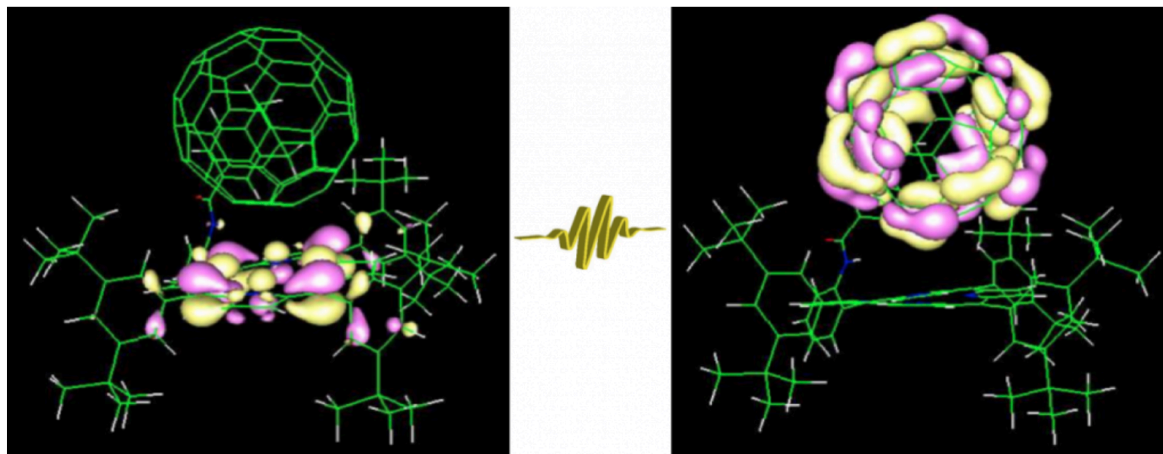


Light-matter interaction

We develop and use electronic structure calculation methods, the fundamental tools for understanding and utilizing the game of electrons and photons



Materials physics

Materials are the most important premise for engineering technology. Therefore, we develop and use electronic structure calculation methods and other modeling approaches for materials physics, the fundamental tools for understanding materials properties and development of better and new materials.

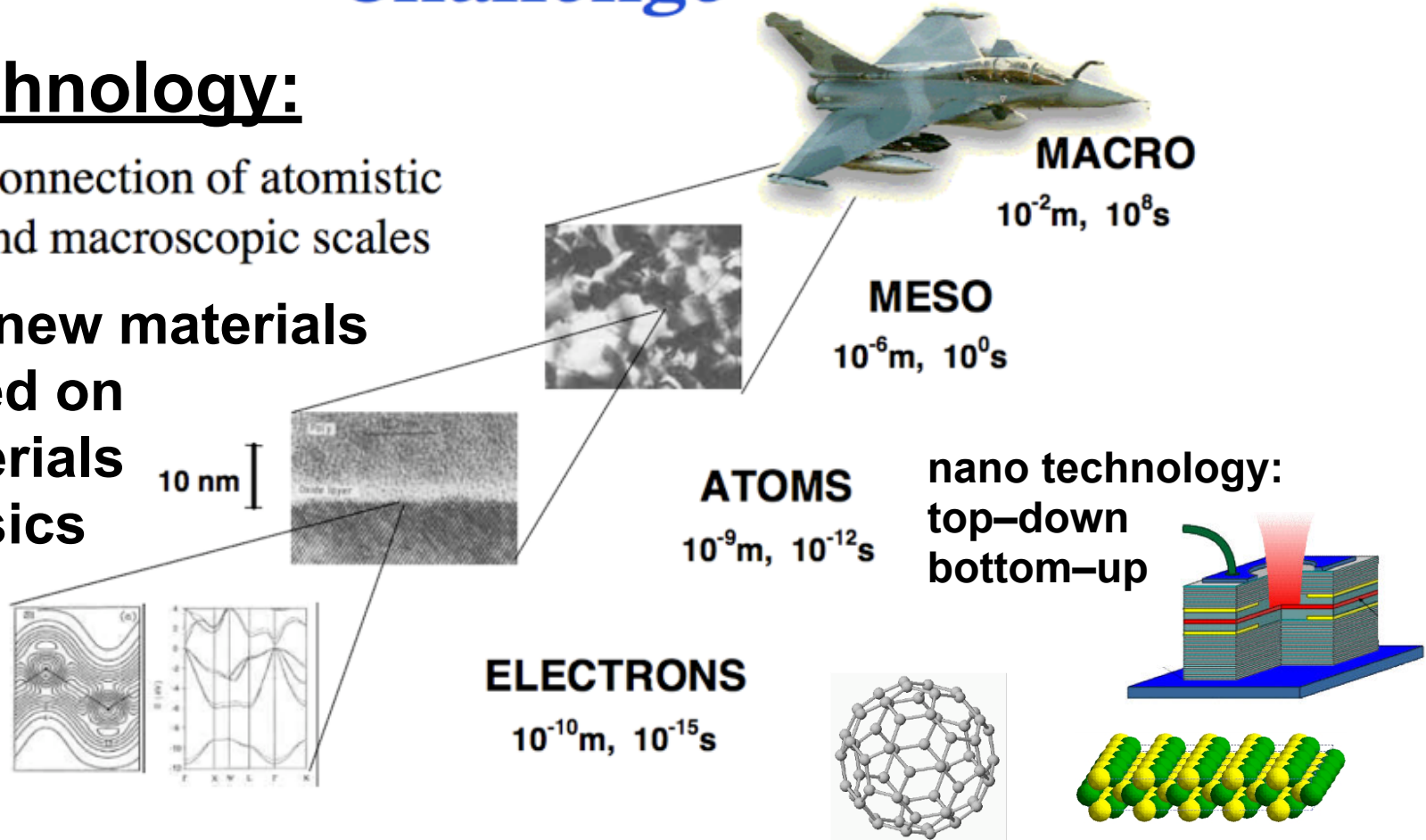
ENGINEERING AND TECHNOLOGY

Challenge

Technology:

Connection of atomistic
and macroscopic scales

and new materials
based on
materials
physics

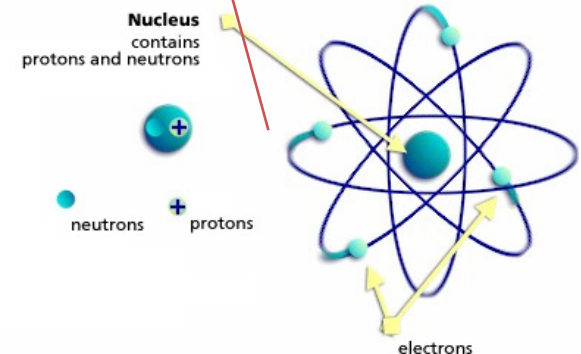
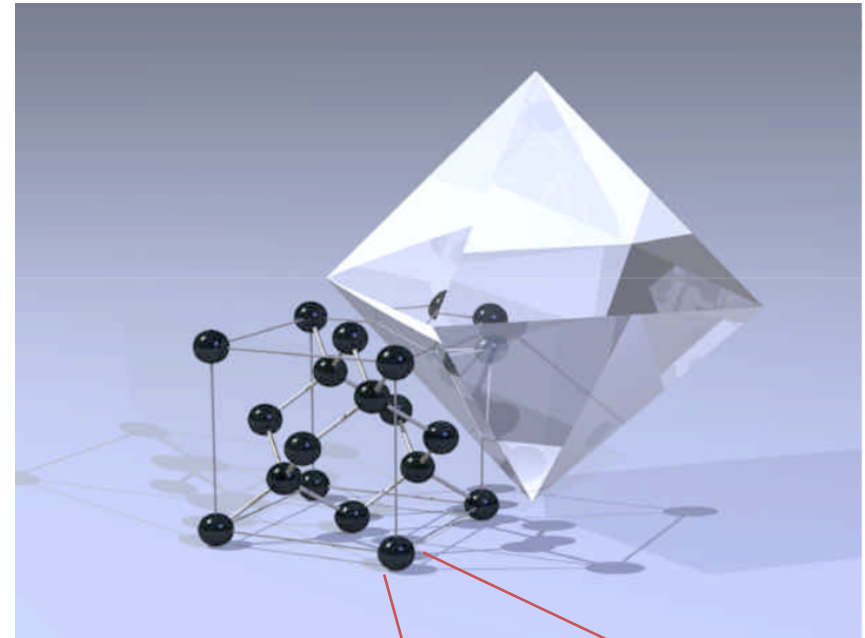


MATERIALS PHYSICS

EST field of science

Materials physics

- properties of matter
- understanding with intuitive models
- prediction
- design of new materials with controlled properties or upgrading old ones

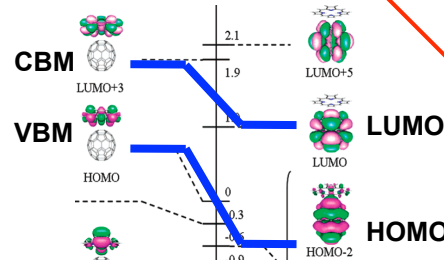
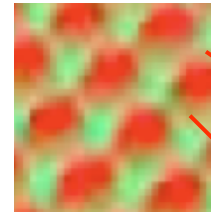
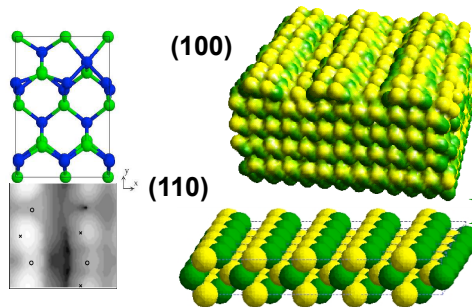
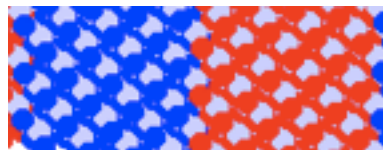
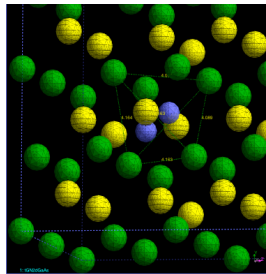


THEORETICAL AND COMPUTATIONAL MATERIALS PHYSICS @ EST

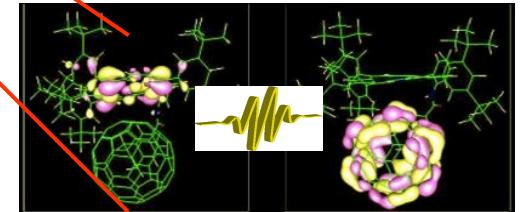
4

H-P. Komsa: PhD Thesis (2008)

Compound semiconductor physics



O. Cramariuc: PhD Thesis (2006)
(Bio)molecular
O. Kontkanen: PhD Thesis (2018)
(opto)electronics

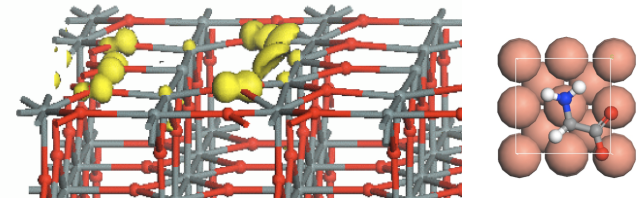


M. Kuisma: PhD Thesis (2014)



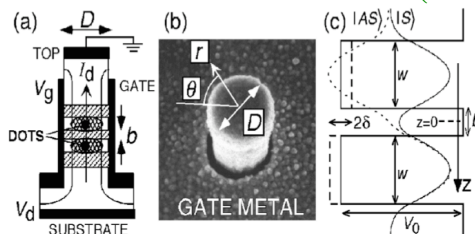
Surface science

M. Viitala: PhD Thesis (2012)



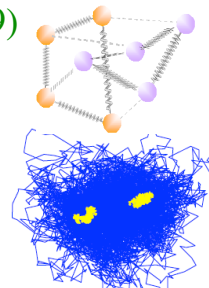
Path-Integral Quantum Monte Carlo

I. Ruokosenmäki: PhD (2019)

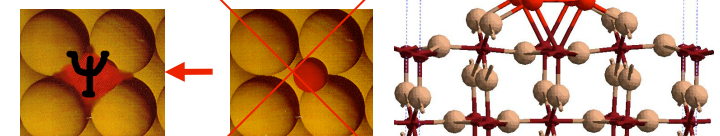


J. Tiihonen: PhD (2019)

I. Kylänpää: PhD (2011)



M. Mäki-Jaskari: PhD Thesis (2004)



M. Leino: PhD (2007)

SOFTWARE: DFT

ACADEMIC/COMMERCIAL CODES:

- PlaneWave basis



CASTEP

abinit.org

PBC

- localized (atomic) basis

DMol³



finite

- Real-space grid



TURBOMOLE GmbH



PBC and finite

ASE: abinit

Asap Dacapo



EMT



- (Gromacs for molecular dynamics)

MOTIVATION FOR METHOD DEVELOPMENT

Electronic structure is the **key quantity to materials properties** and related phenomena:
Mechanical, thermal, electrical, optical,... .

Conventional *ab initio* / first-principles type methods

- suffer from laborious description of electron–electron **correlations** (CI, MCHF, DFT-functionals)
- typically ignore nuclear quantum and thermal dynamics and coupling of electron–nuclei dynamics (**Born–Oppenheimer approximation**)
- give the **zero-Kelvin description, only.**
- are typically good for **stationary states, only.**

PATH INTEGRALS IN REAL AND IMAGINARY TIME

7

$$H\psi(x, \tau) = -\frac{\partial\psi(x, \tau)}{\partial\tau} \quad \xleftarrow{\tau = it} \quad H\psi(x, t) = i\frac{\partial\psi(x, t)}{\partial t}$$

$$\psi(x, \tau) = \int G(x, \tau; x_a, \tau_a) \psi(x_a, \tau_a) dx_a$$

$$\psi(x, t) = \int K(x, t; x_a, t_a) \psi(x_a, t_a) dx_a$$

$$\rho(x_b, \tau_b; x_a, \tau_a) = \int_{x_a}^{x_b} \exp(-S[x_b, x_a]) \mathcal{D}x(\tau)$$

$$K(x_b, t_b; x_a, t_a) = \int_{x_a}^{x_b} \exp(iS[x_b, x_a]) \mathcal{D}x(t)$$

Quantum statistical physics in equilibrium
at temperature T , $\tau_b - \tau_a = \beta = 1/k_B T$

Real Time Path Integrals (RTPI):
Time evolution in real time

$$\psi(x, \tau) = \sum_{n=0}^{\infty} C_n \phi_n(x) \exp[-E_n \tau]$$

$$\psi(x, t) = \sum_{n=0}^{\infty} C_n \phi_n(x) \exp[-iE_n t]$$

Diffusion Monte Carlo (DMC)

Stationary states from incoherent RTPI

Feynman–Hibbs, *Quantum Mechanics and Path Integrals*, (McGraw-Hill, 1965)

PATH INTEGRALS IN IMAGINARY AND REAL TIME

$$H\psi(x, \tau) = \frac{\partial \psi(x, \tau)}{\partial \tau}$$

$$\leftarrow \tau = it$$

$$H\psi(x, t) = i \frac{\partial \psi(x, t)}{\partial t}$$

$$\psi(x, \tau) = \int G(x, \tau; x_a, \tau_a) \psi(x_a, \tau_a) dx_a$$

$$\psi(x, t) = \int K(x, t; x_a, t_a) \psi(x_a, t_a) dx_a$$

--- PATH INTEGRAL APPROACHES ---

τ DMC

The
conventional
Diffusion Monte
Carlo (DMC)

$$G = G_{\text{diff}} G_B$$

$$G_{\text{diff}} = C_1 \exp(-\Delta x^2 / 2\tau)$$

$$G_B = C_2 \exp[-(\bar{V} - E_T)\tau]$$

everywhere real
and positive !

PIMC

$$\rho = \int \exp(-S) Dx(\tau)$$

Quantum statistical
physics in
equilibrium at
temperature $T > 0$,

$$\tau_b - \tau_a = \beta = 1/k_B T$$

Feynman–Hibbs, *Quantum Mechanics and Path Integrals*,
(McGraw-Hill, 1965)

RTPI

$$K = \int \exp(iS) Dx(t)$$

$$S[x_b, x_a] = \int_{t_a}^{t_b} L_x dt$$

Coherent time evolution in real time
and stationary eigenstates from
incoherent evolution

tDMC

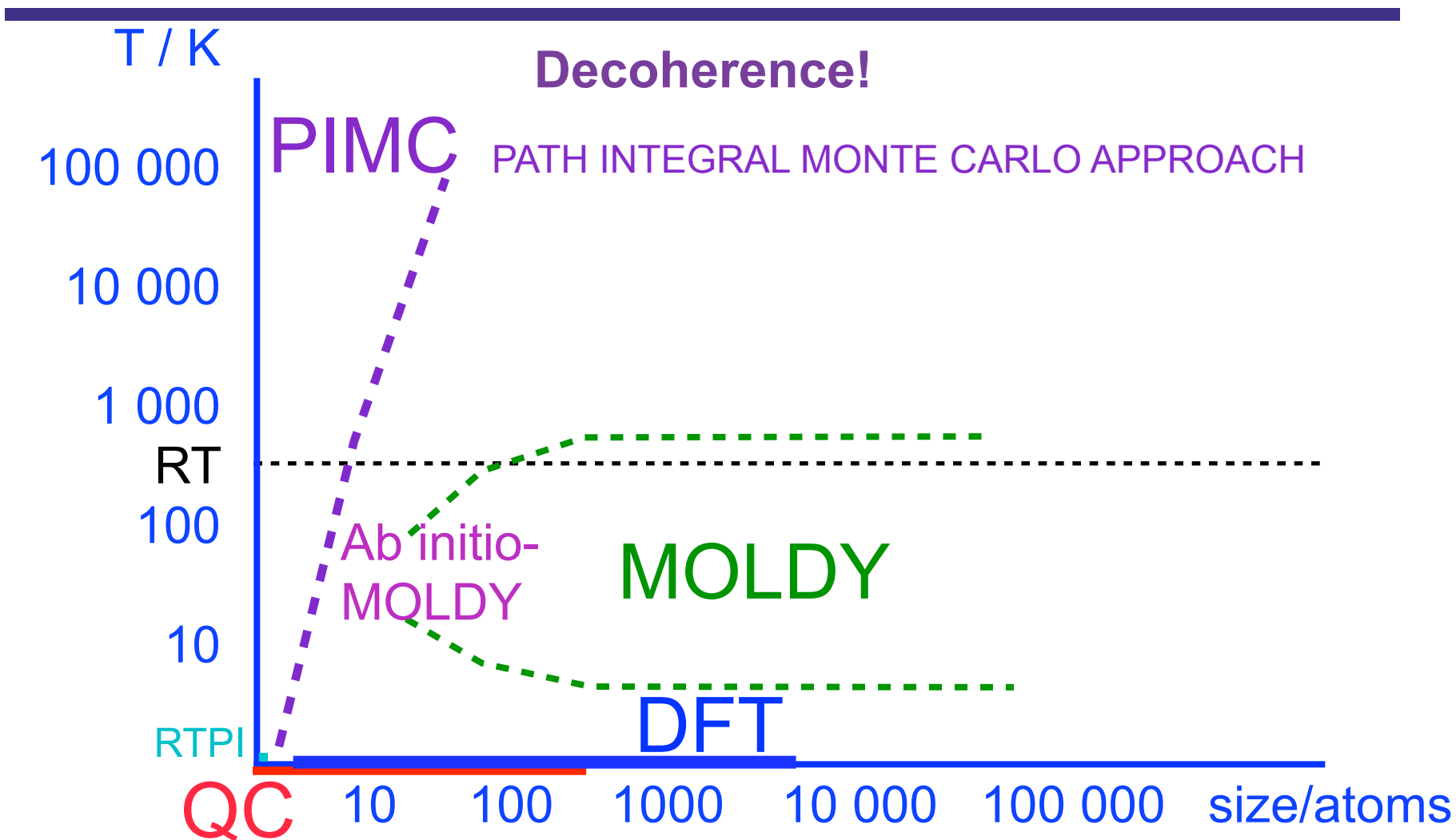
$$K = C \exp(i\phi)$$

complex function !

QUANTUM / CLASSICAL APPROACHES TO DYNAMICS

time dependent	MOLECULAR DYNAMICS	Wave packet approaches RTPI	RTPI	TDDFT RTPI	Car–Parrinello and
$T > 0$ equilibrium	MOLECULAR DYNAMICS Metropolis Monte Carlo	PIMC Rovibrational	PIMC	PIMC	<i>ab initio</i> MOLDY
$T = 0$	Molecular mechanics	approaches	RTPI DMC VMC	<i>ab initio</i> Quantum Chemistry / DFT / semiemp.	
electronic dyn.:			Q	Q	Q
nuclear dyn.:	Class	Q	Q		Class

SIZE AND TEMPERATURE SCALES

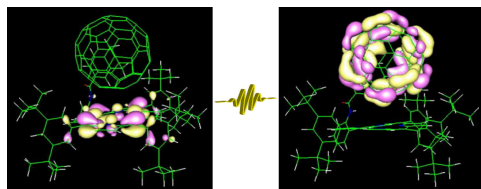


ELECTRONIC STRUCTURE THEORY

with applications and method development

for materials physics, engineering and quantum chemistry

Light–Matter Interaction

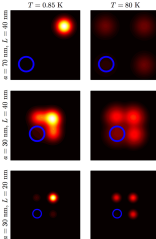


Applications to

- solar cells
- heterogeneous catalysis
- information tech. (QD-QCA)

Sharma, TTR, Hoggan: QMC for heterog. catalysis, *Int. J. Q. Chem* (2020), and *JPCC* (2020); Golovanova *et al.*, Solar irradiation . . . catalyst, *Appl. Catal. B* (2021)

M. Kuisma: GLLB
PhD Thesis (2014)



Teaching activities

- FYS-1470 Aineen rakenne
- FYS-1550 Fysiikan seminaari / Physics seminar
- FYS-4706 Quantum Theory of Electronic Structures

Nobel-
iltapäivä



Path Integral Approach to Quantum Mechanics

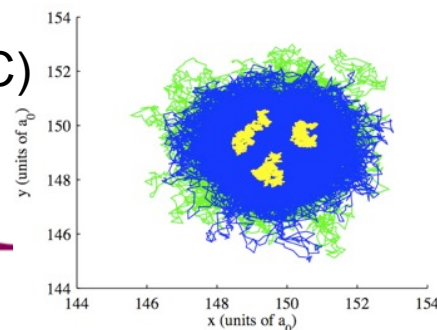
$$\psi(x, t) = \int K(x, t; x_a, t_a) \psi(x_a, t_a) dx_a \longleftrightarrow H\psi(x, t) = i \frac{\partial \psi(x, t)}{\partial t}$$

- fundamental approach to quantum many-body theory
- quantum dynamics and thermal equilibrium ($T > 0$)
- **numerical approaches** with Path Integral Monte Carlo (PIMC) Real Time Path Integral (RTPI) **software development** and **number crunching**

I. Kylänpää: PhD Thesis (2011)

I. Ruokosenmäki: PhD Thesis (2019)

J. Tiihonen: PhD Thesis (2019)



<http://iki.fi/trantala/paths>

QMC Optical Hyper Polarizabilities for Photonics

- full quantum approach to photonics/optical materials
- search for the underlying structure–function relations

GRAND CHALLENGE:
take path integrals to
quantum chemistry

<http://orcid.org/0000-0001-8581-502X>

<http://iki.fi/trantala/papers>

QMC FOR PHOTONICS

QMC evaluation of optical hyper polarizabilities of 2D materials for photonics:

Materials response to the external electric field, mainly with PIMC, i.e., at *ab initio* level for

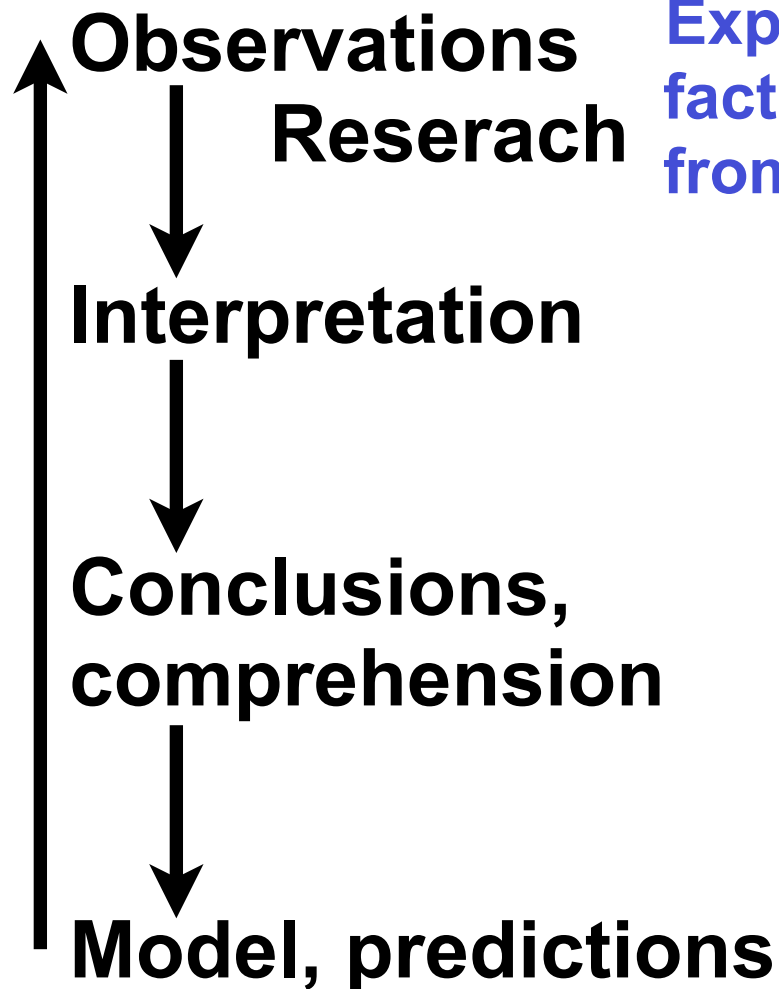
- photonics relevant materials like ENZ**
- nanostructures, structured light**
- dynamics: pulses**

David Trejo Garcia (QMC, PIMC)

Saijad Ahmadi (QMC, RTPI)

int. collaborators (DFT, QMC)

SCIENCE



Experiments with control of relevant factors or systematic data collection from observations

Specific features:

- general concepts, no cultural dependence
- truth or (high) probability
- no contradictions
- publicity, no authors
- (self-)criticism: self-correcting
- cumulative: "progressive"

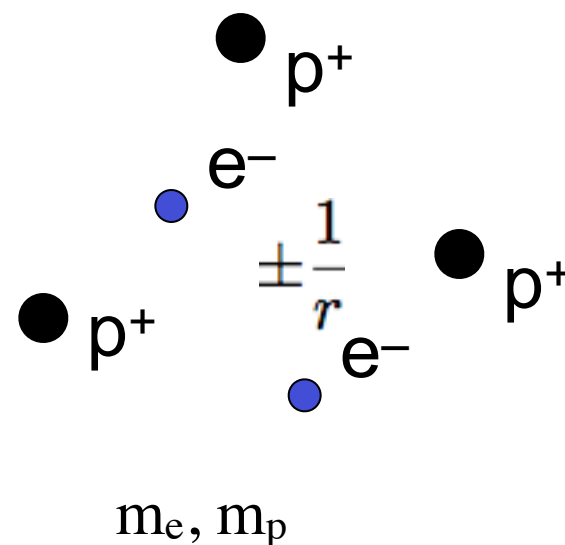
Resulting in the most reliable information

$$\beta = \frac{1}{kT}$$

H₃⁺ MOLECULE

Quantum statistical physics of two electrons and three nuclei (five-particle system) as a function of temperature:

- Structure and energetics:
 - quantum nature of nuclei
 - pair correlation functions, contact densities, ...
 - dissociation temperature
- Comparison to the data from conventional quantum chemistry.



Ab initio or first-principles!

QUANTUM DOTS IN QCA

- Finite temperature and electron delocalization

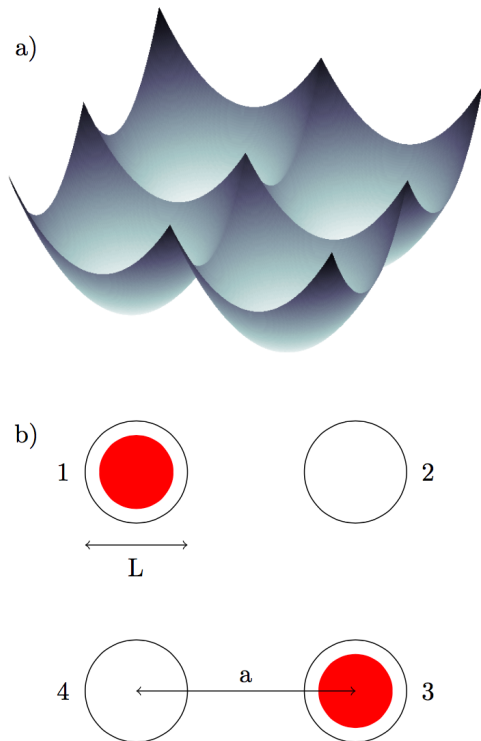


FIG. 1. (a) A visualization of harmonic confinement potential of our QCA cell model. (b) Schematic picture of an ideal QCA setup, where the two electrons occupy either "0" bit (sites 1 & 3) or "1" bit (sites 2 & 4). The site separation a and QD size L are marked.

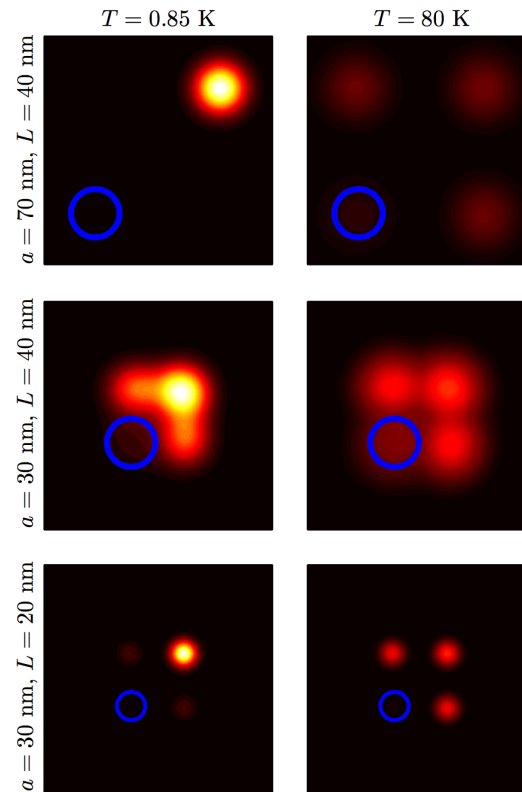


FIG. 3. The density distribution of one electron is plotted according to the reference electron (blue circle) at $T = 0.85$ K (left) and $T = 80$ K (right) with different separation distances and QD sizes. The normalization is the same in both temperatures.

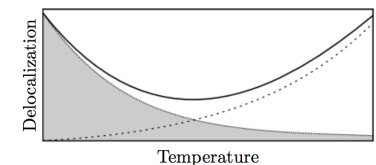
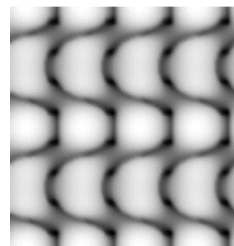
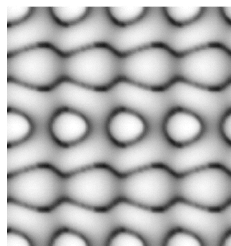
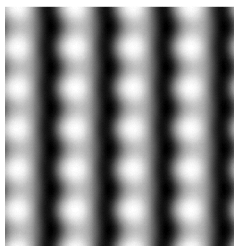


FIG. 6. A schematic separation of the total delocalization (solid line) to thermal part (dashed) and quantum mechanical part (dotted) as functions of temperature. The gray area causes the difference in fidelity between full quantum and classical data.

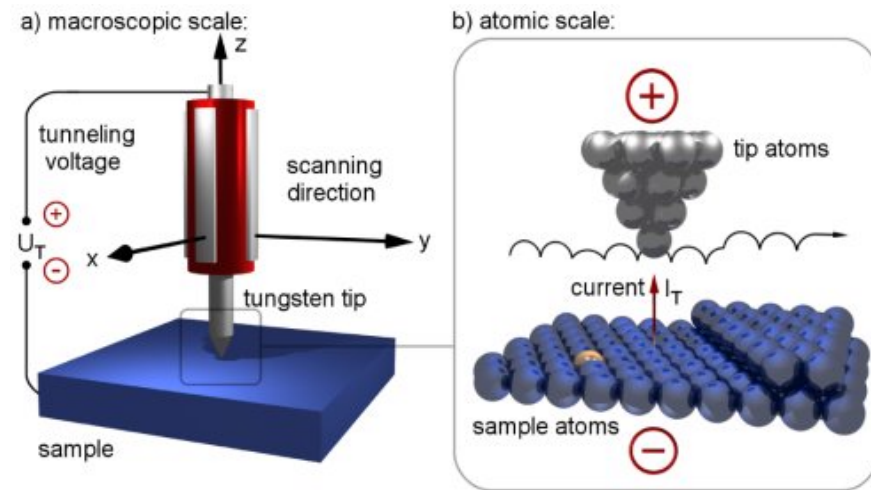
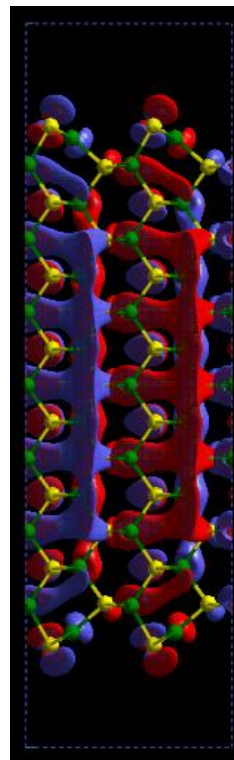
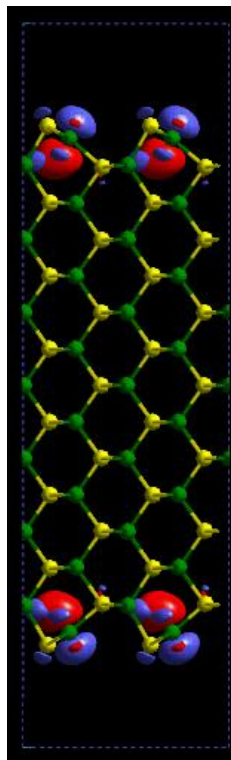
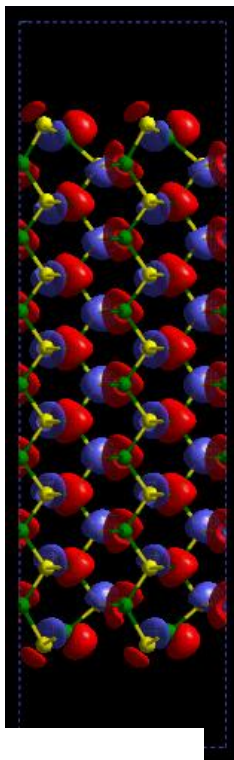
STM IMAGE SIMULATION OF GaAs (110) SURFACE

16



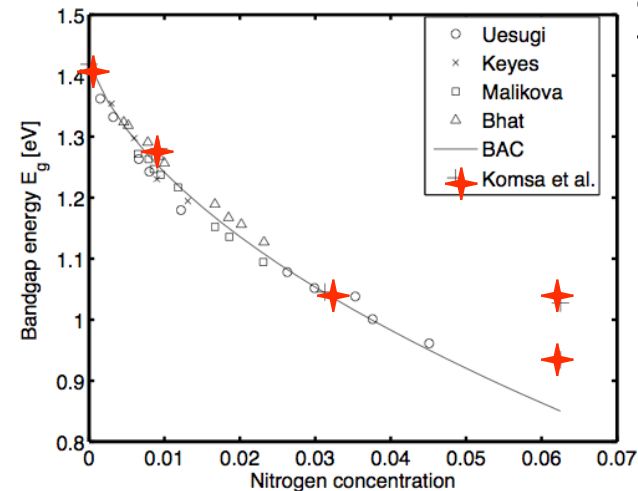
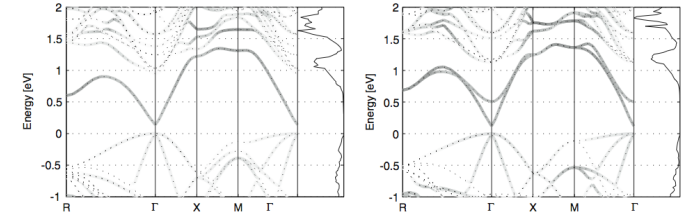
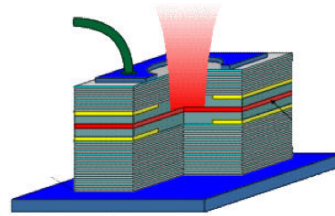
Ville Arpiainen, Jouko Nieminen and Tapio T. Rantala, *Interpretation of orientational contrast in STM images of GaAs(110) cleavage surface*, **Surface Science**, 584/1, 27–34 (2005).

SCANNING TUNNELING MICROSCOPE (STM)

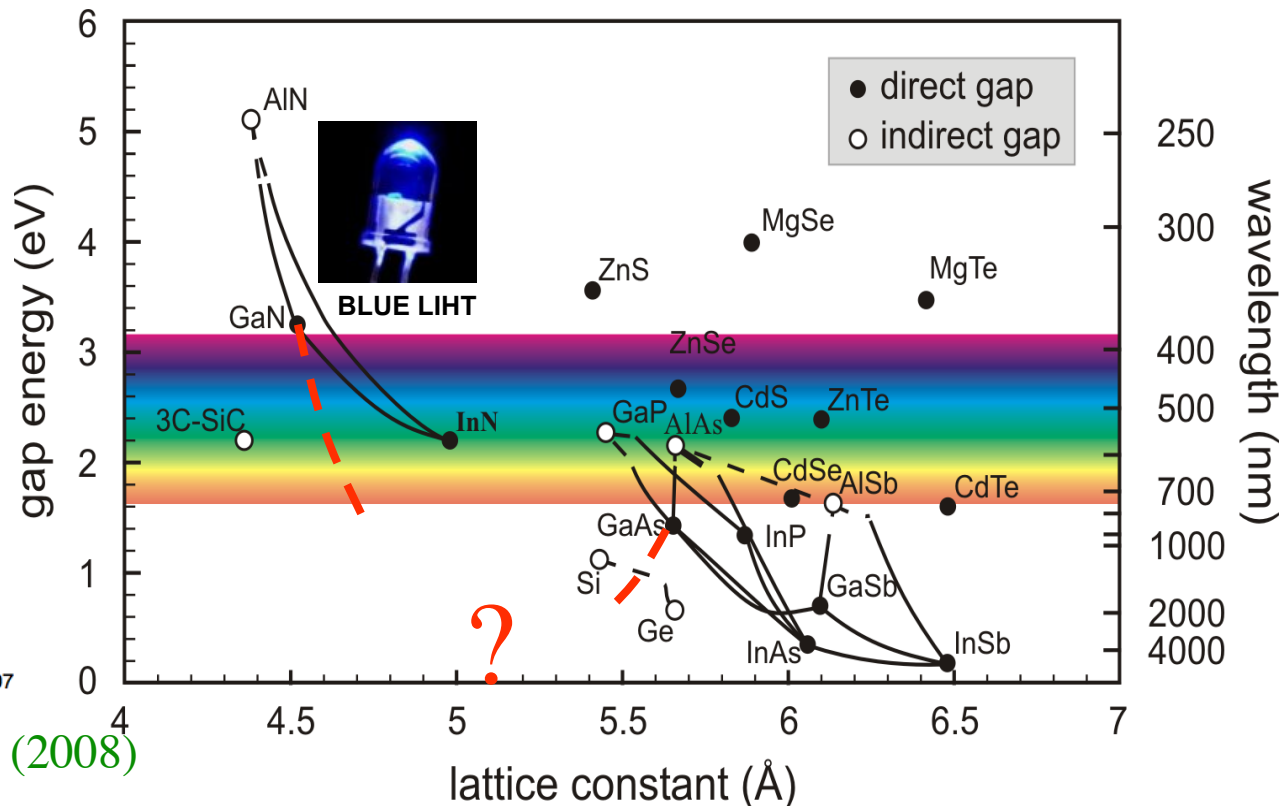


GaAs_{1-x}N_x AND GaN_{1-y}As_y

Central compounds
in optoelectronic
applications,
GaAs: opt. comm.
GaN: blue light
GaAsN: band
bowing



H-P. Komsa: PhD Thesis (2008)



ELECTRONIC STRUCTURE

Ground State and Excited States

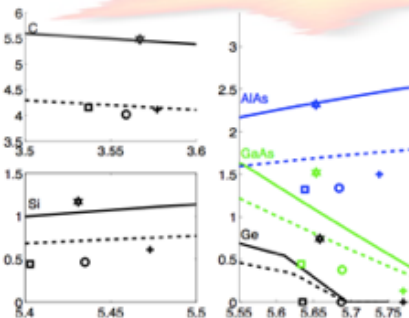
Eigenvalue Problem

- At zero-Kelvin

$$\hat{H}\Psi_k = E_k \Psi_k$$

- Hartree–Fock, CI, MCHF
- Density Functional Theory (DFT – “the work horse”)

Robust Solution to the Semiconductor BAND GAP PROBLEM



- Evaluation of the missing discontinuity: Total (solid curve), LDA-KS (square) and GGA-KS (circle) compared with the experimental (star).
- Further work ongoing

Electronic structure is the basic concept behind structure and properties of matter!

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Explicit Time Propagation

- At zero-Kelvin
- Time-Dependent DFT (TDDFT)



Temperature or Time Dependent States

Quantum Statistical Physics

- Feynman path-integral approach

$$\rho(R(0), R(\beta)) = \int_{R(0)}^{R(\beta)} e^{-S(R(\tau))} \mathcal{D}R(\tau)$$

$$Z(\beta) = \text{Tr} \rho$$

Path Integral Monte Carlo (PIMC)

- Explicitly temperature dependent NVT-ensemble simulation
- Full account of electronic correlations
- Allows model and calculations beyond Born–Oppenheimer approximation, i.e., potential energy surface (PES)
- Accepting the challenge of

FERMION SIGN PROBLEM !

T>0 Ab Initio Quantum Chemistry