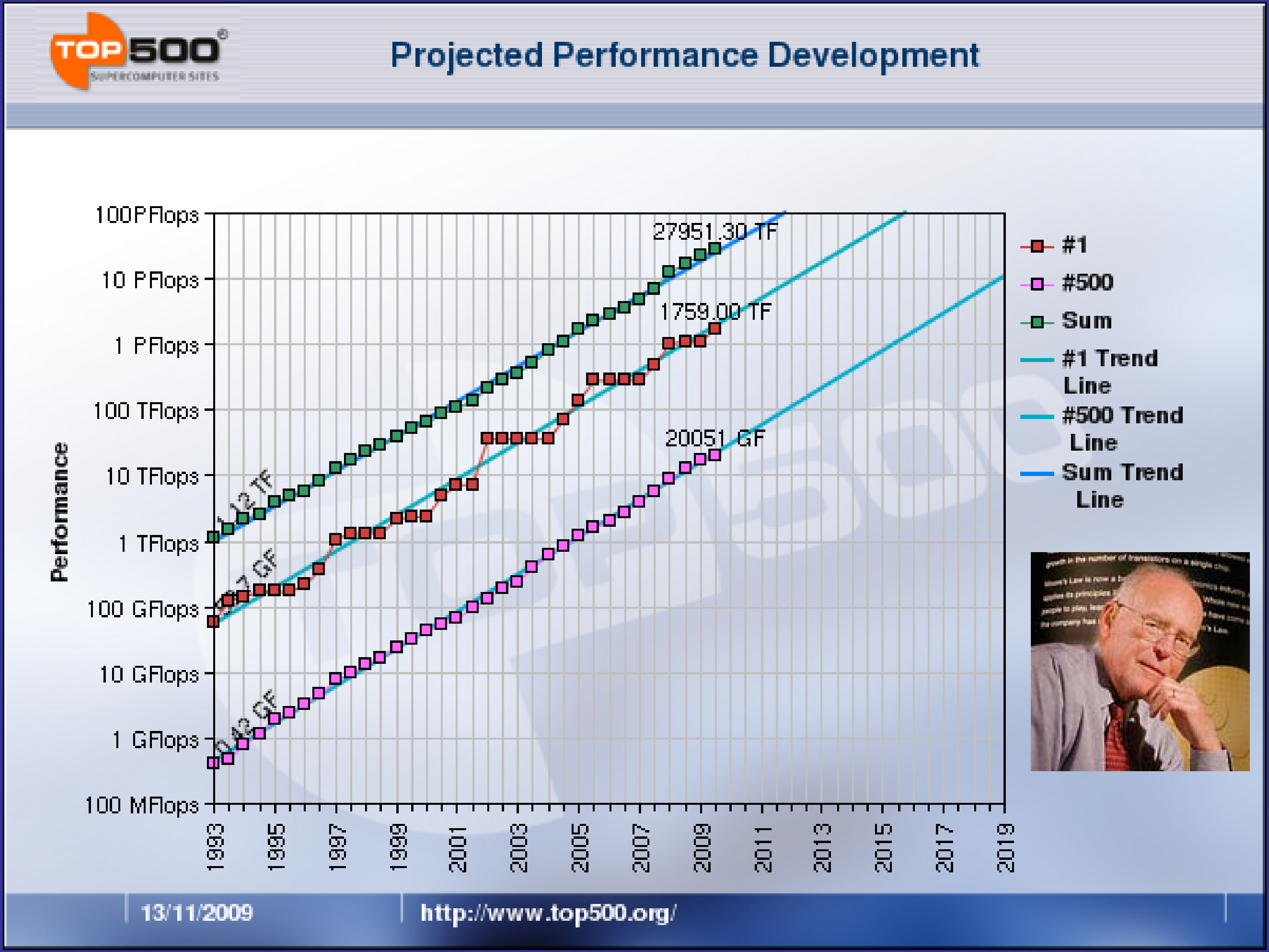
Information at your fingertips, everywhere

HPC and Moore's Law



A computation that in 1980 took 1 full year
to complete can today be done in ~ 5 seconds!

Trends in high-performance computing

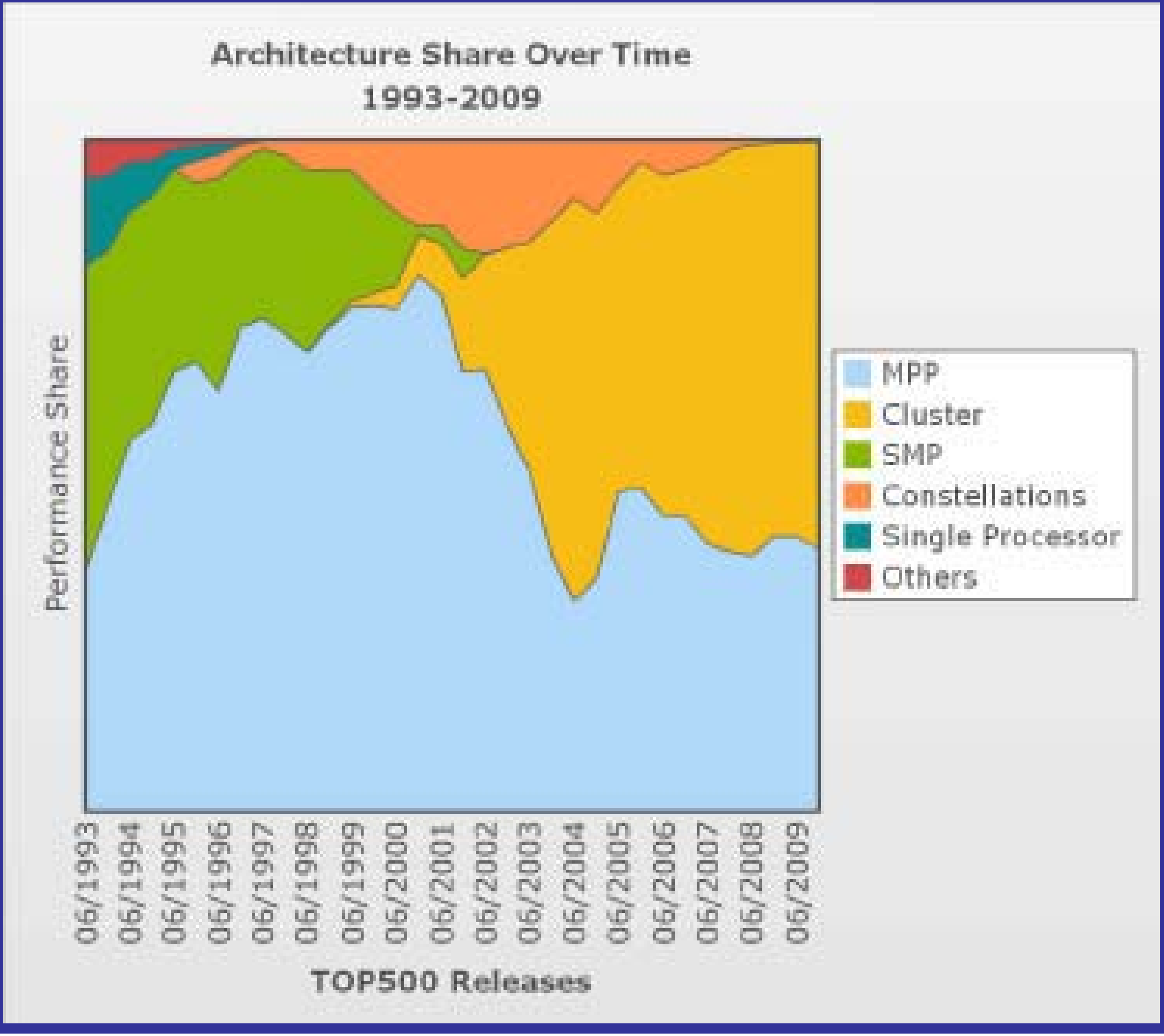


Projected Performance Development

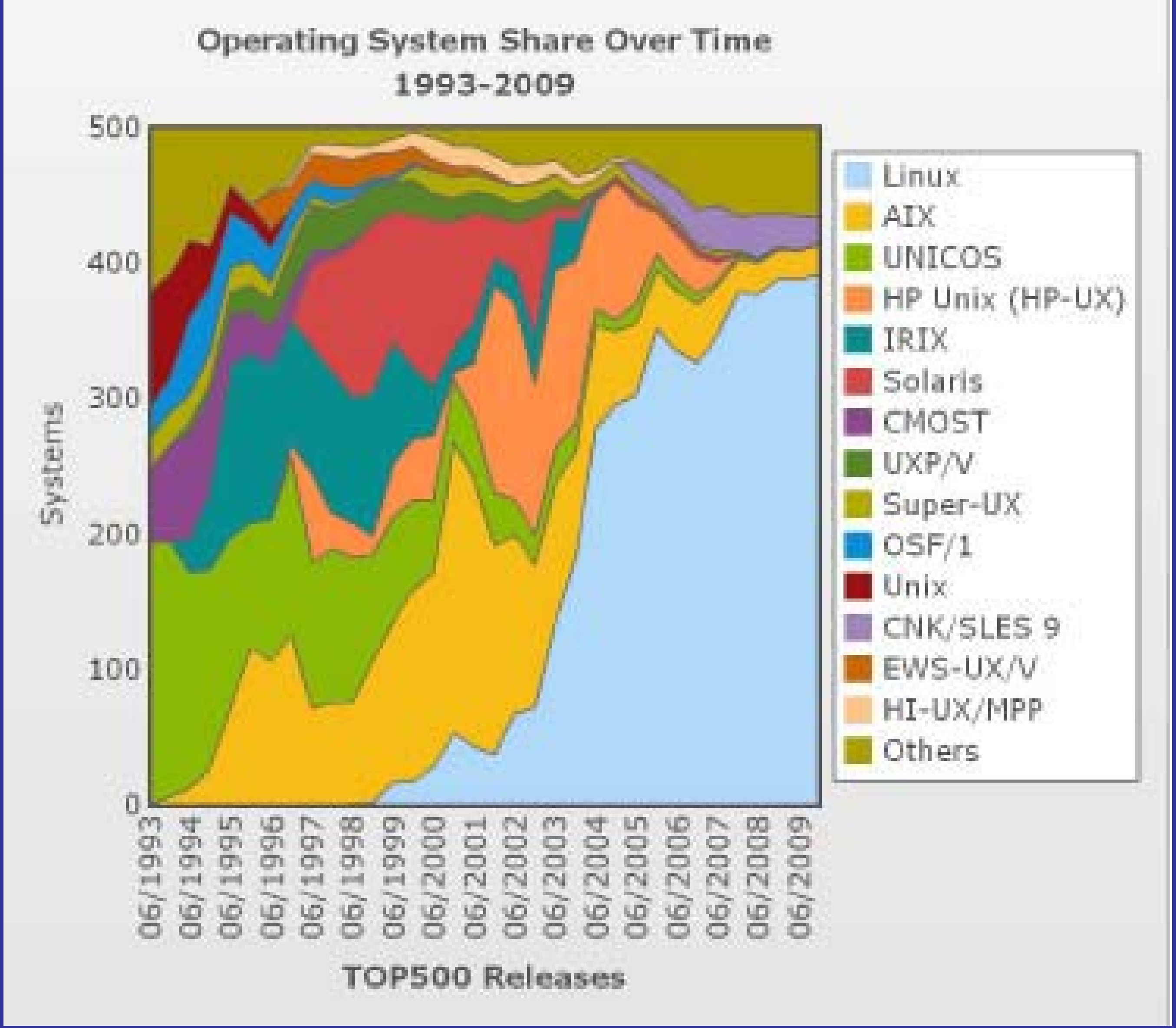
13/11/2009

http://www.top500.org/

Trends in high-performance computing



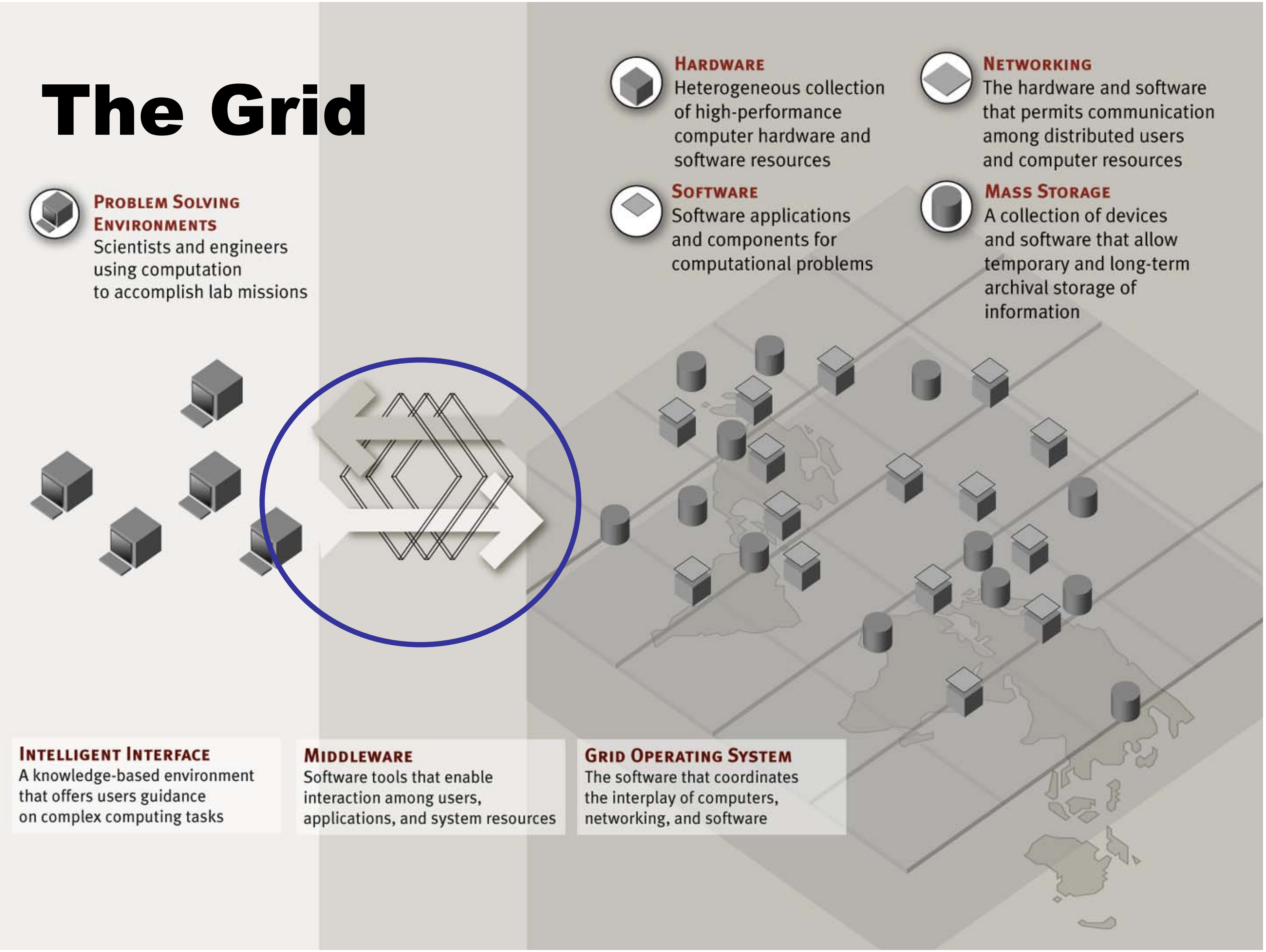
Trends in high-performance computing



Evolving Computational Pyramid: from "Metacomputing" to "Grid Computing" to "Cloud Computing"

- Larry Smarr (NCSA) 1992 -
- Ian Foster *et al.* (Argonne) 1998 –
- First implementations (data intensive challenges – CERN LCG *etc.*) 2000 –
- NSF Foundational Research in Data-Centric Computing 2010 -

The Grid



Problem Solving Environments
Scientists and engineers using computation to accomplish lab missions

Hardware
Heterogeneous collection of high-performance computer hardware and software resources

Networking
The hardware and software that permits communication among distributed users and computer resources

Software
Software applications and components for computational problems

Mass Storage
A collection of devices and software that allow temporary and long-term archival storage of information

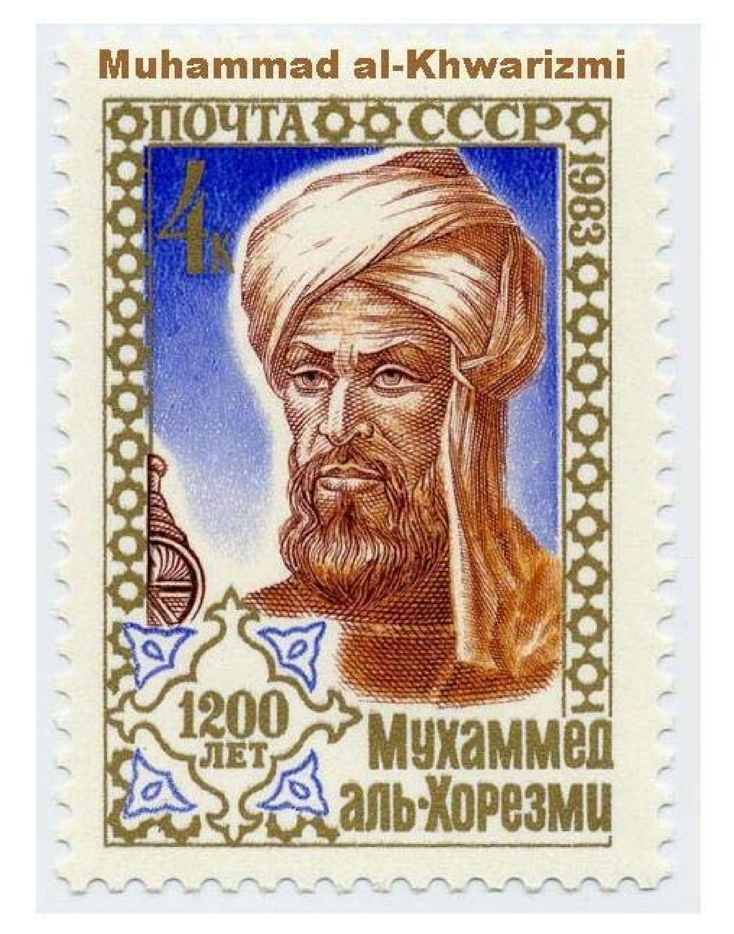
Intelligent Interface
A knowledge-based environment that offers users guidance on complex computing tasks

Middleware
Software tools that enable interaction among users, applications, and system resources

Grid Operating System
The software that coordinates the interplay of computers, networking, and software

GRID projects: DEISA, PRACE,…

The importance of algorithms



SOME MAJOR DEVELOPMENTS IN SCIENTIFIC COMPUTING

(29 of them)

Before 1940

Newton's method
least-squares fitting
Gaussian elimination
Gauss quadrature
Adams formulae
Runge-Kutta formulae
finite differences

1940-1970

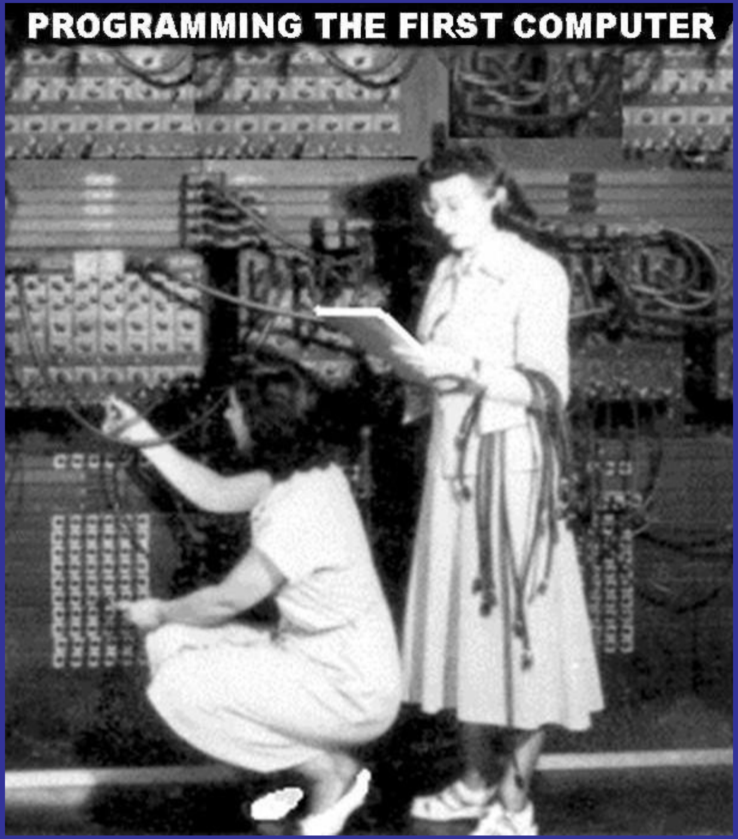
floating-point arithmetic
splines
Monte Carlo methods
simplex algorithm
conjugate gradients & Lanczos
Fortran
stiff ODE solvers
finite elements
orthogonal linear algebra
QR algorithm
Fast Fourier Transform
quasi-Newton iterations

1970-2000

preconditioning
spectral methods
MATLAB
multigrid methods
IEEE arithmetic
nonsymmetric Krylov iterations
interior point methods
fast multipole methods
wavelets
automatic differentiation

The future facilities for HPC will have hundreds of thousands of processors.

This implies the need for massive re-design of algorithms, compilers and and programming tools.



(F. Gygi)

SCALABILITY

Let N measure the problem size (e.g. "number of electrons" in first-principles molecular dynamics)

Strong scalability

- Fixed problem size, increase N_{CPU}
- Ideally, time ~ $O(1/N_{CPU})$
- Hard to achieve

Weak scalability

- Fixed problem size, increase N_{CPU}
- Not well defined if cost is not $O(N)$
- Cost is often polynomial in N or NlogN

LIMITS FOR COMPUTATIONAL EFFICIENCY

- Time scales

- one floating point operation (add or multiply): 125 ps
- fetch a double-precision number from memory: 4 ns
- fetch a double-precision number from another node: 8 ns

- The only viable strategy is to overlap communication and computation

- reuse data in processor cache
- use asynchronous communication

- Try to achieve $t_{compute} > t_{communicate}$

LIMITS FOR COMPUTATIONAL EFFICIENCY

- Fundamental characteristics

F = flop rate (*e.g.* AMD Opteron: 8 Gflop/s)
B = bandwidth (*e.g.* Infiniband 1 GB/s)
S = local data size (*e.g.* matrix block size 8 MB)
N(S) = number of operations (*e.g.* matrix multiply $N(S) = S^{3/2}$)

$t_{compute} = N(S)/F$
$t_{communicate} = S/B$

$N(S)/S > F/B$

LIMITS FOR COMPUTATIONAL EFFICIENCY

- Trends of new CPU architectures

Multicore processors: flop rate (F) increases
Bandwidth (B) ~ constant

$$N(S)/S > F/B$$

Only possible for very large problems (S)

N(S) must be superlinear

ON THE ROAD TO PETASCALE COMPUTING

- Future HPC platforms will consist of O(10^6) CPUs

- CPUs do not get much faster

- We can use the extra computational power to
  - simulate moderate-sized systems faster (requires strong scalablity)
  - use more accurate and sophisticated theory/models

- Petascale computing will require new algorithms
  - main issues: data compression, simplified communication patterns

- New bottlenecks appear:
  - CPU architectures change fast – software must adapt quickly
  - I/O performance will become critical
  - Fault-tolerant algorithms may become a necessity

"The general theory of quantum mechanics is now almost complete. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

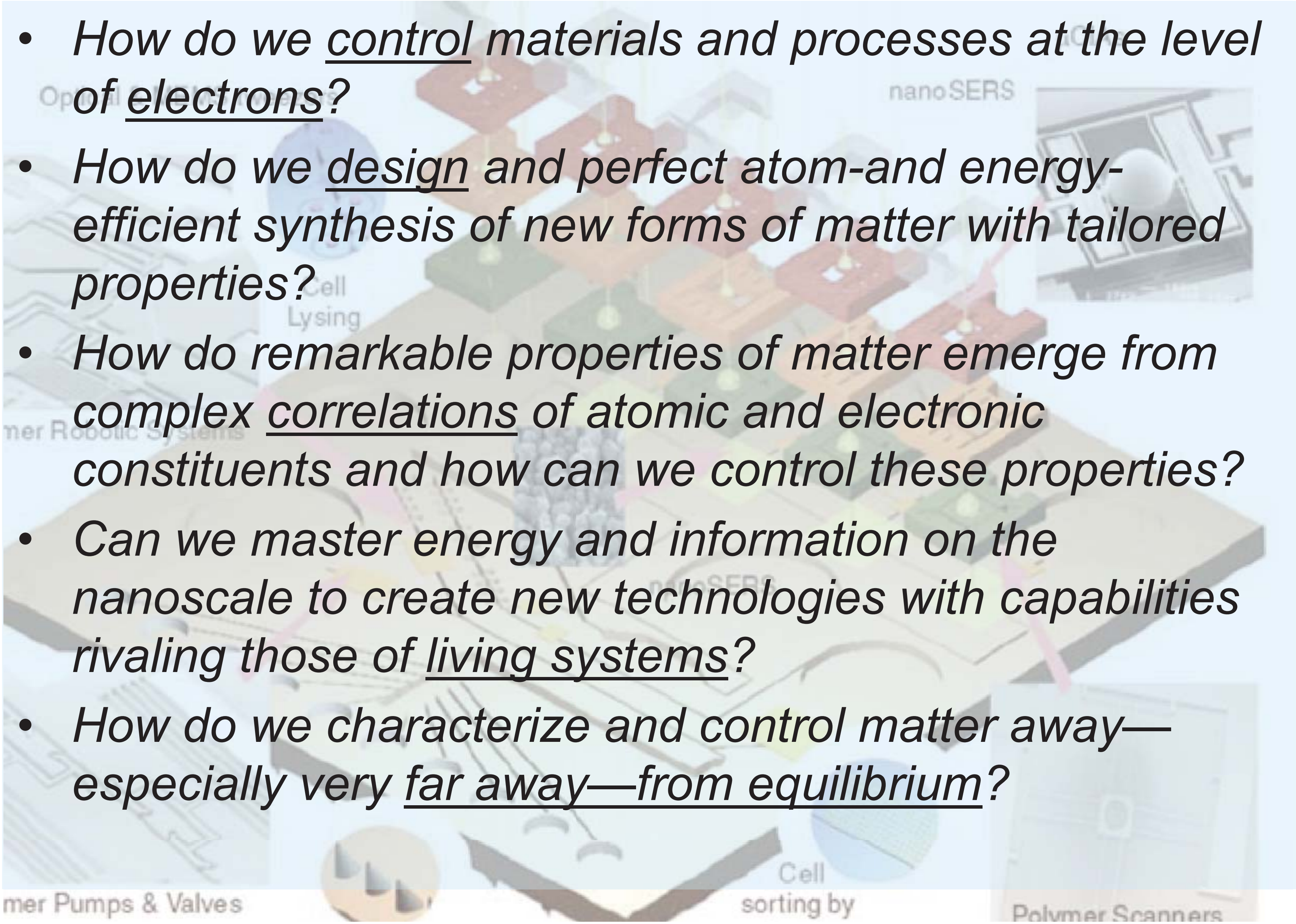
It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

P.A.M. Dirac, 1929

1902-1984

Physics Nobel Prize 1933 (with E. Schrödinger)

Five Grand Challenges for Science and the Imagination (courtesy of Mark Ratner)



- *How do we control materials and processes at the level of electrons?*
- *How do we design and perfect atom-and energy-efficient synthesis of new forms of matter with tailored properties?*
- *How do remarkable properties of matter emerge from complex correlations of atomic and electronic constituents and how can we control these properties?*
- *Can we master energy and information on the nanoscale to create new technologies with capabilities rivaling those of living systems?*
- *How do we characterize and control matter away—especially very far away—from equilibrium?*

NANOWORLD:

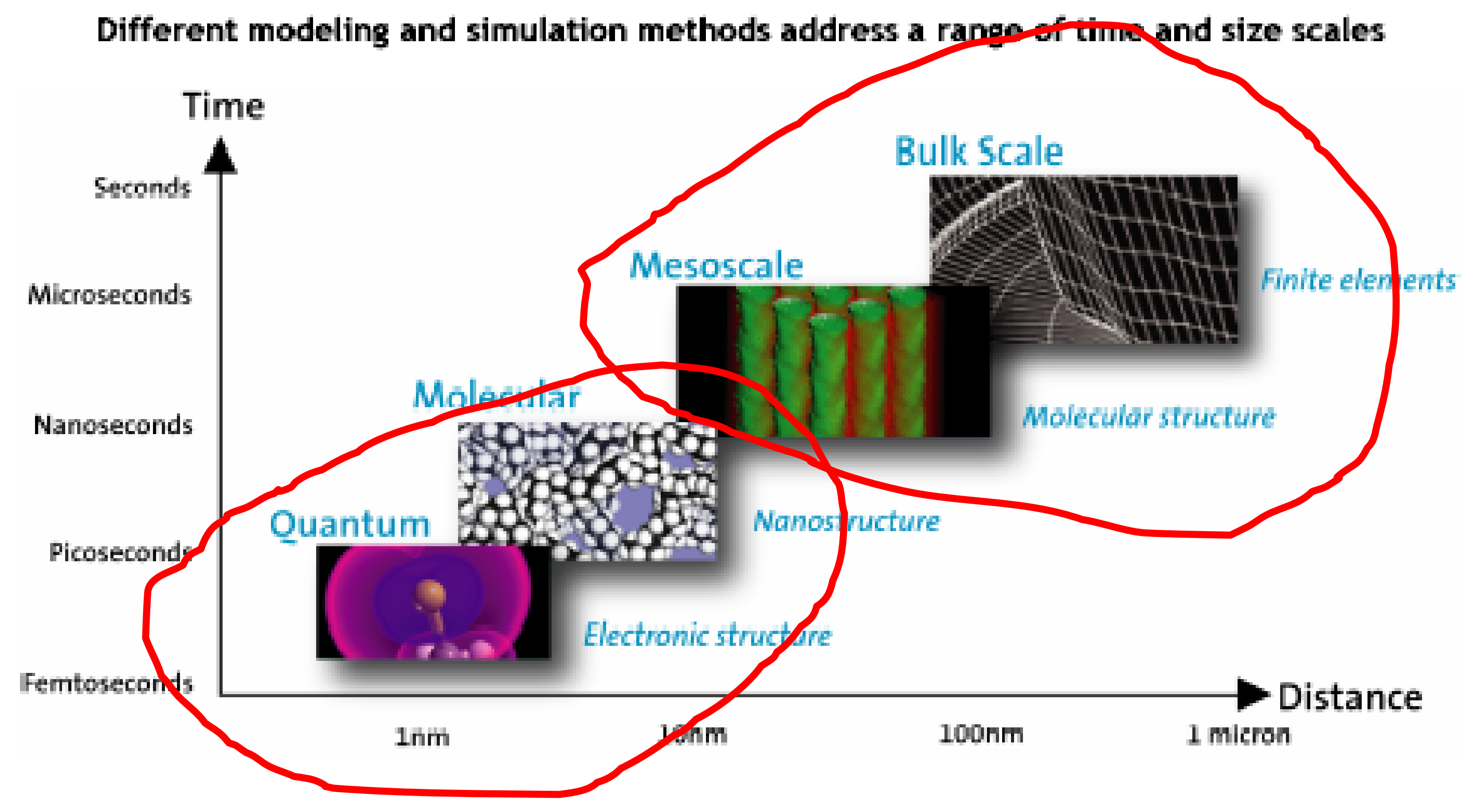
Handshaking of…..

- quantum and classical phenomena
- equilibrium and non-equilibrium phenomena
- top-down and bottom-up approaches
- reductionist and emergent viewpoints ("more is different")

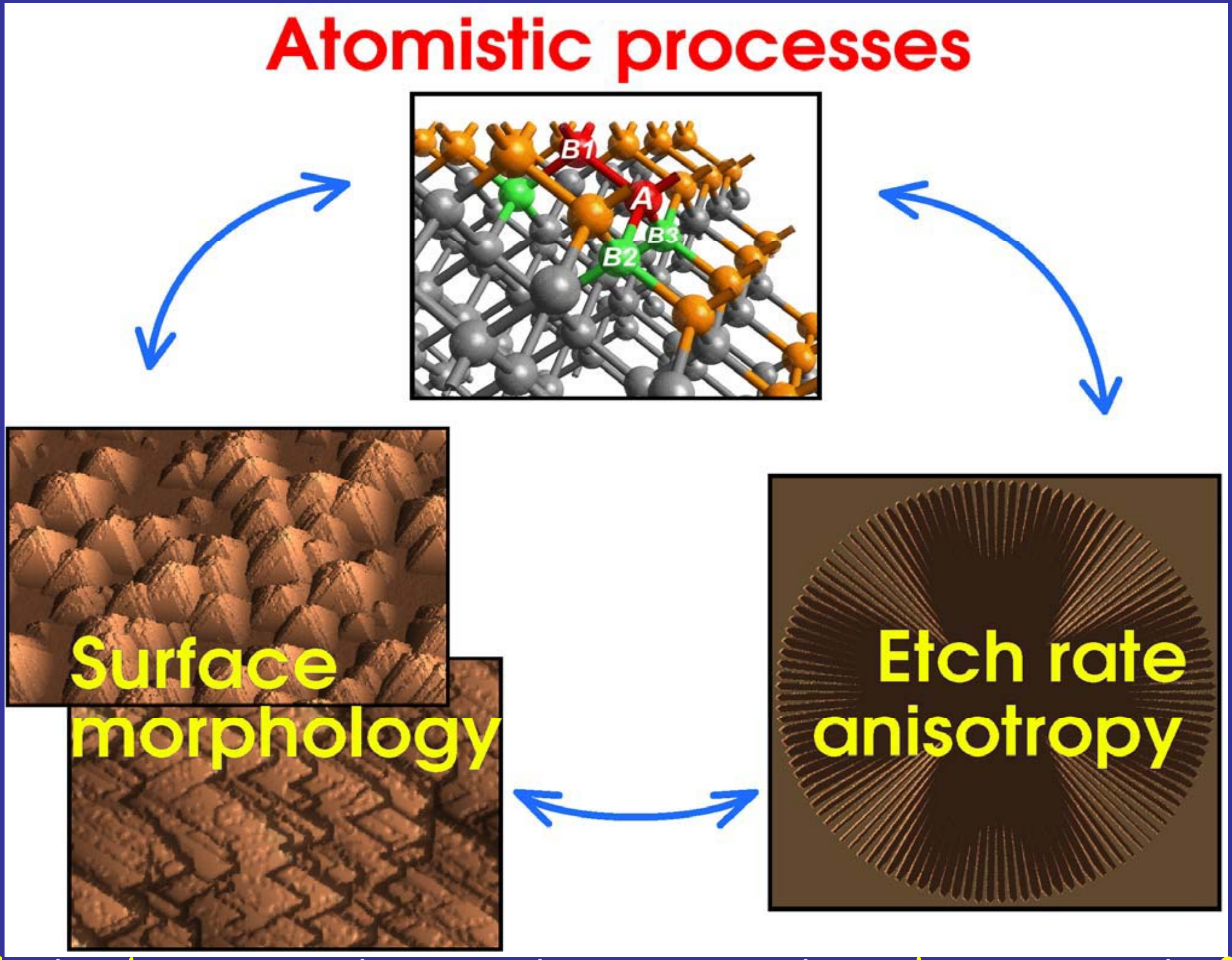
QUANTUM WORLD:

- "weird" = counterintuitive : wave-particle dualism
- inherently "parallel" : quantum computing
- phase information
- many-particle symmetry/antisymmetry :
  mathematical description of electrons very complex
  ("fermion sign problem")
- coupling to (classical) environments: decoherence, dissipation

Multi-scale materials modelling and simulation: bridging length and time scales

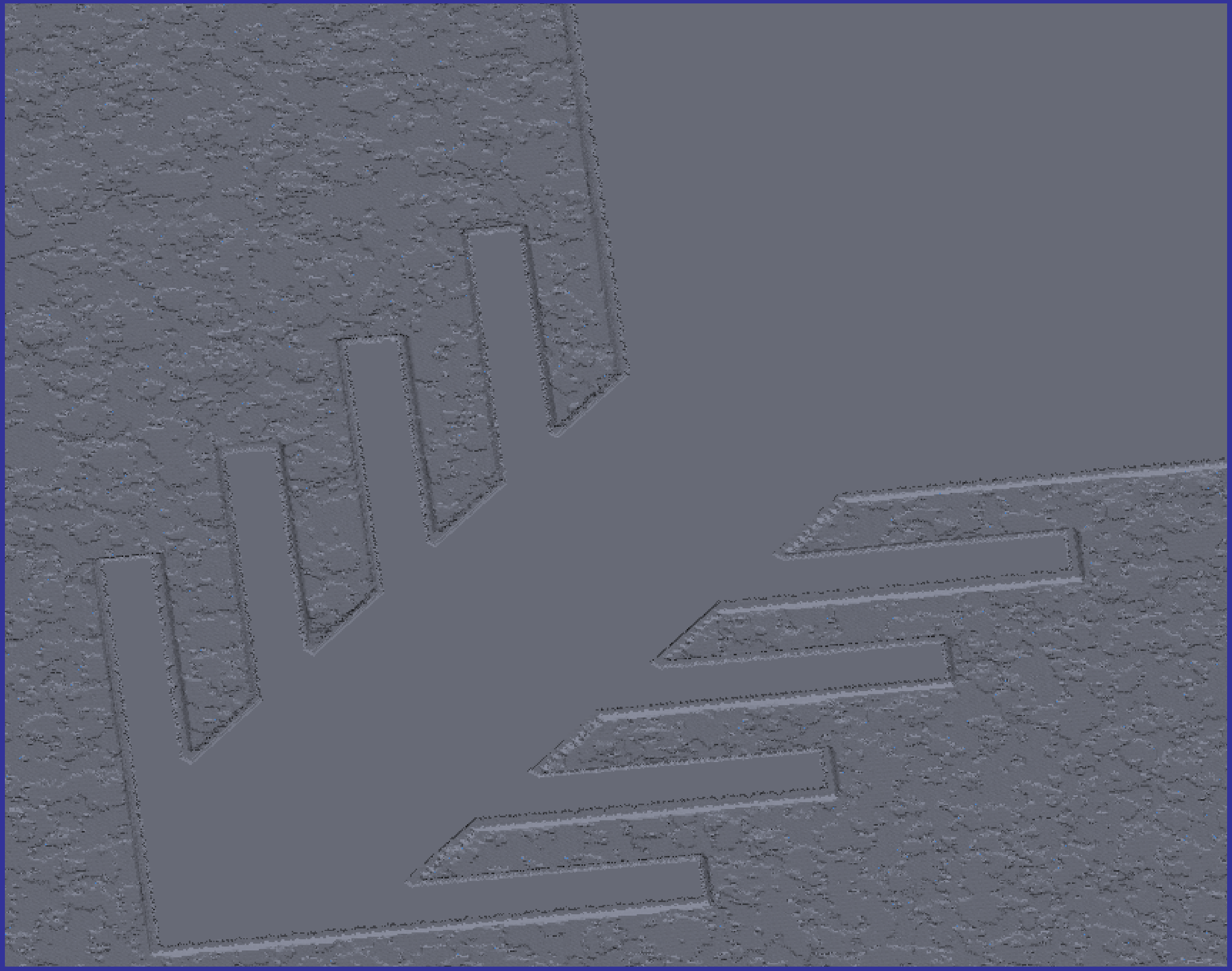


Bridging the different length scales: three-dimensional etching Si MEMS



Interrelation between microscopic, mesoscopic and macroscopic features of the etching process

Corner Compensation Simulation using Monte Carlo Atomistic Method

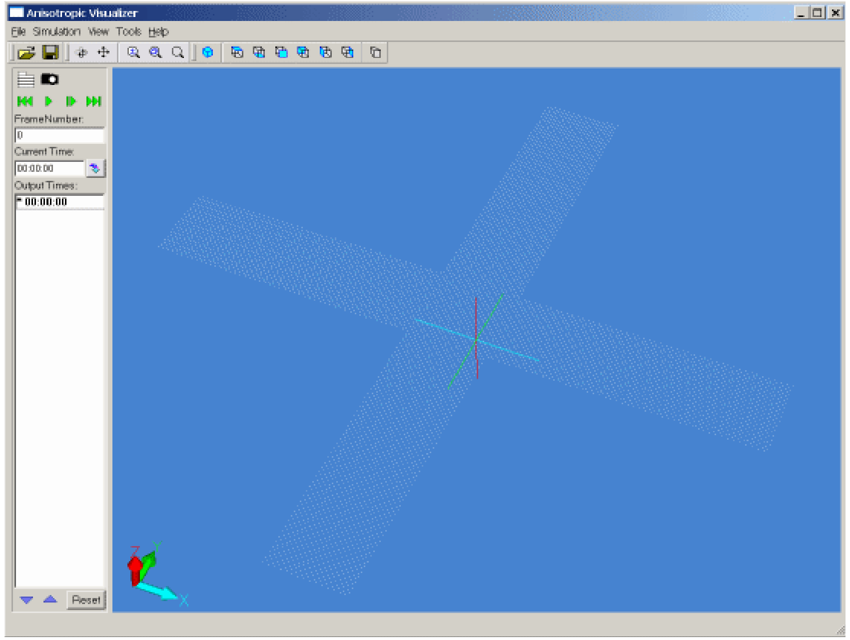


ETCH3D

COVENTOR™

WHAT'S NEXT. AND NEXT. AND NEXT.™

- Results from ETCH3D Anisotropic Etch Simulator



FrameNumber: 0

Current Time: 00:00:00

Output Times: 00:00:00

Scientific software used at COMP

QUANTUM SCALE

QMC

Quantum Monte Carlo

ABINIT VASP
CASTEP WIEN2k
FHI-AIMS OCTOPUS
SIESTA GPAW

Density-functional theory

ATOMISTIC SCALE

CPMD GROMACS MOLDY
CASHEW

Molecular dynamics

MESOSCOPIC SCALE

KMC CASINO
TAPAS

Kinetic Monte Carlo
Cellular automata

CONTINUUM SCALE

ELMER

Finite-element methods

Anatomy of a package: GPAW

https://wiki.fysik.dtu.dk/gpaw
Psi-k Highlight April 2010
J. Phys. CM: Condensed Matter (to be published)

- Real-space grid: finite-differences
- Projector-augmented-wave for the core electrons
- Static and time-dependent DFT
- LDA, GGA, hybrid, van der Waals
- TDDFT: linear-response and time propagation
- Many utilities

PAW: Projector-augmented wave approach (Peter Blöchl)

$$\psi_n(\mathbf{r}) = \hat{\mathcal{T}}\tilde{\psi}_n(\mathbf{r}).$$

$$\hat{\mathcal{T}} = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle)\langle\tilde{p}_i^a|,$$

$$\phi_i^a(\mathbf{r}) = \tilde{\phi}_i^a(\mathbf{r}),\ |\mathbf{r} - \mathbf{R}^a| > r_c^a$$

$$\langle\tilde{p}_{i_1}^a|\tilde{\phi}_{i_2}^a\rangle = \delta_{i_1 i_2}.$$

Total energy

$$\begin{aligned} E &= \tilde{E} + \sum_a \Delta E^a \\ &= \tilde{E}_{\text{kin}} + \tilde{E}_{\text{coul}} + \tilde{E}_{\text{xc}} + \tilde{E}_{\text{zero}} \\ &+ \sum_a (\Delta E_{\text{kin}}^a + \Delta E_{\text{coul}}^a + \Delta E_{\text{xc}}^a + \Delta E_{\text{zero}}^a). \end{aligned}$$

Generalised eigenvalue problem

$$\hat{H}\tilde{\psi}_n = \epsilon_n \hat{S}\tilde{\psi}_n,$$

Hamiltonian

$$\begin{aligned} \hat{H} &= -\frac{1}{2}\nabla^2 + \tilde{v} + \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle \Delta H^a_{i_1 i_2} \langle \tilde{p}^a_{i_2}|, \\ \Delta H^a_{i_1 i_2} &= \frac{\partial \Delta E^a}{\partial D^a_{i_1 i_2}} + \int d\mathbf{r}\,\tilde{v}_{\mathrm{coul}}(\mathbf{r}) \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial D^a_{i_1 i_2}}, \end{aligned}$$

Overlap matrix

$$\hat{S} = \hat{\mathcal{T}}^{\dagger}\hat{\mathcal{T}} = 1 + \sum_a \sum_{i_1 i_2} |\tilde{p}^a_{i_1}\rangle \Delta S^a_{i_1 i_2} \langle \tilde{p}^a_{i_2}|,$$

$$\Delta S^a_{i_1 i_2} = \langle \phi^a_{i_1} | \phi^a_{i_2} \rangle - \langle \tilde{\phi}^a_{i_1} | \tilde{\phi}^a_{i_2} \rangle.$$

Potential

$$\tilde{v} = \frac{\delta \tilde{E}}{\delta \tilde{n}} = \tilde{v}_{\mathrm{coul}} + \tilde{v}_{\mathrm{xc}} + \sum_a \bar{v}^a,$$

Grid-based approach: finite differences

$$\nabla^2 f(\mathbf{r}) = \sum_{\alpha=1}^{D} \sum_{n=-N}^{N} b_\alpha c_n^N f(\mathbf{r} + n\mathbf{h}_\alpha) + O(h^{2N}),$$

Iterative solution (RMM-DIIS, CG, Davidson,…)

Residuals, preconditioning

$$R_n = (\hat{H} - \epsilon_n \hat{S})\tilde{\psi}_n .$$

Exchange and correlation: GGA, meta-GGA, EEX, hybrids, …

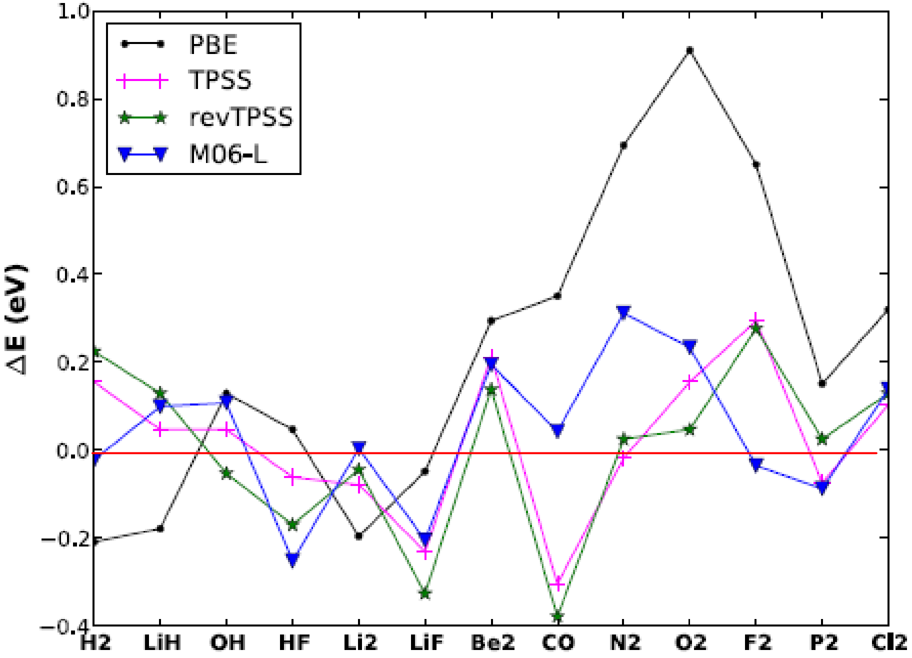


Figure 1: PBE, TPSS, revTPSS and M06-L non-self-consistent atomization energies errors, with respect to experiments, calculated with GPAW for small molecules, in eV. The MGGA GPAW values are obtained from PBE orbitals at experimental geometries. Experimental values are as in Ref. [49].

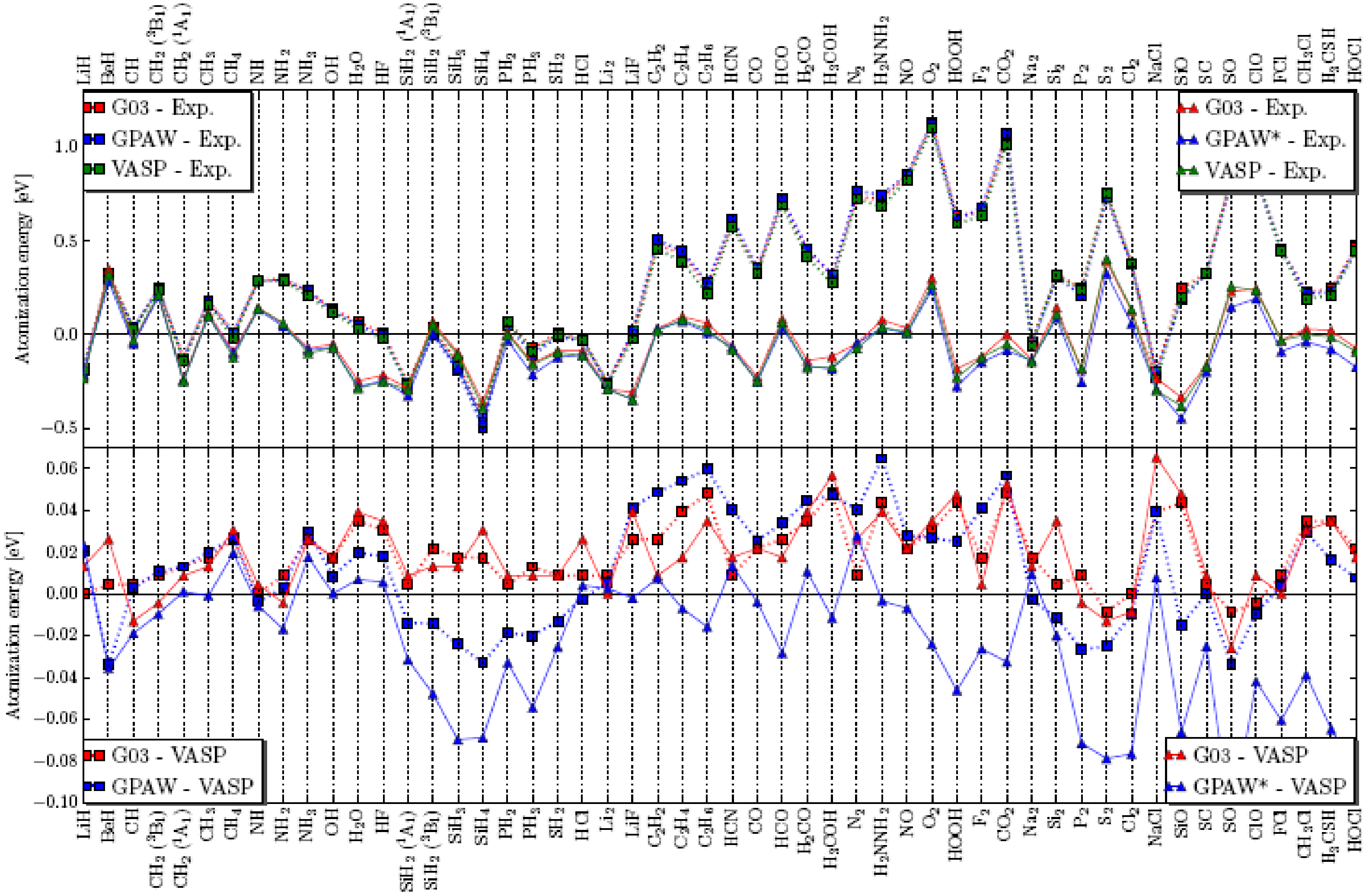


Figure 2: Calculated atomization energies using PBE (dotted) and PBE0 (solid) functionals compared to experimental values (top) and to VASP (bottom). GPAW PBE0 values are not geometry optimized (evaluated at PBE geometries)

The role of the van der Waals interaction in the adsorption of organic molecules on surfaces

Is van der Waals interaction weak?

K. Autumn et al., PNAS 99, 11993 (2002)

vdW-DF correlation energy: Langreth, Lundqvist et al.

$$E_c^{nl} = \int \rho(\vec{r'})\phi(\vec{r'},\vec{r})\rho(\vec{r})d^3r d^3r'$$

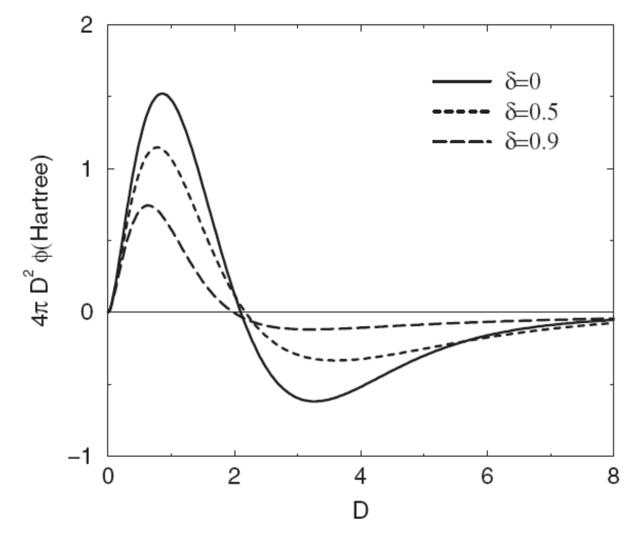
$$\epsilon_c^{nl}(r) = \frac{1}{2}\int \phi(r,r')n(r')d^3r'$$

Tabulated conveniently

$$\phi = \phi(D,\delta)$$

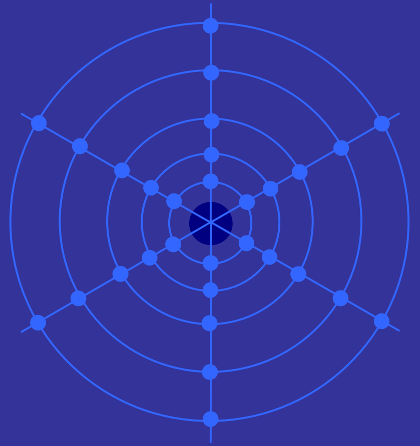
$$D(r_1,r_2) = \frac{(q_0(r_1)+q_0(r_2))r_{12}}{2}$$

$$\delta(r_1,r_2) = \frac{q_0(r_1)-q_0(r_2)}{q_0(r_1)+q_0(r_2)}$$



Phys. Rev. Lett. **95**, 109902(E) (2005)

The integral is evaluated on adaptive grid

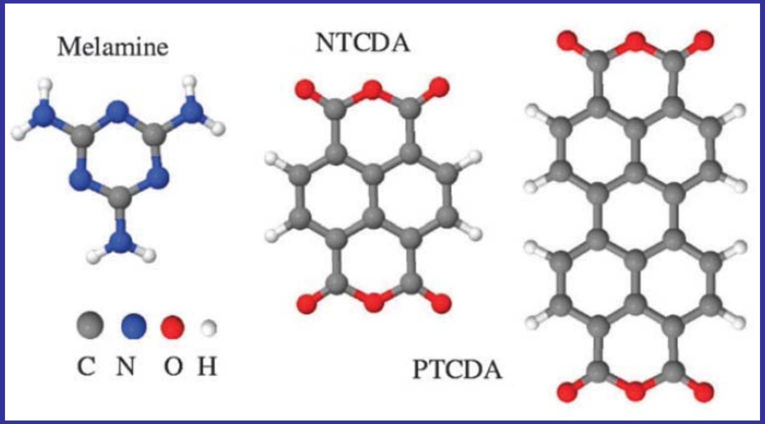


$$v_c^{nl}(r) = \frac{\delta E_c^{nl}}{\delta n}$$

Contains also $\frac{\partial \phi(D,\delta)}{\partial D}$ and $\frac{\partial \phi(D,\delta)}{\partial \delta}$

Phys. Rev. B **79**, 201105 (2009)

Adsorption of planar molecules on Au(111)



Adsorption energies (eV)

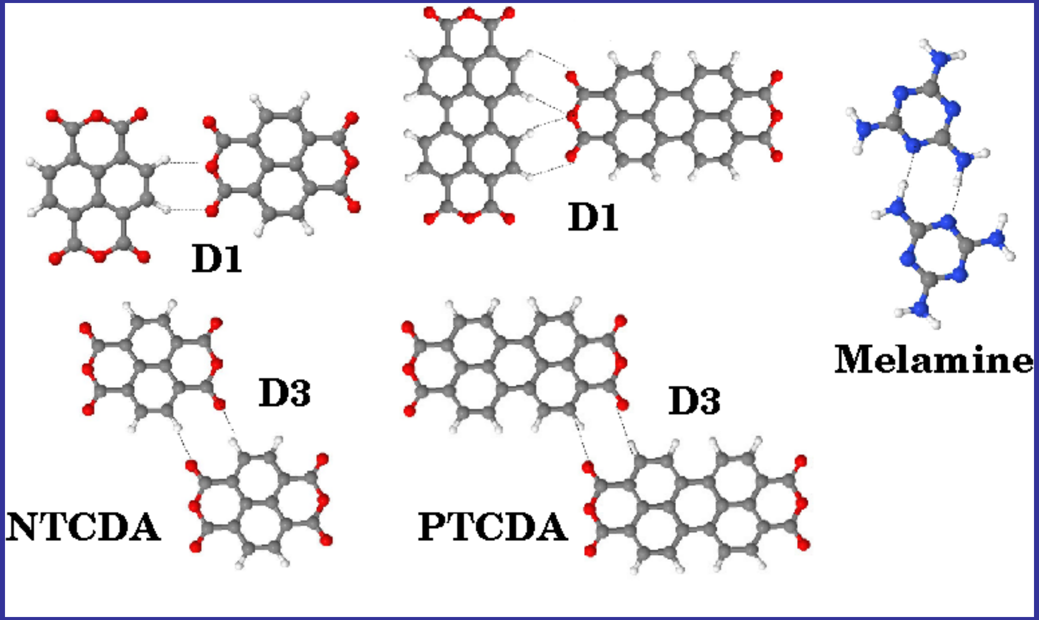
	PBE	vdW-DF
Melamine	-0.25	-0.88
NTCDA	-0.10	-1.31
PTCDA	-0.17	-1.88
Melamine dimer	–	-2.08

The vdW interaction contributes to the adsorption considerably

Andris Gulans *et al.*

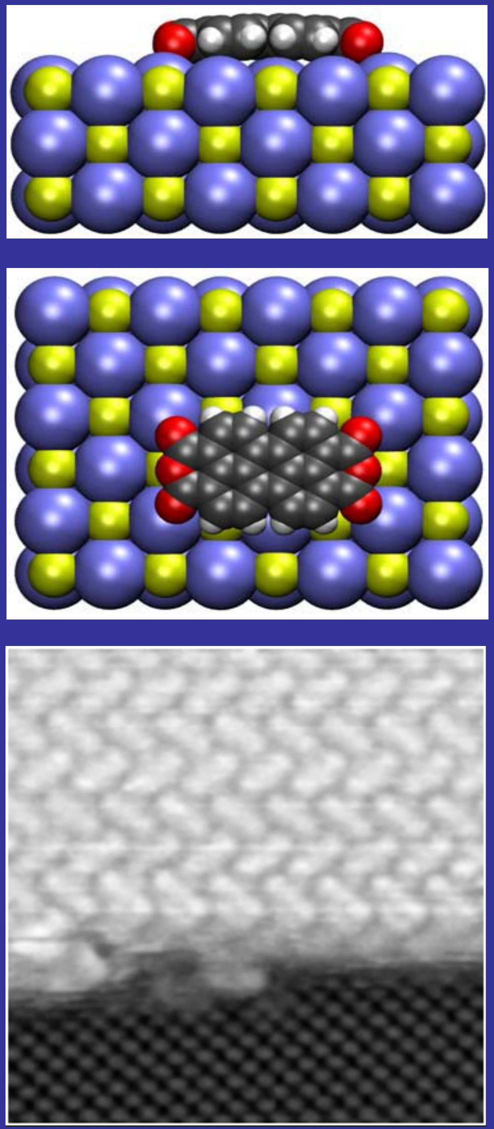
Phys. Chem. Chem. Phys. **12**, 4759 (2010)

Interaction of molecular dimers



dimers	PBE	vdW-DF	MP2
M-M	-0.48 [15]	-0.42	-0.49
NTCDA (D1)	-0.06	-0.18	-0.19
NTCDA (D3)	-0.16	-0.28	-0.28
PTCDA (D1)	-0.23	-0.38	-0.45
PTCDA (D3)	-0.25	-0.38	-0.35

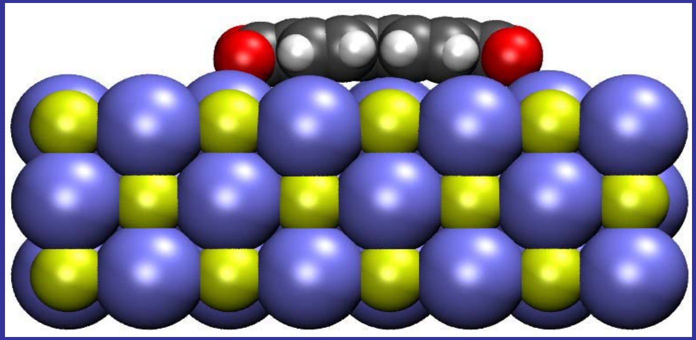
PTCDA molecule

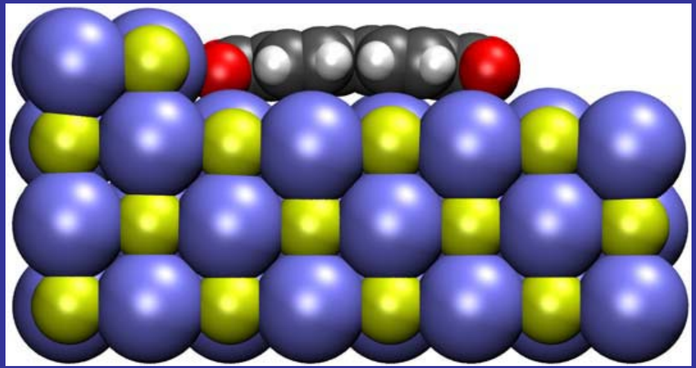


- PTCDA (3,4,9,10-perylene-…) is an organic semiconductor
- derivatives are suitable for manufacturing solar cells
- organizes in well-ordered films on substrates

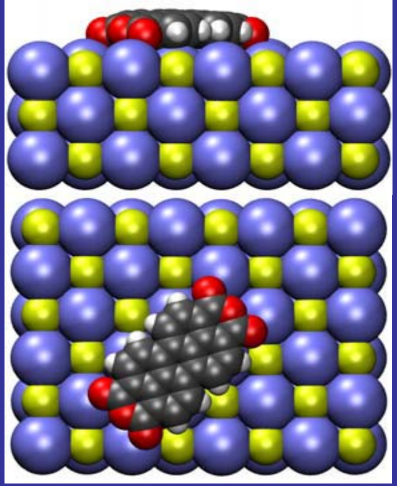
Computational details

- Surface is modelled by slabs with 3-4 atomic layers
- DFT calculations done with the LCAO code SIESTA
- PBE and vdW-DF xc-functionals
- Double-zeta with polarisation basis set
- BSSE estimated using counterpoise correction scheme

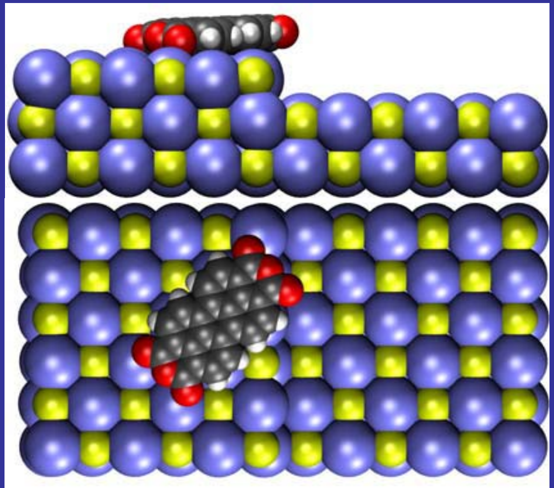




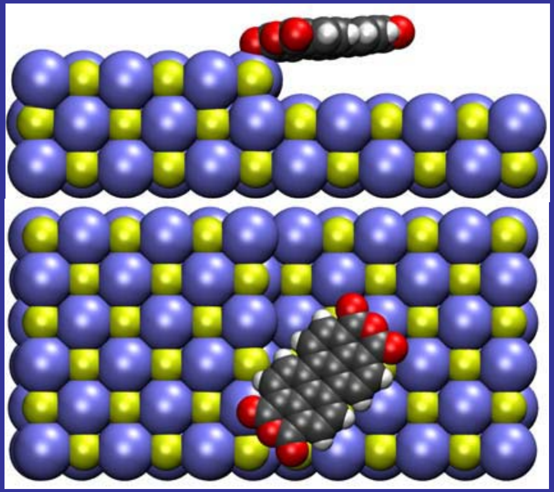
Diffusion over a step on KBr (100) surface (GGA results)



-0.50 eV



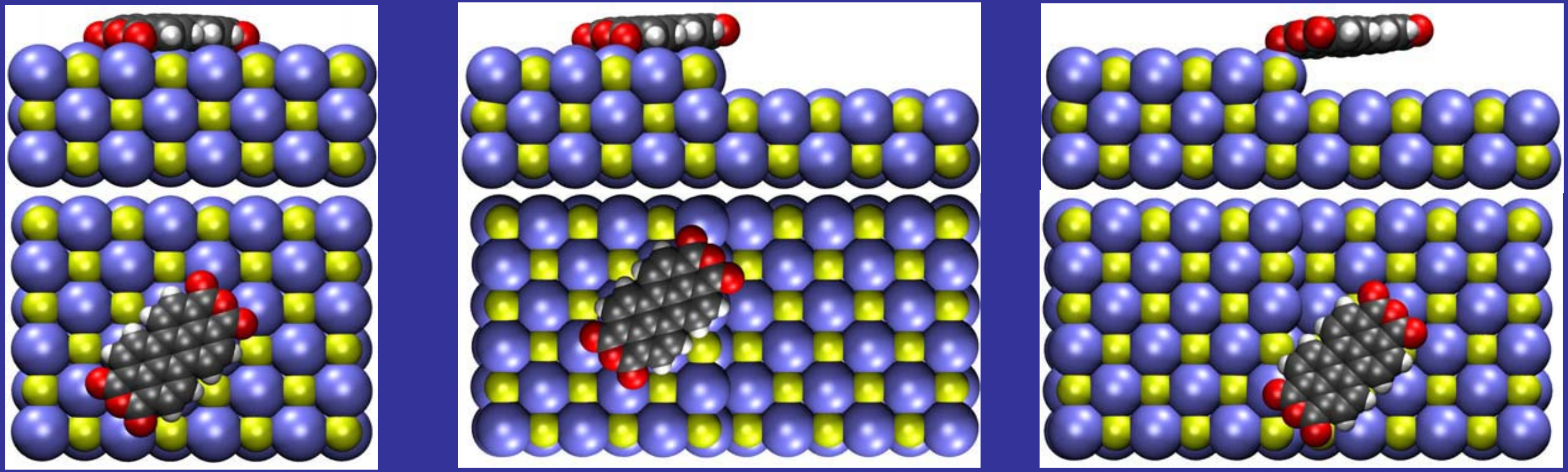
-0.24 eV



-0.07 eV

The molecules are likely to detach during the diffusion over the step

Diffusion over a step (revised)



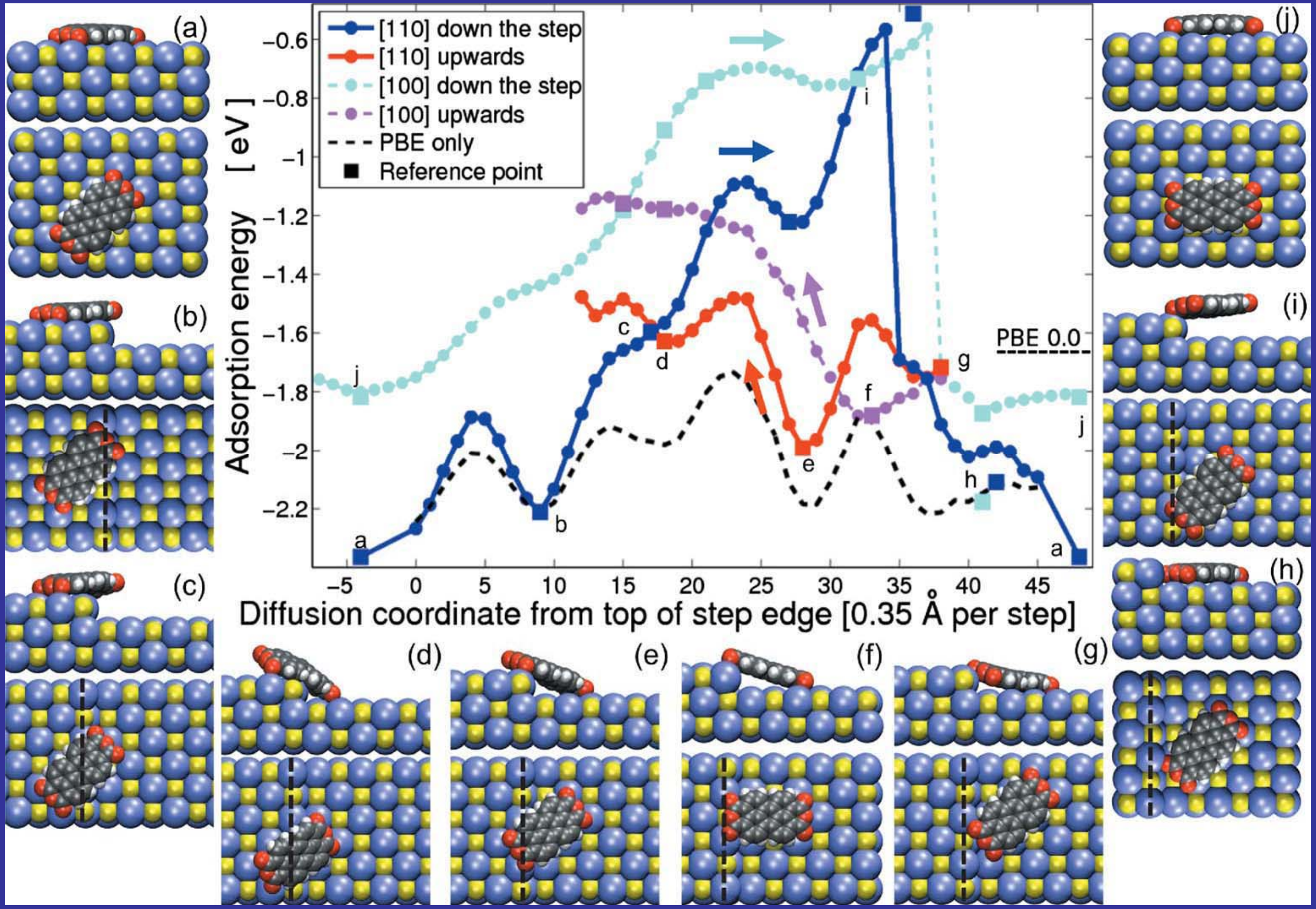
vdW-DF

-2.36 eV -1.63 eV -0.51 eV

PBE

-0.50 eV -0.24 eV -0.07 eV

Diffusion diagram



*The PBE curve is displaced in the energy scale

Phys. Rev. B **80**, 085401 (2009)

- GGA fails in cases where the adsorption is dominated by the vdW interaction. This may have also implications on the accuracy of diffusion calculations.

- The interaction energies of the molecular dimers are influenced not only by hydrogen bonds (electrostatic interaction), but also by dispersion.

Non-covalent interactions are particularly tricky for common DFT methods. Yet there are approaches to overcome these difficulties.

Time-dependent DFT: time-propagation

$$i\frac{\partial}{\partial t}\psi_n(t) = \hat{H}(t)\psi_n(t),$$

Assume: overlap matrix independent of time

$$i\hat{S}\frac{\partial}{\partial t}\tilde{\psi}_n(t) = \hat{H}(t)\tilde{\psi}_n(t).$$

Time propagation: Crank-Nicolson with predictor-corrector steps

Initial (time-dependent) perturbation

External (electromagnetic) vector potential

Nonlinear effects included

Time-dependent DFT: linear reponse

Transition energies between initial and final states

$$\Omega F_I = \omega_I^2 F_I,$$

$$\begin{aligned}\Omega_{ij\sigma,kl\tau} \quad = \quad & \delta_{ik}\delta_{jl}\delta_{\sigma\tau}\,\varepsilon_{ij\sigma}^2 + \\ & 2\sqrt{f_{ij\sigma}\varepsilon_{ij\sigma}f_{kl\tau}\varepsilon_{kl\tau}}K_{ij\sigma,kl\tau},\end{aligned}$$

Coupling matrix

$$K_{ij\sigma,kl\tau} = K_{ij\sigma,kl\tau}^{C} + K_{ij\sigma,kl\tau}^{xc}$$

Time-dependent DFT: kernel for linear response

Coulomb part (Random Phase Approximation)

$$K^{C}_{ij\sigma,kl\tau} = (n_{ij\sigma}|n_{kl\tau})$$

Exchange-correlation part

$$K^{xc}_{ij\sigma,kq\tau} = \int d\mathbf{r}_1 d\mathbf{r}_2 \; n^{*}_{ij\sigma}(\mathbf{r}_1) \, \frac{\delta^2 E_{xc}}{\delta n_{\sigma}(\mathbf{r}_1)\delta n_{\tau}(\mathbf{r}_2)} \, n_{kq\tau}(\mathbf{r}_2),$$

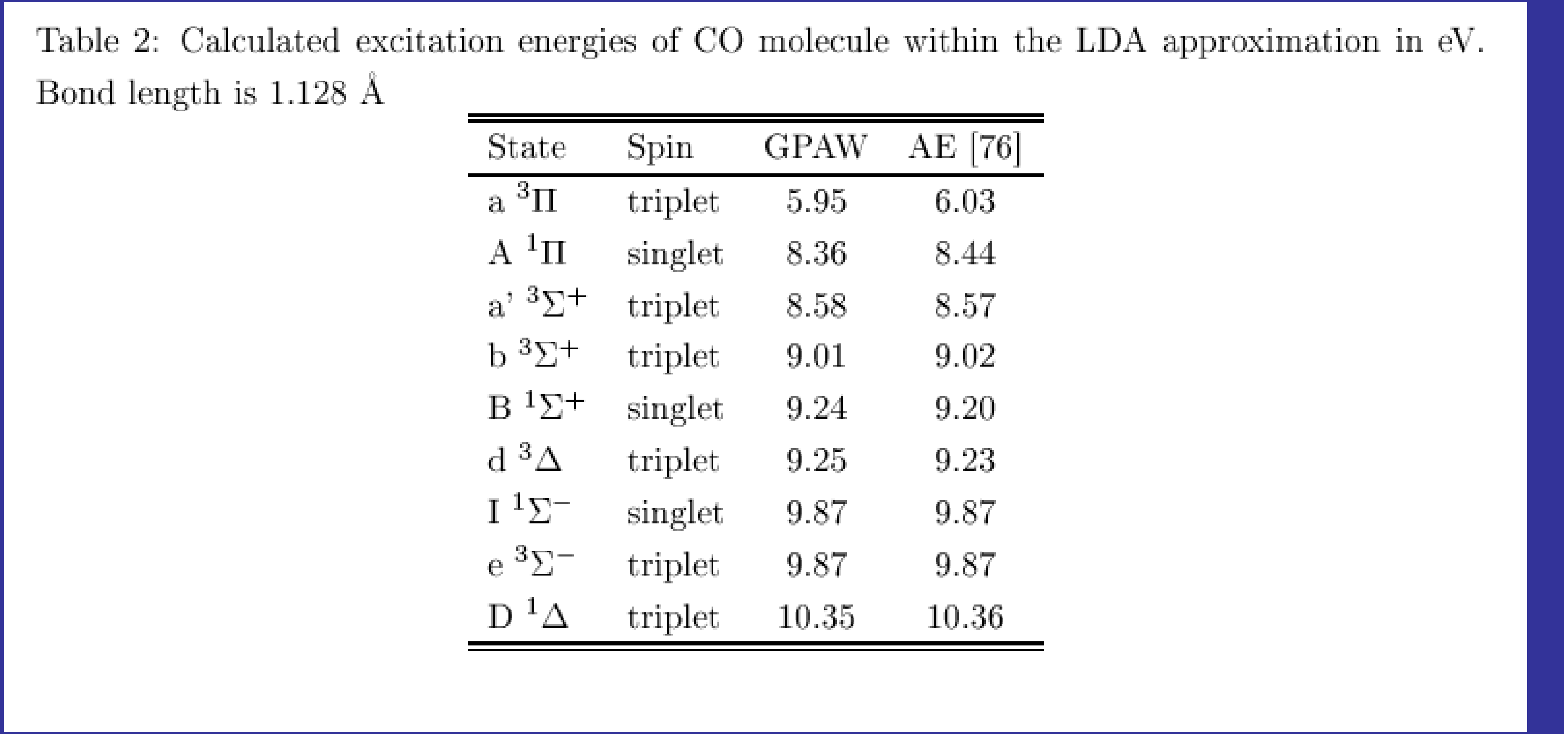


Table 2: Calculated excitation energies of CO molecule within the LDA approximation in eV. Bond length is 1.128 Å

State	Spin	GPAW	AE [76]
a $^{3}\Pi$	triplet	5.95	6.03
A $^{1}\Pi$	singlet	8.36	8.44
a' $^{3}\Sigma+$	triplet	8.58	8.57
b $^{3}\Sigma+$	triplet	9.01	9.02
B $^{1}\Sigma+$	singlet	9.24	9.20
d $^{3}\Delta$	triplet	9.25	9.23
I $^{1}\Sigma^{-}$	singlet	9.87	9.87
e $^{3}\Sigma^{-}$	triplet	9.87	9.87
D $^{1}\Delta$	triplet	10.35	10.36

Excitation energies from linear response (ALDA)

TDDFT: Optical absorption

$$\mathbf{E}(t) = \epsilon \mathbf{k}^{\mathbf{o}} \delta(t),$$

Delta pulse excitation

$$\psi(t = 0^+) = \exp\left(i \frac{\epsilon}{a_0} \mathbf{k}^{\mathbf{o}} \cdot \mathbf{r}\right) \psi(t = 0^-).$$

Time propagation: record time-dependent dipole moment $\mu(t)$
Fourier transform → dipole strength tensor,
oscillator strengths

Linear response: eigenvectors needed

$$\mu_{ij\sigma} = \langle \psi_{i\sigma} | \mathbf{r} | \psi_{j\sigma} \rangle$$

Kohn-Sham
transition dipoles

Oscillator strengths

$$f_{I\alpha} = \left| \sum_{ij\sigma}^{f_{i\sigma} > f_{j\sigma}} (\mu_{ij\sigma})_\alpha \sqrt{f_{ij\sigma} \, \varepsilon_{ij\sigma}} \, (F_I)_{ij\sigma} \right|^2 .$$

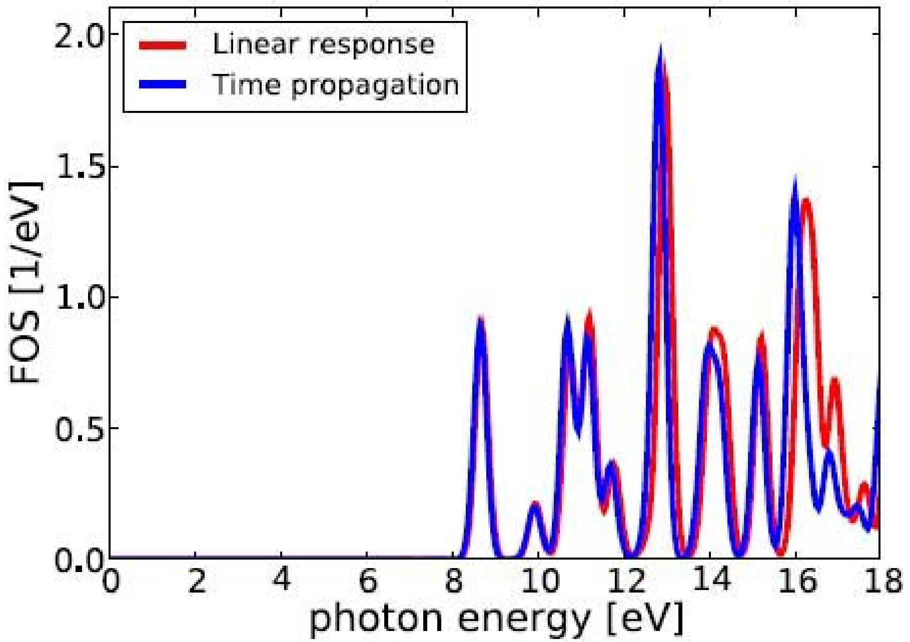


Figure 5: Calculated optical absorption spectra of CH_4 molecule presented as folded oscillator strengths (FOS). The calculation is performed both with the time-propagation and the linear-response method.

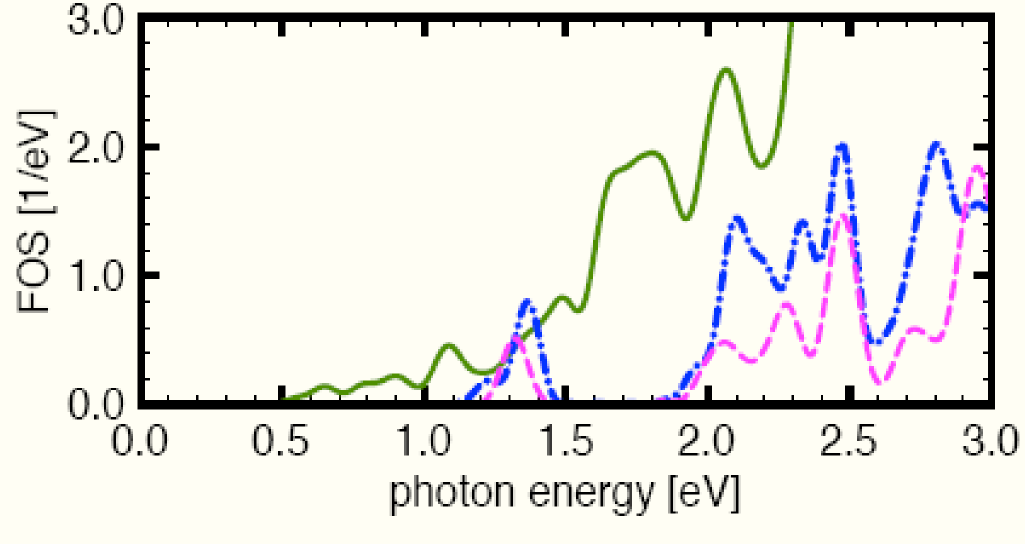


Figure 6: Optical absorption spectra of $Au_{25}(S\text{-}CH_3)_{18}^-$ (dashed magneta), $Au_{25}(S\text{-}CH_2\text{-}CH_2\text{-}C_6H_5)_{18}^-$ (dash-dotted blue), and $Au_{102}(S\text{-}CH_3)_{44}$ (solid green).

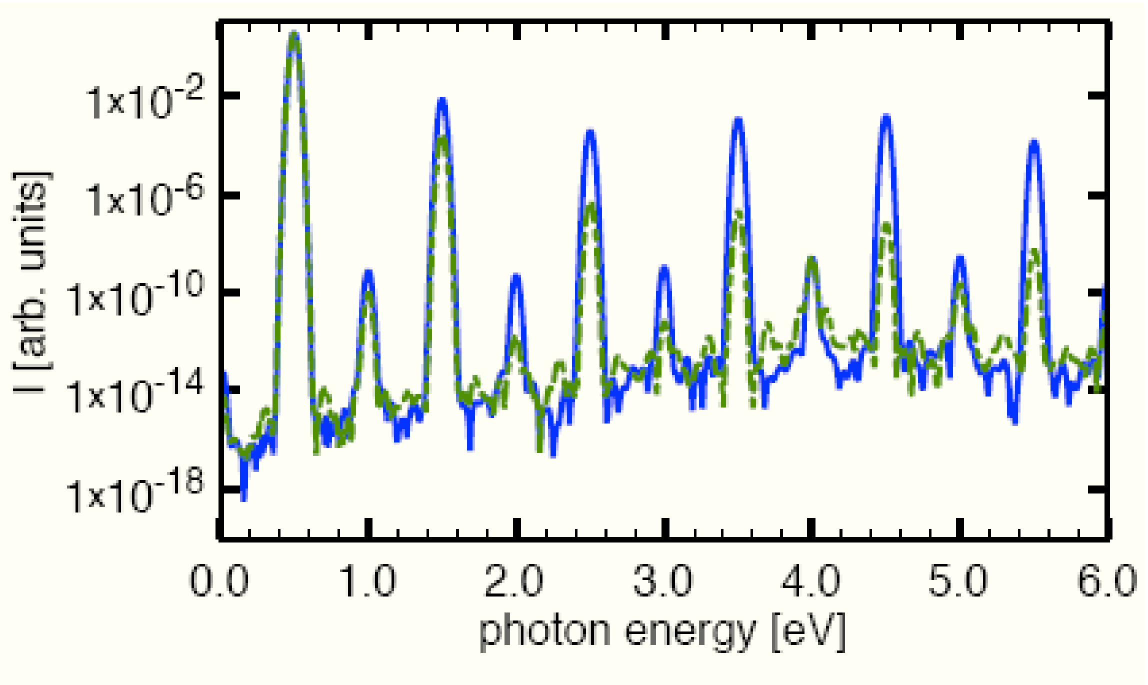


Figure 7: Non-linear emission spectra of Mg atom in a laser field of frequency 0.5 eV and strength of 0.01 (solid blue) and 0.05 (dashed green) atomic units. Strong harmonic frequency generation is observed at odd multiples of the laser field frequency.

Nonlinear effects: higher harmonics in emission spectra

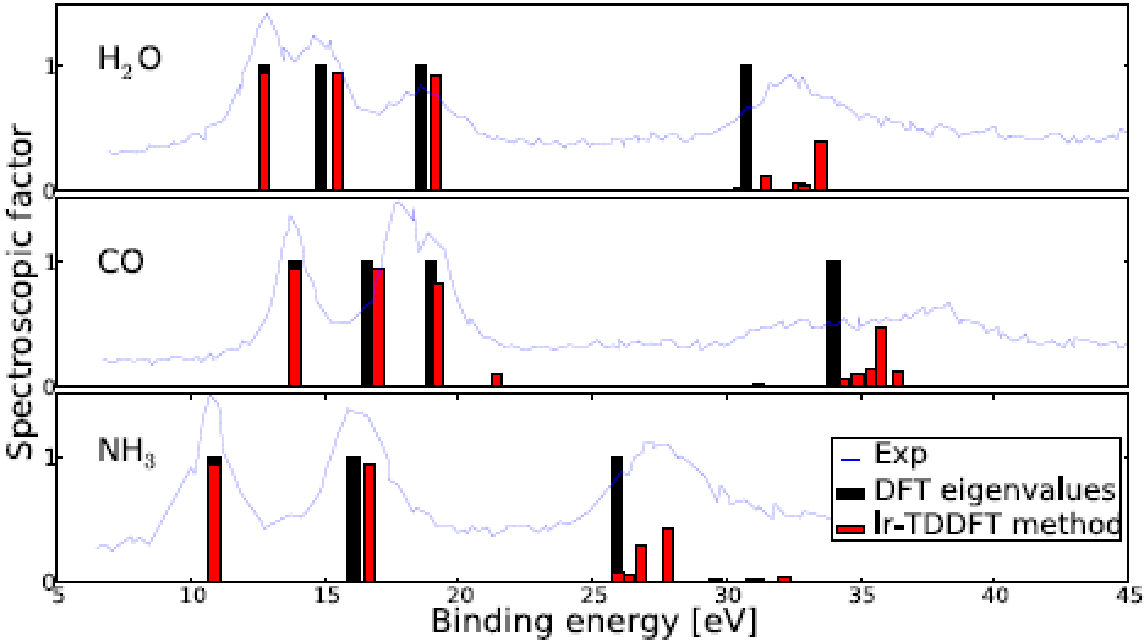


Figure 8: Experimental photoelectron cross sections (adapted from ref. [81]) compared with spectroscopic factors from TDDFT and Kohn-Sham approaches.

Photoelectron cross sections

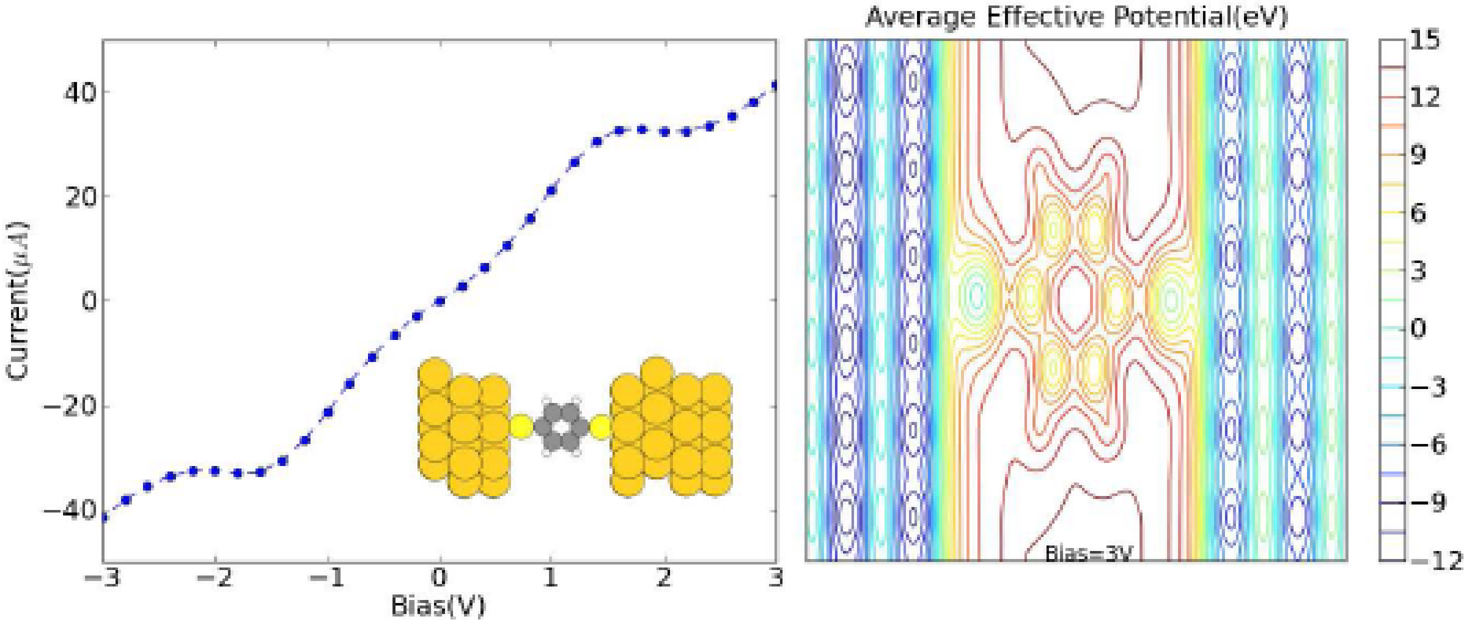


Figure 9: Left: Calculated IV curve for the Au/benzene-dithiolate junction shown in the inset. Right: Effective potential at a bias voltage of 3 volts.

Transport: open boundaries, finite-bias Landauer - Büttiker

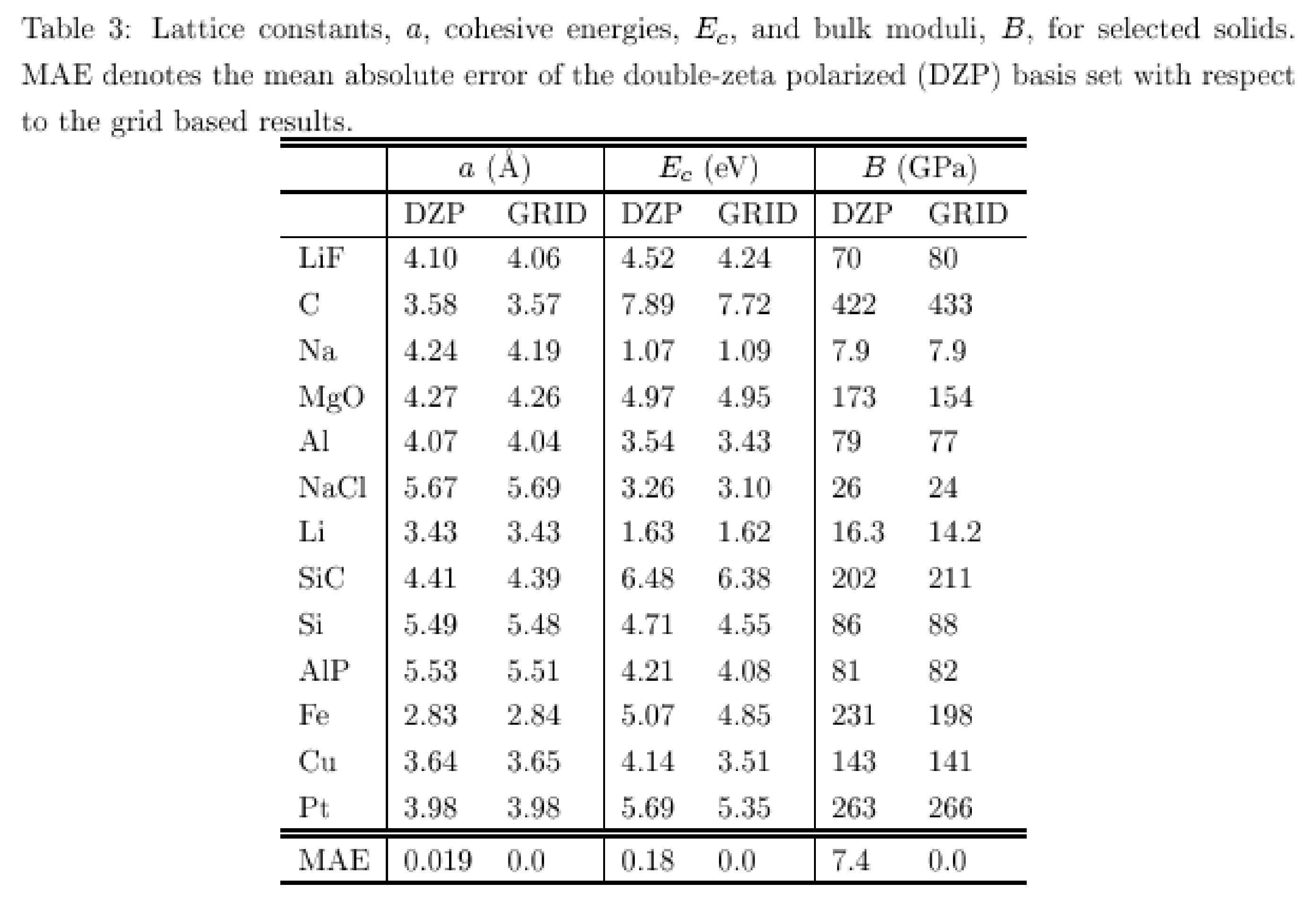


Table 3: Lattice constants, a, cohesive energies, E_c, and bulk moduli, B, for selected solids. MAE denotes the mean absolute error of the double-zeta polarized (DZP) basis set with respect to the grid based results.

	a (Å)		E_c (eV)		B (GPa)	
	DZP	GRID	DZP	GRID	DZP	GRID
LiF	4.10	4.06	4.52	4.24	70	80
C	3.58	3.57	7.89	7.72	422	433
Na	4.24	4.19	1.07	1.09	7.9	7.9
MgO	4.27	4.26	4.97	4.95	173	154
Al	4.07	4.04	3.54	3.43	79	77
NaCl	5.67	5.69	3.26	3.10	26	24
Li	3.43	3.43	1.63	1.62	16.3	14.2
SiC	4.41	4.39	6.48	6.38	202	211
Si	5.49	5.48	4.71	4.55	86	88
AlP	5.53	5.51	4.21	4.08	81	82
Fe	2.83	2.84	5.07	4.85	231	198
Cu	3.64	3.65	4.14	3.51	143	141
Pt	3.98	3.98	5.69	5.35	263	266
MAE	0.019	0.0	0.18	0.0	7.4	0.0

Also: localised basis sets

Other utilities

- ΔSCF
- Wave function overlaps
- X-ray absorption spectra
- Wannier orbitals
- Density analysis and partitioning

Parallel calculations

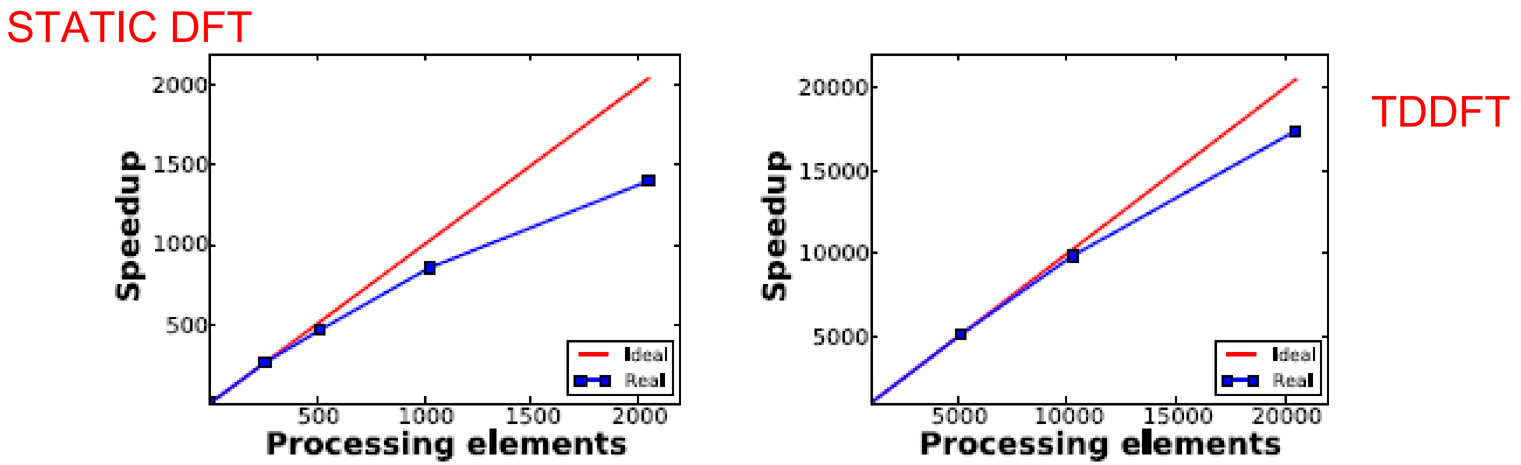


Figure 14: Parallel scaling for ground state total energy calculation (left) and for real-time propagation (right). The calculations are performed on a Cray XT5 systems at CSC and at Oak Ridge National Laboratory. The speedup is normalized so that at the first data point (256 PEs on left and 5000 PEs on right) the speed-up equals the number of PE's.

Key issue: real-space domain decomposition

(Mark Ratner)

Overall Challenge: *Making the Leap from Observation Science to Control Science*

The things we want to do (i.e. designing materials to have the properties we want & directing synthesis to achieve them) require the ability to see functionality at the relevant time, length & energy scales.

We will need to develop & disseminate new tools capable of viewing the inner workings of matter—transport, fields reactivity, excitations & motion

This new generation of instruments will naturally lead to devices capable of directing matter at the level of electrons, atoms, or molecules.