Electronic States at Low-angle Grain Boundaries in Polycrystalline Naphthalene

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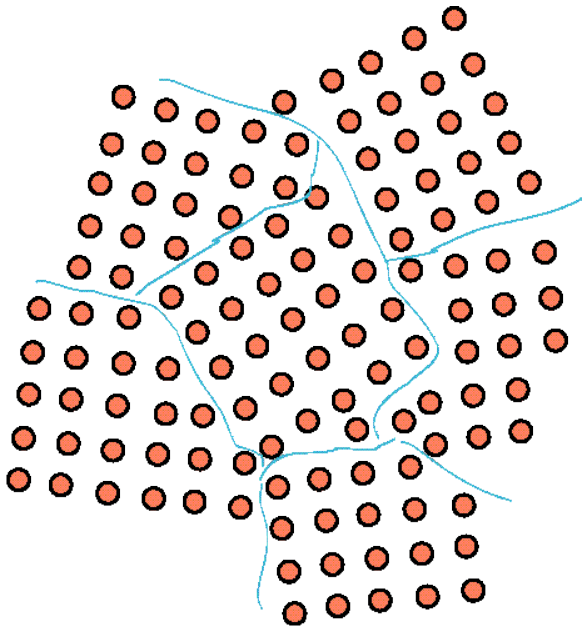
Grain boundaries in organic semiconductors

- Thin films of crystalline organic semiconductors have a polycrystalline form - they contain grains with different crystalline orientations.
- Grain boundaries affect material properties, but it is not clear how.
- It is believed that grain boundaries introduce trap states in the band gap of a material.
- There are suggestions that grain boundaries act as barriers for charge carriers.

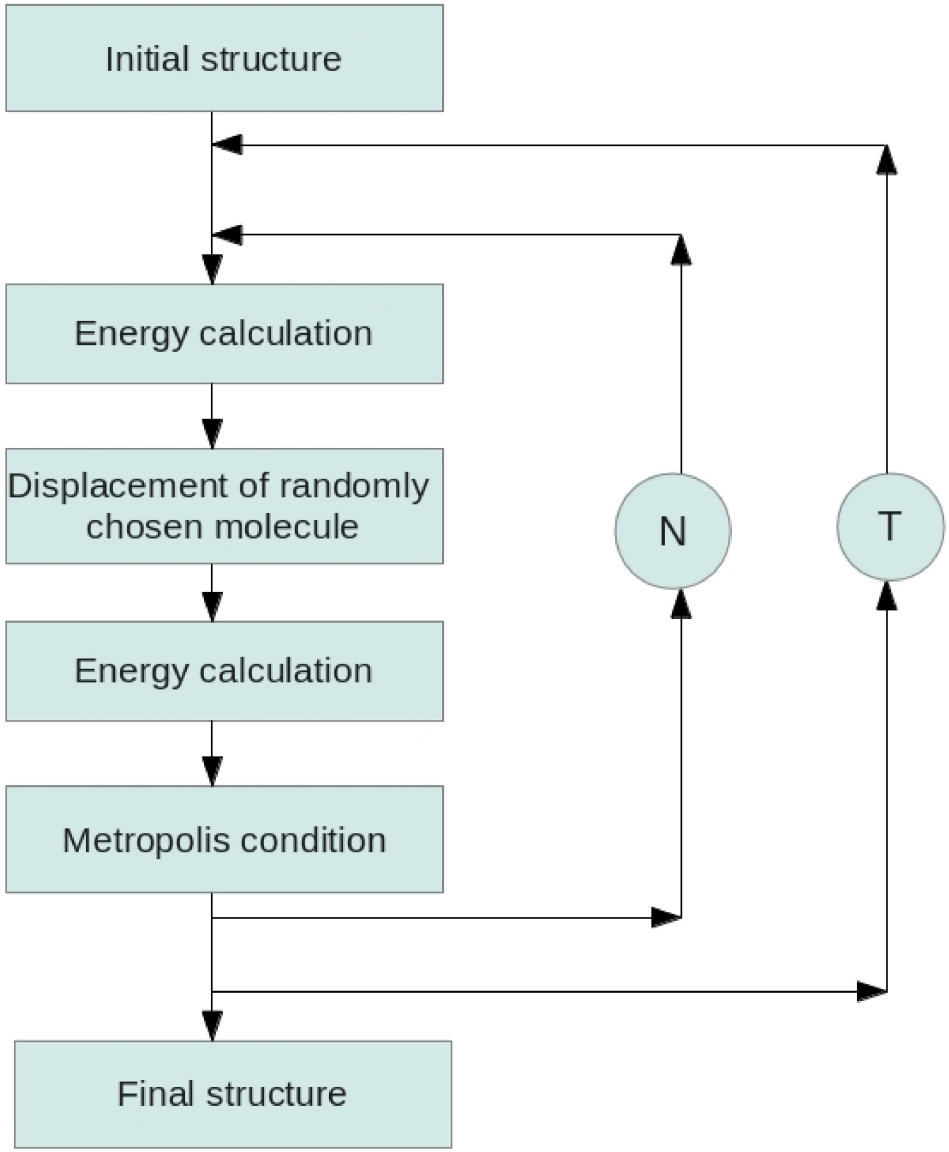


Grain boundaries in organic semiconductors

- Chwang, Frisbie *J. Appl. Phys.* (2011): transport in single grain boundary transistor limited by grain boundary
- Horowitz, Hajlaoui *Adv. Mater.* (2000): pronounced dependence of mobility in oligothiophene transistors on the grain size
- Kalb, Hass, Krellner, Mathis, Batlogg *Phys. Rev. B* (2010): strong difference between the characteristics of single crystal and polycrystalline transistors based on the same material
- Kaake, Barbara, Zhu *J. Phys. Chem. Lett.* (2010): grain boundaries act as a barriers and charge carriers are trapped by the grains
- Verlaak, Hermans, *Phys. Rev. B* (2007): microelectrostatic calculations indicate the presence of trapping centers at the grain boundary

Method for atomic structure calculations

Monte Carlo method



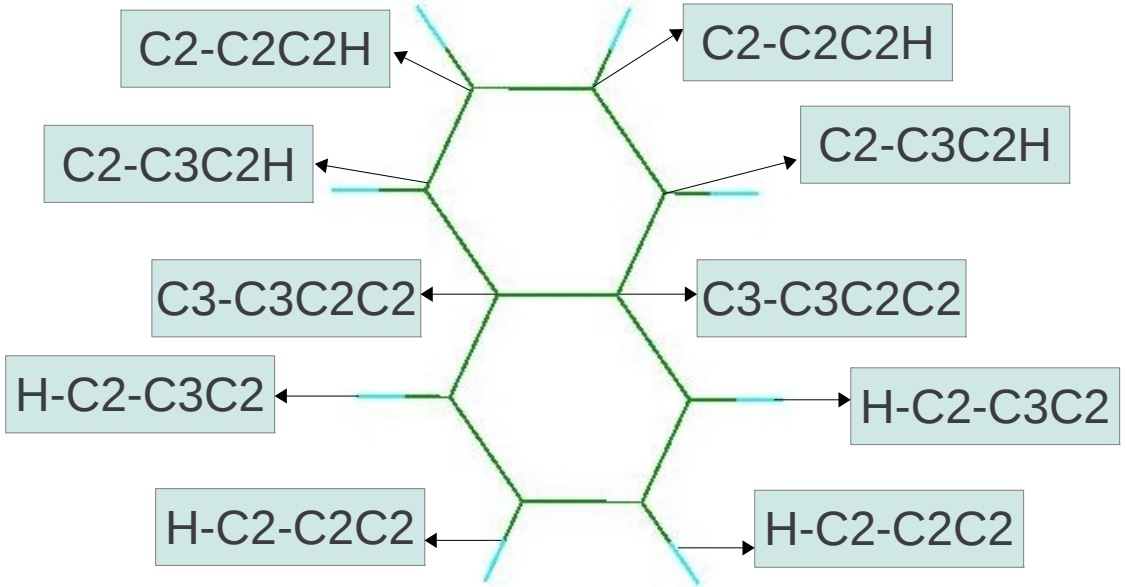
Method for atomic structure calculations

- Initial structure: two joined monocrystal grains
- Energy calculation: sum of the interactions between atoms from neighboring molecules, TraPPE potentials used
- Simulations performed at 300 K, followed by slowly cooling to 0 K
- Naphthalene unit cell parameters optimized: *a* = 8.325 Å, *b* = 5.92 Å, c = 7.77 Å, α = 90°, β=63° and γ=90°
- Naphthalene melting temperature calculated: 340 K

Method for electronic structure calculations

Charge patching method

- Motif: description of the environment of an atom
- Motifs in a naphthalene molecule:



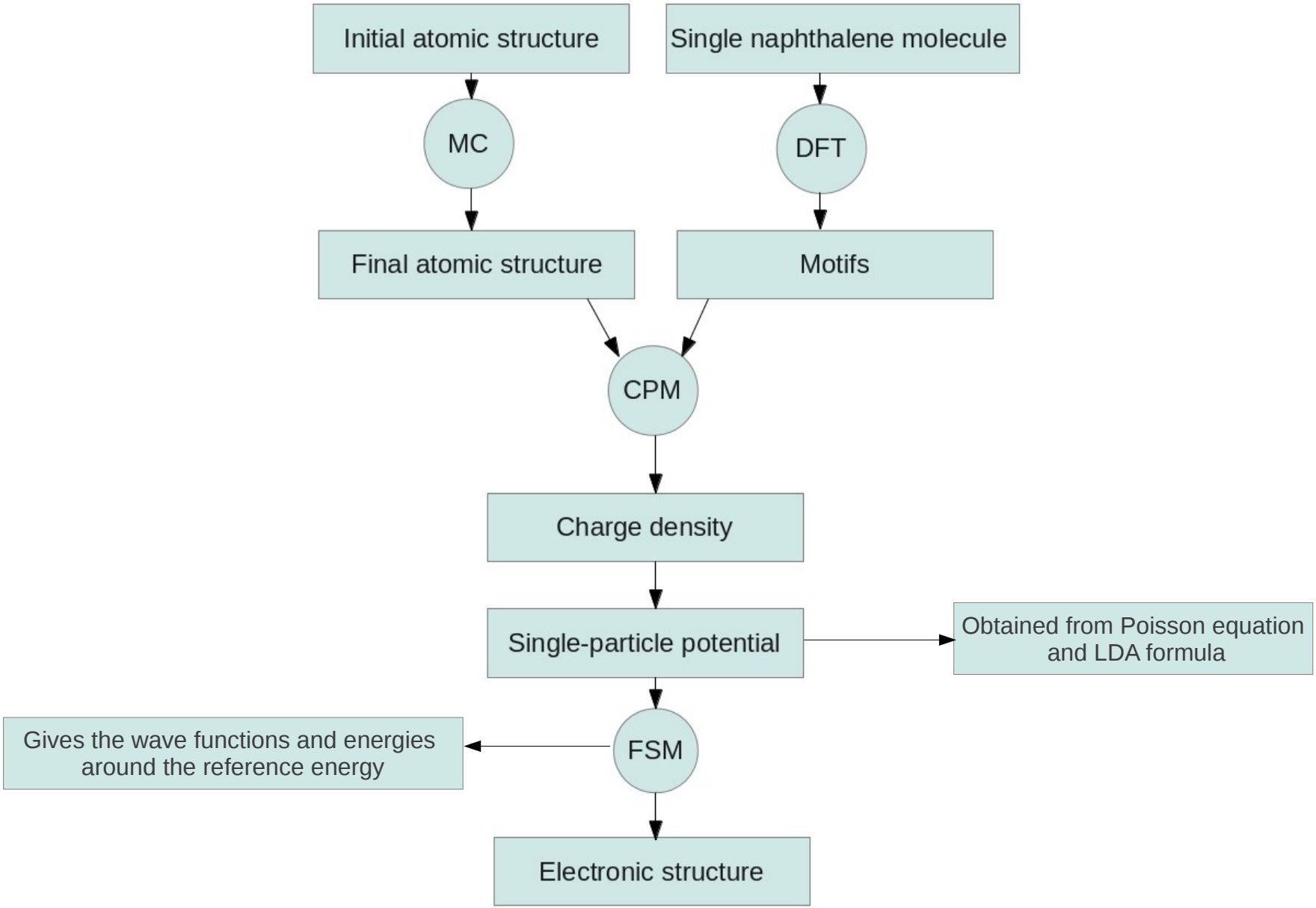
- Contribution of an atom:

$$m_A(\vec{r} - \vec{R_A}) = \frac{w_A(\vec{r} - \vec{R_A})}{\sum_B w_B(\vec{r} - \vec{R_B})}\rho(\vec{r})$$

- Overall charge density:

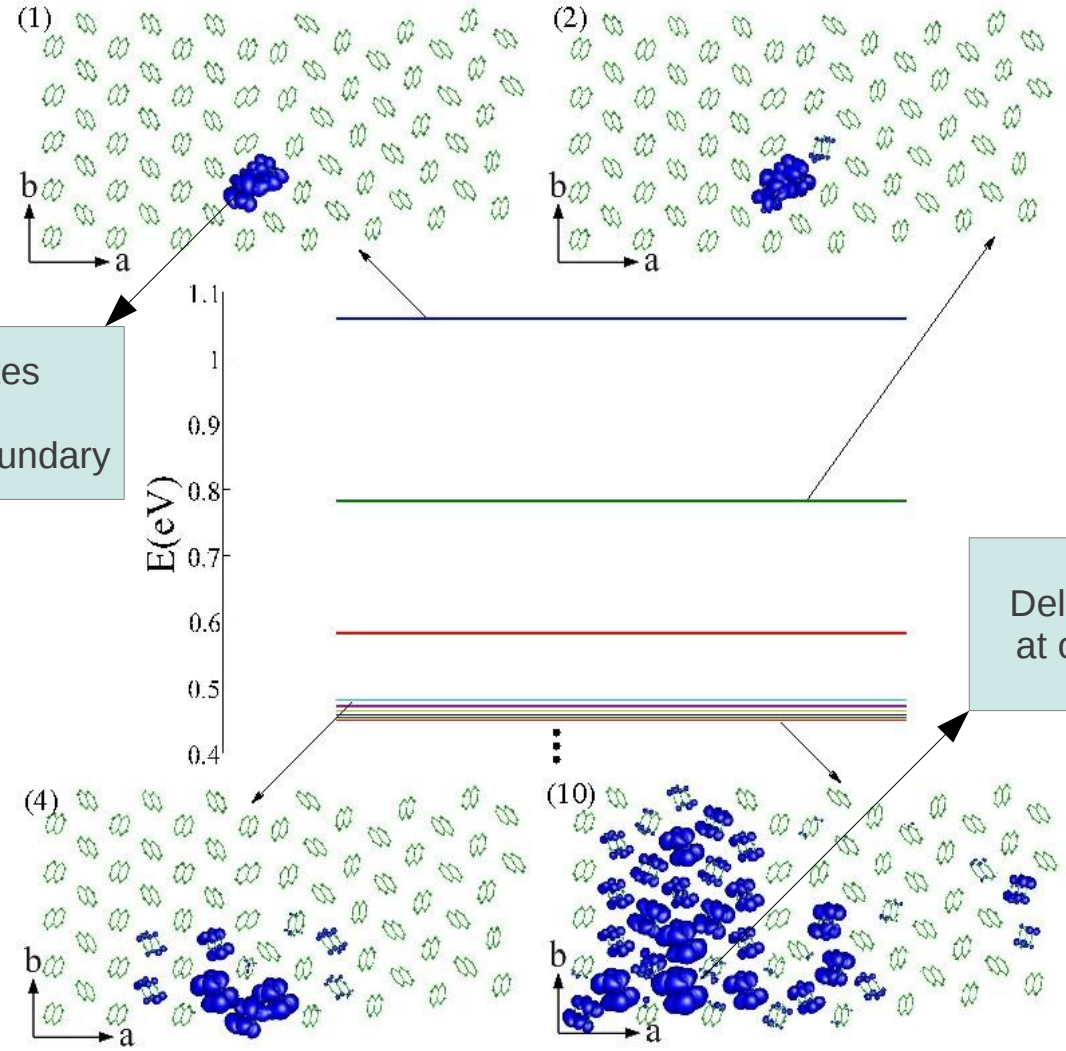
$$\rho(\vec{r}) = \sum_A m_A(\vec{r} - \vec{R_A})$$

Method for electronic structure calculations



Wave functions at grain boundaries

a-boundary system, misorientation angle of 10º

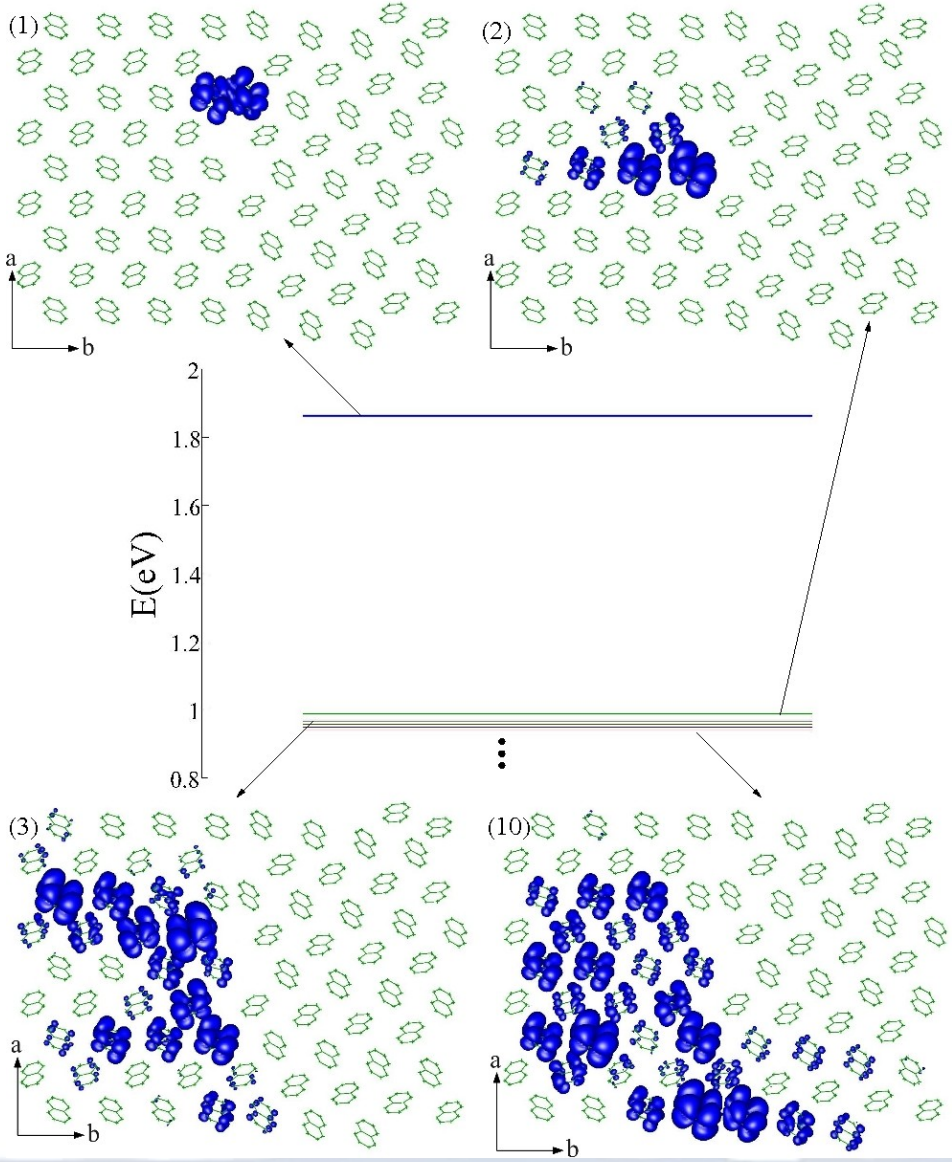


The highest trap states localized on the molecule pairs at the boundary

Delocalized states confined at one side of the boundary

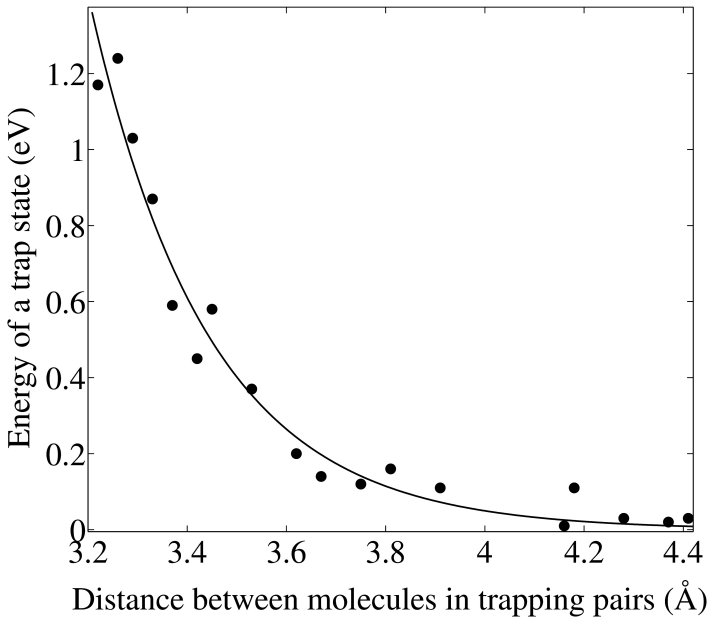
Wave functions at grain boundaries

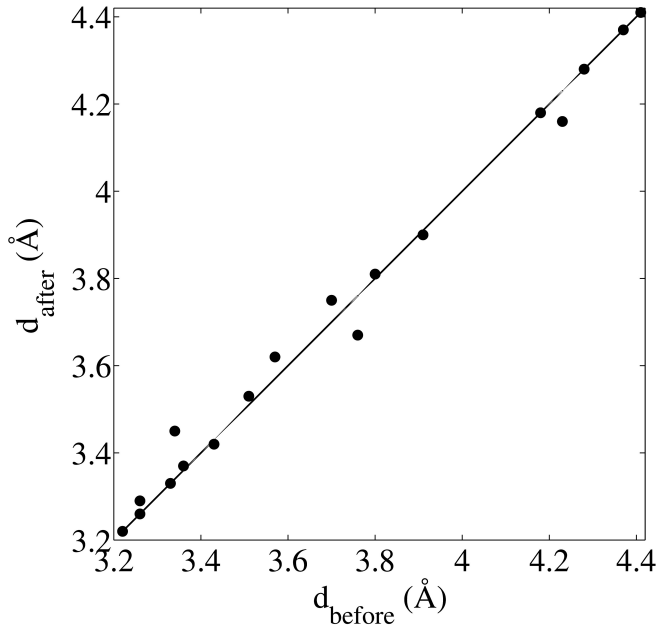
b-boundary system, misorientation angle of 10º



Wave functions at grain boundaries

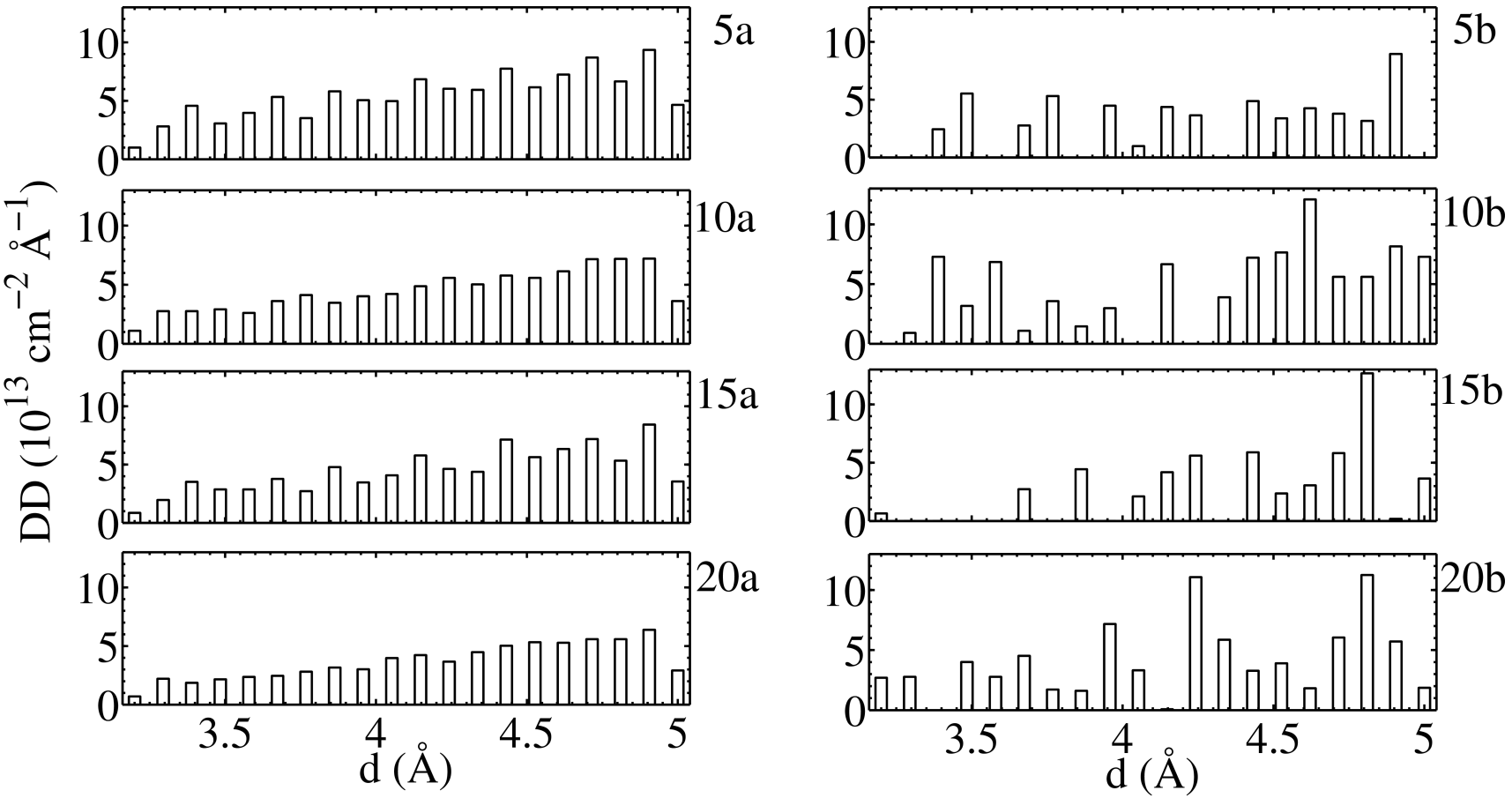
- Trap states with the highest energies relative to the top of the valence band are localized on the molecule pairs with mutual distance significantly smaller than the corresponding distance in a monocrystal (trapping pairs).
- Strong correlation between energy of the trap state and trapping pair mutual distance.
- Atomic structure stays nearly unchanged after the MC relaxation.



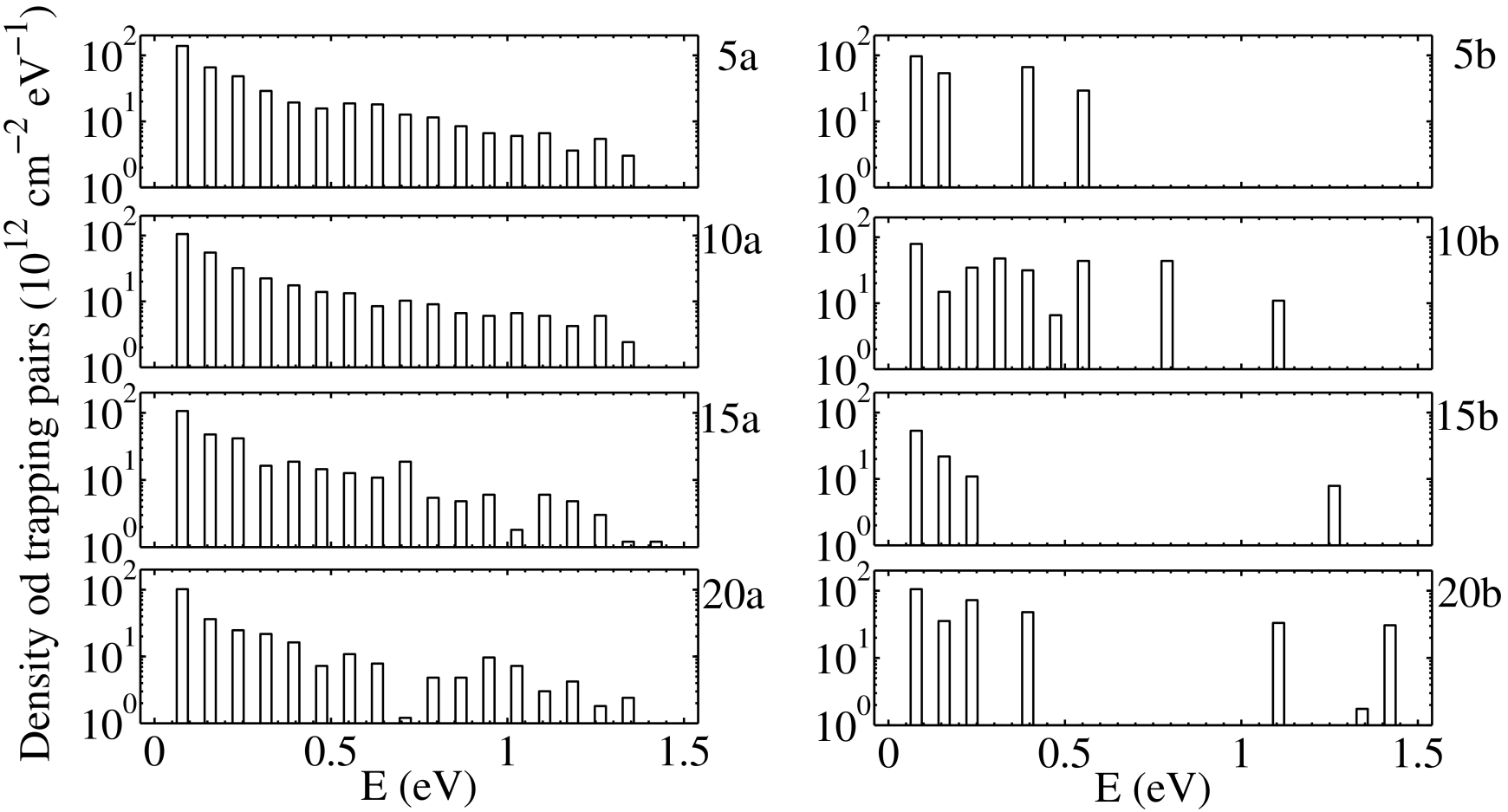


Density of trap states at grain boundaries

- For the density of trap states prediction, only trapping pairs distance distribution is needed.

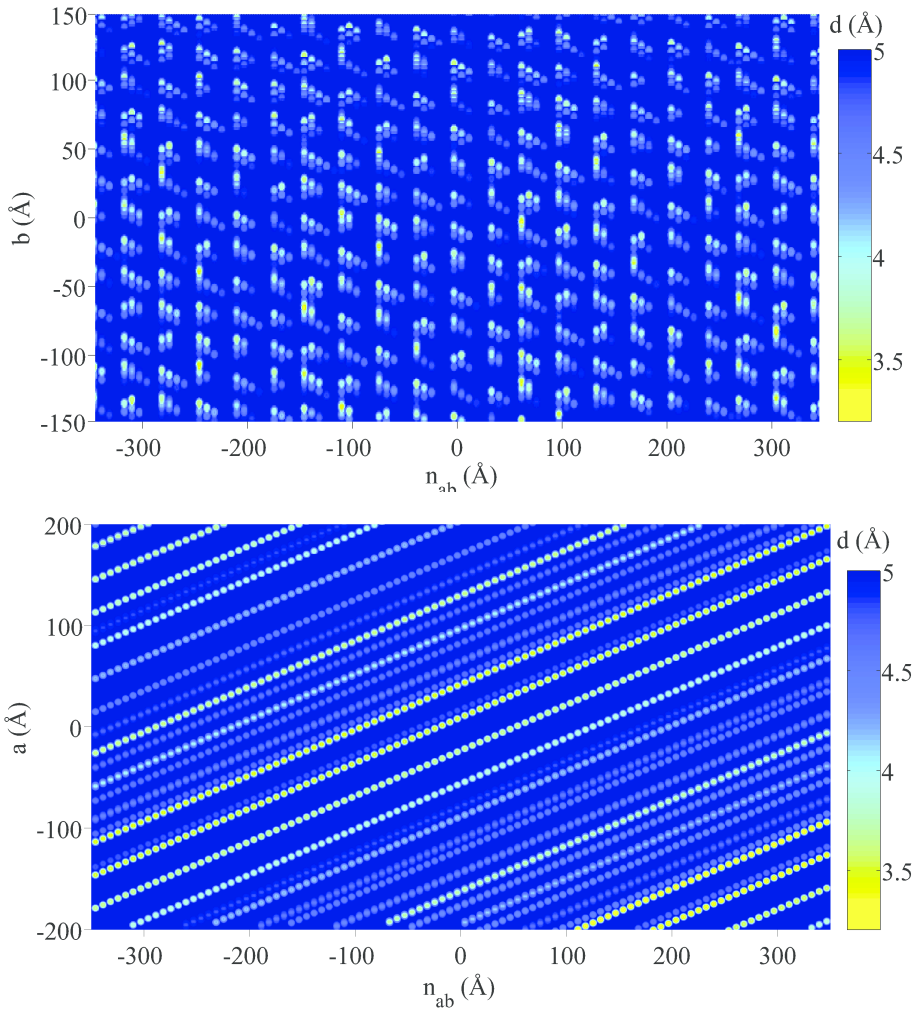


Density of trap states at grain boundaries



Density of trap states at grain boundaries

- Densities of states for *a*-boundary systems are continuous decreasing functions
- Densities of states for *b*-boundary systems are discrete functions with some energies preferred
- *a*-boundary systems have random spatial trapping pairs distance distribution, while *b*-boundary have periodic



Conclusions

- Existence of grain boundary induced trap states is confirmed.
- For the first time, microscopic insight into the trap states is given.
- Method for easy density of trap states prediction is proposed.
- Estimated numbers of trap states per unit of boundary surface and volume are: $3\times10^{13}\,cm^{-2}$ and $6.1\times10^{17}\,cm^{-3}$, respectively, which are of the same order of magnitude as experimental results for similar organic semiconductors.
- Delocalized states at grain boundaries are confined at one grain. In that sense, grain boundaries act as barriers.

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- More details: M. Mladenovic, N. Vukmirovic, I. Stankovic, *J. Phys. Chem. C* (2013) DOI: 10.1021/jp404825h

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