Abinit : Excited states within TDLDA & Langevin molecular dynamics

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Outlook

- Langevin dynamics
  - Background
  - Implementation
  - Test case
  - Examples
    a. Structural optimization via simulated annealing
    b. Structure and dynamics of liquids

- Time dependent LDA
  - Background
  - Implementation
  - Test case
  - Example
    a. TDLDA spectra of carbon and silicon nanoclusters
    b. Discussion TDLDA vs other methods

Finite T Molecular dynamics

- 2 thermostats included
  - Ionmov 8 *Nose-Hoover thermostat*

    Variables : dtion, mditemp, mdftemp, noseinert

  - Ionmov 9 *Langevin thermostat*

    Variables : dtion, mditemp, mdftemp, friction

    mdwall, sigperm,delayperm

Langevin dynamics

Movement equations :

$$m_j \ddot{\vec{R}}_j = \vec{F}(\{R_j\}) - \gamma m_j \dot{\vec{R}}_j + \vec{G}_j$$

$$\gamma = friction\ \ coefficient$$

$$G_j = gaussian\ random\ \ force$$

$$\langle G_i^{\alpha}(t) \rangle = 0$$

$$\langle G_i^{\alpha}(t) G_j^{\beta}(t') \rangle = 2\gamma m_i k_B T \delta_{ij} \delta(t - t')$$

See J. Chelikowsky, J. Phys. D : Appl Phys. 33(2000)R33.

Implementation

- Src9drive/moldyn.f

Tests

- Test_v2/

87. Ge liquid. Test of Nose dynamics. 2 atoms in a cell. Allows 4 time steps. .

88. Ge liquid. Test of Langevin dynamics. 2 atoms in a cell.

Simulated annealing : Clusters optimization

- Variables :

  Ionmov 9
  dtion ~100
  Mditemp 3000
  Mdftemp 300
  Ntime 200

- Optional variables :

  mdwall
  getvel
  signperm
  delayperm

Si_n, Ge_n n<11

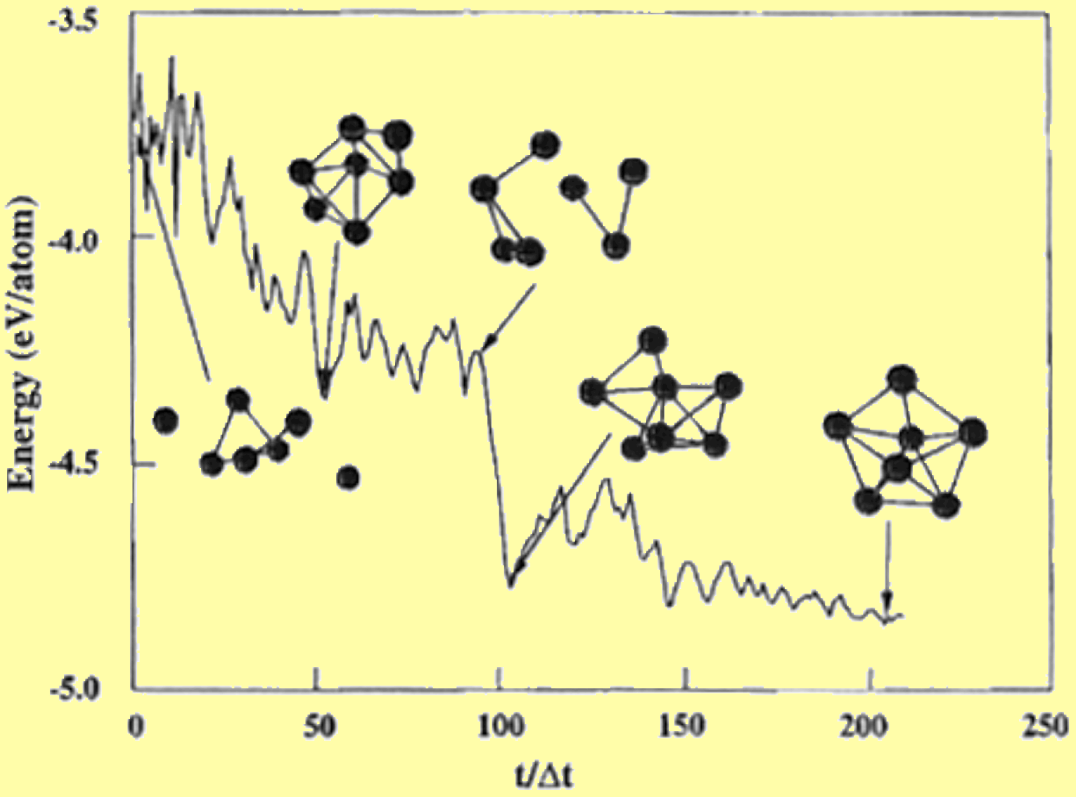


Figure 5. The binding energy of Si_7 during a Langevin simulation. The initial temperature is 3000 K; the final temperature is 300 K. Bonds are drawn for interatomic distances of less than 2.5 Å. The time step is 5 fs.

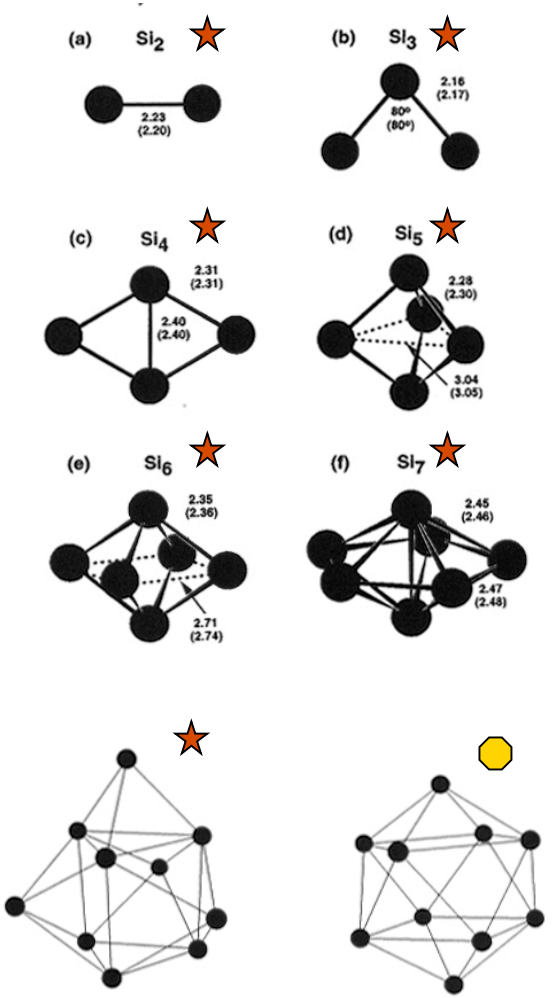


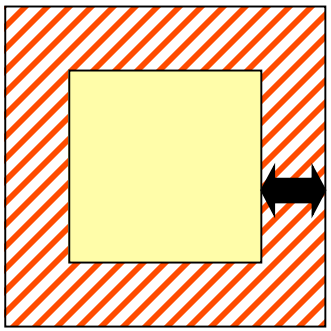
Figure 7. Two possible isomers for Si_{10} or Ge_{10} clusters. (I) is a tricapped trigonal prism cluster and (II) is a bicapped antiprism cluster.

```
#Cluster optimization via simulated annealing
#*******************************************************
   acell 3*25
   xcart  ……
   occopt  4

   ionmov 9            #Langevin dynamics
   ntime 100
   dtion 100

   friction 0.001
   mdwall 3.0          # optional

   mditemp1 3000
   mdftemp1 2500
   tsmear1 0.05
   tolvrs1 1.0d-2

   mditemp2   2500
   mdftemp2   2000
   tsmear2     0.04
   getxcart2   -1
   getvel2     -1
   tolvrs2     1.0d-2
   ……..

# Then end with a Broyden minimization
```

Sample Input

- Adapt tsmear to T_ion
- Getvel -1

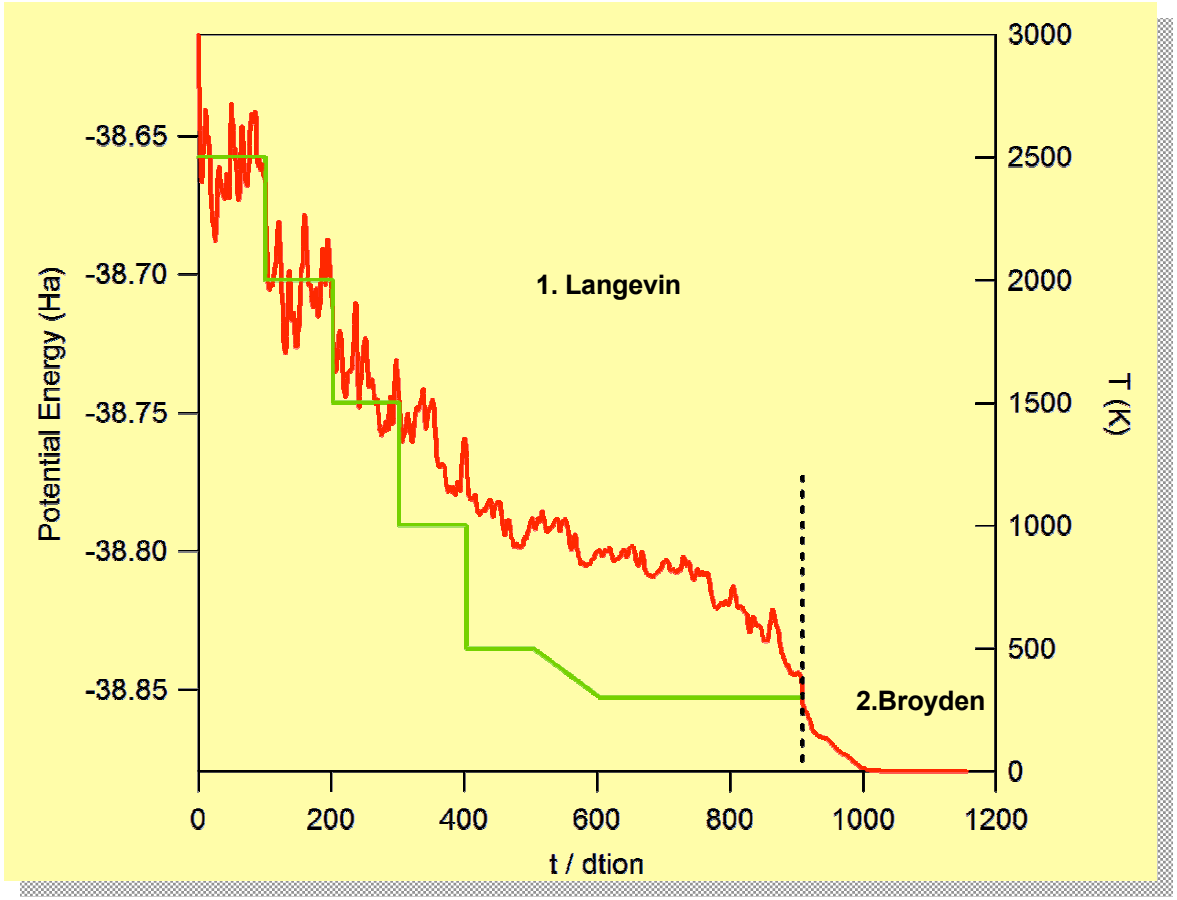
At startup :
If E_kin = 0, atoms are given random velocities (mditemp)
Otherwise, velocities are rescaled to the requested mditemp.

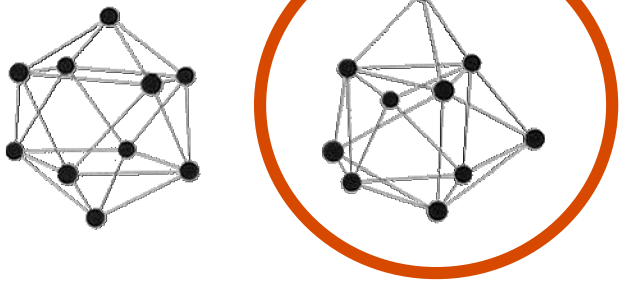


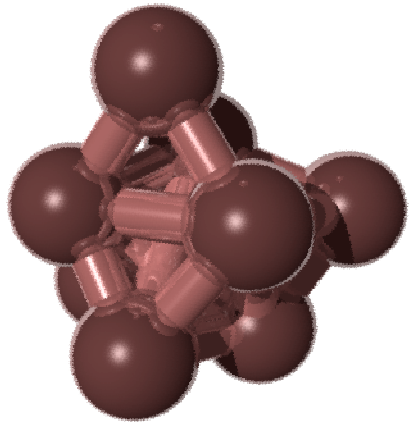
mdwall (a.u.)

Ge10

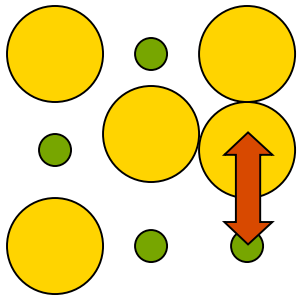
?


Potential Energy (Ha)
-38.65
-38.70
-38.75
-38.80
-38.85
1. Langevin
2.Broyden
0
200
400
600
800
1000
1200
t / dtion
3000
2500
2000
1500
1000
500
0
T (K)





Optional variables



For binary systems :

delayperm : nr of time steps between attemps for exchanging 2 atoms from different type

signperm +1 favors alternation

-1 segregation

Under development, not optimized

Liquids simulation

- System 56 atoms
- GS stuff LDA & GGA
- Molecular dynamics strategy

  1) Random cfg, 5ps at 3000K
  2) Temperature ramp mditemp 3000, mdftemp 700, ntime 1000, dtion 200 (5ps)
  3) Thermalization at mdftemp (typical 5ps)
     - Check : diffusivity + potential energy
  4) Data acquisition

     Keep *friction* as low as possible

Eutectic Ge-Te alloy

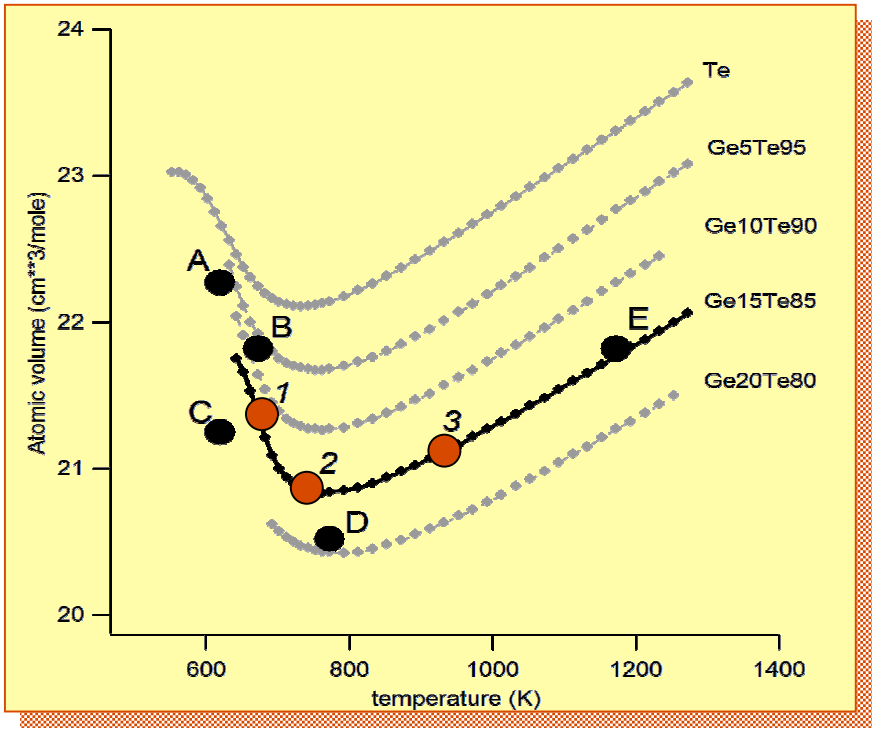
- Why ?

  Glass forming,

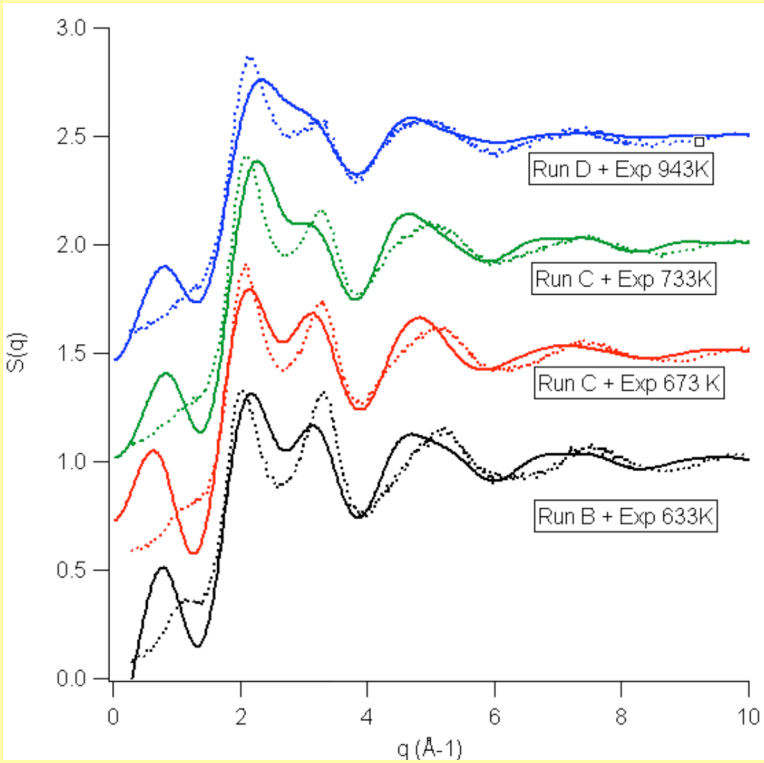
  strong anomalous behavior
  pseudo Liquid-Liquid transition

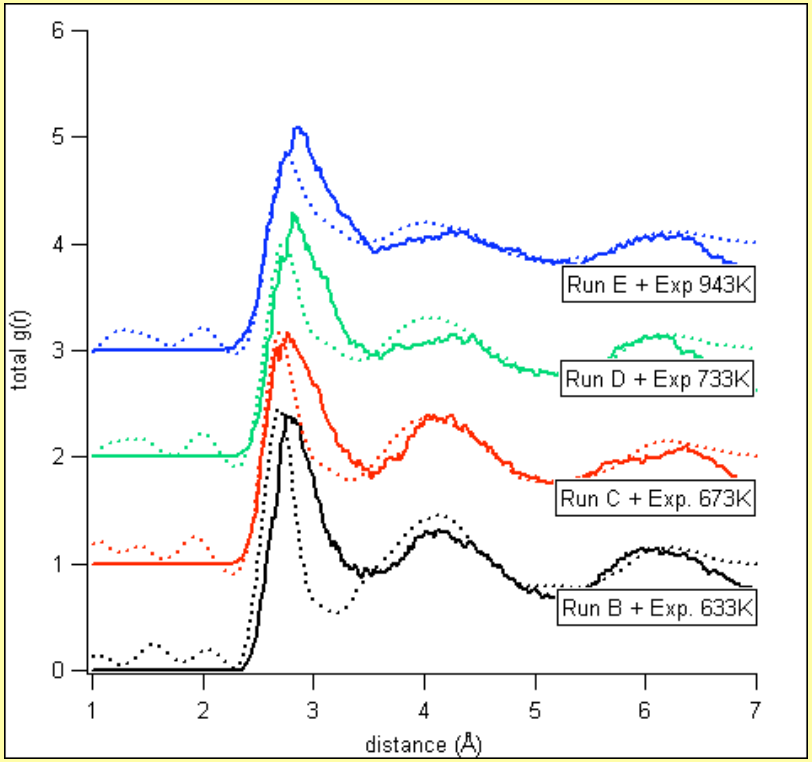
- LDA vs GGA
  - LDA ok GeTe, not that ok for Ge1Te6…

- Limitation : fixed volume
  - Importance of the density



$GeTe_6$: comparison with experiments



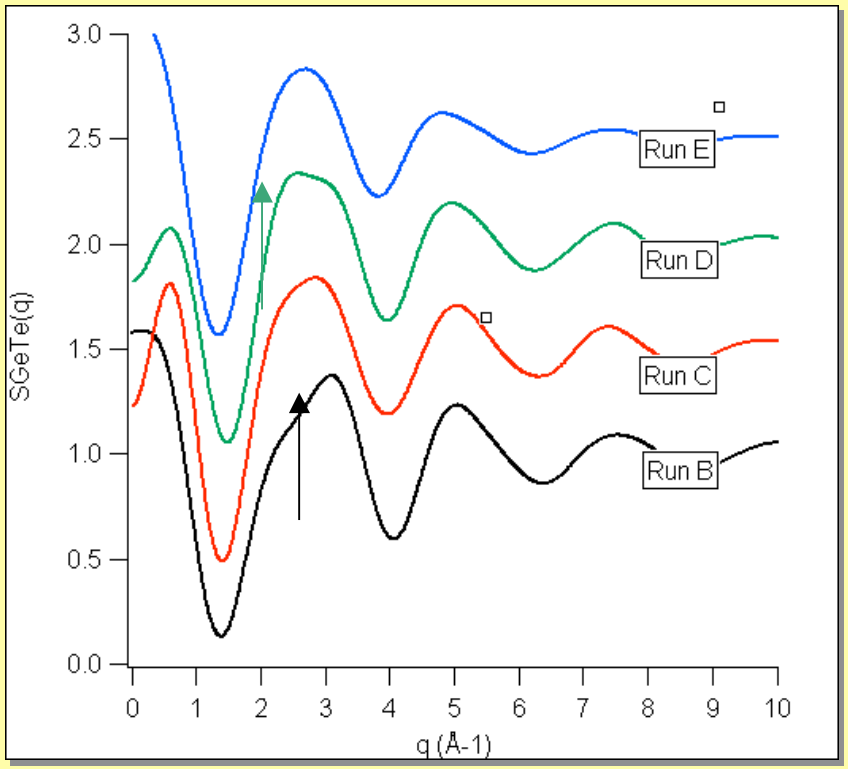


Agreement could be better but general trends OK

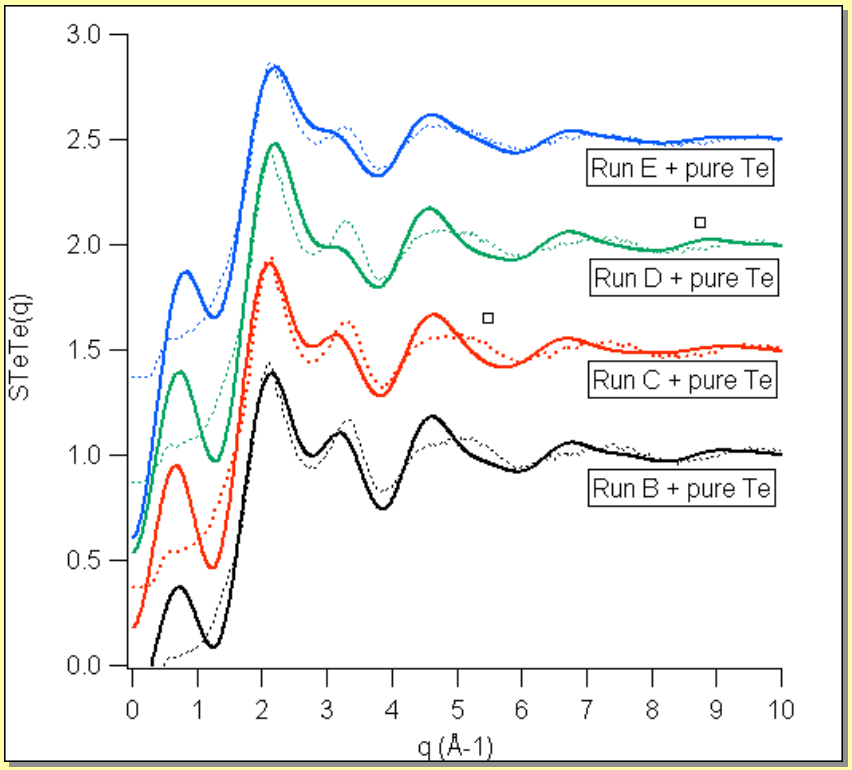
Problems : 85 % Te ! Large temperature fluctuations

$GeTe_6$: partial structure factors

$S_{GeTe}(q)$



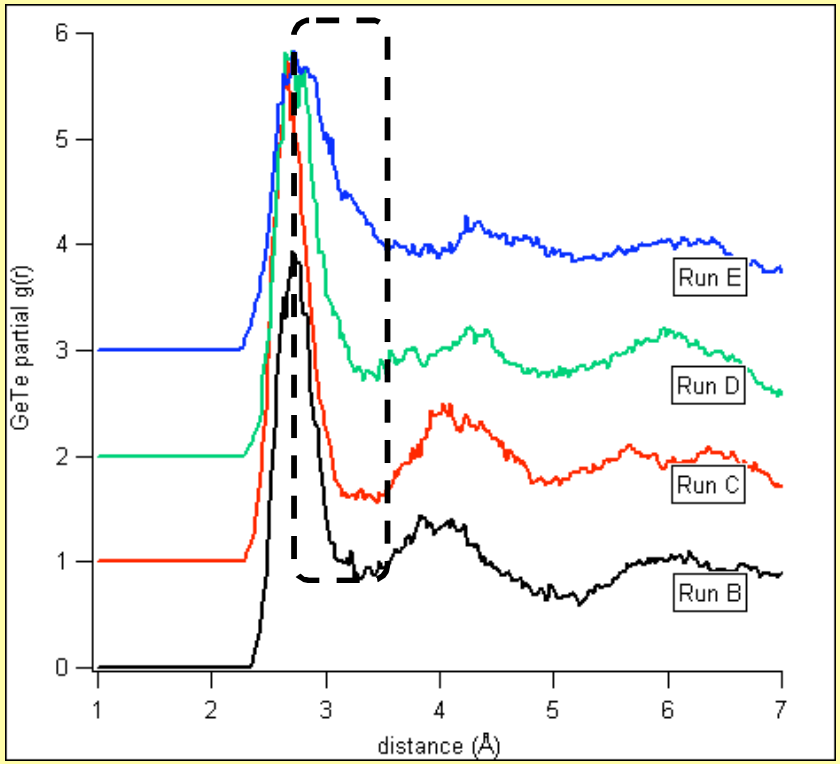
$S_{TeTe}(q)$



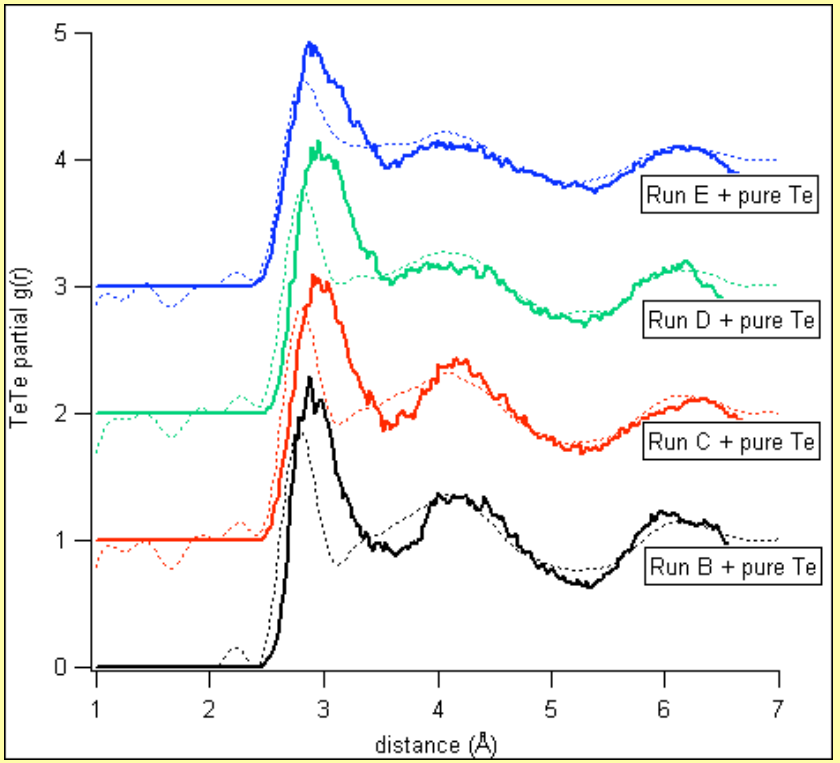
More changes on $S_{GeTe}(q)$ than on $S_{TeTe}(q)$

$GeTe_6$: partial pair correlation functions

$g_{GeTe}(r)$



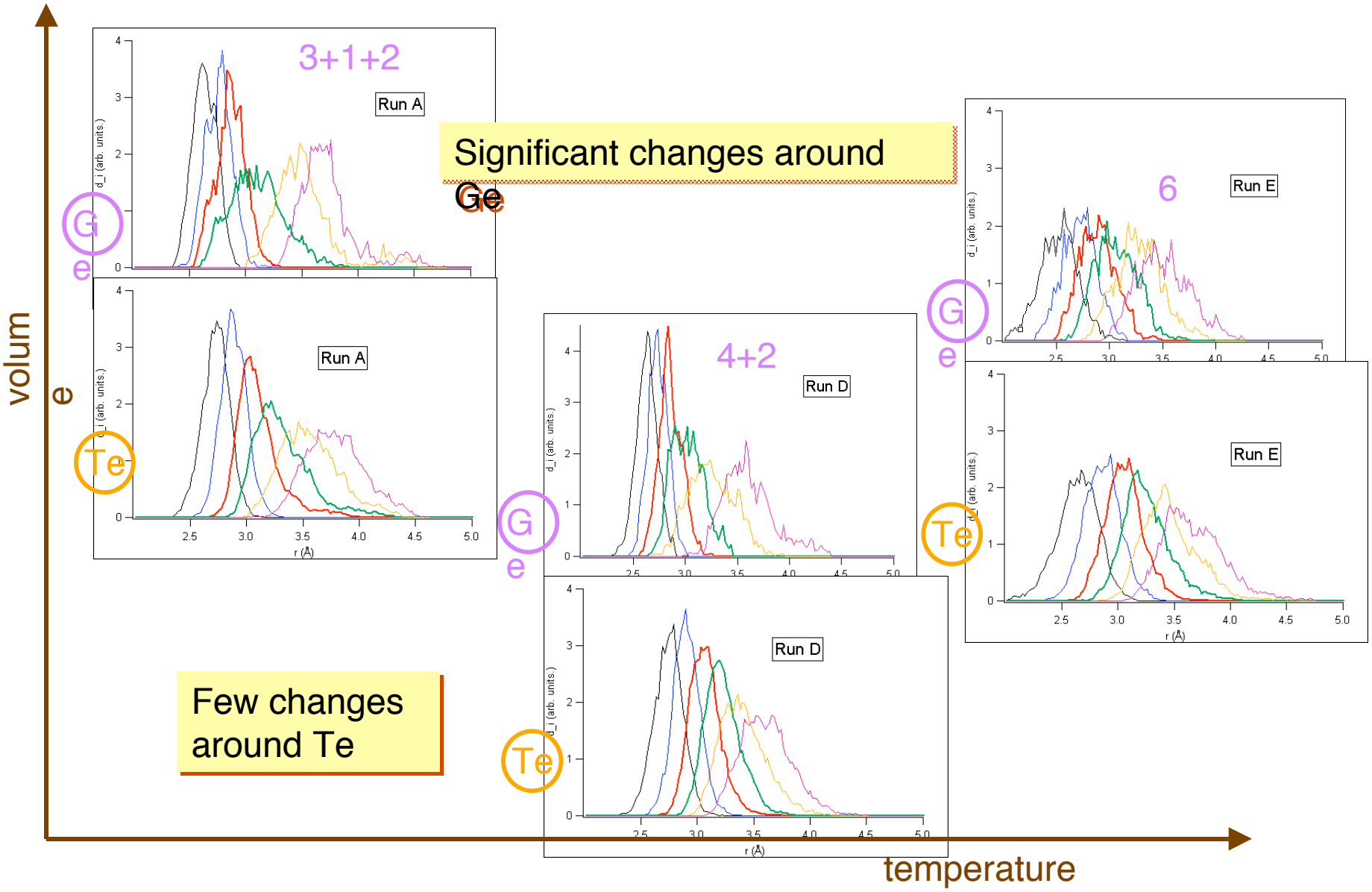
$g_{TeTe}(r)$



first peak of $g_{GeTe}(r)$ becomes broader

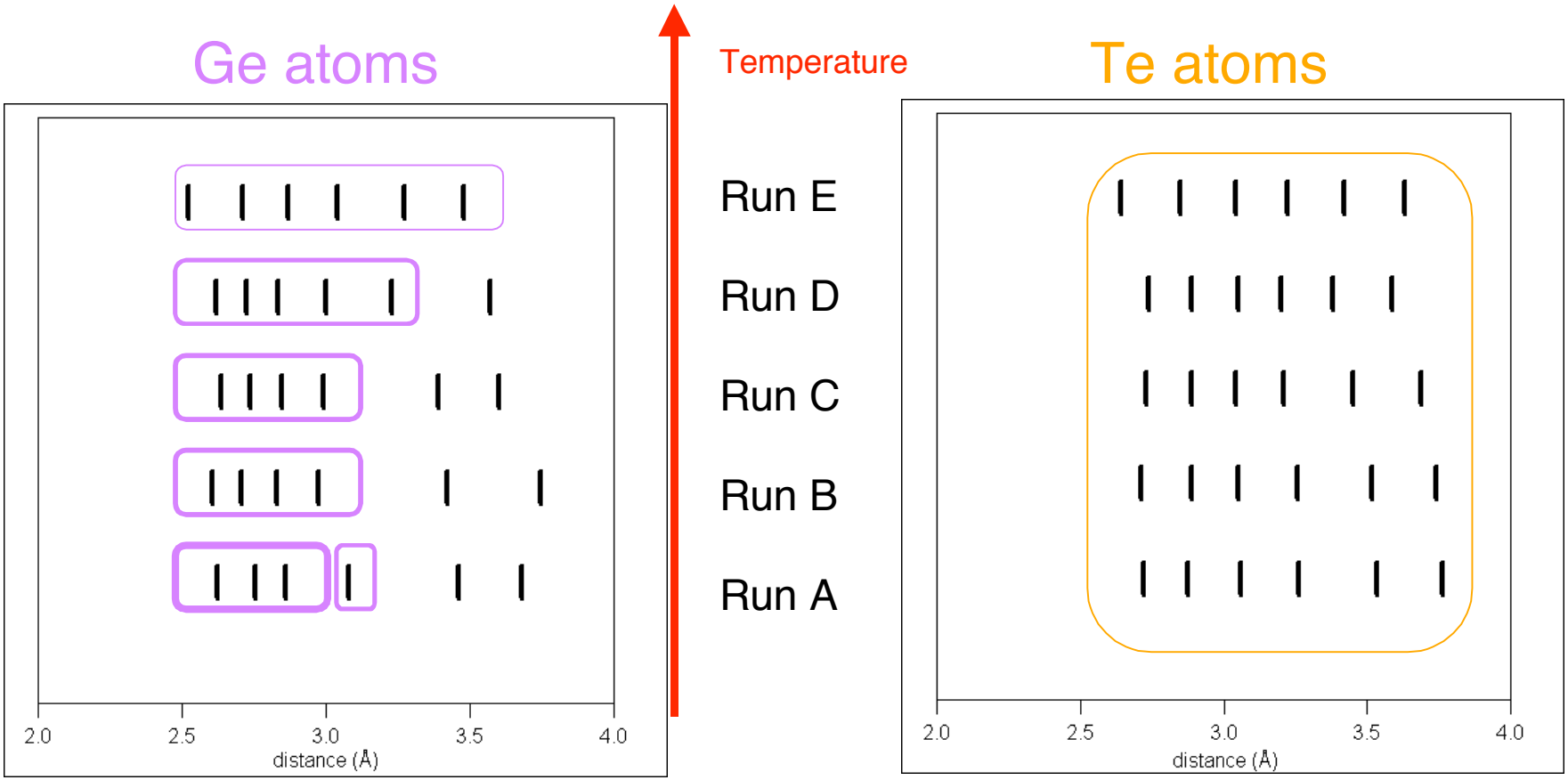
changes localized around Germanium atoms

What kind atomic arrangements ?

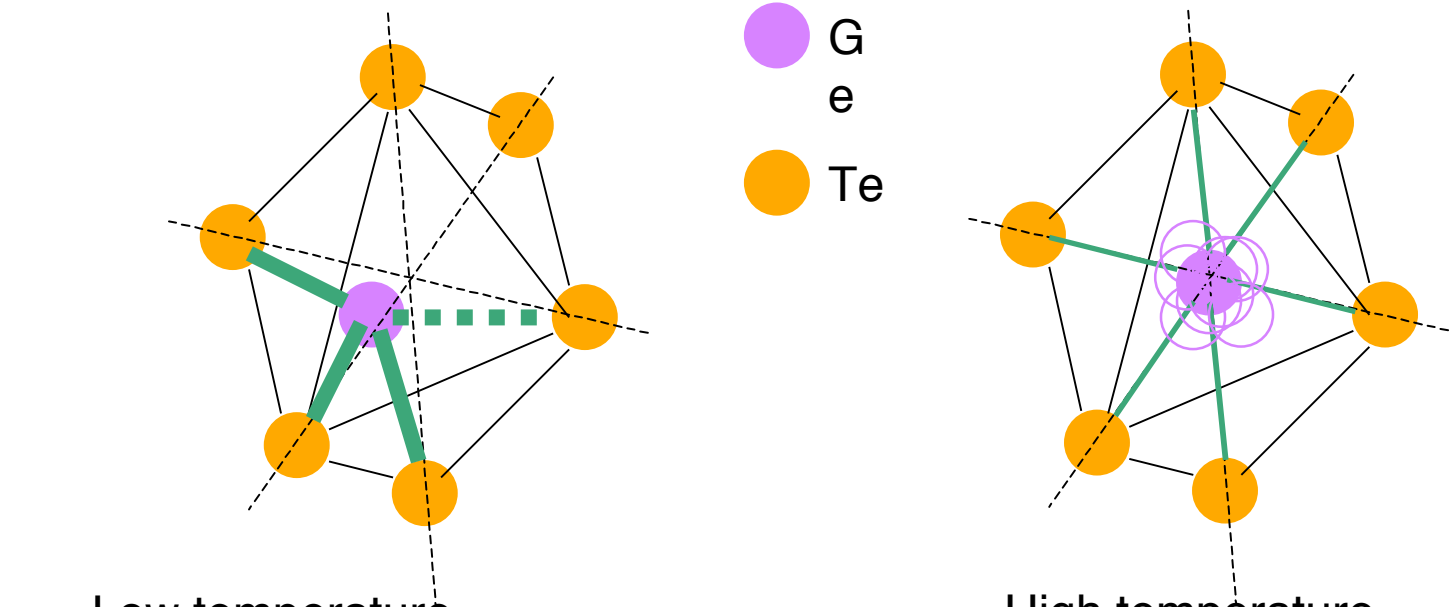


What kind atomic arrangements ?

Average distances of nearest neighbors around



A simple picture



Low temperature

Broken symmetry

Energetically favored
(Peierls like mechanism)

High temperature

More symmetry

Entropically favored
vibrational entropy

Future developments ?

- Constant pressure dynamics !

Excited States : Time dependent LDA

- Need for improved description of the excited states
- Methods available : computationnally demanding
  GW + BSE, DFT + QMC
- TDLDA : ‘cheap’ calculation on top of standart LDA calculation

Time-Dependent DFT
2 ways

- Linear response method (TD-DFRT)

"*Time-Dependent Density Functional Response Theory of Molecular systems: Theory, Computational Methods, and Functionals",* by M.E. Casida, in Recent Developments and Applications of Modern Density Functional Theory, edited by J.M. Seminario (Elsevier, Amsterdam, 1996).)

- Real time method

TDLDA calculation

Simple eigenvalue problem on top of LDA :

$$[\Omega_{ij\sigma}^2 \delta_{ik}\delta_{jl}\delta_{\sigma\tau} + 2\sqrt{f_{ij\sigma}\Omega_{ij\sigma}}\, K_{ij\sigma,kl\tau}\sqrt{f_{kl\tau}\Omega_{kl\tau}}]\,\vec{F}_n = \omega_n^2 \vec{F}_n$$

Where

$\Omega_{ij\sigma} = \varepsilon_{j\sigma} - \varepsilon_{i\sigma}$ are the Kohn-Sham transition energies

$f_{ij\sigma} = n_{i\sigma} - n_{j\sigma}$ are the diff. in occupation numbers

ω_n are the TDDFT excitations energies

$\vec{F}_n$ are related to the oscillator strengths

The coupling matrix K

Adiabatic approximation :

$$v_{xc}^{\sigma}[\rho_t^{\uparrow},\rho_t^{\downarrow}](\vec{r}) = \frac{\partial E_{xc}[\rho_t^{\uparrow},\rho_t^{\downarrow}]}{\partial \rho_t^{\sigma}(\vec{r})}$$

Linear response : $\delta\rho_{\sigma}(\vec{r},\omega) = \sum_{ij} \psi_{i\sigma}(\vec{r})\, \delta P_{ij\sigma}(\omega)\, \psi^{*}_{j\sigma}(\vec{r})$

$\delta P_{ij\sigma}(\omega)$ *linear response to perturbation* $\delta(t)$

$$\delta_{eff}(t) = \delta(t) + \delta v^{SCF}(\vec{r},t)$$

Coupling matrix : $K_{ij\sigma,lk\sigma} = \dfrac{\partial v_{ij\sigma}^{SCF}}{\partial P_{kl\sigma}}$

$$= \iint \psi^{*}_{i\sigma}(\vec{r})\psi_{j\sigma}(\vec{r}) \left(\frac{1}{|\vec{r}-\vec{r}'|} + \frac{\partial v_{\sigma}^{xc}(\vec{r})}{\partial \rho_{\sigma}(\vec{r}')}\right) \psi_{k\sigma}(\vec{r}')\psi^{*}_{l\sigma}(\vec{r}')\, d\vec{r}\, d\vec{r}'$$

xc term

Coulomb term

Oscillator strength : $f_I = \frac{2}{3}(E_I - E_0) \sum_{\alpha=\hat{x},\hat{y},\hat{z}} \left|\langle \psi_0 | \alpha | \psi_I \rangle\right|^2$

Sum rule : $\sum_i f_I = N_e$

Src_5common/tddft.f

$$[\underbrace{\omega_{ij\sigma}^2 \delta_{ik}\delta_{jl}\delta_{\sigma\sigma'} + 2\sqrt{f_{ij\sigma}}\,\omega_{ij\sigma}\,K_{ij\sigma,kl\sigma'}\sqrt{f_{kl\sigma'}}\,\omega_{kl\sigma'}}]\,\vec{F}_n = \Omega_n^2\,\vec{F}_n$$

NxN Matrix to diagonalize with

$$K_{ij\sigma,lk\sigma'} = \iint \varphi_{i\sigma}^*(\vec{r})\,\varphi_{j\sigma}(\vec{r})\left(\frac{1}{|\vec{r}-\vec{r}'|} + \frac{\partial v_{\sigma}^{xc}(\vec{r})}{\partial \rho_{\sigma}(\vec{r}')}\right)\varphi_{k\sigma'}(\vec{r}')\,\varphi_{l\sigma'}^*(\vec{r}')\,d\vec{r}\,d\vec{r}'$$

coupling the excitation i-j with the excitation l-k

- Double loop + Mpi coming (-> src_9seqpar)
- Restart – disabled
- N Excitations window (by default, N= nval x ncond)

  Optional variables : td_maxene, td_mexcit

```
# Magnesium atom. acell much too small.
# Excited states computation

 ndtset    3

  iscf1   5
  nband1   1
  prtden1   1

  iscf2  -1    #non-scf followed by tdlda
  nband2   10
  getden2   1
  getwfk2   1

   iscf3  -1   #same, but with mkmem 0
  nband3  10
  mkmem3   0
  getden3   1
  getwfk3   1

#Common

 acell 17.999   18   18.001
 boxcenter 3*0

 ecut  3.5

 natom  1
  xangst 0 0 0
```

Test_v1/t69

- Iscf -1
- Mkmem 0 (opt) :

  td_matrix is stored on disk

  (for eventual restart – to debug)

  $\Box_i^*(\vec{r})\Box_j(\vec{r}) \quad (i,j) = 1, N$

  are stored on disk

Take center of molecule as boxcenter

+Test_v2/t42.in : ixc=20,21,22

Test_v3/t55.in

```
# N2 system.
# Excited state computation, using LDA/TDLDA
# with different XC kernels

 ndtset    4

#DATASET 1  SCF

#DATASET 2 TDDFT
#Common to all except GS calculations
 getden    1
 tolwfr    1.0d-9
   iscf   -1
 getwfk    1
  nband    12

#DATASET 3  SCF with another ixc
   iscf3   5
  nband3   5
 prtden3   1
 getwfk3   1
 tolwfr3   1.0d-15
    ixc3   7

#DATASET 4 TDDFT
 getden4   3
 getwfk4   3
    ixc4   7

#Common
 acell 6  2*5 Angstrom
 boxcenter 3*0.0d0
 diemac 1.0d0   diemix 0.5d0
 ecut 25
 ixc  1
```

- Test :

TDDFT excitation energies

oscillator strengths,

Polarisability

Cauchy coefficients.

Excitation window :

Default:
N = nval * ncond

Optional :
Td_maxene xxx :
Keep excitation i-j such
E_j-E_i < xxx

Td_mexcit yyy :
Keep yyy lowest KS excitations

***** TDDFT : computation of excited states *****
Splitting of 12 bands in 5 occupied bands, and 7 unoccupied bands, giving 35 excitations.

Kohn-Sham energy differences, corresponding total energies and oscillator strengths (X,Y,Z and average)-
(oscillator strengths smaller than 1.e-6 are set to zero)

Transition (Ha) and (eV) Tot. Ene. (Ha) Aver XX YY ZZ
5-> 6 3.10921E-01 8.46059E+00 -1.92708E+01 0.0000E+00 0.00E+00 0.00E+00 0.00E+00
…
1-> 12 1.20769E+00 3.28629E+01 -1.83740E+01 1.9809E-04 0.00E+00 0.00E+00 5.94E-04
Sum of osc. strength : 2.575099E+00

TDDFT singlet excitation energies (at most 20 of them are printed), and corresponding total energies.
Excit# (Ha) and (eV) total energy (Ha) major contributions
1 3.47969E-01 9.46872E+00 -1.923375E+01 0.74(5-> 6) 0.25(5-> 7)
…
20 5.63495E-01 1.53335E+01 -1.901822E+01 0.76(4-> 11) 0.17(2-> 7)

Oscillator strengths : (elements smaller than 1.e-6 are set to zero)
Excit# (Ha) Average XX YY ZZ XY XZ YZ
1 3.47969E-01 0.000E+00 0.000E+00 0.000E+00 0.000E+00 0.00E+00 0.00E+00 0.00E+00
…
7 3.96426E-01 5.755E-02 0.000E+00 8.722E-05 1.726E-01 0.00E+00 0.00E+00 3.88E-03
…
35 1.21621E+00 2.119E-05 0.000E+00 0.000E+00 6.355E-05 0.00E+00 0.00E+00 1.43E-06
Sum of osc. strength : 2.575099E+00
Cauchy coeffs (au) : (-2)-> 7.978E+00, (-4)-> 2.768E+01, (-6)-> 1.077E+02
(-8)-> 4.672E+02, (-10)-> 2.236E+03, (-12)-> 1.161E+04, (-14)-> 6.415E+04

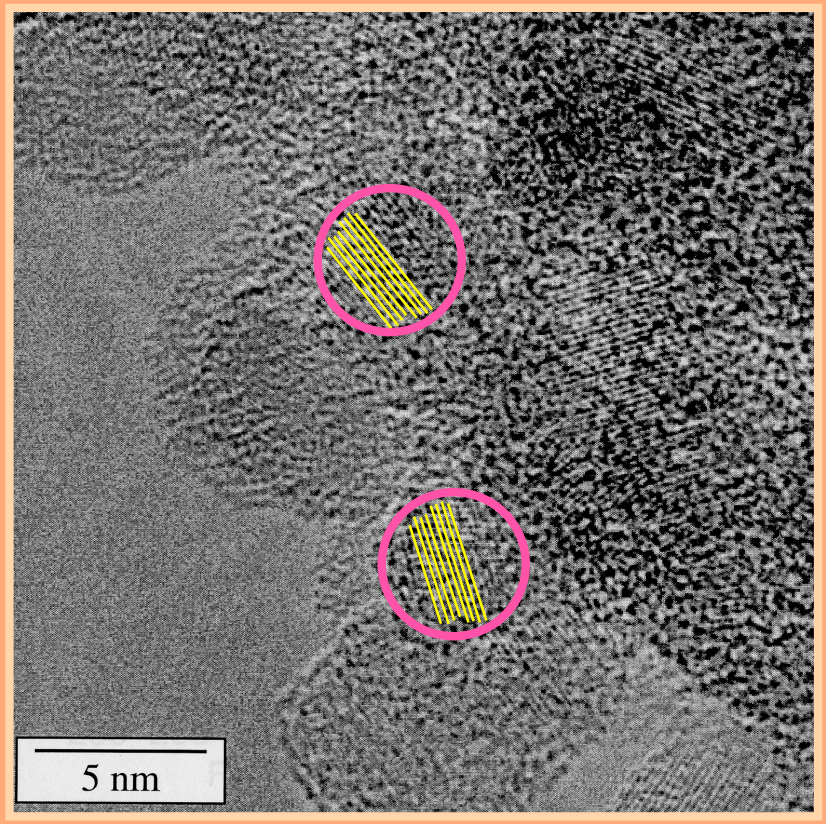
TDDFT triplet excitation energies (at most 20 of them are printed),
and corresponding total energies.
……

Test_v3/t55.out

Application : Nanoclusters

- Carbon & Silicon clusters
- Description
- Convergence vs excitation window
- Nanodiamonds : quantum confinement
- Comparison with experiment Si29H24
- Silicon : comparison with other methods

Nanodiamonds & TDLDA



- They do exist !
- 2-6 nanometers
- Crystalline
- Huge quantum confinement

(still ~1 eV at 35 nm) PRL xxxxxx

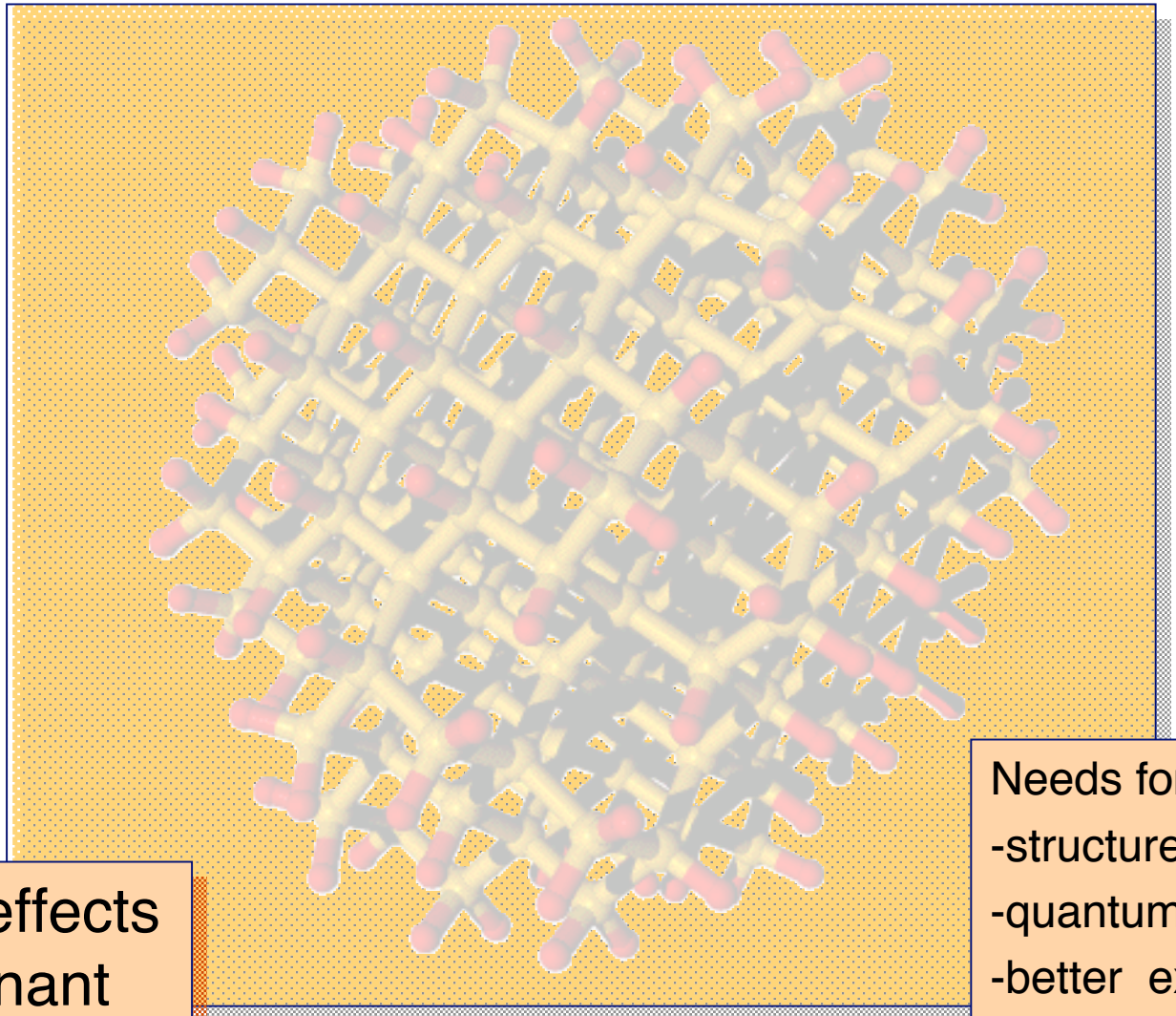
But

- LLNL x-ray exp. show *NO* QC for 3nm particles
- What is the gap of 3 nm particles ? *GGA vs TDLDA*

Simulation

C211H140

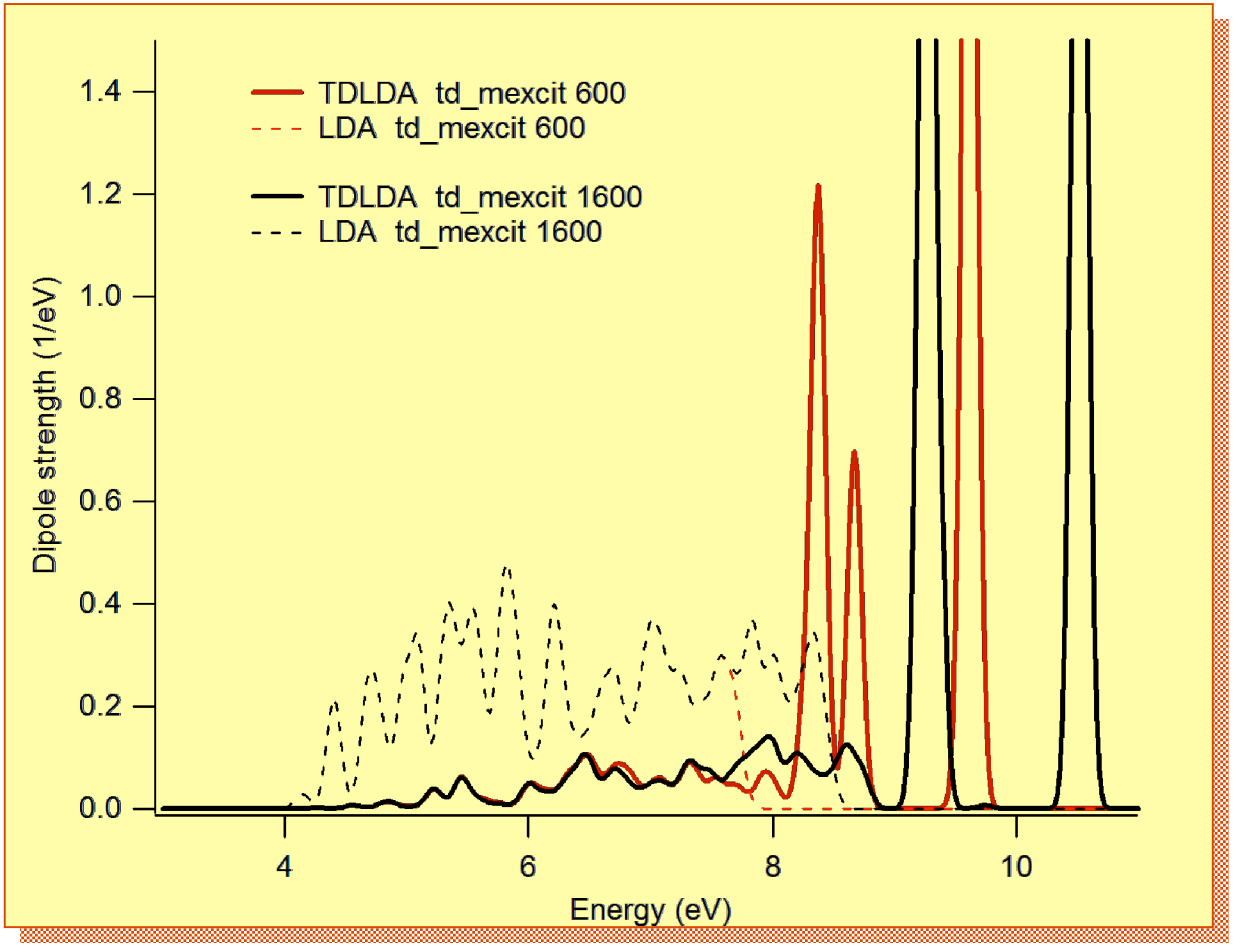
1.4 nm



Surface effects are dominant

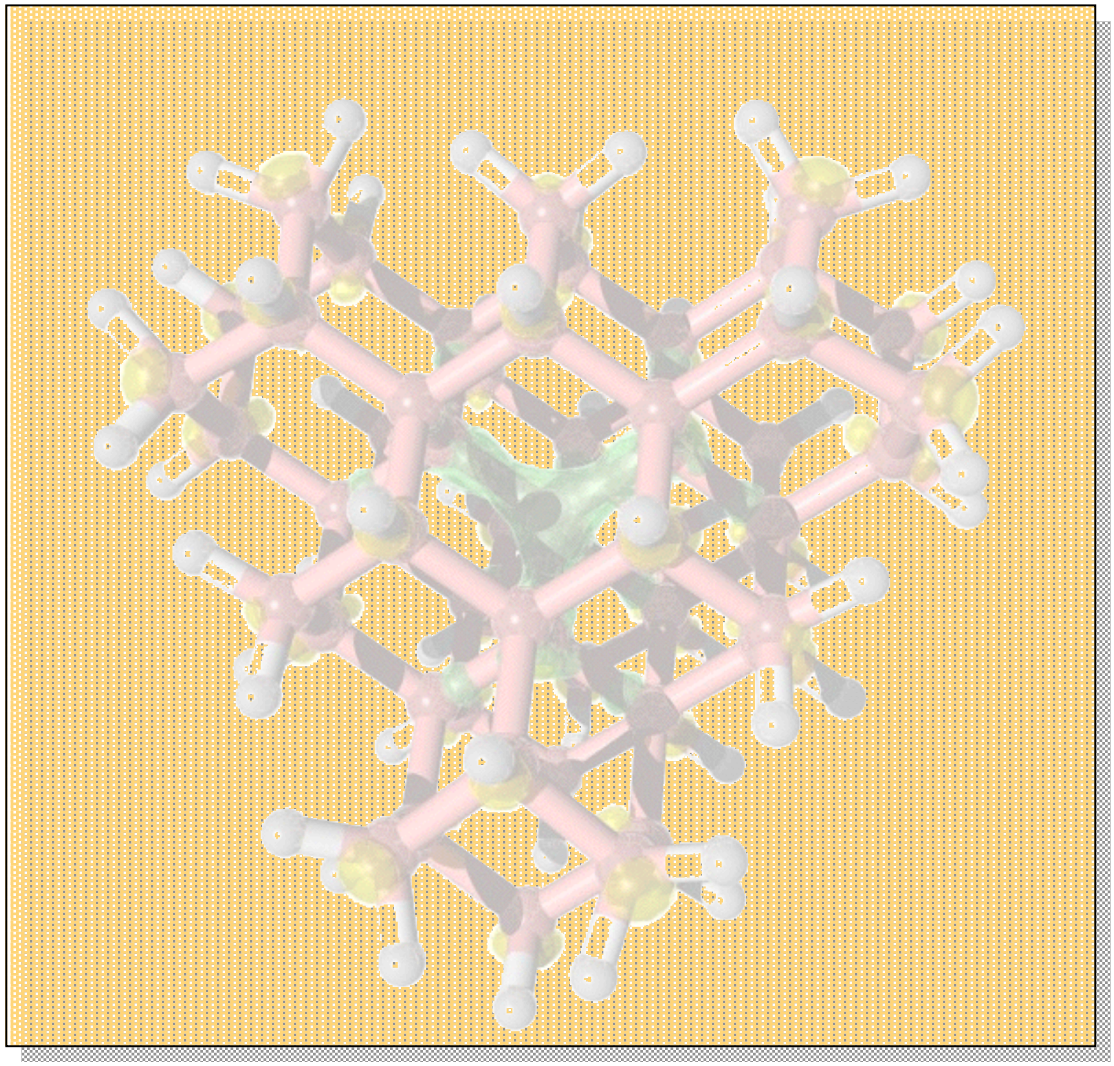
Needs for
-structure optimization
-quantum description
-better excited states

Convergence with excitations window



- Default : N = 52*148 = 7696
- Td_mexcit = 600 : converged on ~2 eV
- Td_mexcit = 1600 : ~3eV

C59H60 GGA



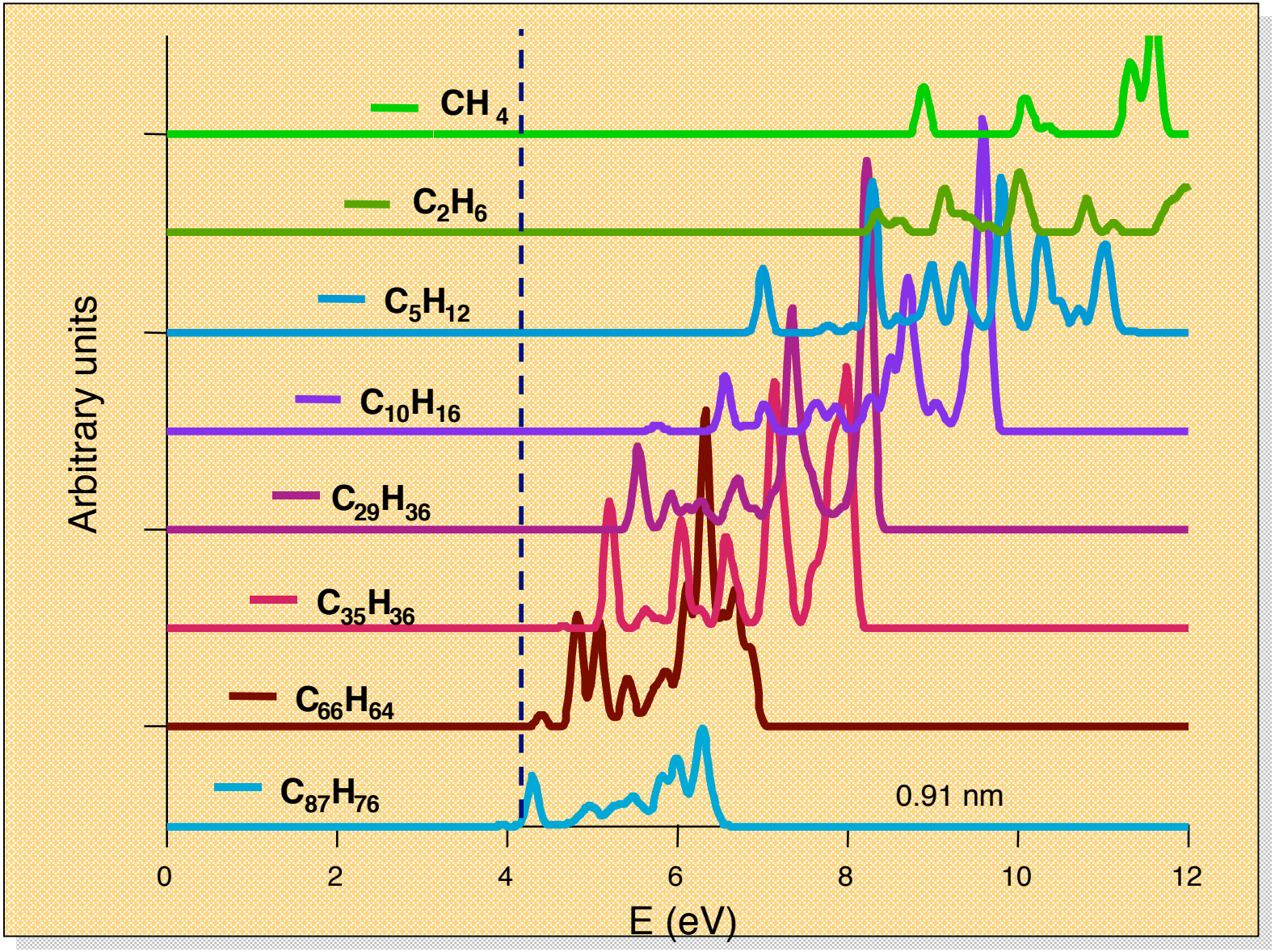
- 0.8 nm
- C-C : 1.61-1.64 Å

  Bulk : 1.54 Å
- HOMO 3x deg.
- E_{gap} = 4.3 eV

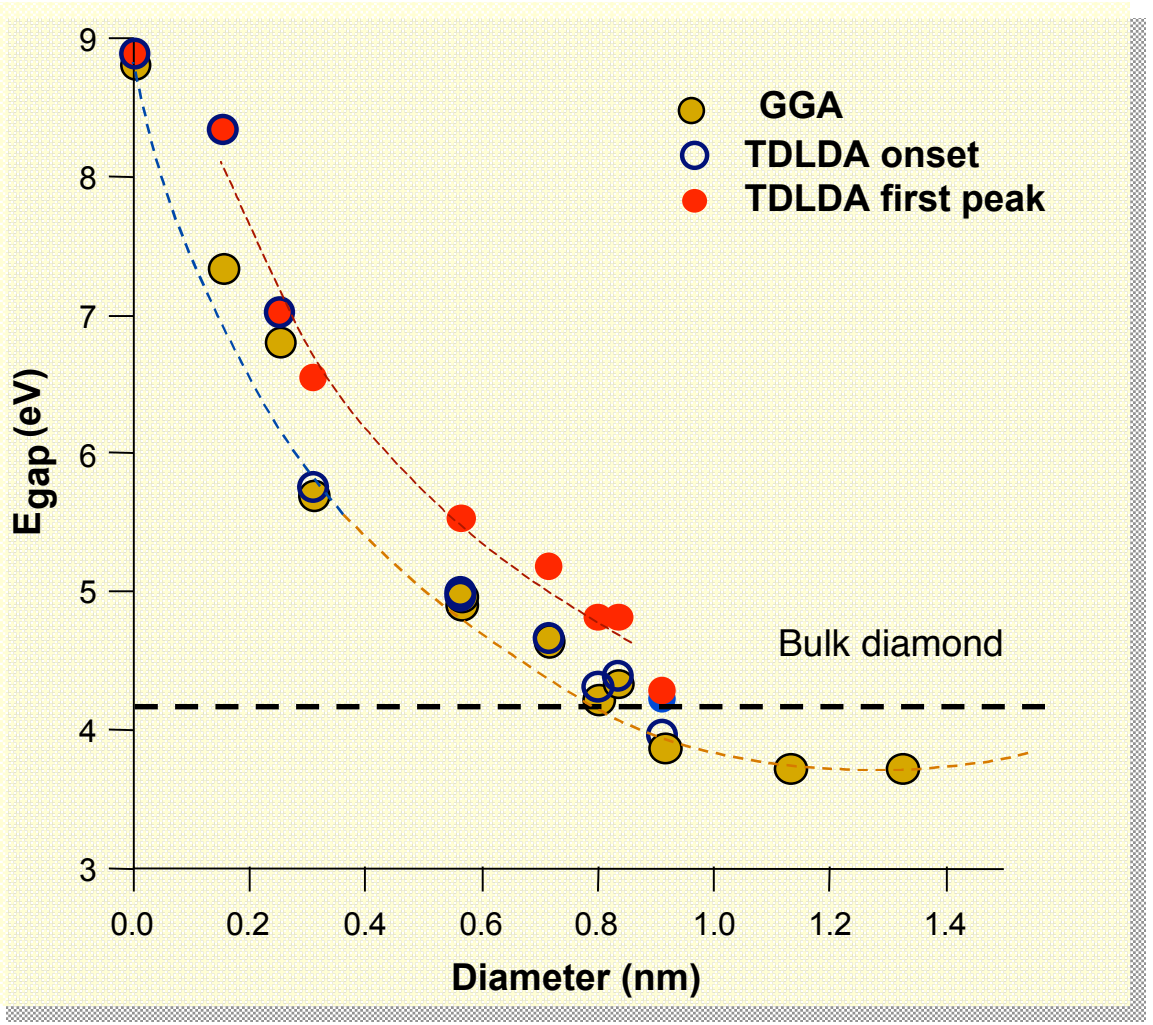
  Bulk : 4.23 eV

Simulation

TDLDA Optical Spectra

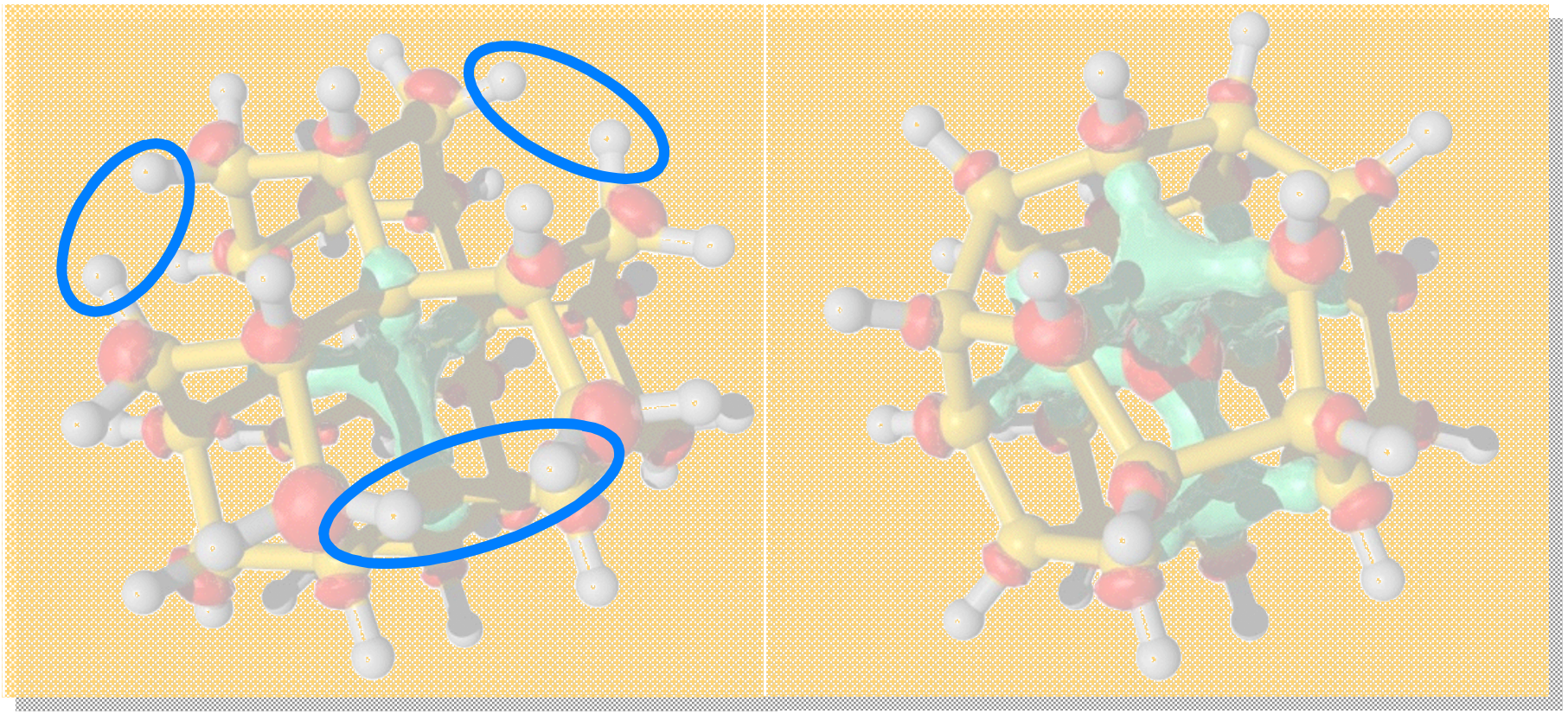


Optical gap vs size



Simulation

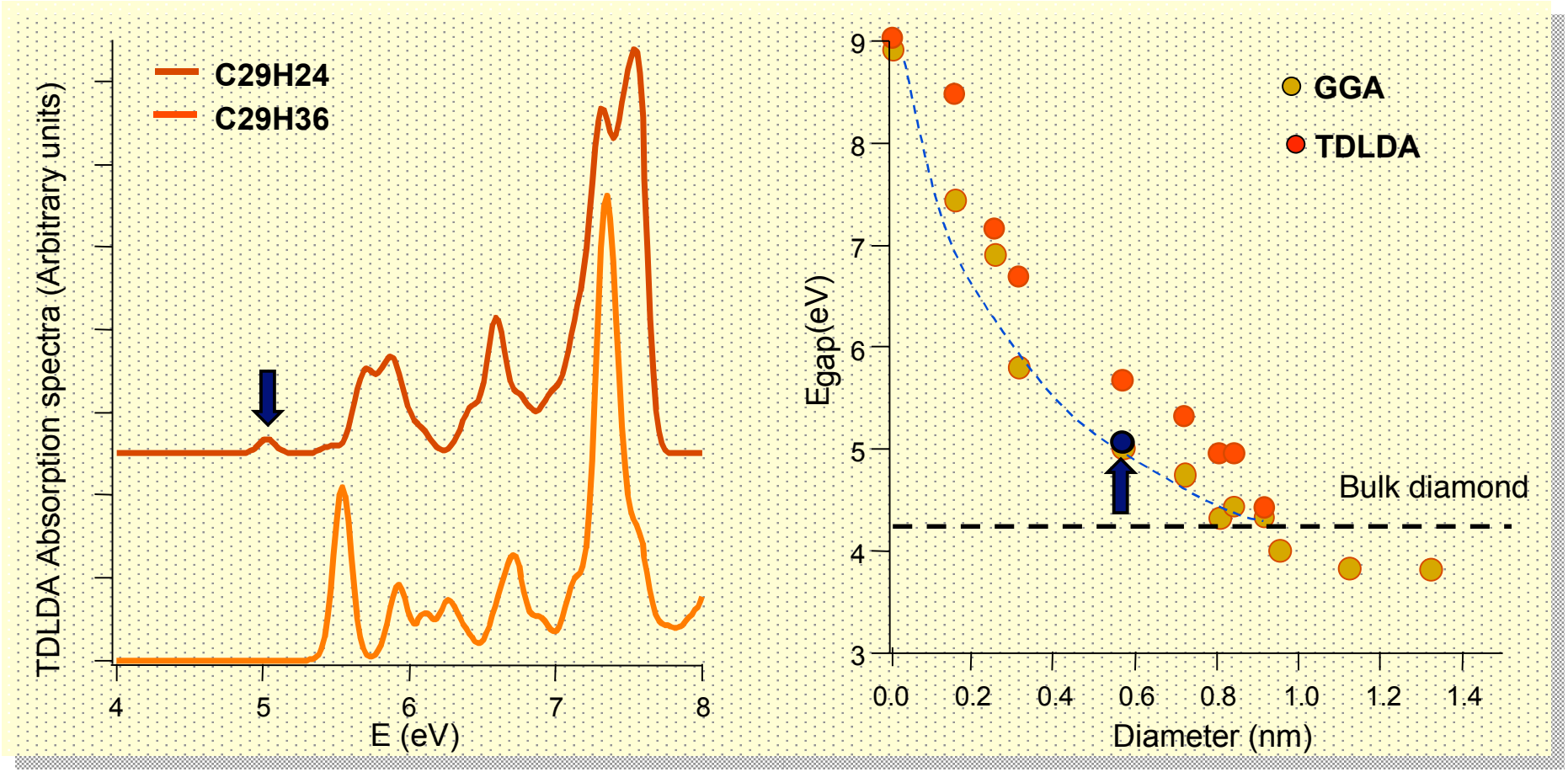
Surface reconstruction



C29H36 – 6 H2 -> C29H24

Simulation

Surface reconstruction effect

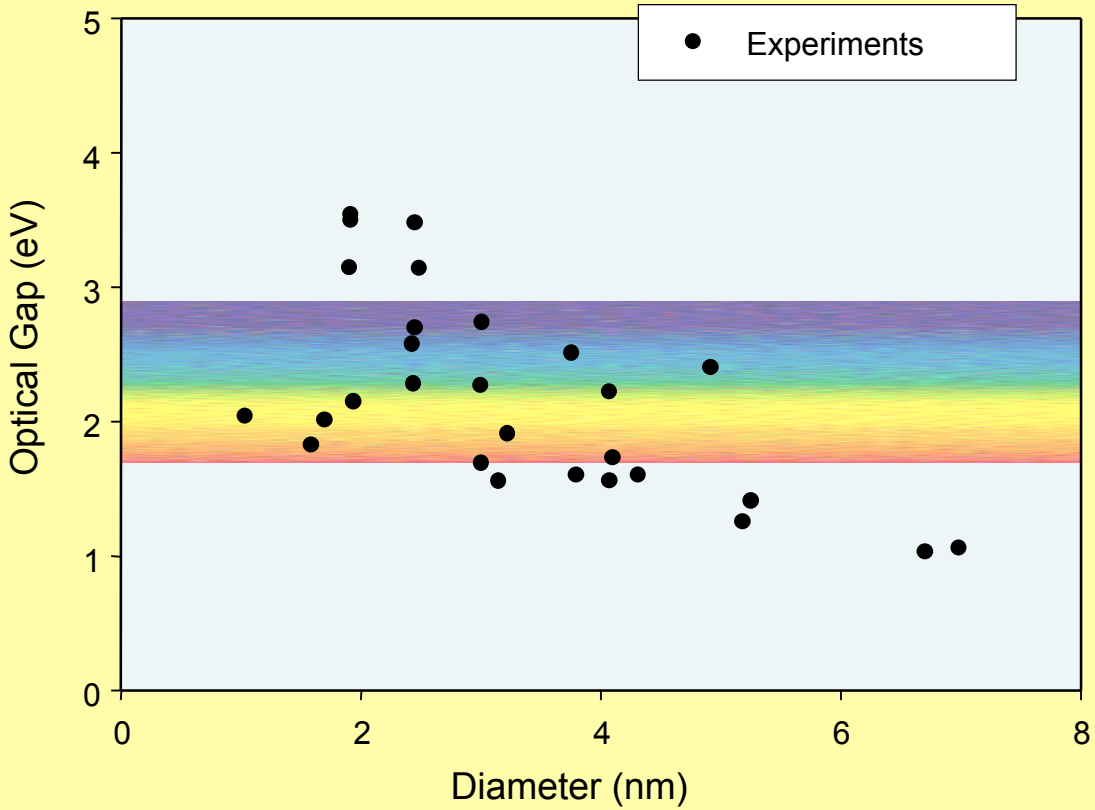


Gap is reduced by ~0.5 eV

No quantum confinement effect for D > 1-2 nm

Simulation

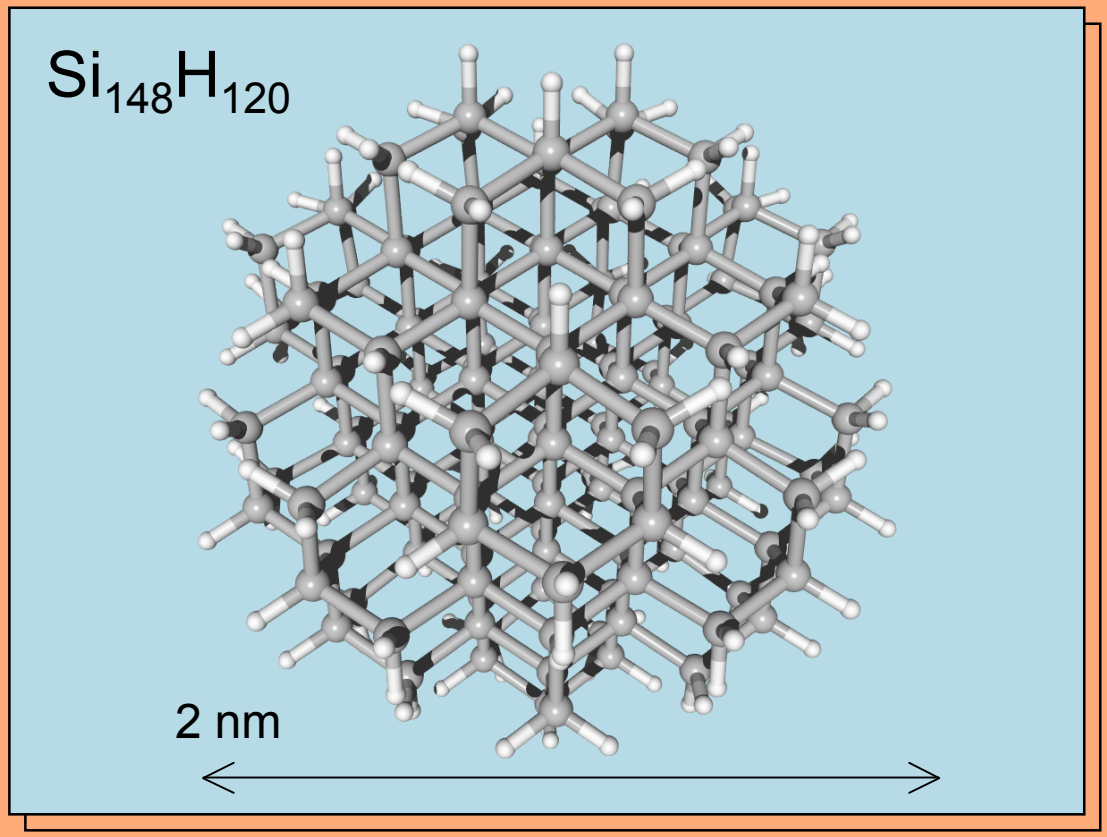
Optical gaps of Si clusters



- Size dependence of model clusters
- Surface effects
- Preparation conditions

Predictive simulation techniques are needed to model and characterize silicon nanostructures

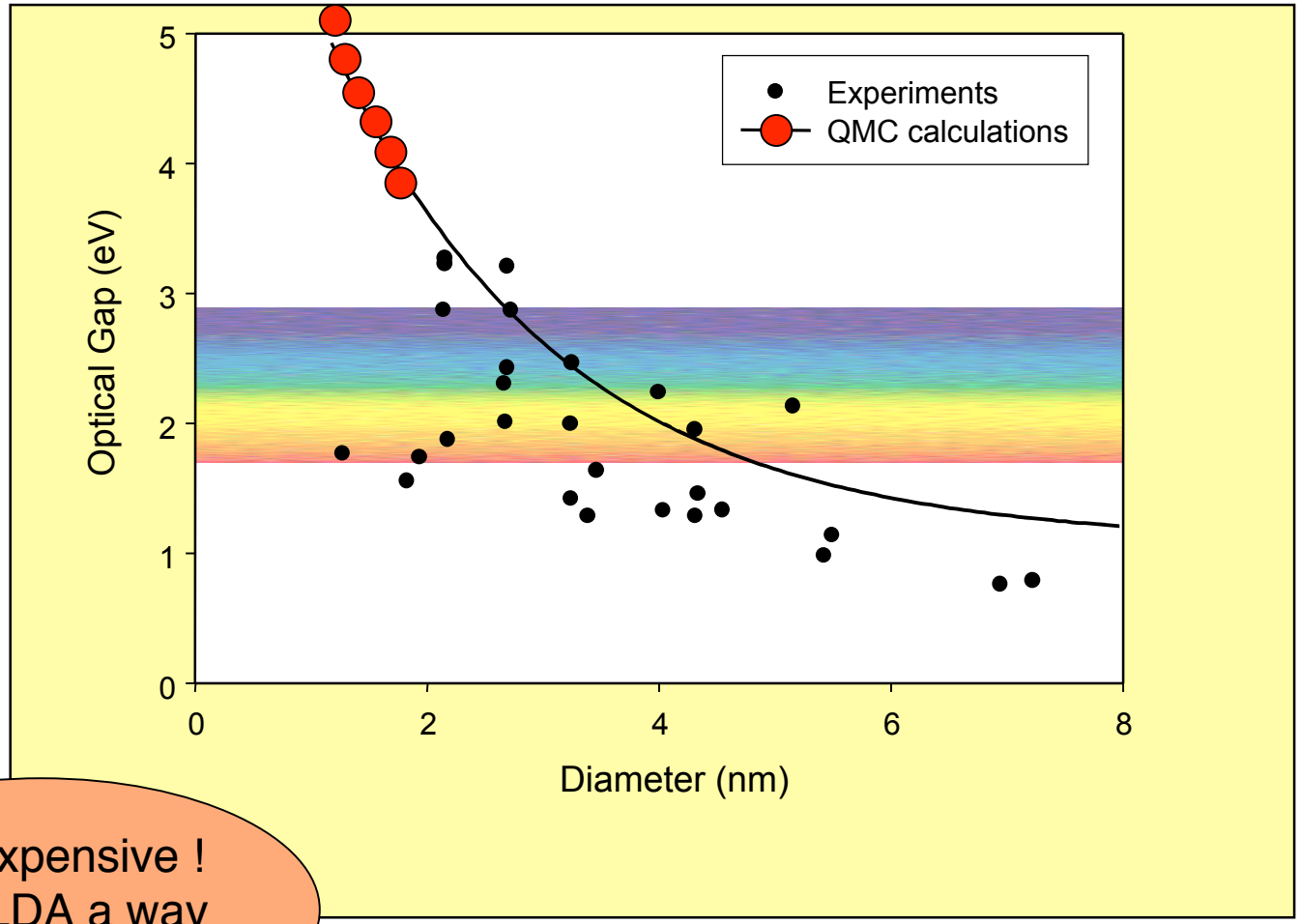
State of the simulations (QMC)



- 2 nm diameter
- 268 atoms
- 712 electrons
- >1000 CPU hours

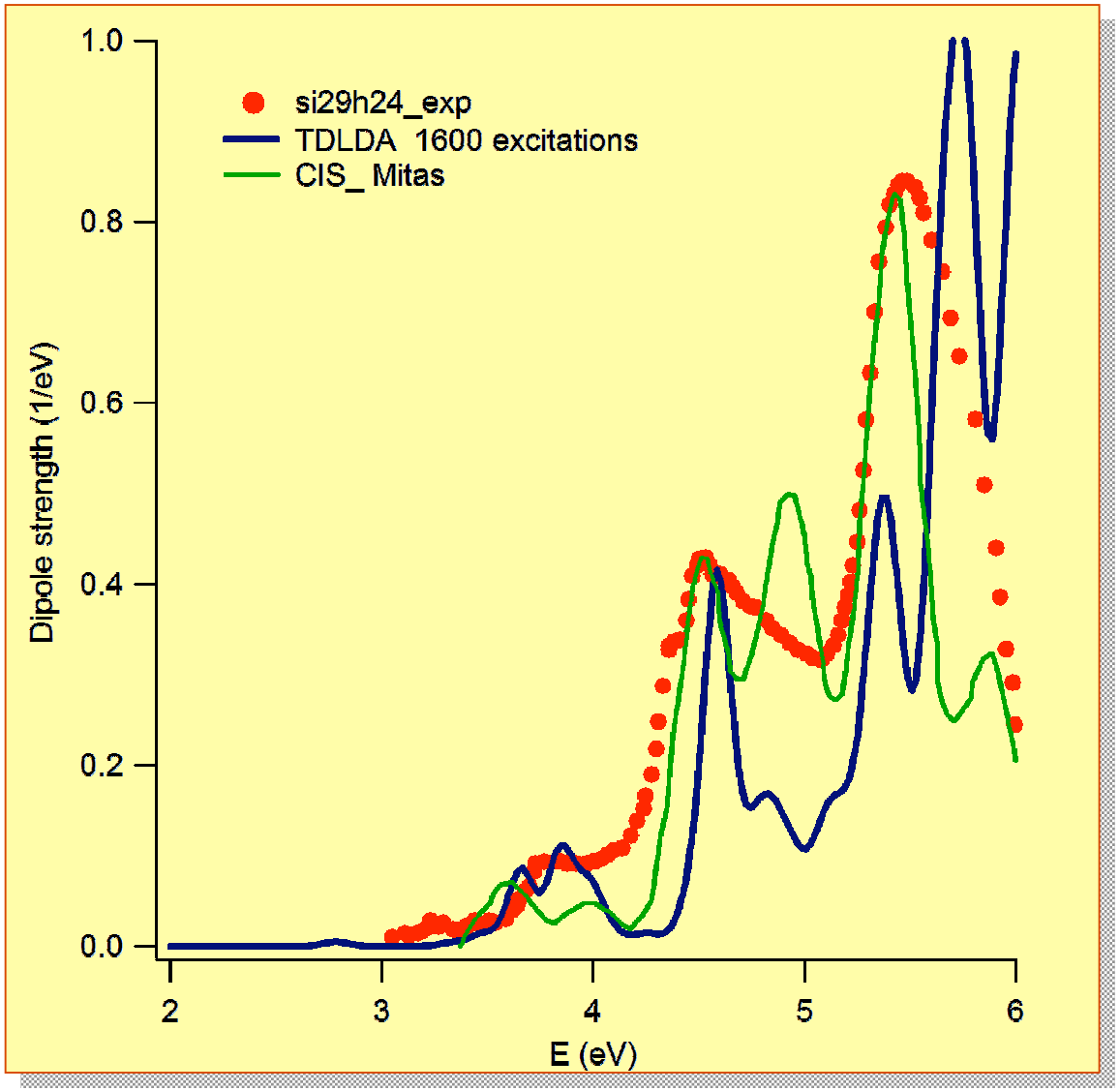
A.J. Williamson *et al.* Physical Review Letters, **87** 246406 (2001)

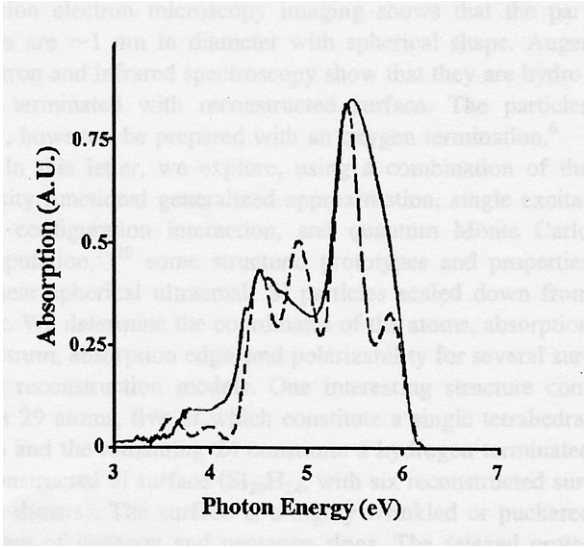
QMC Calculations explain the largest gaps



Too expensive !
Is TDLDA a way to go ?

TDLDA vs Experiment

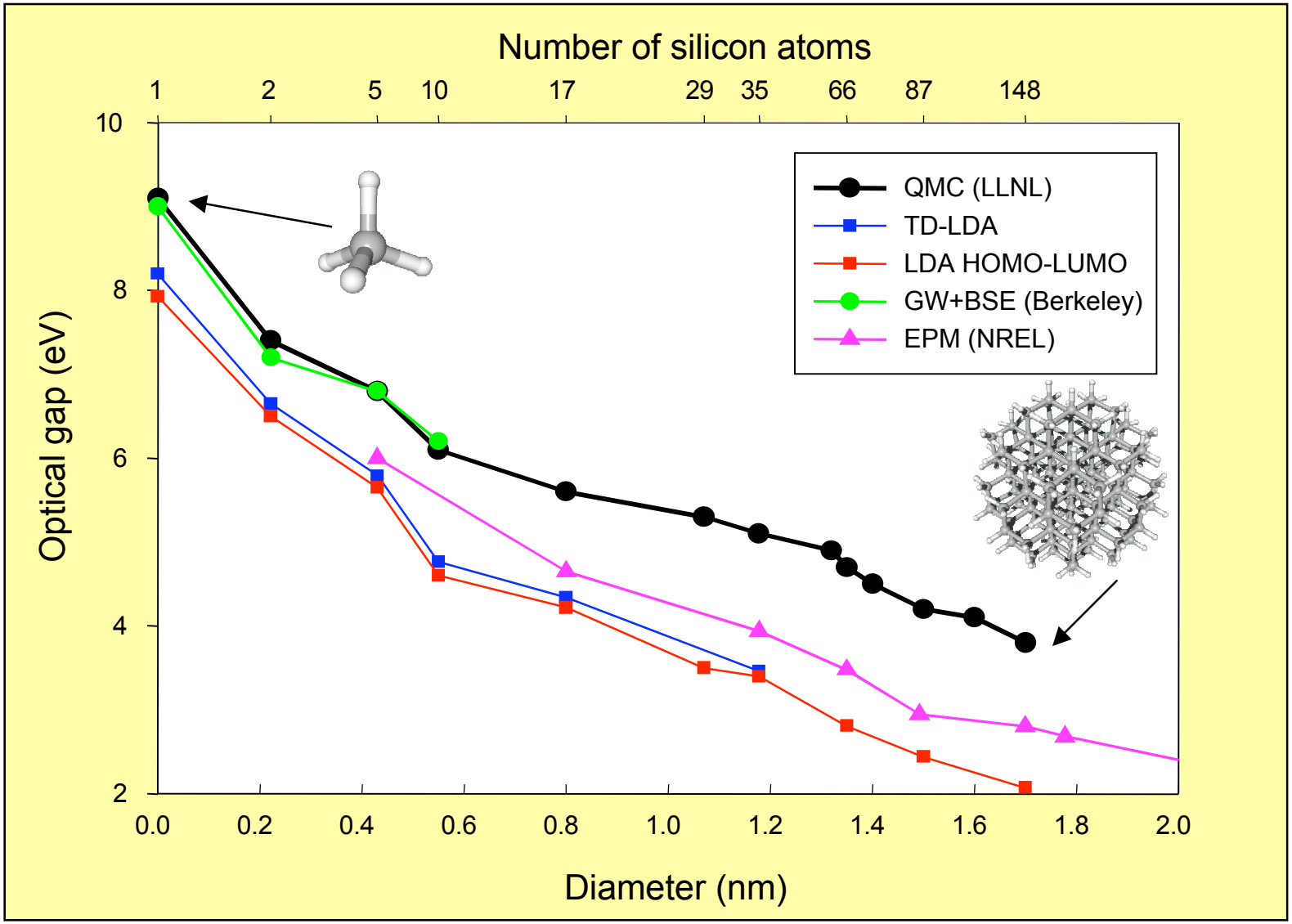




L. Mitas et al.

- Not normalized (sum rule not verified)

Optical Gap of Silicon Dots

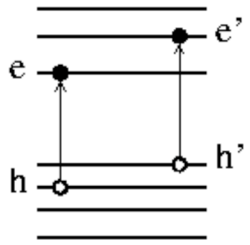


TDLDA vs BSE

Lorin Benedict et al.

Theoretical methods

must involve mixing of configurations



K(eh;e'h') couples (eh) to (e'h')

$$|\text{excited state}\rangle = \sum_{e,h} \Psi(e,h)\,|e,h\rangle$$

equation of motion for electron-hole pair wave function, $\psi(e,h)$:

$$[(E_e - E_h) - E]\psi(e,h) + \sum_{e'h'} K(eh;e'h')\psi(e',h') = 0$$

Bethe-Salpeter equation (BSE), Time-dependent local density approximation (TDLDA), Configuration interaction with singles excitations (CIS)

- 2-stage calculations: Determine single-particle E_e, E_h, ϕ_e, ϕ_h, then calculate $\psi(e,h)$ by solving electron-hole pair equation.

- Determine $\alpha(E)$ from $\psi(e,h)$, E.

TDLDA

- stage 1: determine E_e, E_h, ϕ_e, ϕ_h from LDA.

- stage 2: solve electron-hole pair equation with

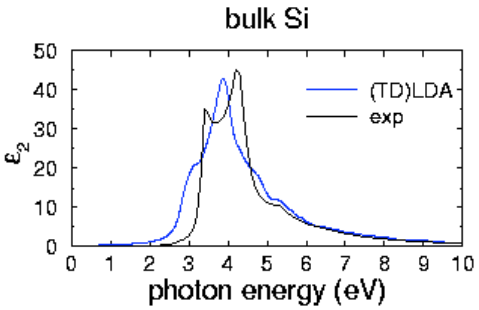
$$K(eh;e'h') = K_{Coul}(eh;e'h') + K_{xc}(eh;e'h')$$

K_{Coul} is a repulsion between the electron and hole. K_{xc} accounts for excitonic binding.

$$K_{Coul}(eh;e'h') = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_e^*(\mathbf{r}_1)\phi_h(\mathbf{r}_1)\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\phi_{e'}(\mathbf{r}_2)\phi_{h'}^*(\mathbf{r}_2)$$

$$K_{xc}(\mathbf{r}_1,\mathbf{r}_2;t,t') = \delta(t-t')\frac{\delta^2 E_{xc}}{\delta\rho(\mathbf{r}_1)\delta\rho(\mathbf{r}_2)}$$

Gives LDA answer for bulk



Bethe-Salpeter Equation

- stage 1: determine E_e, E_h from LDA + GW (including quasiparticle self-energies), ϕ_e, ϕ_h from LDA.

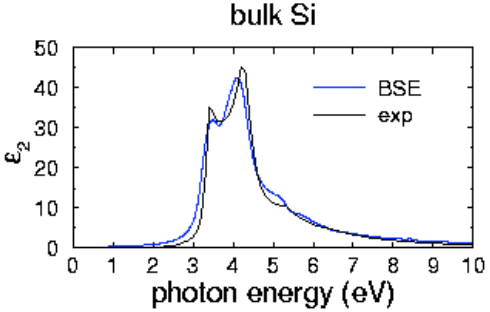
- stage 2: solve electron-hole pair equation with

$$K(eh;e'h') = K_{Coul}(eh;e'h') + K_{dir}(eh;e'h')$$

K_{dir} is attraction between electron and hole.

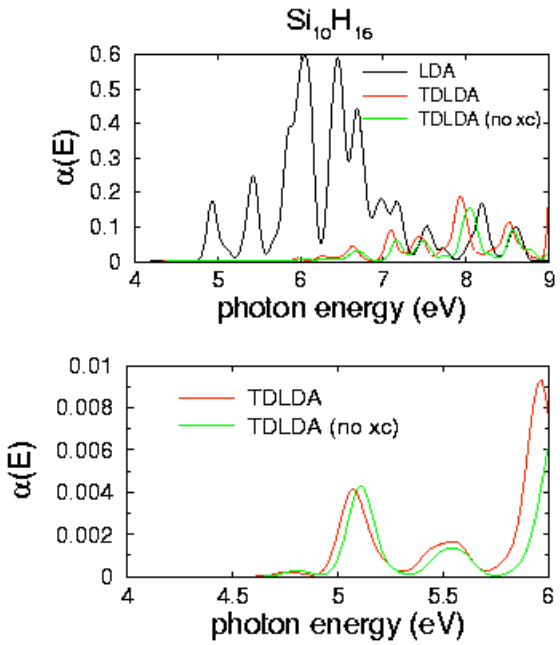
$$K_{dir}(eh;e'h') = \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_e^*(\mathbf{r}_1)\phi_h(\mathbf{r}_2)\frac{-e^2}{\epsilon(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{r}_1-\mathbf{r}_2|}\phi_{e'}(\mathbf{r}_1)\phi_{h'}^*(\mathbf{r}_2)$$

Gives accurate answer for bulk

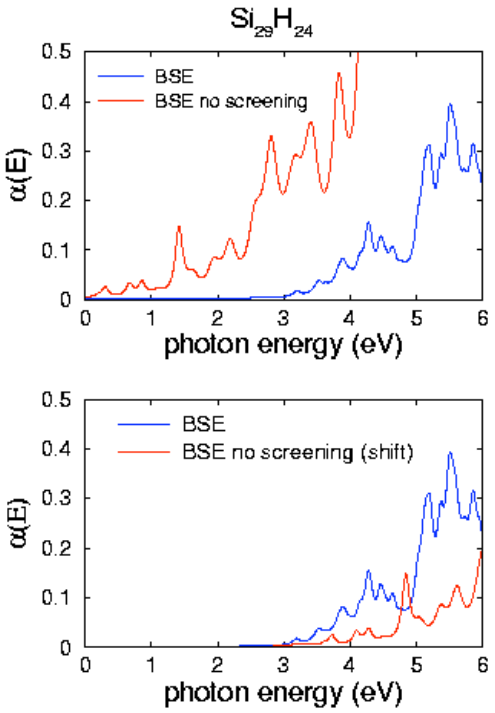


Kcoul, Kxc contributions

TDLDA results, effect of K_{Coul}, K_{xc}



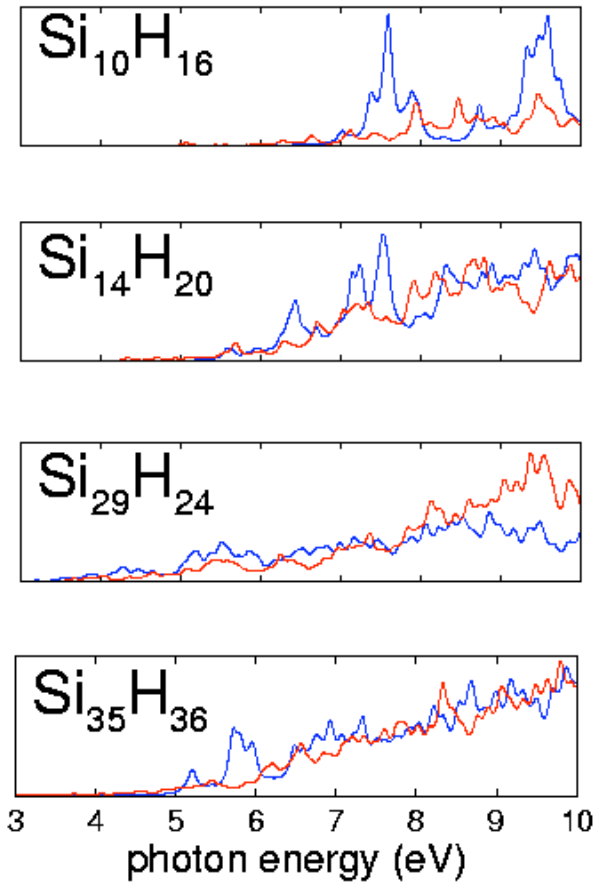
BSE results, effect of screening



K_{Coul} shifts spectral weight to higher energies

K_{xc} has almost no effect

BSE vs TDLDA



K_{Coul} shifts intensity to high E in BSE and TDLDA

K_{dir} gives rise to more structure at low E

K_{xc} has practically no effect

Future developments

- MPI version
- Other functionals

  (TDLDA/LB94, TDLDA/ACLDA)

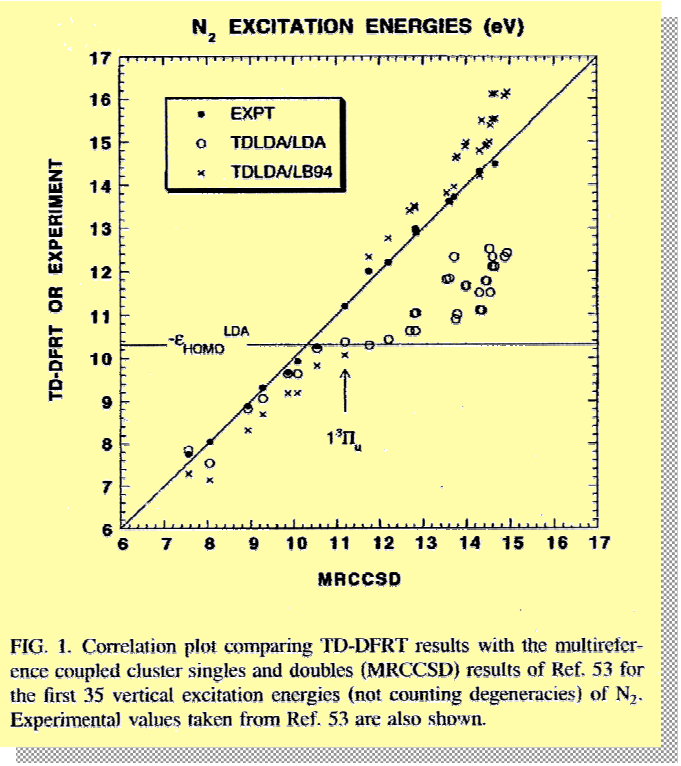


FIG. 1. Correlation plot comparing TD-DFRT results with the multireference coupled cluster singles and doubles (MRCCSD) results of Ref. 53 for the first 35 vertical excitation energies (not counting degeneracies) of N_2. Experimental values taken from Ref. 53 are also shown.

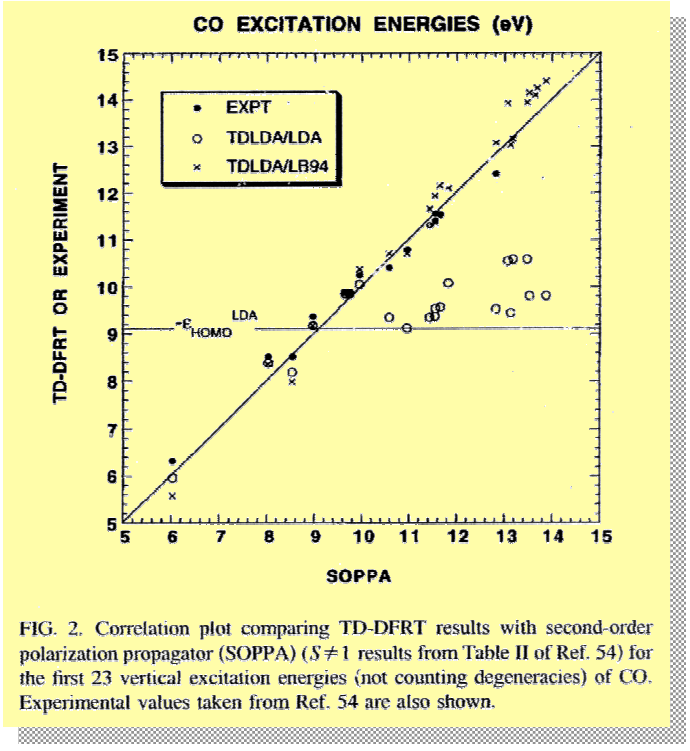


FIG. 2. Correlation plot comparing TD-DFRT results with second-order polarization propagator (SOPPA) ($S \neq 1$ results from Table II of Ref. 54) for the first 23 vertical excitation energies (not counting degeneracies) of CO. Experimental values taken from Ref. 54 are also shown.

M. Casida et al. J. Chem. Phys. 108 (1998) 4439

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