50 years of the Institute of High Pressure Physics Polish Academy of Sciences

Highlights in III-V semiconductors, THz physics and nanomaterials

Anniversary Symposium „Unipress 50”

Ab initio many-body perturbation theory (MBPT) for solids exposed to pressure, temperature and light

Małgorzata Wierzbowska (NL3)

Problems and methods

Modern physics and technology requires very advanced methods for a description of the phenomena in solids beyond the ambient conditions, such as

- light-matter interaction
- high pressure and temperature
- spin-states at defects under n-type and p-type doping

- The popular ground-state methods such density-functional theory (DFT)
- or molecular dynamics (MD) are **not able** to treat such problems.

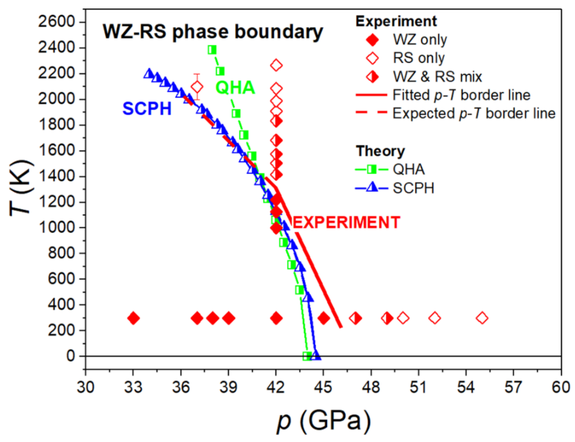
Interaction of fermions and bosons can be **successfully described** by the *ab initio* many-body perturbation theory (MBPT).

Ab initio MBPT approaches start with the Bloch functions obtained for the ground state using the DFT method and add the „diagramatic” terms to the Hamiltonian intentionally constructed for the interacting state. Three examples:

- temperature-dependent anharmonic phonons (Alamode code)
- light absorption/emission, excitonic properties (Yambo code)
- g-factor of defected solids in high charge states (Quantum ESPRESSO GIPAW code)

GaN wurtzite to rock-salt phase transition under high temperature and pressure - self-consistent phonon (SCPH) approach

The border line of the structural phase transition in GaN is a non-linear curve on a plot of pressure and temperature dependence Theoretical description of such effects requires the *ab initio* MBPT.



The total energy of each structural phase is given by the Gibbs potential that contains the pressure dependent part (pV) with the crystal volume V and temperature dependent part including the atomic vibrations.

$$G(p,T) = \overbrace{E_{el.}(V, T=0) + pV}^{G_I - \text{staticpart}} + F_{\text{vib.}}(V,T)$$

The static part is the total energy of the electronic and electron-nucleus interactions obtained form hte DFT. The vibrational part depends on the temperature as the function of β=1/kT and can divided to the harmonic term (**quasi harmonic approximation – QHA**), where phonon frequencies $\omega_{\mathbf{q}\nu}$ **do not depend on temperature** and are obtained with the density functional perturbation theory DFPT as a linear responce to the atomic displacements (using PHONON code),

$$F_{\text{vib.}}^{(QHA)}(V,T) = \frac{1}{N_q}\sum_{\mathbf{q}\nu}\left[\frac{\hbar\omega_{\mathbf{q}\nu}(V)}{2} + \frac{1}{\beta}\ln\left(1 - e^{-\beta\hbar\omega_{\mathbf{q}\nu}(V)}\right)\right]$$

and the anharmonic term, where the **phonon frequencies are dependent on temperature in the 4-th order term of the perturbative expansion in the interatomic forces**. Such approach is called the self-consistent phonon (**SCPH**) method and can be performed within the frozen-phonon approach implemented in the Alamode code.

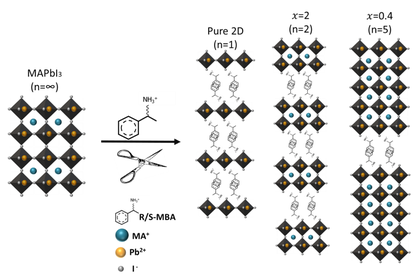
$$F_{\text{vib.}}^{(SCPH)}(V,T) = \overbrace{F_{\text{vib.}}^{QHA}(V,T)}^{G_{II}-\text{QHApart}} + \overbrace{\Delta F_{\text{vib.}}^{\text{corr}}(V,T)}^{G_{III}-\text{SCPHpart}}$$

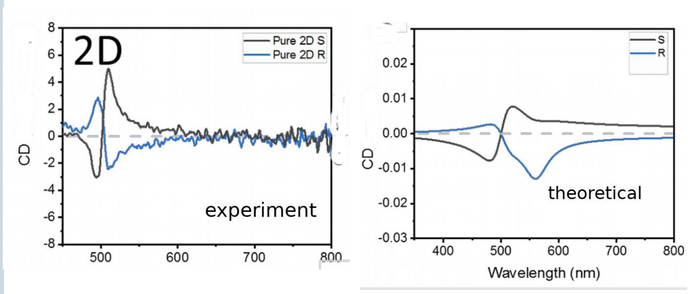
$$= \overbrace{\frac{1}{N_q}\sum_{\mathbf{q}\nu}\left[\frac{\hbar\omega_{\mathbf{q}\nu}(V)}{2} + \frac{1}{\beta}\ln\left(1 - e^{-\beta\hbar\omega_{\mathbf{q}\nu}(V)}\right)\right]}^{G_{II}-\text{QHApart}} - \overbrace{\frac{1}{4N_q}\sum_{\mathbf{q}\nu}\left[\Omega_{\mathbf{q}\nu}^2(V,T) - \omega_{\mathbf{q}\nu}^2(V)\right]\alpha_{\mathbf{q}\nu}}^{G_{III}-\text{SCPHpart}}$$

Experimental and theoretical evidence of the temperature-induced wurtzite to rocksalt phase transition in GaN under high pressure
Bohdan Sadovyi, Małgorzata Wierzbowska, Svitlana Stelmakh, Silvia Boccato, Stanislaw Gierlotka, Sylwester Porowski and Izabella Grzegory
Physical Review B | (2020) 102, 235109

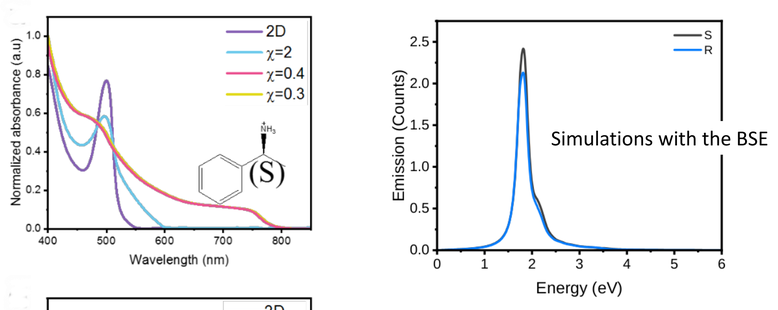
2D lead halide perovskites with chiral barrier molecules as solar cells - experiment vs. TDDFT and BSE

2D lead halide perovskite
with two chiral barrier molecules:
(S)-(+)-α-Methylbenzylamine
(R)-(+)-α-Methylbenzylamine
and various perovskite thickness.





Comparison of the experimental and theoretical spectra of the circular dichroism in pure 2D structures with chiral molecules. Simulations were done with the **time-dependent DFT (TDDFT)** using the Yambo code.

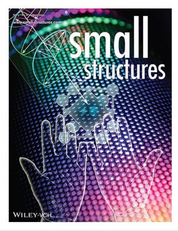


Comparison of the experimental absorption spectra (left) and the theoretical emission spectra obtained with the **Bethe-Salpeter equation (BSE)** (right).

BSE is the linear response theory which includes the electron-hole interactions, and thus it takes into account the exciton binding energy. The Yambo code was used.

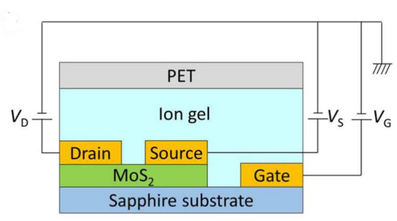
Publication includes the solar cell parameters obtained for the studied systems: the PCE, Voc, Jsc and fill factor.

Ruddlesden–Popper two-dimensional chiral perovskite based solar cells
Adva Shpatz Dayan, Małgorzata Wierzbowska and Lioz Etgar
Small Structures, 70026 (2022)
https://doi.org/10.1002/sstr.202270026

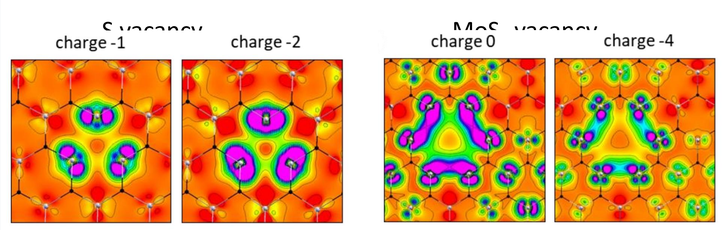


MoS_2 (monolayer and multilayered) with magnetic and charged defects in transistor configurations - operando ESR vs. g-factor (GIPAW)

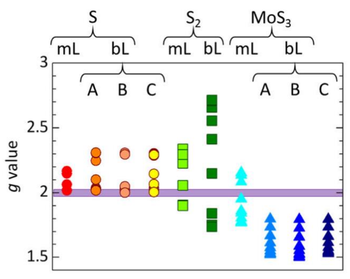
Experimental setup:
MoS_2 layers
(mono-, bi-, trilayers) with vacancies (S, S_2, MoS_3, MoS_6)
are in transistor structures which enable the n-type doping.



Vacancies bear the localized spin states dependent on the charge.

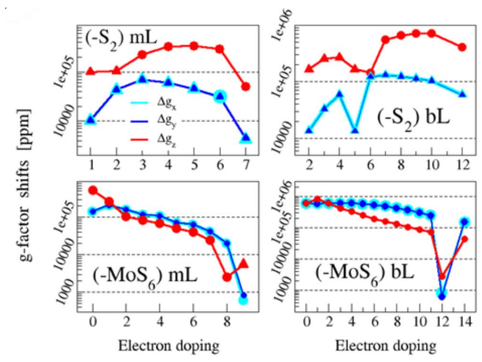


Comparison of the values of g-factor extracted from the operando ESR experiment and that obtained from the calculations performed for the system with various vacancies at many charge levels enables to characterize the mesaurd samples and correlate their transport properties with the exsitence of the specific defects.



Calculation of the g-factor with the GIPAW method implemented in the Quantum ESPRESSO code: The spin-polarized DFT results (eigenstates) are passed to the perturbative approach for the inclusion of the spin-orbit coupling. Further, the g-factor is extracted from certain terms of the perturbed Hamiltonian.

Anisotropic, in plane (g_x and g_y) and out-of-plane (g_z), g-factor shifts of defected monolayers (mL) and bilayers (bL) at various electron doping levels.



Spin-states in MoS_2 thin-film transistors distinguished by operando electron spin resonance
Naho Tsunetomo, Shohei Iguchi, Małgorzata Wierzbowska, Akiko Ueda, Yousang Won, Sinae Heo, Yesul Jeong, Yutaka Wakayama and Kazuhiro Marumoto
COMMUNICATIONS MATERIALS | (2021) 2:27 | https://doi.org/10.1038/s43246-021-00129-y

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