Excitons in Organic Semiconductors, Carbon Nanotubes, and Nano-Peapods

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Abstract

The exciton binding energy (BE) is a central quantity in the photophysics of (organic) semiconductors since it is intimately related to the probability of radiative emission/absorption and electric-field induced generation of free charge carriers. It is defined as the energy required to separate a bound electron-hole pair, the exciton, into a free electron and a free hole. Here, we show for the prototypical *organic* semiconductors, i.e. the series of oligoacene molecular crystals, that the BE is inversely proportional to the molecular length. The BE is also strongly dependent on the strength of intermolecular interactions. Also, a strong effect of the resonant-antiresonant coupling terms is observed. For the zig-zag carbon nanotube (10,0) we evaluate the excitonic properties, and for the nano-hybrid system composed of poly-acetylene inside (10,0) we analyze the coupling between CNT and polymer optical excitations.

Theory

The Bethe-Salpeter equation, the equation of motion for two-particle electron-hole correlation function, provides a rigorous framework for the treatment of optical excitations. The interaction between the electron and the hole is accounted for by an effective interaction kernel, H^{e-h}, comprised of an attractive direct interaction, H^{dir}, and a repulsive exchange interaction H^x:

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{vc\mathbf{k}} \qquad H^{e-h} = H^{diag} + H^{dir} + 2H^{x}$$

The eigenvalues E^{λ} are the excitation energies, the eigenvectors A^{λ} describe the e-h coupling coefficient from which the electron-hole wave function as well as the imaginary part of the dielectric function is obtained. Details about our implementation into the all-electron framework of the full-potential linearized augment plane wave method (FP-LAPW) can be found in Ref. (2).

Organic Semiconductors – Oligoacenes
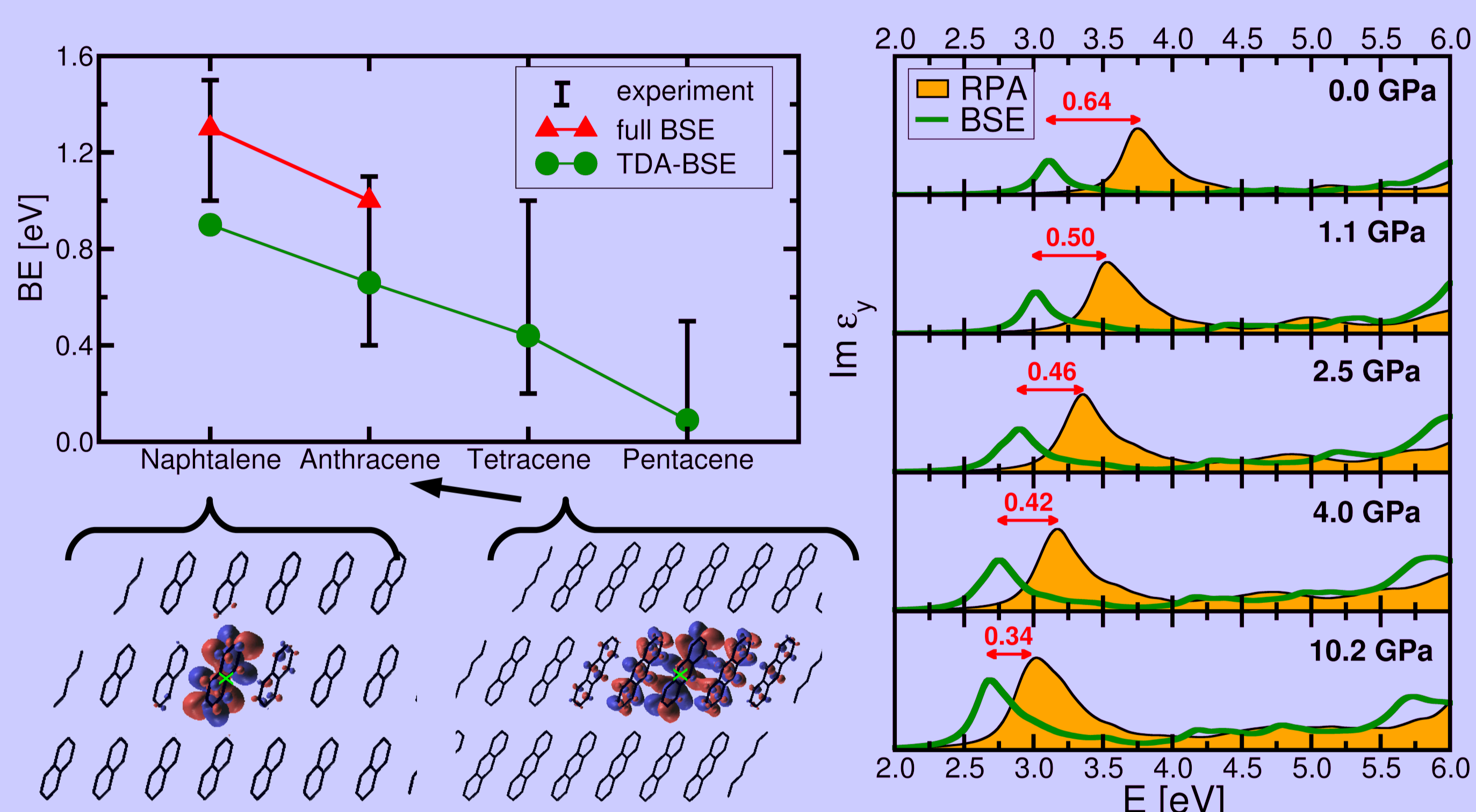
Fig. 1: *Left*: Dependence of the exciton binding energy (BE) on the molecular length. With increasing size the BE of the lowest lying exciton is reduced and the its spatial extent is enhanced as illustrated for naphthalene and anthracene. Note the pronounced effect of the resonant-antiresonant coupling terms in the BSE on the BE (full BSE). *Right*: Pressure dependence of the exciton BE in anthracene highlighting its dependence on the strength of intermolecular interactions.

Carbon Nanotubes: zig-zag (10,0) CNT
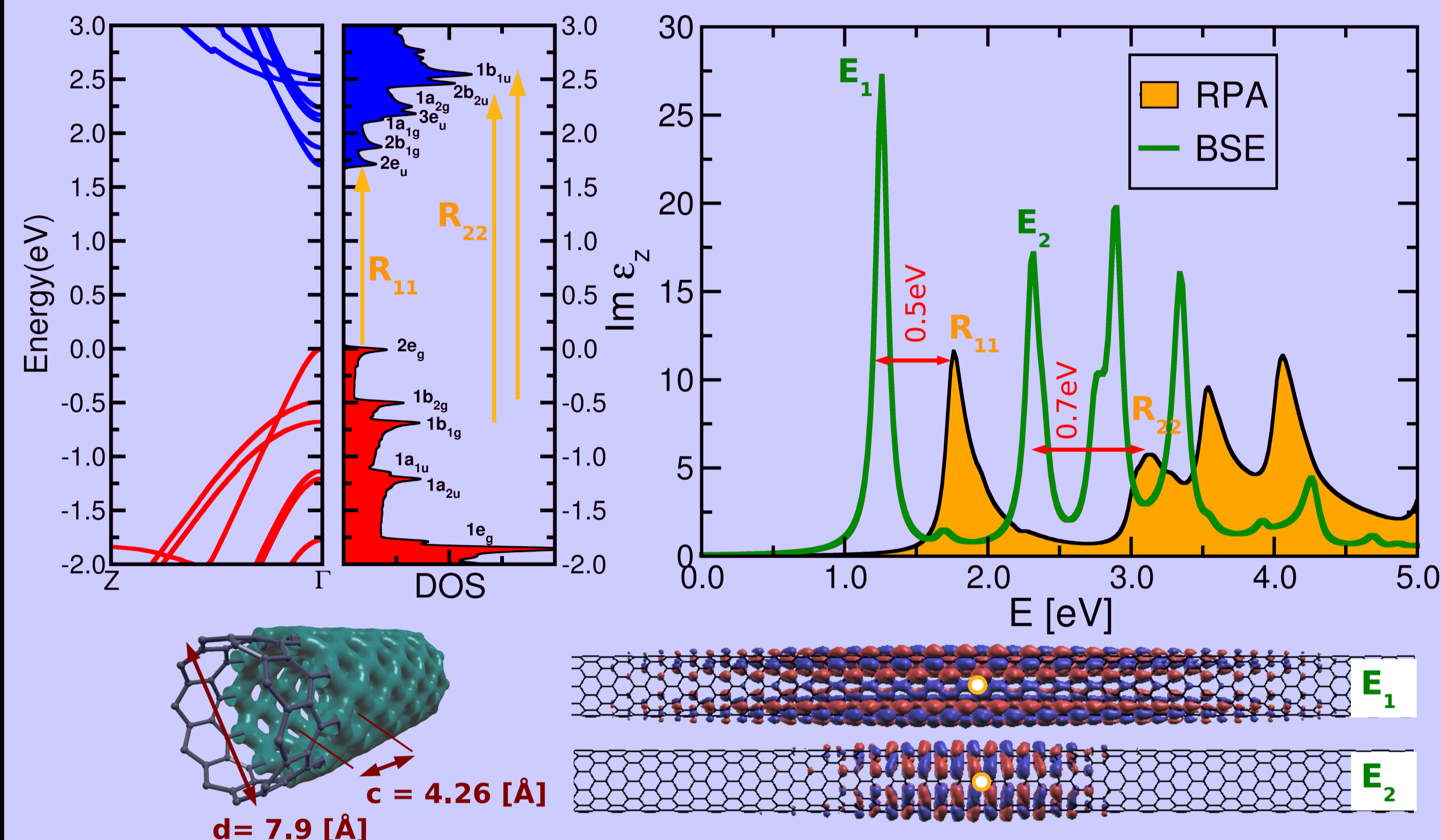
Fig. 2: The zig-zag single-wall CNT (10,0) with a diameter of 7.9 A exhibits a band gap of about 1.7 eV (GGA-DFT gap is 0.7 eV, corrected by a scissors shift of 1.0 eV). The solution of the BSE reveals strong electron-hole correlations resulting in bound excitons E1 and E2 with binding energies of 0.5 and 0.7 eV, respectively.

Nano-Peapods: Polyacetylene (PA) inside the (10,0) SWCNT
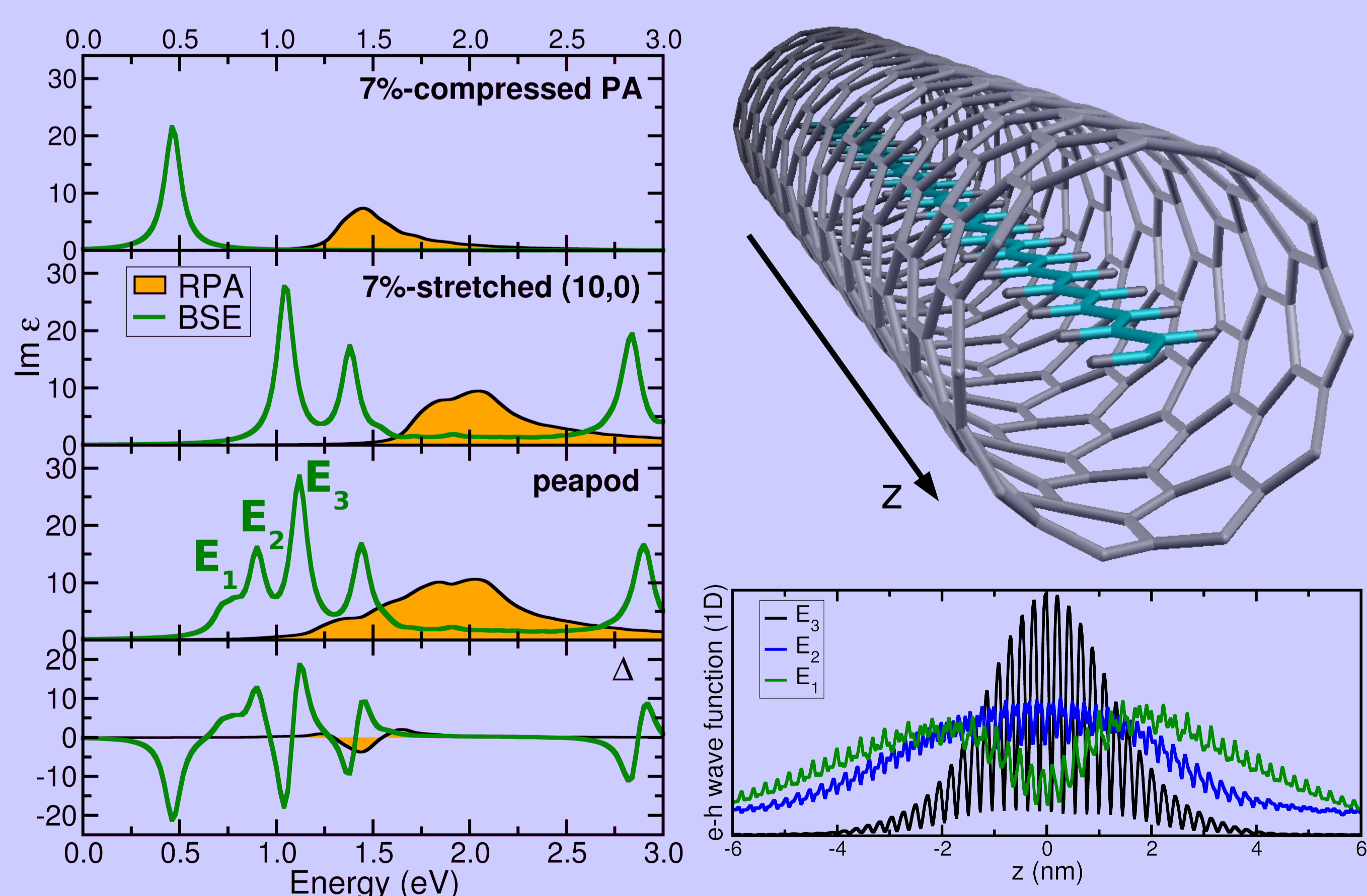

Fig. 3: We consider a nano-hybrid system composed of a photo-active organic semiconductor (*pea*) inside a carbon nanotube (*pod*). We show results for a model system consisting of trans-polyacetylene (PA) inside a (10,0) CNT. In contrast to RPA, which gives merely a superposition of optical spectra, the inclusion of electron-hole correlations within the BSE leads to a strong coupling between PA and CNT transitions.
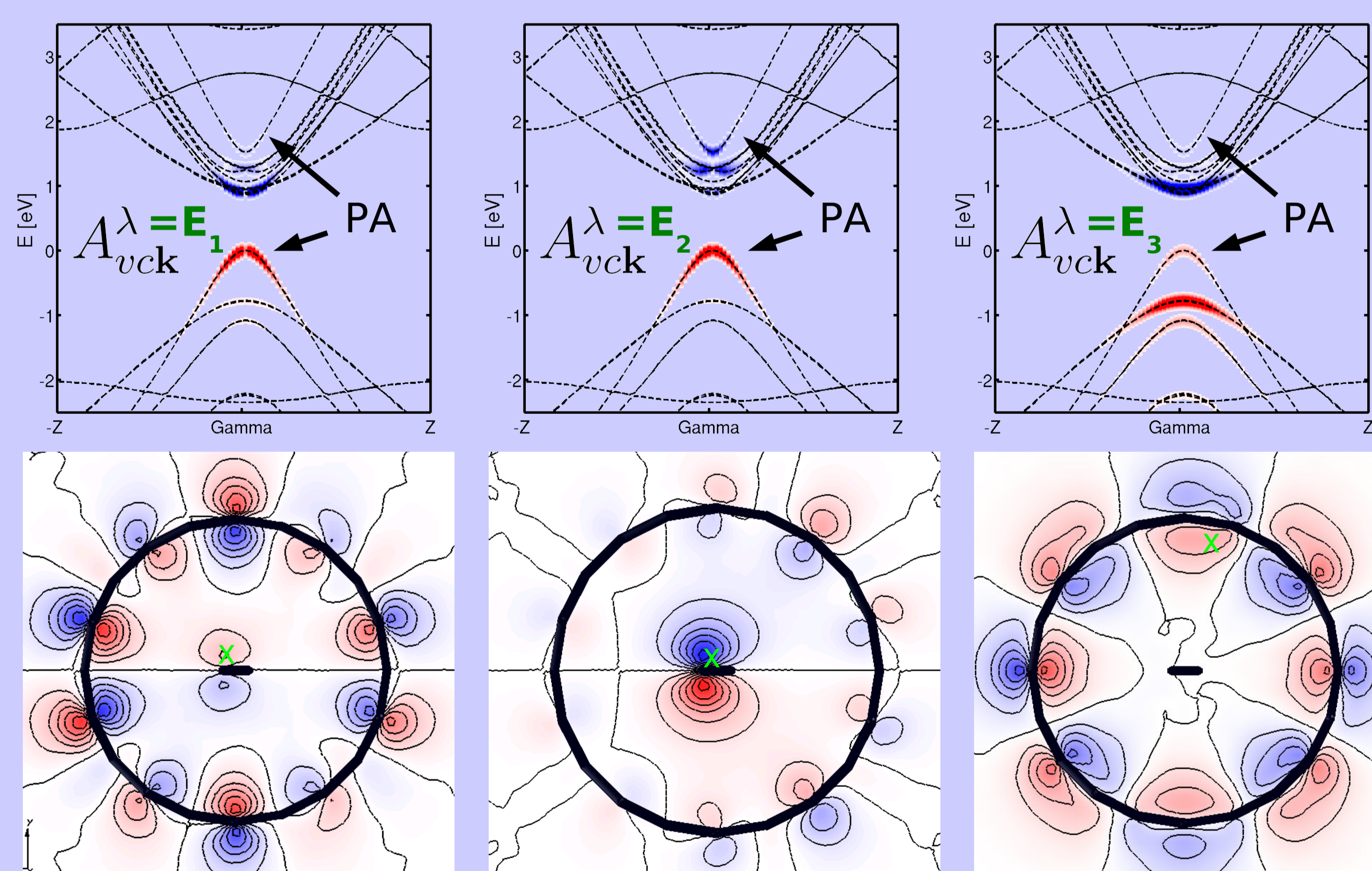
Fig. 4: We analyze the structure of the lowest-lying excitons E_1, E_2, E_3 by plotting the electron-hole (e-h) coupling coefficients A^{λ} color-coded on top of the band structure (top) and by drawing the e-h wave function (bottom) for fixed hole-positions indicated by the green cross.

Acknowledgments
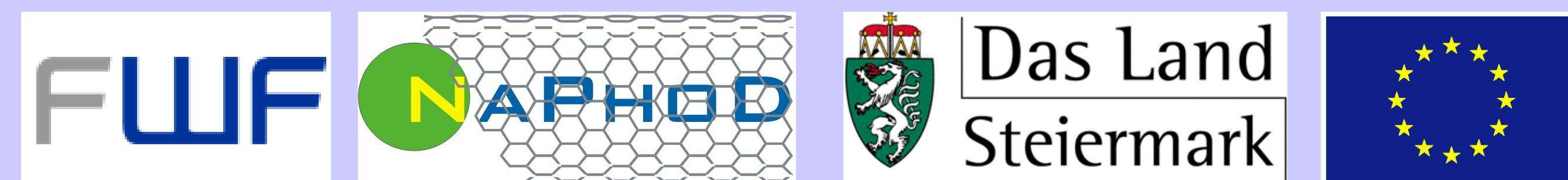
References

(1) P. Puschnig and C. Ambrosch-Draxl, *Phys. Rev. Lett.* **89**, 056405 (2002).

(2) P. Puschnig and C. Ambrosch-Draxl, *Phys. Rev. B* **66**, 165105 (2002).

(3) K. Hummer, P. Puschnig and C. Ambrosch-Draxl, *Phys. Rev. Lett.* **92**, 147402 (2004).

(4) K. Hummer, P. Puschnig, S. Sagmeister and C. Ambrosch-Draxl, *Mod. Phys. Lett. B* **20**, 261-280 (2002).

(5) P. Puschnig and C. Ambrosch-Draxl, *C. R. Phys.* **10**, 504-513 (2009).