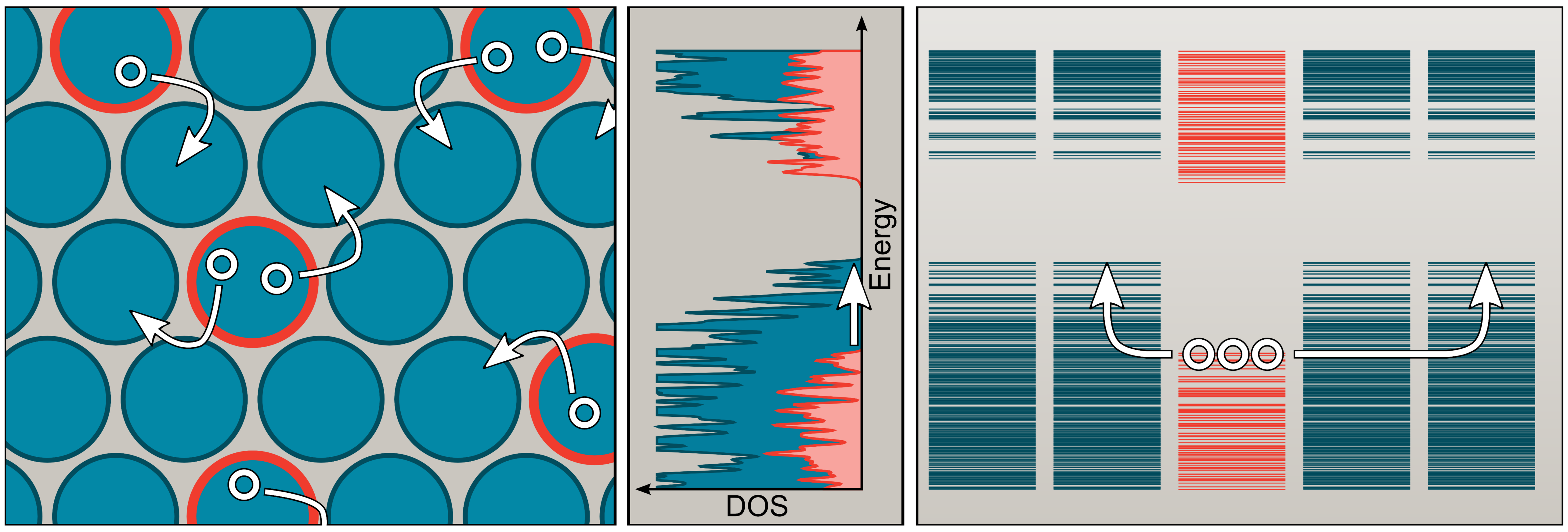
FSCOSD – Physics of Semiconductors, Optoelectronics and Disordered Systems, University of Aveiro

Metadopants for Semiconductor Nanocrystal Superlattices



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Objectives

- Achieve high electrical conductivity in solid films of small semiconductor nanocrystals (NCs). Look for affective doping strategies;
- Show that suitable engineered NCs (referred to as *metadopants*) can lead to a controllable and athermal activation of carriers.

Methods and techniques

- Large-scale first-principles calculations;
- Density functional theory (AIMPRO code), along with the local spin-density approximation to the correlation energy;
- Pseudopotentials for atomic core states and linear combinations of Gaussians functions for valence states;
- Superlattice (SL), atomic and electronic *relaxation* of several NCSLs per cell (Fig. 1);
- Location of acceptor levels of *metadopants* with respect to the conduction band bottom of a nanocrystal SL, E_c-E(-/0), estimated by comparing electron affinities (EA) taken from pristine and *metadoped* SLs as E_c-E(-/0) = EA_p - EA_{md}, where $EA_p \equiv E_c$ can be interpreted as the conduction band bottom of the pristine SL;
- Cancelation of image-charge interactions in charged systems with periodic boundary conditions;
- Projected density of states (PDOS) produced from Mulliken gross populations obtained after projecting the Kohn-Sham eigenstates onto all atom-centered basis functions.

Results

- *Metadopants* based on size-tuning [Table I (b)] and core-shell structuring (e) did not lead to sizable improvements in hole binding energy values (E_h);
- The higher-lying valence band top of the Ge-NCSL with respect to the Si-NC HOMO (Fig. 2 (c) – left) results in the athermal transfer of the hole from the *metadopant* to the surrounding Ge-NCs.
- Halide-terminated Si-NCs show dramatic EA and IP offsets with respect to H-terminated Si-NCs [Fig. 2 (c)].
- NC solids and SLs can be doped with help of dispersed and suitably engineered NCs (*metadopants*), consisting of doped structures whose intrinsic redox levels are calibrated to drive acceptor levels (donor levels) below the valence band top (above the conduction band bottom) of the solid.

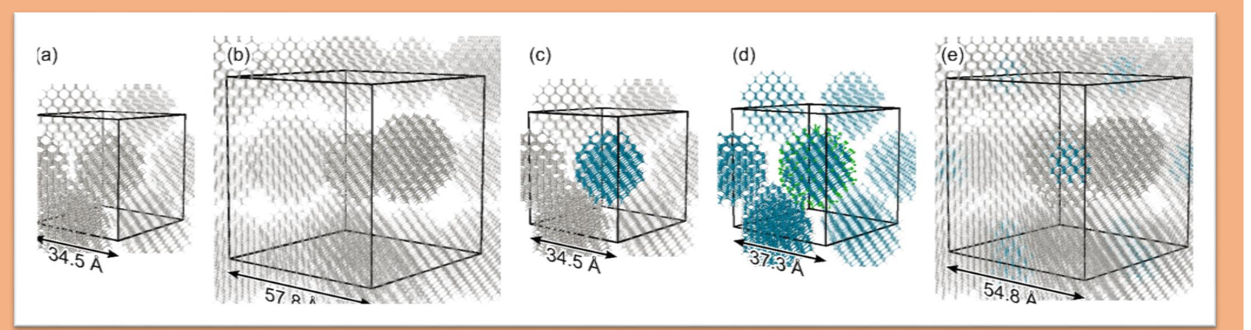

Fig. 1 – Some superlattice structures studied in this work along with their conventional (cubic) unit cells and respective equilibrium lattice parameters. See Table I for chemical composition and size information.

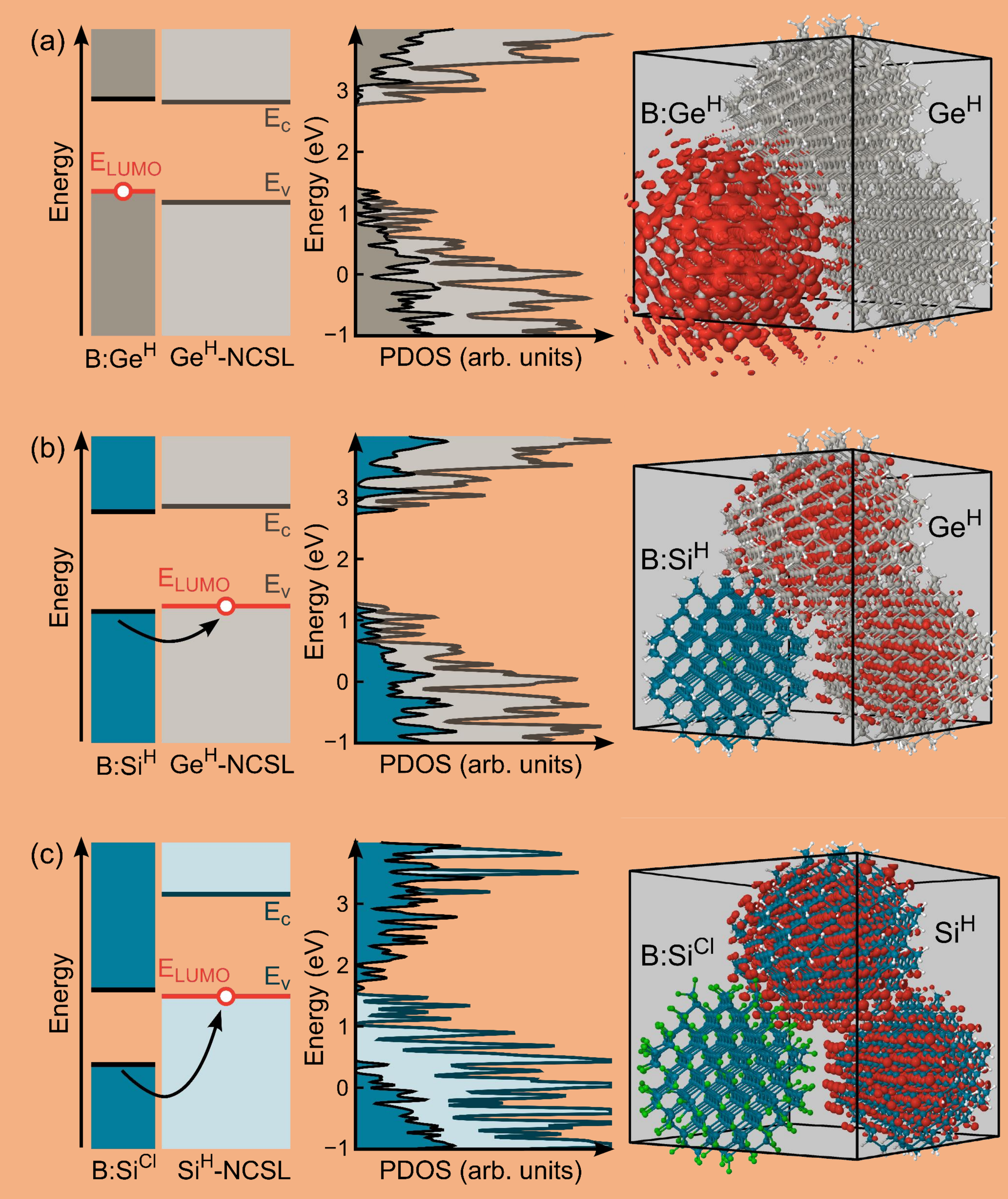

Fig. 2 – Level offset diagrams across metadopants ($B{:}X^{Y}$) and undoped NCs in $X'^{Y'}$ NCSLs (left), Kohn-Sham projected density of states (PDOS) over the metadopant and neighboring nanocrystals (middle), and isosurface of constant electron density shown in orange (right) for three p-doped NCSLs, namely (a) $B_S{:}Ge^H_{2.46\,nm}/3Ge^H_{2.46\,nm}$, (b) $B_S{:}Si^H_{2.38\,nm}/3Ge^H_{2.46\,nm}$ and (c) $B_S{:}Si^{Cl}_{2.85\,nm}/3Si^H_{2.38\,nm}$. In each unit cell the metadopant is represented on the lower left corner.

	Type	Unit Cell	E_h (eV)
(a)	sc	$B_S{:}Ge^H_{2.46\,nm}/3Ge^H_{2.46\,nm}$	0.23
(b)	fcc	$B_S{:}Ge^H_{2.46\,nm}/Ge^H_{3.19\,nm}$	0.22
(c)	sc	$B_S{:}Si^H_{2.38\,nm}/3Ge^H_{2.46\,nm}$	0.04
(d)	sc	$B_S{:}Si^{Cl}_{2.85\,nm}/3Si^H_{2.38\,nm}$	-0.04
(e)	fcc	$cs{-}B_S{:}SiGe^H_{3.16\,nm}/Ge^H_{3.19\,nm}$	0.19
(f)	sc	$B_S{:}Si^F_{2.85\,nm}/3Si^H_{2.38\,nm}$	-0.06

Table I – Superlattice type (sc: simple cubic; fcc: face-centered cubic), and hole binding energy (E_h) of p-type metadopants in several NCSLs.

Publications

[1] Coutinho, *et al.*, *Submitted to Phys. Rev. X* (2014).
[2] Pereira, *et al.*, Nano Lett. **14** 3817 (2014).
[3] Carvalho, *et al.*, Phys. Rev. B **86** 045308 (2012).

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FCT Fundação para a Ciência e a Tecnologia
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