JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

Ground- and excited-state properties of tetraphenyl compounds

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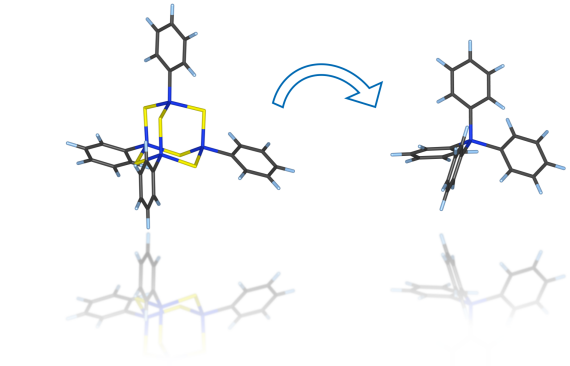
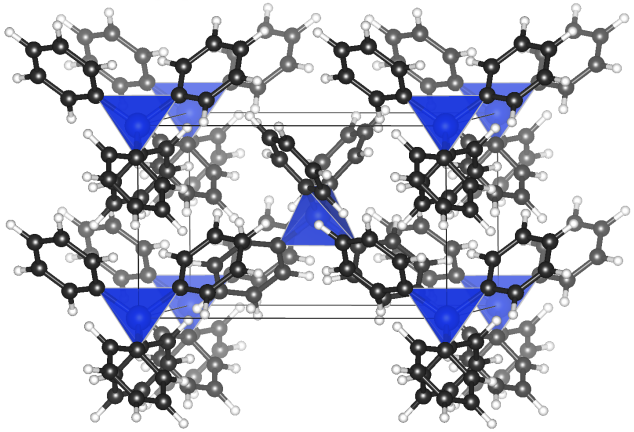
Introduction

Tetraphenyl compounds with adamantane core are investigated because of their special optical properties, which depend on the structural properties (crystalline vs. amorphous). Due to the system size of typically ~700 electrons, calculations are performed with smaller prototypes.

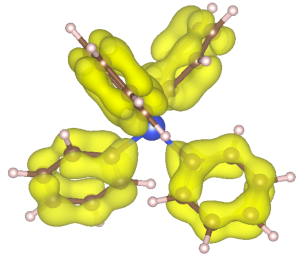
To this end, we employed DFT to calculate the ground state wave functions of Ph_4X crystals with X being a tetravalent element (C, Si, Ge, Sn, Pb). After obtaining a reliable structure by minimization of the forces with special regard to dispersion forces, we make use of the wave functions to calculate further spectroscopic properties and relate them to structural and chemical trends.

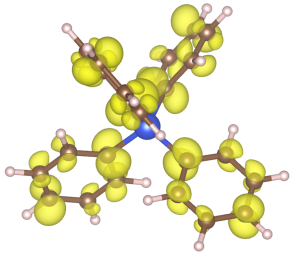
Ph_4Si crystal from molecule





HOMO





LUMO

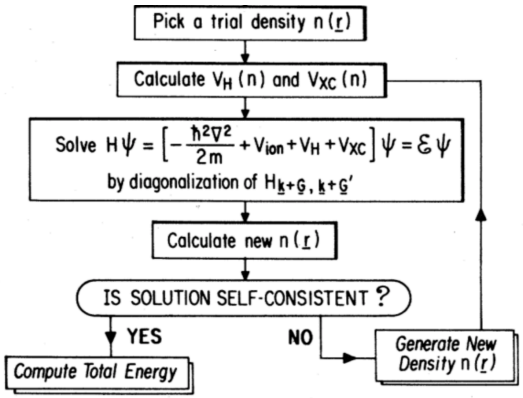
Partial charge distributions correspond to delocalized π orbitals and localized p_z orbitals, respectively.

Method: Why DFT at HLRS?

DFT and methods based on its wave functions allow us to calculate optical properties from first principles. Also, the performance tests show favorable speedup for calculating the wave functions. Spectroscopic signatures typically require a large number of k-points and future calculations are performed on larger, more demanding systems.

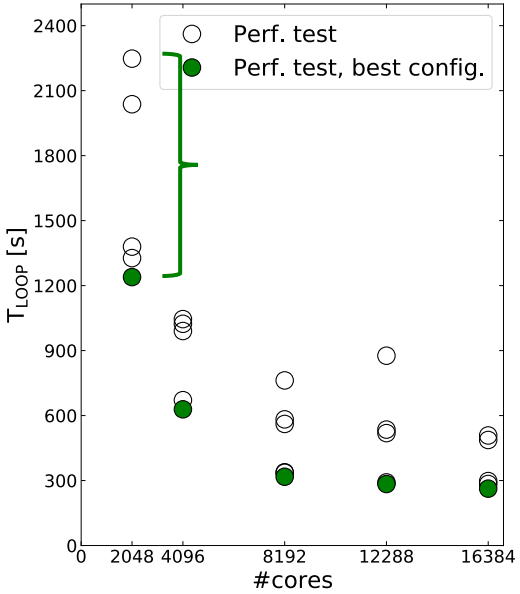
Methods

- DFT as implemented in VASP, numerically mainly matrix diagonalization
- Libraries: FFTW, LAPACK, ScaLAPACK and MPI
- PAW potentials, PBE (XC), DFT-D3 (dispersion forces)
- Plane wave basis expanded up to 460 eV
- BZ integration: 2x2x4 Monkhorst-Pack grid
- Geometry optimization until forces ≤ 0.001 eV/Å



Performance

Parallelization controlled by grouping of bands (NPAR) and k-points (KPAR)



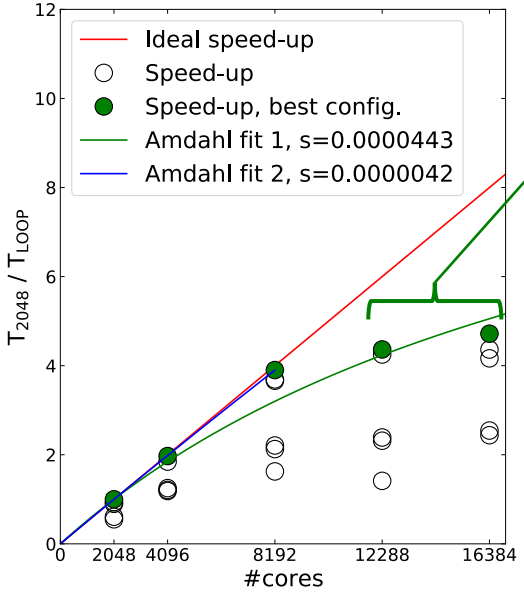
NPAR

Read the manual!

128 MPI tasks per node (not hybrid)

Parallelization cost: Memory demand!

Scaling efficiency of 96 % at 8192 cores!



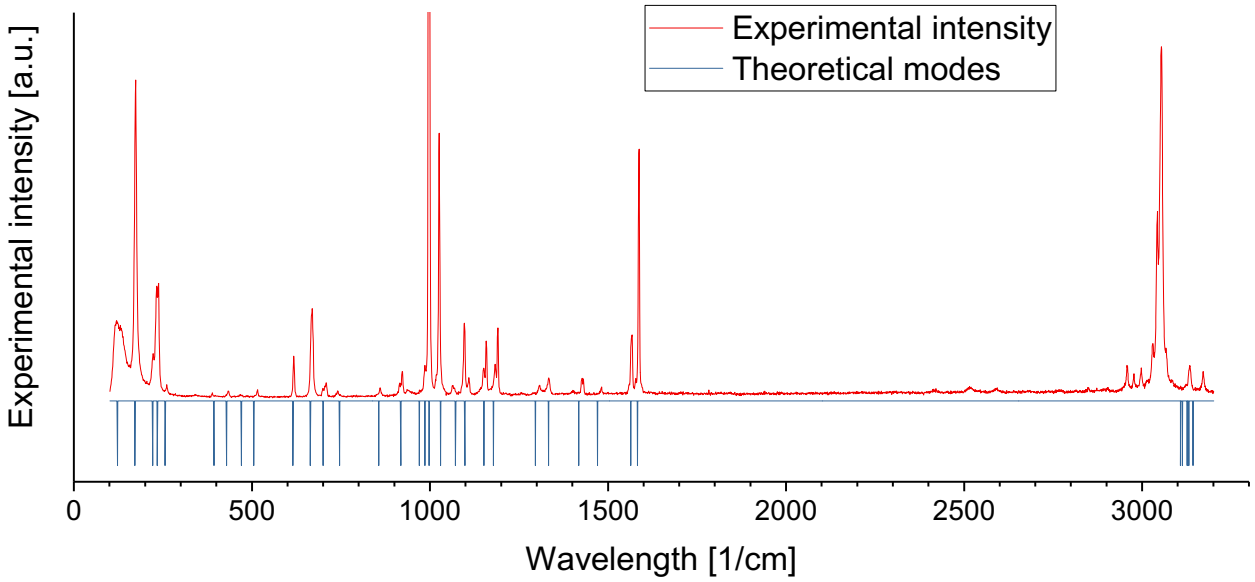
Too many nodes to successfully employ KPAR

A better scaling is expected for even more demanding calculations with a larger number of k-points to be distributed among the nodes.

Geometric properties

- Zero damping DFT-D3 vdW correction
- Nice agreement with experiment
- Also true for frozen phonon calculations, which allow to assign modes (symmetry, displacement) to spectral features

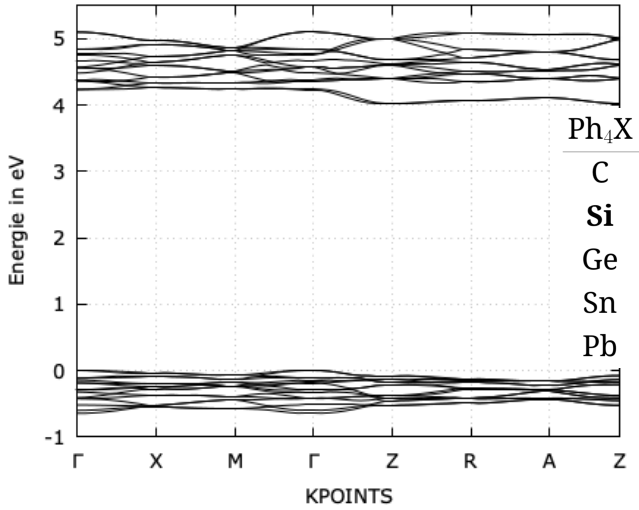
	Unit	PBE-D3	EXP	Δ
Si-Si	Å	8.683 – 9.079	8.792	0.022
Si-C	Å	1.883 – 1.891	1.875	0.014
C-Si-C	°	108.78 – 109.90	109.63	0.12
c	Å	6.158 – 7.285	6.762	0.020
a	Å	11.374 – 11.761	11.477	0.040
a/c	1	1.614 – 1.865	1.697	0.011



Summary

- Parallelization by k-points allows high scaling efficiency (associated with larger memory demand)!
- Calculations of optical properties employ the wave functions, which allow for a better understanding of experimental results.

(Non-)Linear optical spectra



Ph_4X	Bandgap [eV]
C	4.354
Si	**4.022**
Ge	3.817
Sn	3.739
Pb	4.028

$$\vec{P} = \epsilon_0 \chi \vec{E} + \vec{P}^{(2)} + \vec{P}^{(3)} + \dots$$
$$= \epsilon_0 \chi \vec{E} + \epsilon_0 \chi^{(2)} \vec{E}\vec{E} + \epsilon_0 \chi^{(3)} \vec{E}\vec{E}\vec{E} + \dots$$