Physics of Semiconductors (6)

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k·p perturbation method

$$\hat{H}\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \qquad \psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\boldsymbol{r}}u_{\boldsymbol{k}}(\boldsymbol{r})$$

$$\left[-\frac{\hbar^2\boldsymbol{\nabla}^2}{2m_0} + V(\boldsymbol{r}) + \frac{\hbar^2\boldsymbol{k}^2}{2m_0} \underbrace{- i\frac{\hbar^2}{m_0}\boldsymbol{k}\cdot\boldsymbol{\nabla}}_{\hat{H}'}\right] u_{n\boldsymbol{k}}(\boldsymbol{r}) = E_n u_{n\boldsymbol{k}}(\boldsymbol{r})$$

perturbation

$$u_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{j=0}^{\infty} c_{nj}(\boldsymbol{k})u_{j0}(\boldsymbol{r})$$

non-degenerate case

$$u_{i\boldsymbol{k}}(\boldsymbol{r}) = u_{i0}(\boldsymbol{r}) + \sum_{j\neq i}\frac{\langle j|\hat{H}'|i\rangle}{E_i - E_j}u_{i0}(\boldsymbol{r}),$$

$$E_i(\boldsymbol{k}) = E_i(0) + \langle i|\hat{H}'|i\rangle + \sum_{j\neq i}\frac{|\langle i|\hat{H}'|j\rangle|^2}{E_i - E_j}$$

k·p perturbation method

degenerated case Assume $u_{00}(\boldsymbol{r})$ has n-fold degeneracy.

An orthogonal basis $\{u^{j}_{00}(\boldsymbol{r})\}$ (j = 1,..., n) $u^{i}_{0\boldsymbol{k}}(\boldsymbol{r}) = \sum_{j=1}^{n} A_{ij}(\boldsymbol{k}) u^{j}_{00}(\boldsymbol{r})$

$\langle u^{i}_{00}| \quad \rightarrow \quad [\hat{H}_0 + \hat{H}' - E_0(\boldsymbol{k})] u_{0\boldsymbol{k}}(\boldsymbol{r}) = 0 \qquad |u^{i}_{00}\rangle = |0i\rangle$

$$\sum_{j=1}^{n} A_{ij}(\boldsymbol{k}) [\langle 0i|\hat{H}_0|0j\rangle + \langle 0i|\hat{H}'_0|0j\rangle - \langle 0i|E_0(\boldsymbol{k})|0j\rangle]$$

$$= \sum_{j=1}^{n} A_{ij}(\boldsymbol{k}) [\langle 0i|\hat{H}'|0j\rangle + (E_0 - E_0(\boldsymbol{k}))\delta_{ij}] = 0$$

$$|\langle 0i|\hat{H}'|0j\rangle + (E_0 - E_0(\boldsymbol{k}))\delta_{ij}| = 0$$

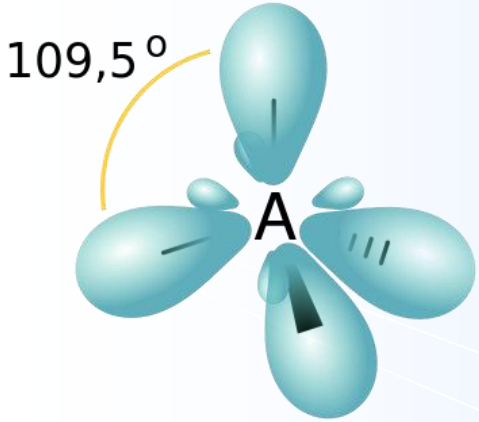
Spin-orbit interaction

Spin-orbit Hamiltonian

$$\hat{H}_{\mathrm{so}} = -\frac{\hbar}{4m_0^2c^2}\boldsymbol{\sigma}\cdot\boldsymbol{p}\times(\nabla V) \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},\ \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},\ \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\left[\frac{p^2}{2m_0} + V + \frac{\hbar^2k^2}{2m_0} + \frac{\hbar}{m_0}\boldsymbol{k}\cdot\boldsymbol{\pi} + \frac{\hbar}{4m_0^2c^2}\boldsymbol{p}\cdot\boldsymbol{\sigma}\times\nabla V\right] u_{n\boldsymbol{k}} = E_n(\boldsymbol{k})u_{n\boldsymbol{k}},$$

$$\boldsymbol{\pi} \equiv \boldsymbol{p} + \frac{\hbar}{4mc^2}\boldsymbol{\sigma}\times\nabla V,$$



Crystal formation from sp^3 hybridization.

use s, p^+, p^0, p^- orbitals instead of sp^3 hybrids

$$|S\rangle,\ \ |+\rangle \equiv (|X\rangle + i|Y\rangle)/\sqrt{2},\ \ |0\rangle \equiv |Z\rangle,\ \ |-\rangle \equiv (|X\rangle - i|Y\rangle)/\sqrt{2}$$

⟶ 8x8 determinant

k·p method for diamond and zinc-blende

perturbation Hamiltonian $\hat{H}' + \hat{H}_{\mathrm{SO}} = -i\frac{\hbar^2}{m_0}\boldsymbol{k}\cdot\boldsymbol{\nabla} - \frac{\hbar}{2}\xi(\boldsymbol{r})\boldsymbol{l}\cdot\boldsymbol{\sigma}$

$$P \equiv -i\frac{\hbar^2}{m_0}\langle S|\frac{\partial}{\partial X}|X\rangle \qquad \Delta_0 \equiv \frac{3}{2}\hbar^2\langle +|\xi|+\rangle$$

E_c, E_v : conduction and valence edges in non-perturbed state

For simplicity $\boldsymbol{k}$ = (0, 0, k) then 8x8 matrix is reduced to 4x4.

$$\begin{vmatrix} E_c-\lambda & 0 & Pk & 0 \\ 0 & E_v-\lambda-\frac{\Delta_0}{3} & \frac{\sqrt{2}\Delta_0}{3} & 0 \\ P^*k & \frac{\sqrt{2}\Delta_0}{3} & E_v-\lambda & 0 \\ 0 & 0 & 0 & E_v-\lambda+\frac{\Delta_0}{3} \end{vmatrix} = 0$$

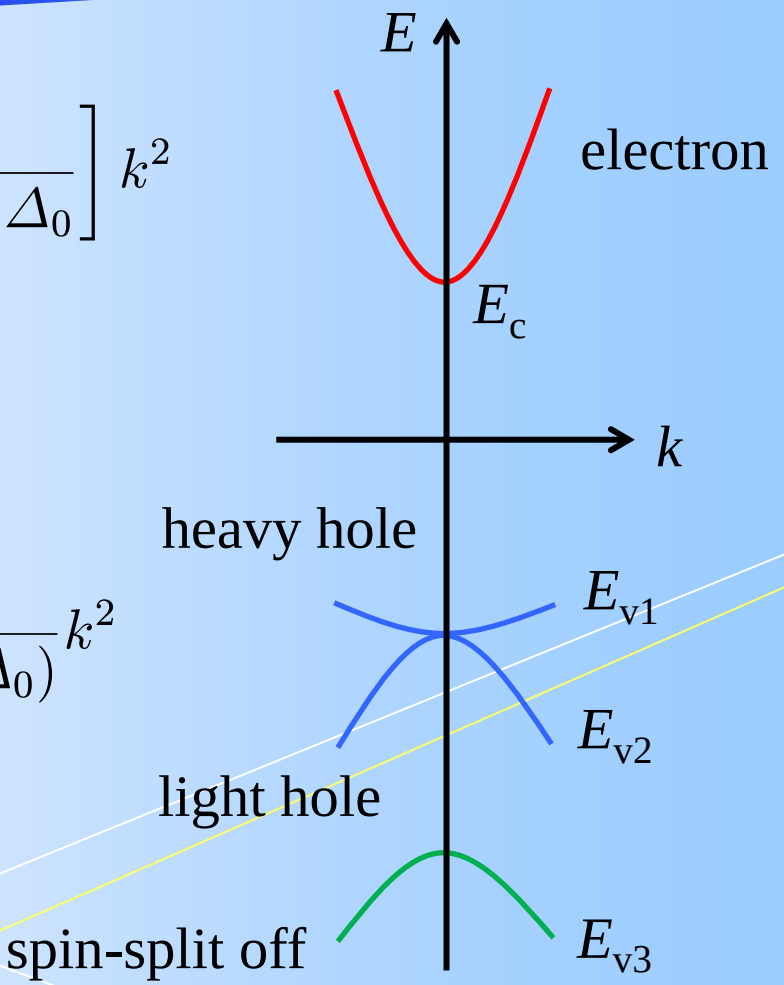
k·p method for diamond and zinc-blende

$$E_c(\boldsymbol{k}) = E_c + \frac{\hbar^2 k^2}{2m_0} + \frac{|P|^2}{3}\left[\frac{2}{E_\mathrm{g}} + \frac{1}{E_\mathrm{g}+\Delta_0}\right]k^2$$

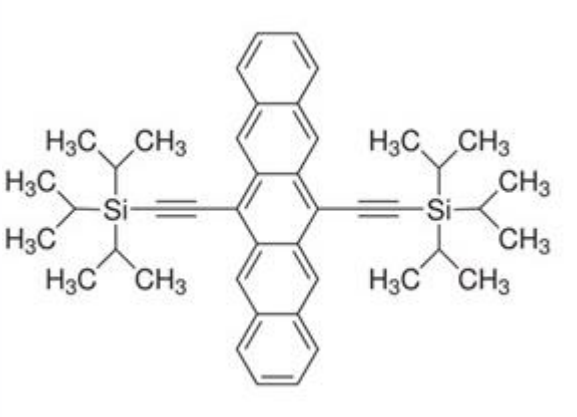
$$E_{v1}(\boldsymbol{k}) = E_v + \frac{\Delta_0}{3} + \frac{\hbar^2 k^2}{2m_0}$$

$$E_{v2}(\boldsymbol{k}) = E_v + \frac{\Delta_0}{3} + \frac{\hbar^2 k^2}{2m_0} - \frac{2|P|^2}{3E_\mathrm{g}}k^2$$

$$E_{v3}(\boldsymbol{k}) = E_v - \frac{2\Delta_0}{3} + \frac{\hbar^2 k^2}{2m_0} - \frac{|P|^2}{3(E_\mathrm{g}+\Delta_0)}k^2$$

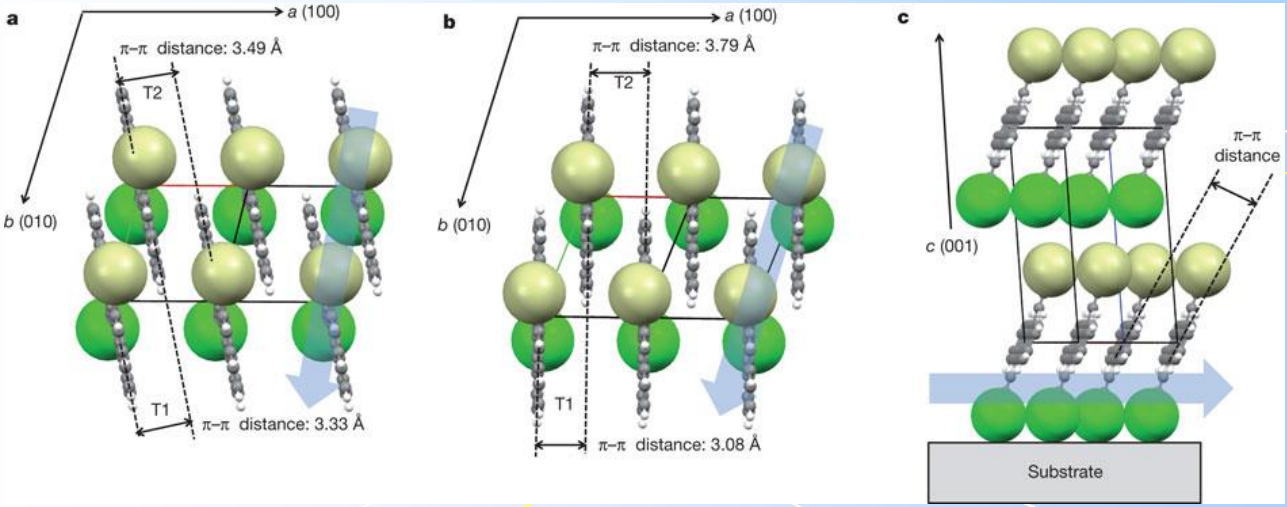


Organic semiconductors



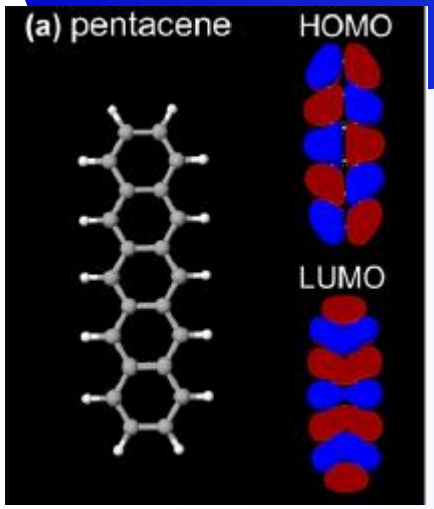
Ex) Pentacene

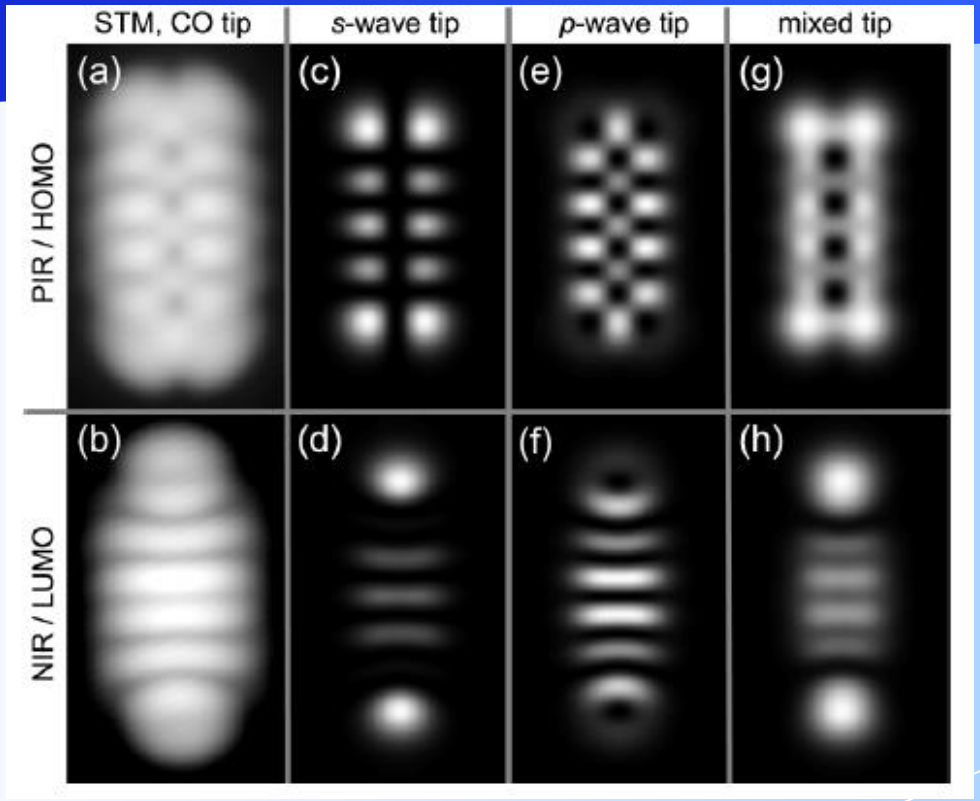
Strong intra-molecule bonding: covalent, ionic
Weak inter-molecule bonding: van der Waals

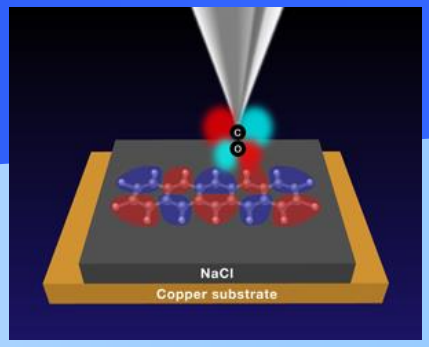


G Giri *et al. Nature* **480**, 504-508 (2011) doi:10.1038/nature10683

Organic semiconductors







L. Gross *et al.*
PRL **107**, 086101 (2011).

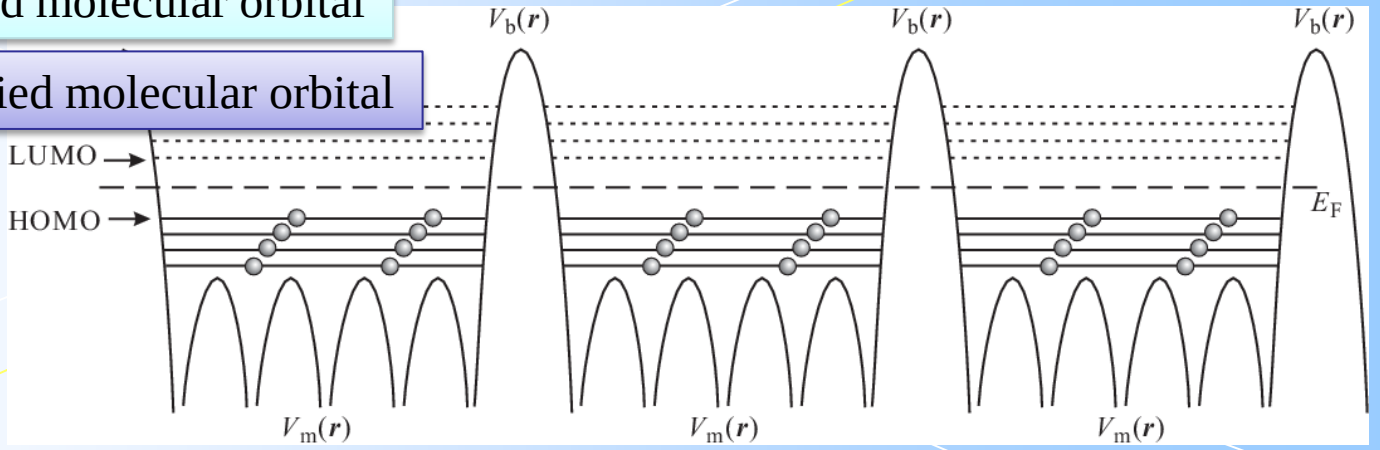
frontier orbital

HOMO: highest occupied molecular orbital

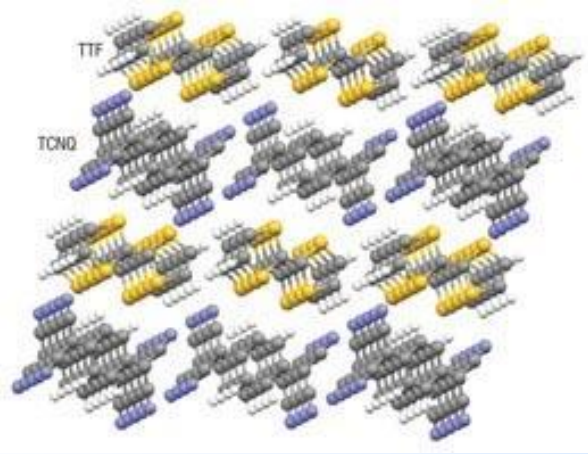
LUMO: lowest unoccupied molecular orbital

(Ken-ichi Fukui 1952)

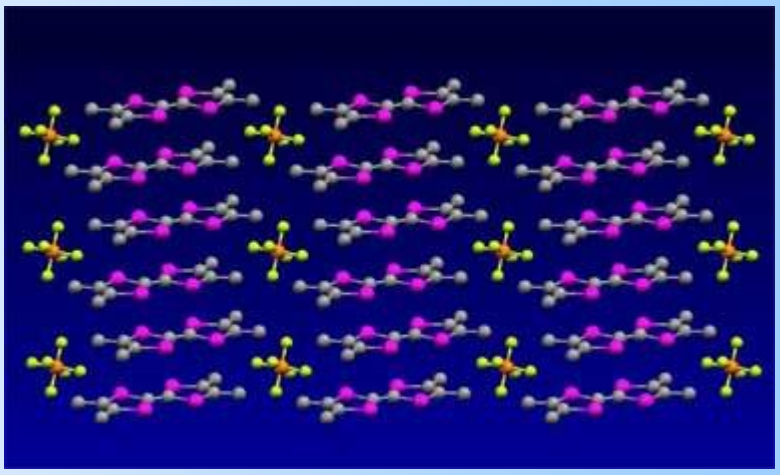
valence band
conduction band



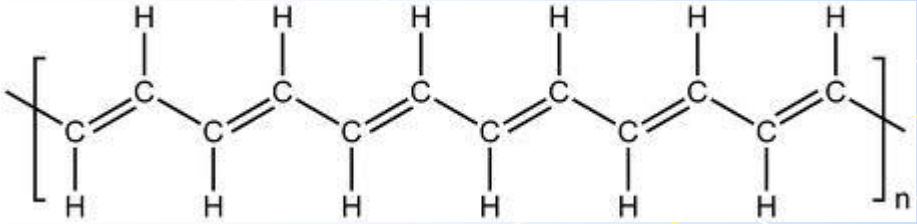
Organic semiconductors



TTF-TCNQ

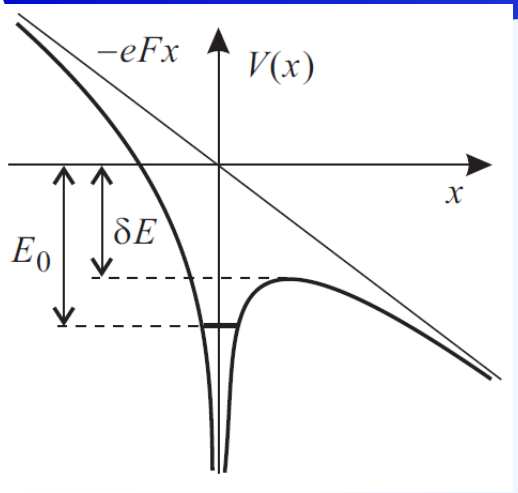


$(TMTSF)_2PF_6$



polyacetylene

Poole-Frenkel model

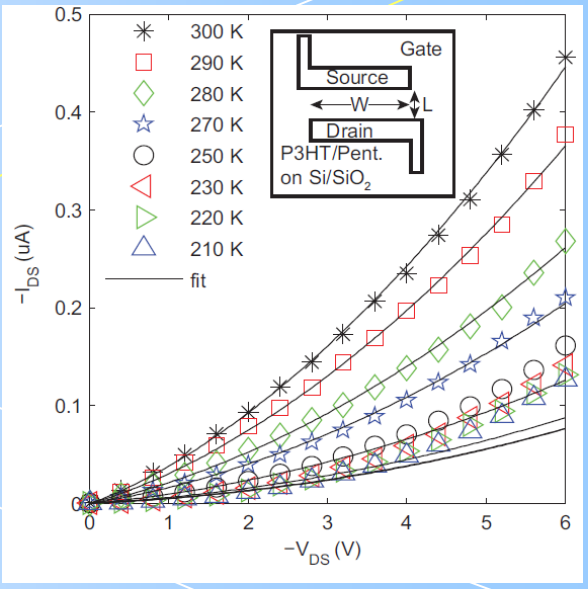


trap potential $$V(\boldsymbol{r}) = -\frac{e^2}{4\pi\epsilon\epsilon_0 r} - eFx$$

$$\delta E = \sqrt{\frac{e^3 F}{\pi\epsilon\epsilon_0}}$$

$$\mu(F) = \mu_0 \exp\left[-\frac{E_0 - \delta E}{k_\mathrm{B}T}\right] = \mu(0)\exp\left[\frac{\delta E}{k_\mathrm{B}T}\right] \equiv \mu(0)\exp(\beta(T)F^{1/2})$$

$$\beta(T) = (e^3/\pi\epsilon\epsilon_0)^{1/2}/k_\mathrm{B}T$$ Poole-Frenkel coefficient



J. H. Worne *et al.*
APL **96**, 053308 (2010).

Exercise

1. Derive the expression for built-in potential V_{bi} simply by considering that the right and the left ends of a *pn* junction should have the same expressions for chemical potential as those in bulk p and n doped semiconductors.

2. A pn junction in equilibrium has a double space charge region and thus has an effective electric capacitance. Obtain the expression for the capacitance as a function of donor and acceptor concentrations, energy gap and temperature.