Part III

Self-energy and excitonic corrections in nanostructures

Outline

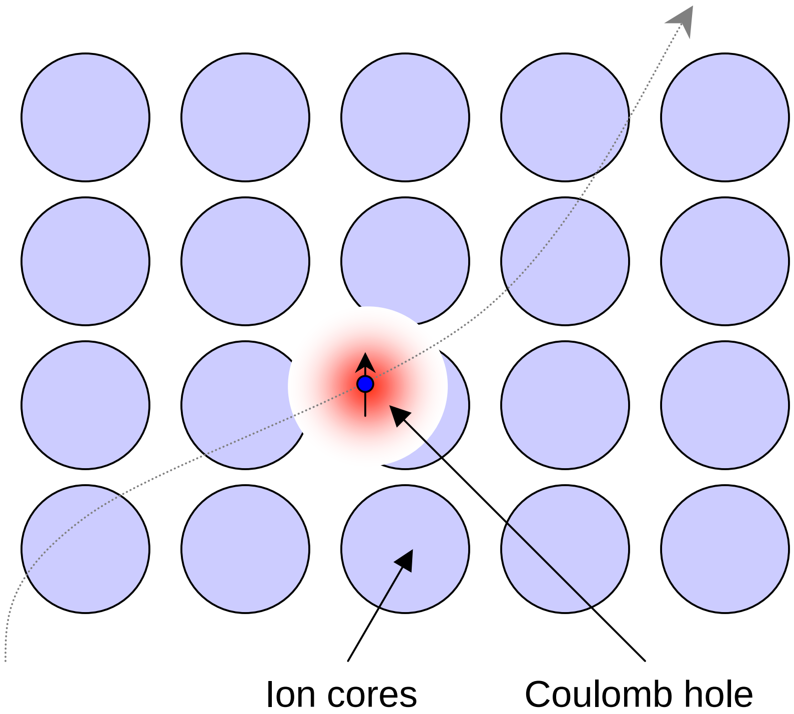
- **III.1** :
  The « self-energy » correction

- **III.2** :
  The exciton

III.1 : The « self-energy » correction

The self-energy problem (I)

- Let us add an electron to an otherwise neutral solid...

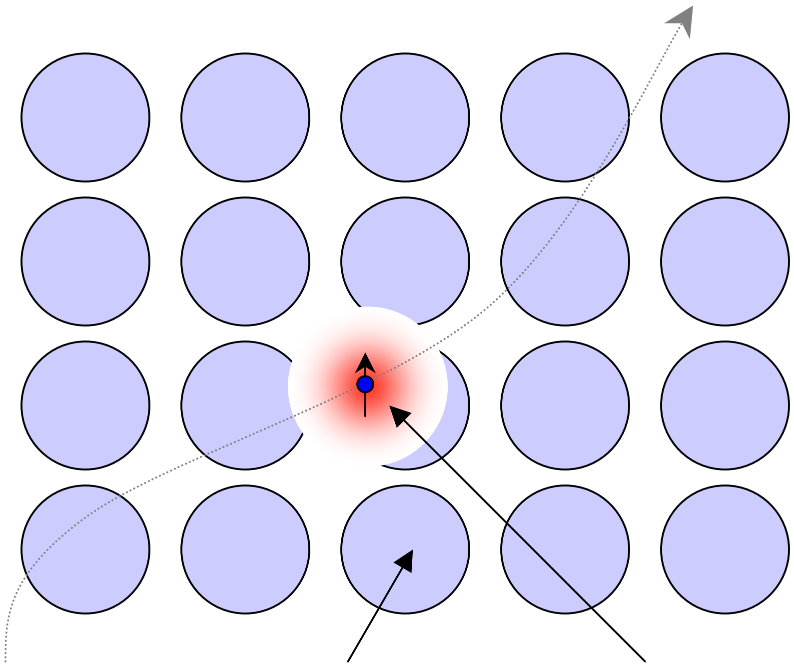


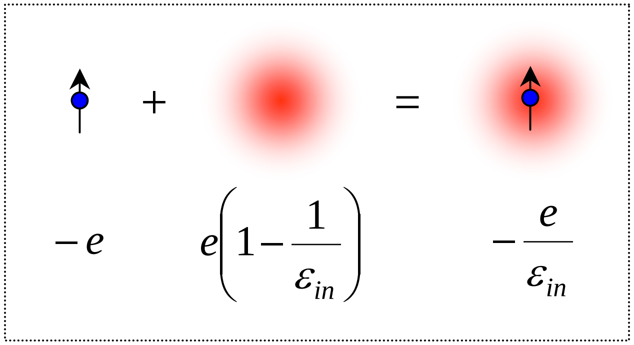
This electron repells nearby valence electrons, thus leaving partially « naked » ion cores around him.

The electron is thus « clothed » by a cloud of positive charges (also known as a **Coulomb hole**) that screens its interactions with the other particles. This Coulomb hole follows the electron travelling in the solid.

The self-energy problem (II)

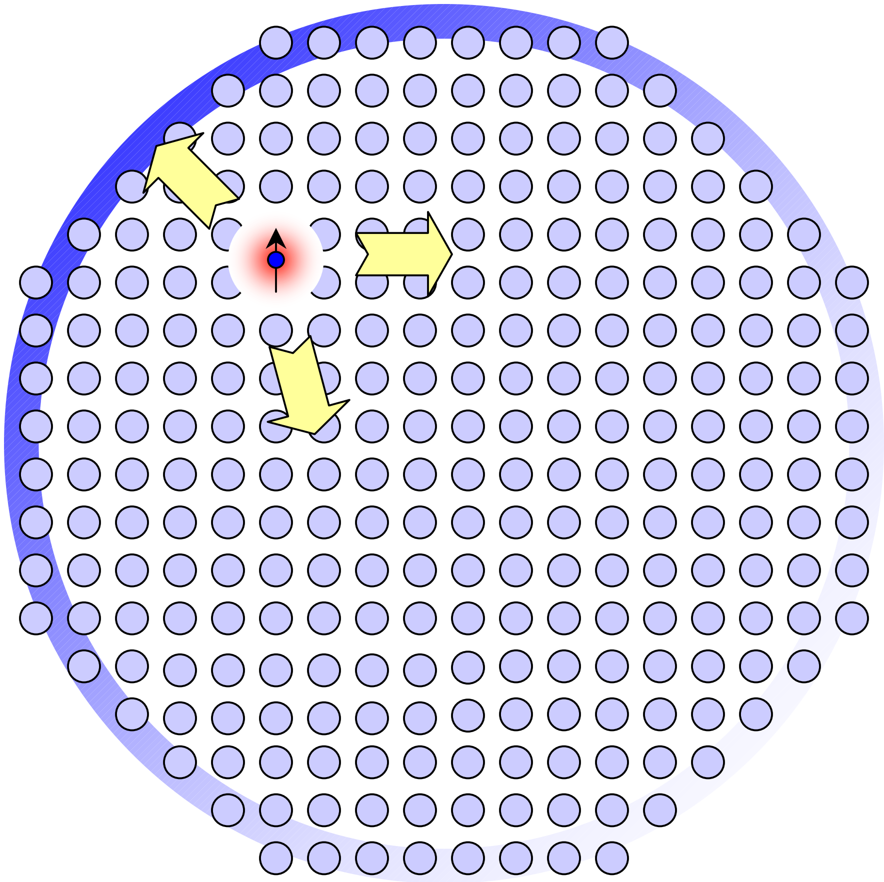
- Let us add an electron to an otherwise neutral solid...





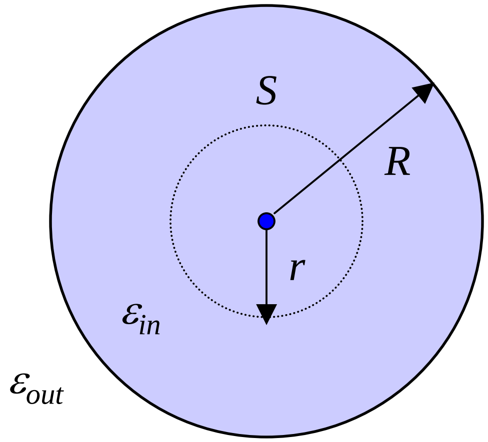
- The charge $q = -e(1-1/\varepsilon_{in})$ cast out from the Coulomb hole is expelled to « infinity » and does not interact any more with the additional electron…

The self-energy problem (III)



- In finite-size nanostructures however, the charge cast out from the Coulomb hole is expelled onto the surfaces of the system, and thus still interacts with the additional electron…
- The interaction of the electron with the so-called **image charges** it has **itself** induced on the surfaces of the system is responsible for large « **self-energy** » corrections to the electronic structure.

Classical electrostatics (I)



- Gauss theorem for a single electron at the center of a nanocrystal with radius R and dielectric constant ε_{in} embedded in a medium with dielectric constant ε_{out} :

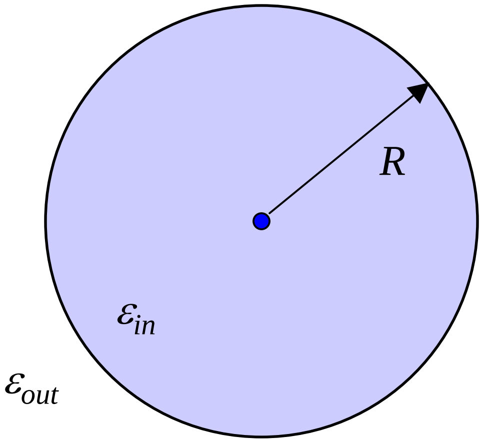
$$\int_S \varepsilon \mathbf{E} \cdot d\mathbf{S} = 4\pi r^2 \varepsilon(r) E(r) = 4\pi Q_i = -4\pi e$$

$$\begin{cases} 4\pi\varepsilon_{in} r^2 E(r) = -4\pi e \text{ if } r < R \\ 4\pi\varepsilon_{out} r^2 E(r) = -4\pi e \text{ if } r > R \end{cases} \Rightarrow \begin{cases} E(r) = -\dfrac{e}{\varepsilon_{in} r^2} \text{ if } r < R \\ E(r) = -\dfrac{e}{\varepsilon_{out} r^2} \text{ if } r > R \end{cases} \Rightarrow \begin{cases} V(r) = -\dfrac{e}{\varepsilon_{in} r} + C \text{ if } r < R \\ V(r) = -\dfrac{e}{\varepsilon_{out} r} \text{ if } r > R \end{cases}$$

where C is a constant such that $\lim_{r \to R^-} V(r) = \lim_{r \to R^+} V(r)$, ie :

$$C = -\frac{e}{\varepsilon_{out} R} + \frac{e}{\varepsilon_{in} R}$$

Classical electrostatics (II)



$$V(r) = -\frac{e}{\varepsilon_{in} r} + \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{R} \quad \text{if} \quad r < R$$

$$V(r) = -\frac{e}{\varepsilon_{out} r} \quad \text{if} \quad r > R$$

- The potential created by the electron can be split in two parts $V(r) = V_b(r) + V_s(r)$, where :

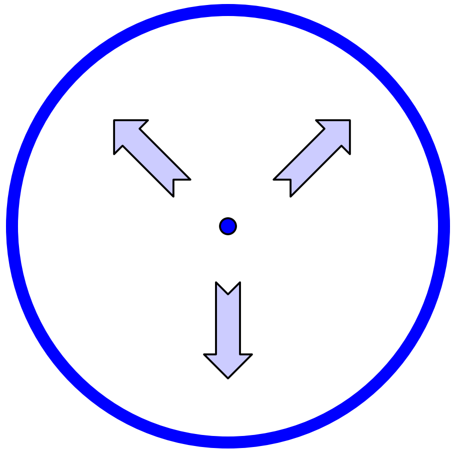
$$V_b(r) = -\frac{e}{\varepsilon_{in} r}$$

$$V_s(r) = \begin{cases} \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{R} & \text{if} \quad r < R \\ \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{r} & \text{if} \quad r > R \end{cases}$$

$V_b(r)$ is the potential created in vacuum by the electron plus its « local » Coulomb hole.

$V_s(r)$ is the potential created in vacuum by the (uniform) image charge distribution at the surface of the nanocrystal.

Classical electrostatics (III)

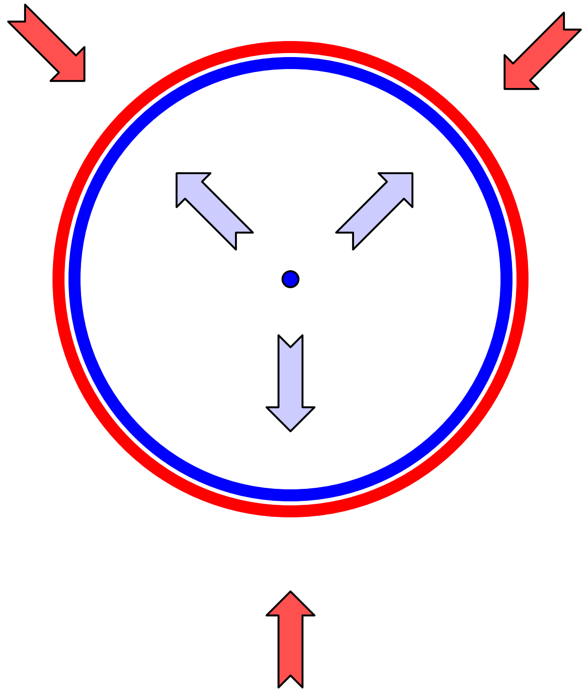


$$V_s(r) = \begin{cases} \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{R} & \text{if } r < R \\ \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{r} & \text{if } r > R \end{cases}$$

is actually the potential created in vacuum by a surface charge density $\sigma_s = \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{4\pi R^2}$.

- If $\varepsilon_{out} = 1$, $4\pi R^2 \sigma_s = -e(1-1/\varepsilon_{in})$ is the charge expelled from the Coulomb hole around the electron. In particular, the total charge of the system (electron + Coulomb hole + surface image charges) is $-e$, so that the potential outside the nanocrystal is just $V(r) = -e/r$.

Classical electrostatics (IV)

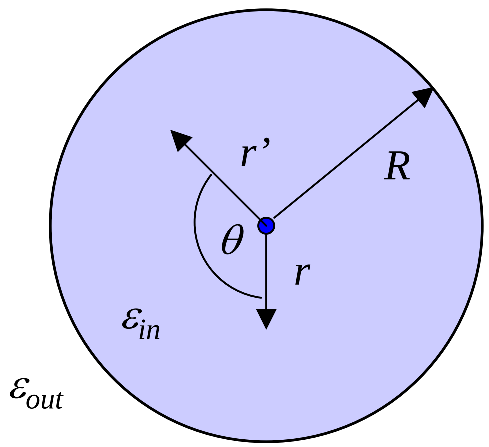


$$V_s(r) = \begin{cases} \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{R} & \text{if} \quad r < R \\ \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{r} & \text{if} \quad r > R \end{cases}$$

is actually the potential created in vacuum by a surface charge density $\sigma_s = \left(\frac{1}{\varepsilon_{in}} - \frac{1}{\varepsilon_{out}}\right)\frac{e}{4\pi R^2}$.

- If $\varepsilon_{out} \neq 1$, $4\pi R^2\sigma_s = -e(1/\varepsilon_{out} - 1/\varepsilon_{in})$ can be seen as the charge $q = -e(1-1/\varepsilon_{in})$ expelled from the Coulomb hole plus a charge $q' = e(1-1/\varepsilon_{out})$ brought by the embedding medium to screen the electron. In particular, $\sigma_s = 0$ if $\varepsilon_{in} = \varepsilon_{out}$.

Classical electrostatics (V)



- **Generalization** : The potential created at point **r'** by an electron at point **r** in a nanocrystal with radius R and dielectric constant ε_{in} embedded in a medium with dielectric constant ε_{out} is :

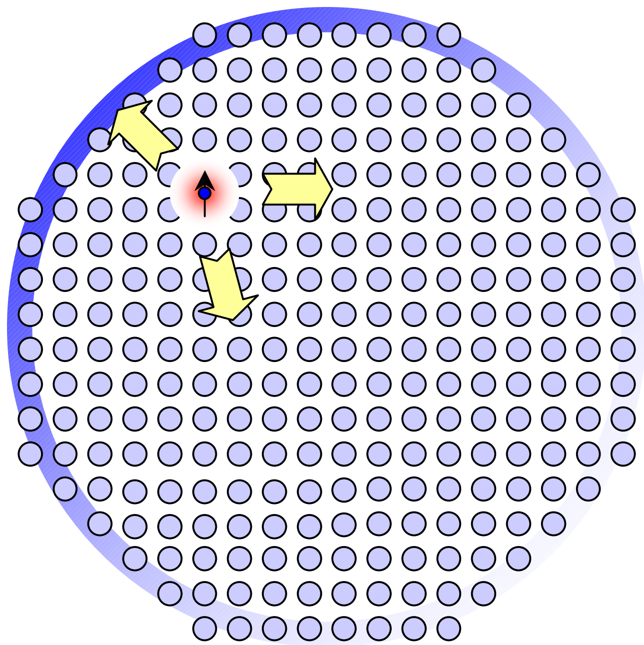
$$V(\mathbf{r},\mathbf{r}') = V_b(\mathbf{r},\mathbf{r}') + V_s(\mathbf{r},\mathbf{r}')$$

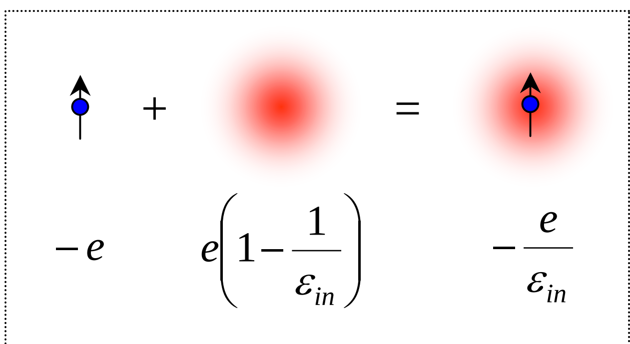
where :

$$\begin{cases} V_b(\mathbf{r},\mathbf{r}') = -\dfrac{e}{\varepsilon_{in}\left|\mathbf{r}-\mathbf{r}'\right|} \\ V_s(\mathbf{r},\mathbf{r}') = -e\displaystyle\sum_{n=0}^{\infty}\dfrac{(n+1)(\varepsilon_{in}-\varepsilon_{out})\left|\mathbf{r}\right|^n\left|\mathbf{r}'\right|^n P_n(\cos\theta)}{\varepsilon_{in}\left[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})\right]R^{2n+1}} \quad \text{if } r<R \text{ and } r'<R \end{cases}$$

$P_n(x)$ is the Legendre ploynomial of order n (cf. spherical harmonics).

The self-energy correction : semi-classical theory (I)





- Let us consider an additional electron at point $\mathbf{r}$. This electron creates at point $\mathbf{r'}$ a potential :

$$V(\mathbf{r},\mathbf{r'}) = V_b(\mathbf{r},\mathbf{r'}) + V_s(\mathbf{r},\mathbf{r'})$$

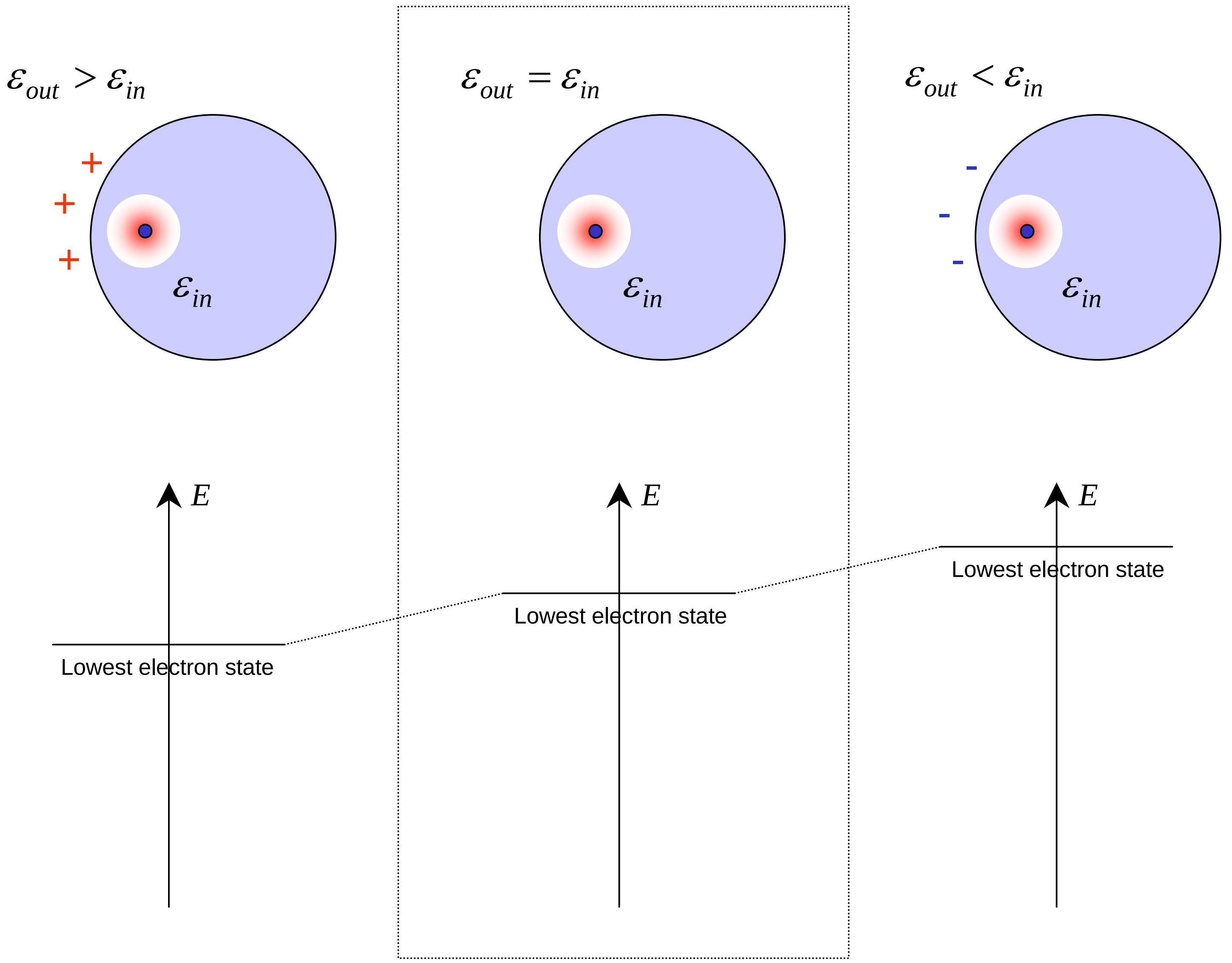
where $V_b(\mathbf{r},\mathbf{r'}) = -e/\varepsilon_{in}\left|\mathbf{r}-\mathbf{r'}\right|$ is the potential created by the electron plus its Coulomb hole and $V_s(\mathbf{r},\mathbf{r'})$ is the potential created by the surface image charges. The latter thus act back onto the electrons with a potential :

$$\Sigma_e(\mathbf{r}) = -eV_s(\mathbf{r},\mathbf{r})$$

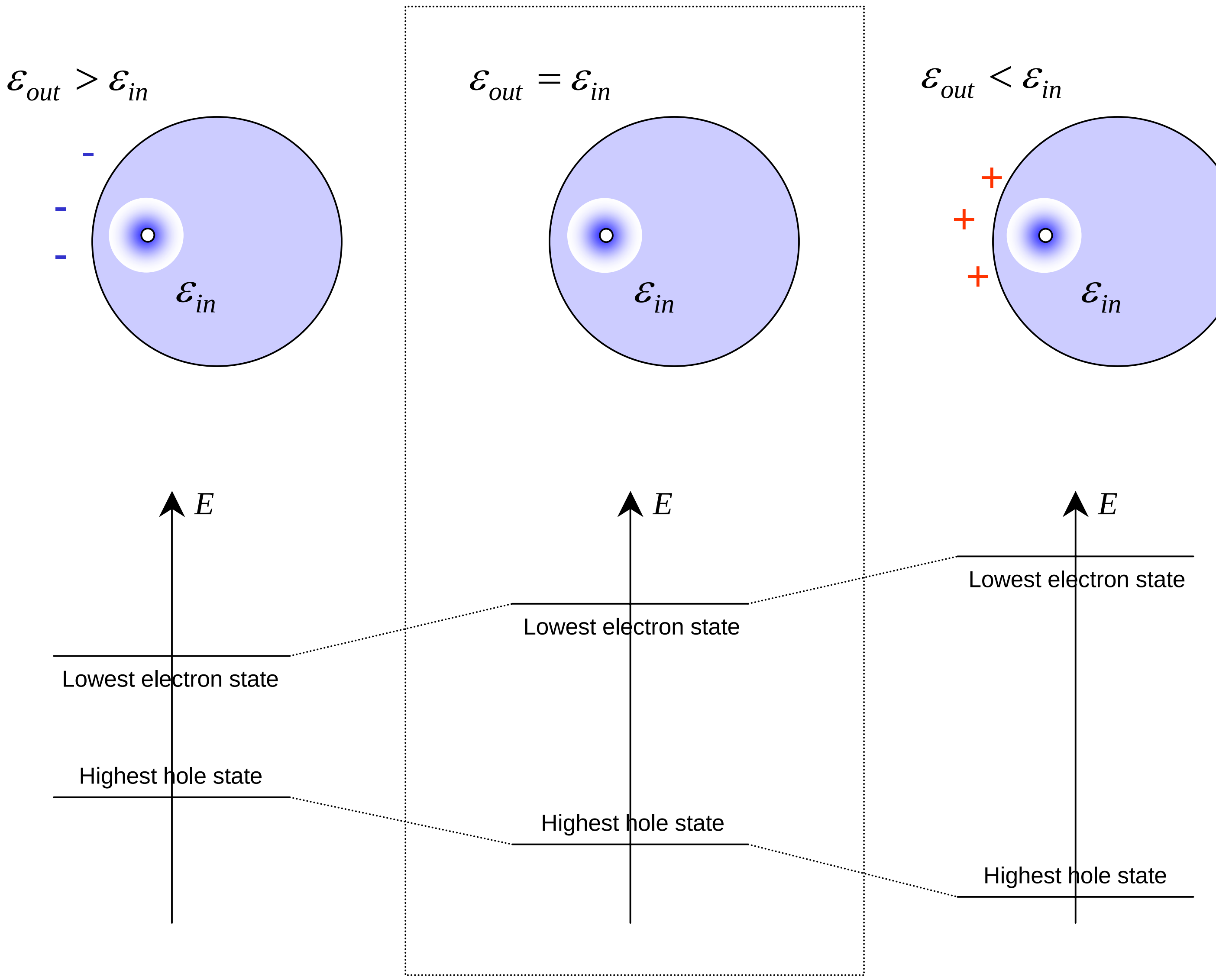
A more refined theory where the electron is introduced « adiabatically » into the system actually yields :

$$\Sigma_e(\mathbf{r}) = -eV_s(\mathbf{r},\mathbf{r})/2$$

The self-energy correction : semi-classical theory (II)

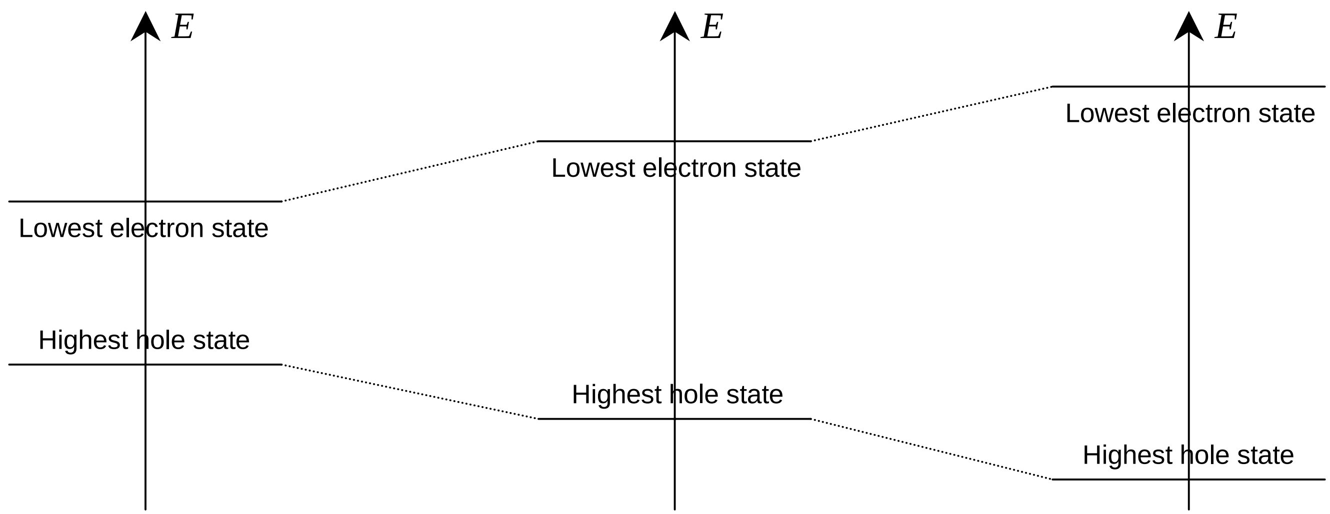


The self-energy correction : semi-classical theory (III)

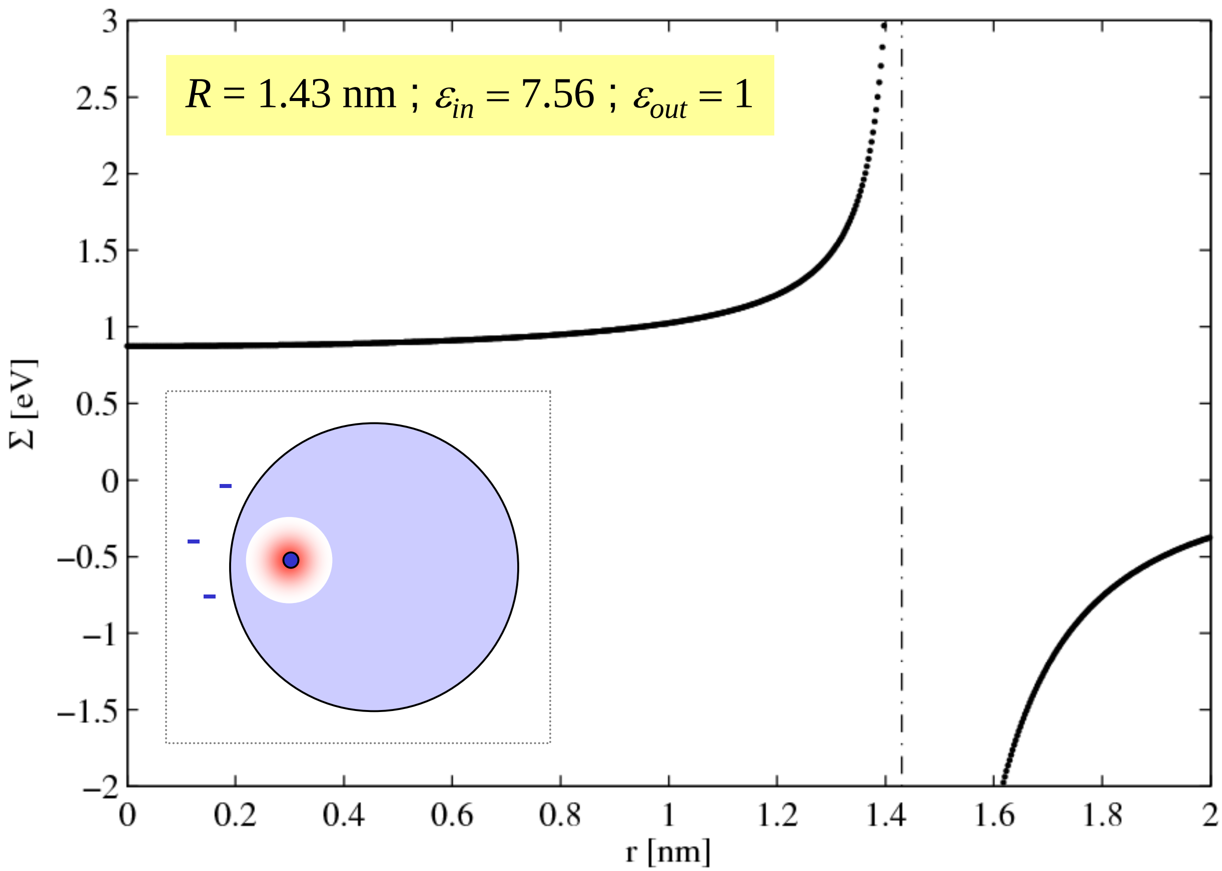


The self-energy correction : semi-classical theory (IV)

The hole feels a potential $\Sigma_h(\mathbf{r}) = -\Sigma_e(\mathbf{r})$!!



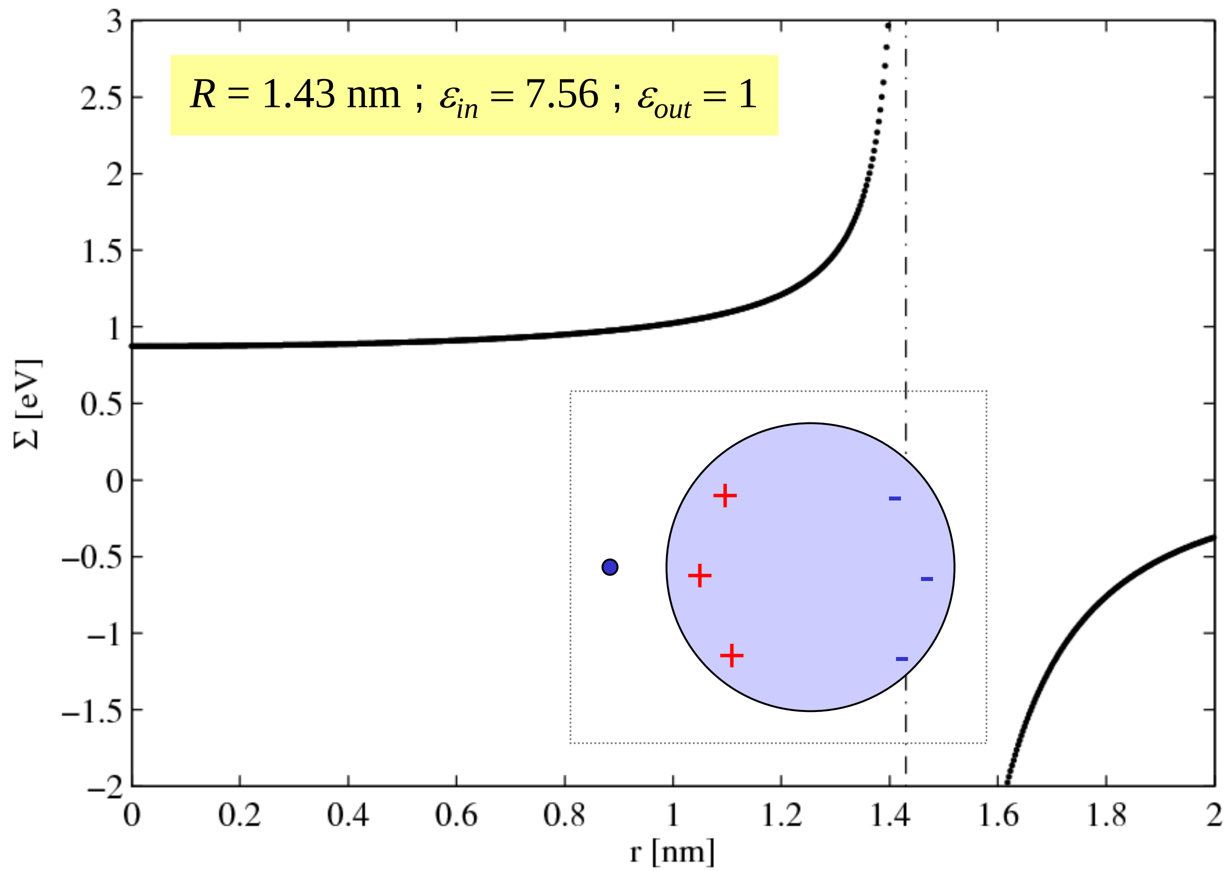
The self-energy potential $\Sigma_e(\mathrm{r})$ (I)



- The semi-classical self-energy potential $\Sigma_e(\mathrm{r})$ is positive inside the nanocrystal…

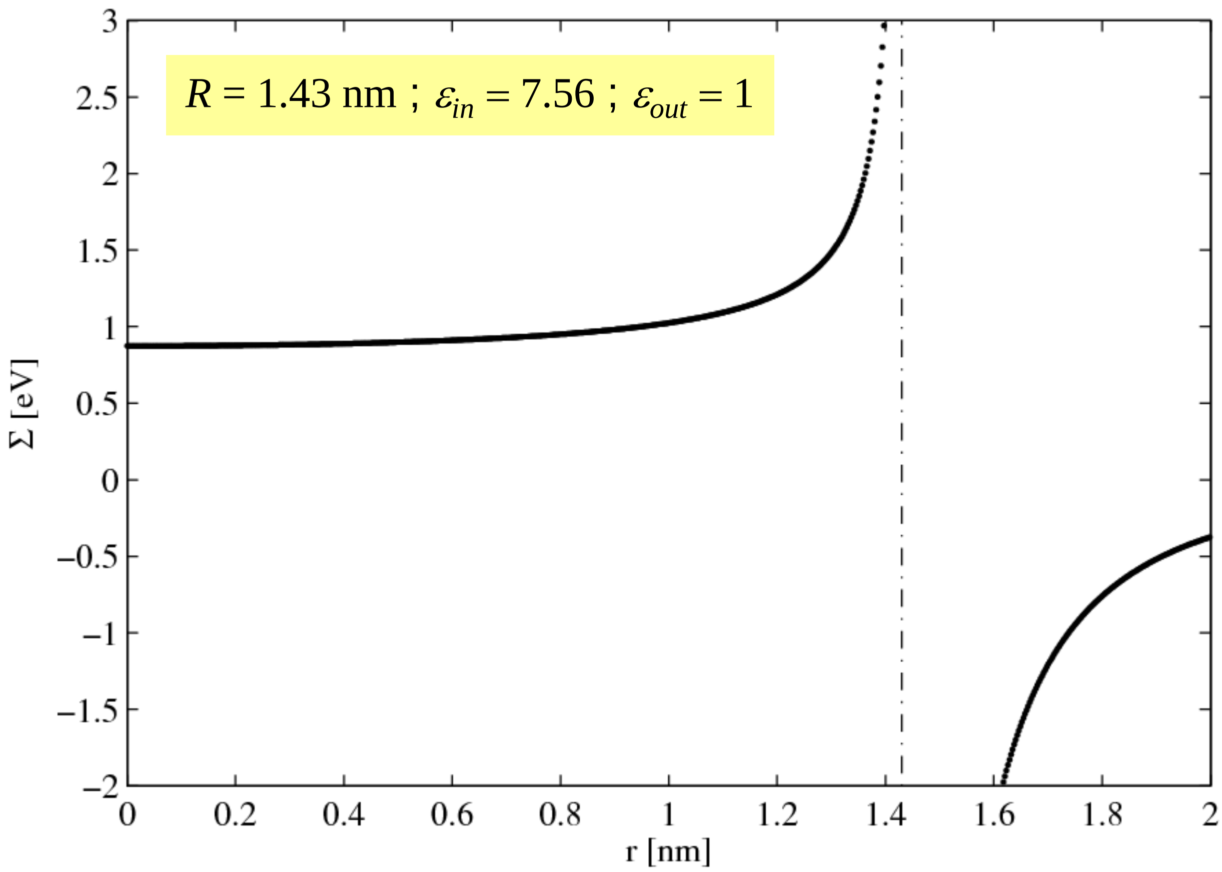
$$\Sigma_e(\mathbf{r}) = -\frac{e}{2}V_s(\mathbf{r},\mathbf{r}) = \frac{e^2}{2}\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_{in}-\varepsilon_{out})|\mathbf{r}|^{2n}}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}} \quad \text{if } r < R$$

The self-energy potential $\Sigma_e(r)$ (II)



- …negative outside (the electron polarizes the nanocrystal and attract positive charges on its side),…

The self-energy potential $\Sigma_e(r)$ (III)



- …and diverges as the electron approaches the image charges at the surface of the nanocrystal (this divergence actually disappears in a more refined many-body approach).

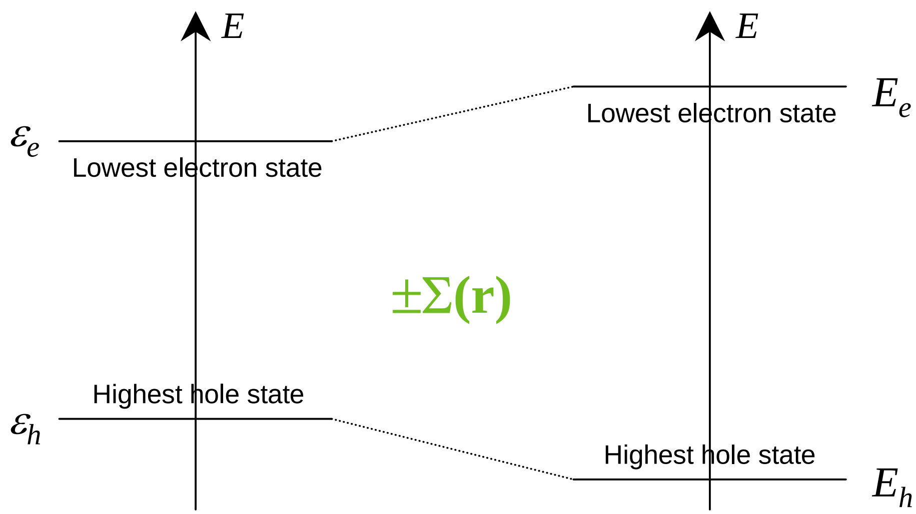
First-order perturbation theory (I)

- Let :

$$\begin{cases} \varphi_e(\mathbf{r}) \text{ and } \varepsilon_e \text{ be the lowest electron wavefunction and energy} \\ \varphi_h(\mathbf{r}) \text{ and } \varepsilon_h \text{ be the highest hole wavefunction and energy} \end{cases}$$

… without self-energy potential. The first-order self-energy corrections read :

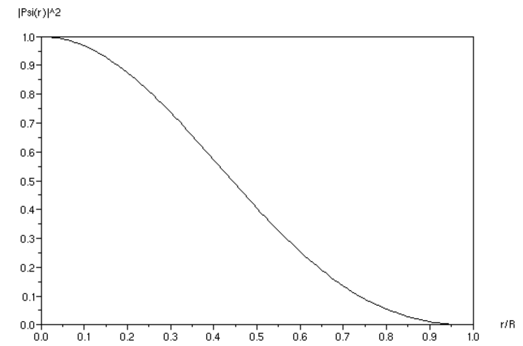
$$\begin{cases} E_e = \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle \\ E_h = \varepsilon_h - \langle \varphi_h | \Sigma | \varphi_h \rangle \end{cases} \quad \text{where } \Sigma(\mathbf{r}) = \Sigma_e(\mathbf{r}) = -\Sigma_h(\mathbf{r})$$



First-order perturbation theory (II)

- We can hopefully get a reasonnable approximation for $\langle\varphi_e|\Sigma|\varphi_e\rangle$ and $\langle\varphi_h|\Sigma|\varphi_h\rangle$ using an effecive mass ansatz for the wavefunctions $\varphi_e(\mathbf{r})$ and $\varphi_h(\mathbf{r})$:

$$\begin{cases} \varphi(r) = \dfrac{1}{\sqrt{2\pi R}}\dfrac{1}{r}\sin\left[\dfrac{\pi}{R}r\right] \text{ if } r < R \\ \varphi(r) = 0 \text{ if } r > R \end{cases}$$



Then,

$$\langle\varphi|\Sigma|\varphi\rangle = \int d^3r\Sigma(\mathbf{r})|\varphi(\mathbf{r})|^2 = 4\pi\int_0^R dr\Sigma(r)|\varphi(r)|^2$$

where :

$$\Sigma(r) = \frac{e^2}{2}\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_{in}-\varepsilon_{out})r^{2n}}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}}$$

First-order perturbation theory (III)

- This finally yields, in the limit $\varepsilon_{in} + \varepsilon_{out} >> 1$,

$$\begin{cases} E_e = \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle \\ E_h = \varepsilon_h - \langle \varphi_h | \Sigma | \varphi_h \rangle \end{cases} \text{ where } \Sigma(\mathbf{r}) = \Sigma_e(\mathbf{r}) = -\Sigma_h(\mathbf{r})$$

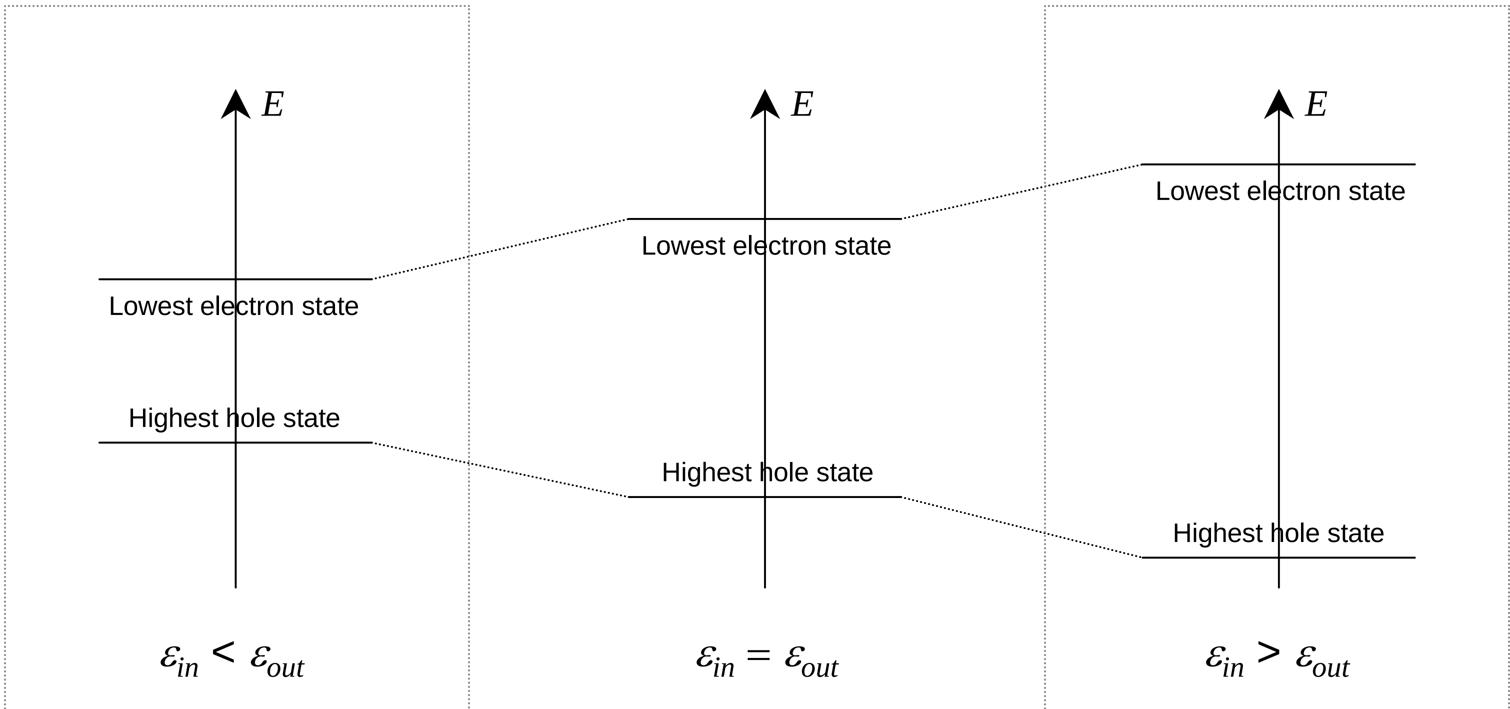
and :

$$\langle \varphi_e | \Sigma | \varphi_e \rangle \approx \langle \varphi_h | \Sigma | \varphi_h \rangle \approx \frac{1}{2}\left(\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right)\frac{e^2}{R} + 0.47\frac{e^2}{\varepsilon_{in} R}\left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}}\right)$$

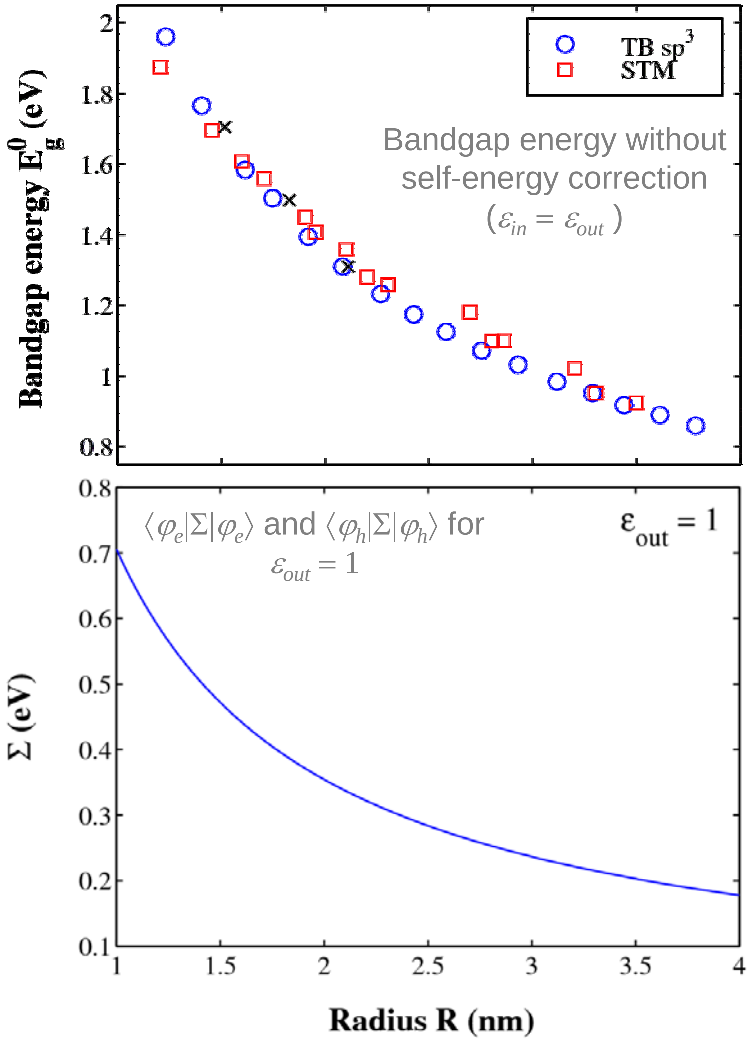
First-order perturbation theory (IV)

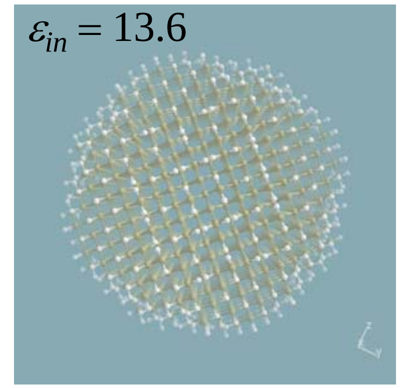
$$\langle \varphi_e | \Sigma | \varphi_e \rangle \approx \langle \varphi_h | \Sigma | \varphi_h \rangle \approx \frac{1}{2}\left(\frac{1}{\varepsilon_{out}} - \frac{1}{\varepsilon_{in}}\right)\frac{e^2}{R} + 0.47\frac{e^2}{\varepsilon_{in} R}\left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}}\right)$$

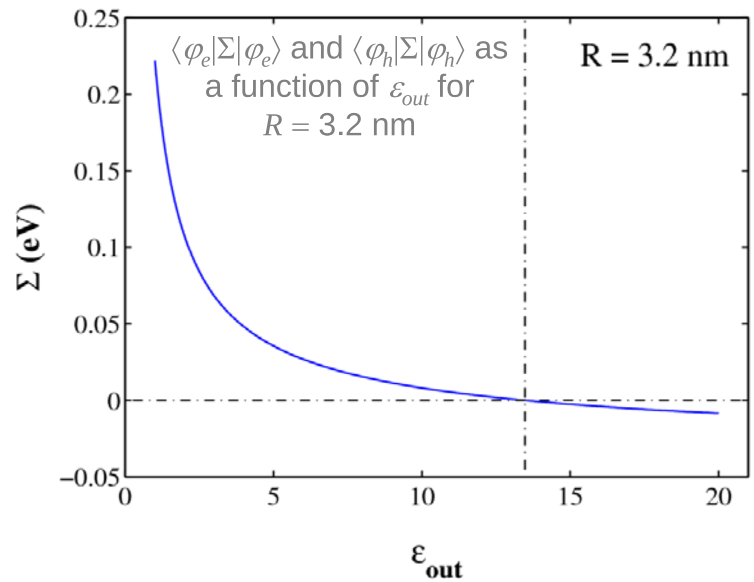
- The self-energy corrections open (resp. close) the quasiparticle gap when $\varepsilon_{in} > \varepsilon_{out}$ (resp. $\varepsilon_{out} > \varepsilon_{in}$). **They decrease in $1/R$, slower than quantum confinement**. They are thus far from negligible in most experimental setups !!



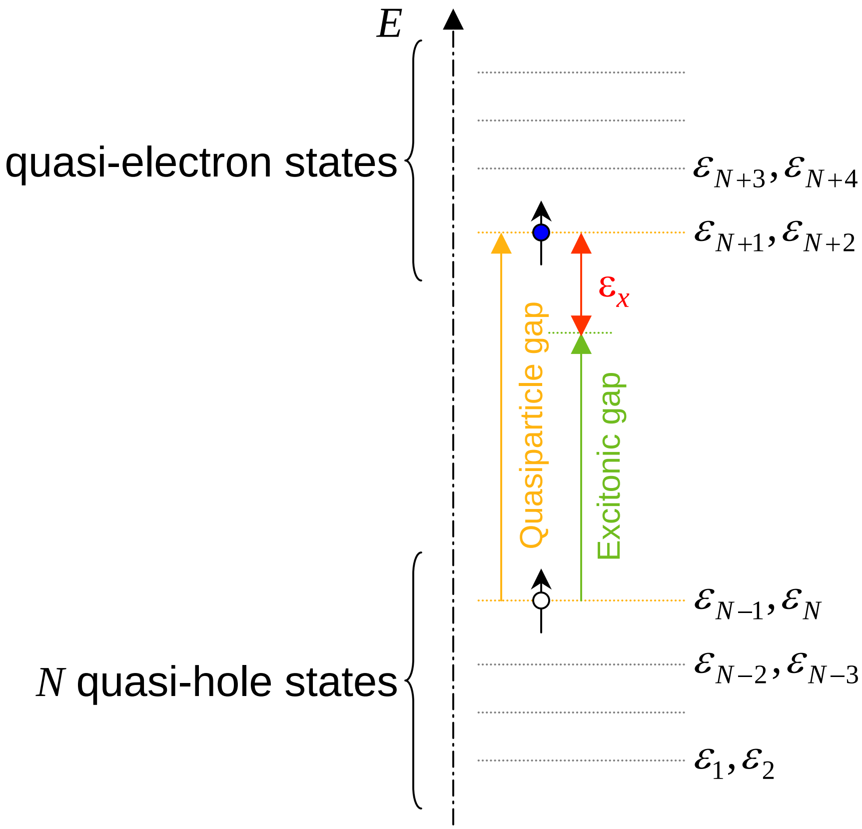
Application : InAs nanocrystals







Quasiparticle and excitonic gaps



- **Quasiparticle gap** :
  Difference between the first ionization energy and the energy gained by an additional electron (electron affinity).

  Probed by transport spectroscopies.

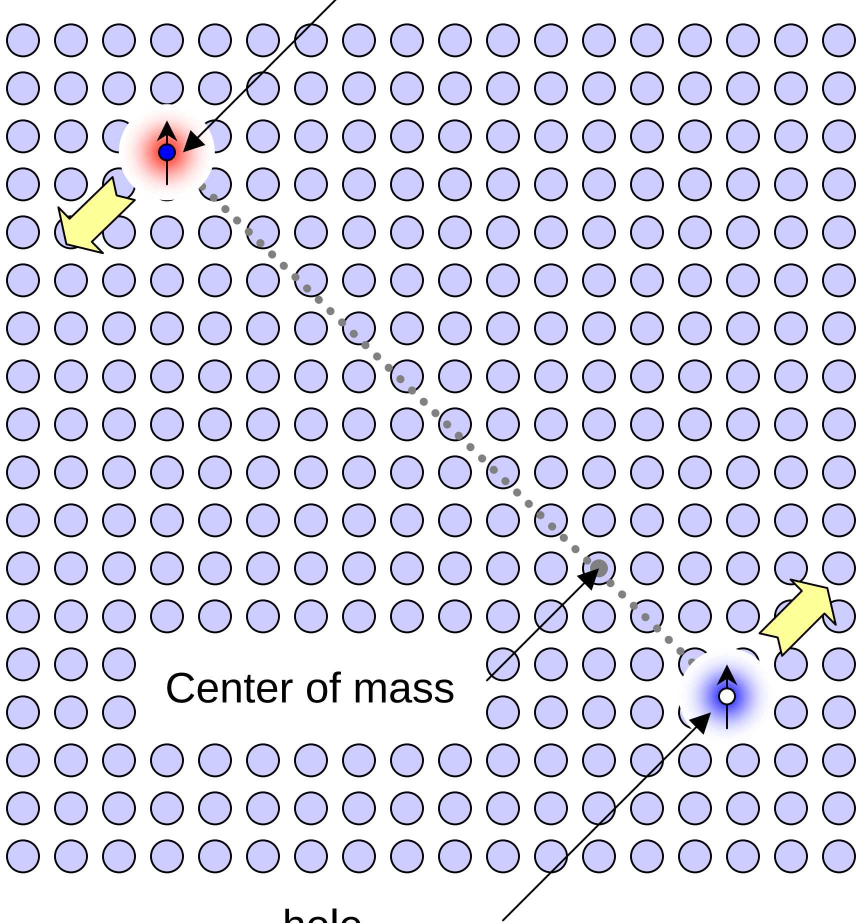
- **Excitonic gap** :
  Lowest excitation energy.

  Probed by optical spectroscopies.

- The difference between the two gaps is the **exciton binding energy** ε_x.

III.2 : The exciton

The exciton in bulk materials (I)



The electron at $\mathbf{r}_e$ and the hole at $\mathbf{r}_h$ attract each other with an effective Coulomb interaction :

$$W(\mathbf{r}_e, \mathbf{r}_h) = -\frac{e^2}{\varepsilon_r |\mathbf{r}_e - \mathbf{r}_h|}$$

provided $|\mathbf{r}_e - \mathbf{r}_h|$ is not too small.

The attraction reduces the energy of the electron-hole pair by the « **exciton binding energy** » ε_x :

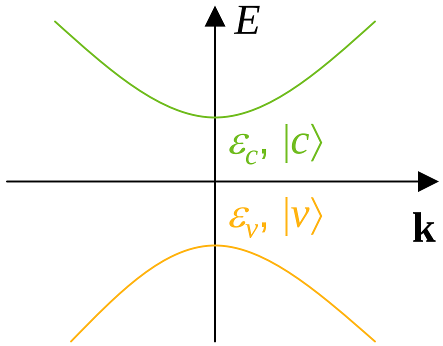
$$h\nu = \varepsilon_{N+1} - \varepsilon_N - \varepsilon_x$$

The **exciton** is (in a first approximation) an hydrogenoid-like bound state between the electron and the hole.

The exciton in bulk materials (II)

- We assume that the independent electron and hole can be described by a single band effective mass model :

$$\begin{cases} -\dfrac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi_e(\mathbf{r}_e) = (\varepsilon_e - \varepsilon_c)\psi_e(\mathbf{r}_e) \\ +\dfrac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi_h(\mathbf{r}_h) = (\varepsilon_h - \varepsilon_v)\psi_h(\mathbf{r}_h) \end{cases}$$



The solution of these equations are indeed Bloch waves :

$$\begin{cases} \varepsilon_e = \varepsilon_c + \dfrac{\hbar^2\mathbf{k}_e^2}{2m_e^*} \text{ and } \psi_e(\mathbf{r}_e) \propto e^{i\mathbf{k}_e\cdot\mathbf{r}_e} \left[\varphi_e(\mathbf{r}_e) = \psi_e(\mathbf{r}_e)\langle\mathbf{r}_e|c\rangle \propto e^{i\mathbf{k}_e\cdot\mathbf{r}_e}\langle\mathbf{r}_e|c\rangle\right] \\ \varepsilon_h = \varepsilon_v - \dfrac{\hbar^2\mathbf{k}_h^2}{2m_h^*} \text{ and } \psi_h(\mathbf{r}_h) \propto e^{i\mathbf{k}_h\cdot\mathbf{r}_h} \left[\varphi_h(\mathbf{r}_h) = \psi_h(\mathbf{r}_h)\langle\mathbf{r}_h|v\rangle \propto e^{i\mathbf{k}_h\cdot\mathbf{r}_h}\langle\mathbf{r}_h|v\rangle\right] \end{cases}$$

We now introduce the electron-hole pair energy $\varepsilon = \varepsilon_e - \varepsilon_h$ and « uncorrelated » envelope function $\psi(\mathbf{r}_e, \mathbf{r}_h) = \psi_e(\mathbf{r}_e)\psi_h(\mathbf{r}_h)$, which satisfy :

$$-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi(\mathbf{r}_e,\mathbf{r}_h) - \frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi(\mathbf{r}_e,\mathbf{r}_h) = (\varepsilon - \varepsilon_g)\psi(\mathbf{r}_e,\mathbf{r}_h)$$

The exciton in bulk materials (III)

- We last switch on the screened Coulomb interaction between the electron and the hole :

$$W(\mathbf{r}_e,\mathbf{r}_h) = -\frac{e^2}{\varepsilon_r\left|\mathbf{r}_e - \mathbf{r}_h\right|}$$

The electron-hole pair energy ε and envelope function $\psi(\mathbf{r}_e, \mathbf{r}_h)$ now satisfy :

$$-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi(\mathbf{r}_e,\mathbf{r}_h) - \frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi(\mathbf{r}_e,\mathbf{r}_h) - \frac{e^2}{\varepsilon_r\left|\mathbf{r}_e - \mathbf{r}_h\right|}\psi(\mathbf{r}_e,\mathbf{r}_h) = (\varepsilon - \varepsilon_g)\psi(\mathbf{r}_e,\mathbf{r}_h)$$

$\psi(\mathbf{r}_e, \mathbf{r}_h)$ can not be written any more as a product $\psi(\mathbf{r}_e, \mathbf{r}_h) = \psi_e(\mathbf{r}_e)\psi_h(\mathbf{r}_h)$ of one electron and one hole wavefunction. Still, the center of mass motion can be decoupled from the relative motion of the electron-hole pair. Let us indeed introduce :

$$\begin{cases} \mathbf{r} = \mathbf{r}_e - \mathbf{r}_h \\ \mathbf{R} = \dfrac{m_e^*}{m_e^* + m_h^*}\mathbf{r}_e + \dfrac{m_h^*}{m_e^* + m_h^*}\mathbf{r}_h \end{cases} \Rightarrow \begin{cases} \mathbf{r}_e = \mathbf{R} + \dfrac{m_h^*}{m_e^* + m_h^*}\mathbf{r} \\ \mathbf{r}_h = \mathbf{R} - \dfrac{m_e^*}{m_e^* + m_h^*}\mathbf{r} \end{cases}$$

The exciton in bulk materials (IV)

$$\begin{cases} \mathbf{r} = \mathbf{r}_e - \mathbf{r}_h \\ \mathbf{R} = \dfrac{m_e^*}{m_e^* + m_h^*}\mathbf{r}_e + \dfrac{m_h^*}{m_e^* + m_h^*}\mathbf{r}_h \end{cases} \Rightarrow \begin{cases} \mathbf{r}_e = \mathbf{R} + \dfrac{m_h^*}{m_e^* + m_h^*}\mathbf{r} \\ \mathbf{r}_h = \mathbf{R} - \dfrac{m_e^*}{m_e^* + m_h^*}\mathbf{r} \end{cases}$$

and $\psi(\mathbf{r}_e, \mathbf{r}_h) \equiv \psi(\mathbf{R}, \mathbf{r})$

- We get :

$$-\frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}_e}\psi(\mathbf{R},\mathbf{r}) - \frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}_h}\psi(\mathbf{R},\mathbf{r}) - \frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r}) = (\varepsilon - \varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2m_e^*}\frac{m_e^{*2}}{(m_e^* + m_h^*)^2}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r}) - \frac{\hbar^2}{2m_e^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2m_h^*}\frac{m_h^{*2}}{(m_e^* + m_h^*)^2}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r}) - \frac{\hbar^2}{2m_h^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r}) - \frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r}) = (\varepsilon - \varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2}\frac{m_e^* + m_h^*}{(m_e^* + m_h^*)^2}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r}) - \frac{\hbar^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r}) - \frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r}) = (\varepsilon - \varepsilon_g)\psi(\mathbf{R},\mathbf{r})$$

$$-\frac{\hbar^2}{2(m_e^* + m_h^*)}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r}) - \frac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r}) - \frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r}) = (\varepsilon - \varepsilon_g)\psi(\mathbf{R},\mathbf{r}) \text{ where } \frac{1}{\mu^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

The exciton in bulk materials (V)

$$-\frac{\hbar^2}{2\left(m_e^*+m_h^*\right)}\Delta_{\mathbf{R}}\psi(\mathbf{R},\mathbf{r})-\frac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi(\mathbf{R},\mathbf{r})-\frac{e^2}{\varepsilon_r|\mathbf{r}|}\psi(\mathbf{R},\mathbf{r})=\left(\varepsilon-\varepsilon_g\right)\psi(\mathbf{R},\mathbf{r})$$

- $\mathbf{R}$ and $\mathbf{r}$ are uncoupled : we can indeed split $\psi(\mathbf{R},\mathbf{r}) = \psi_m(\mathbf{R})\psi_x(\mathbf{r})$, $\varepsilon = \varepsilon_g + \varepsilon_m - \varepsilon_x$ and solve :

$$\begin{cases} -\dfrac{\hbar^2}{2\left(m_e^*+m_h^*\right)}\Delta_{\mathbf{R}}\psi_m(\mathbf{R})=\varepsilon_m\psi_m(\mathbf{R}) \\ -\dfrac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi_x(\mathbf{r})-\dfrac{e^2}{\varepsilon_r|\mathbf{r}|}\psi_x(\mathbf{r})=-\varepsilon_x\psi_x(\mathbf{r}) \end{cases}$$

The solution of the center of mass equation is just :

$$\varepsilon_m=\frac{\hbar^2\mathbf{K}^2}{2\left(m_e^*+m_h^*\right)} \text{ and } \psi_m(\mathbf{R})\propto e^{i\mathbf{K}\cdot\mathbf{R}}$$

where $\mathbf{K}$ is an arbitrary wavector. The ground-state energy for the center of mass motion is thus :

$$\varepsilon_m^0=0$$

The exciton in bulk materials (VI)

$$\begin{cases} -\dfrac{\hbar^2}{2\left(m_e^* + m_h^*\right)}\Delta_{\mathbf{R}}\psi_m(\mathbf{R}) = \varepsilon_m\psi_m(\mathbf{R}) \\ -\dfrac{\hbar^2}{2\mu^*}\Delta_{\mathbf{r}}\psi_x(\mathbf{r}) - \dfrac{e^2}{\varepsilon_r|\mathbf{r}|}\psi_x(\mathbf{r}) = -\varepsilon_x\psi_x(\mathbf{r}) \end{cases}$$

- The equation for the relative motion of the electron and hole is similar to the hamiltonian of the Hydrogen atom, with m_0 replaced by μ^* and e^2 replaced by e^2/ε_r. The ground-state wavefunction and energy for the relative electron-hole motion are thus :

$$\begin{cases} \varepsilon_x^0 = \dfrac{\mu e^4}{2\hbar^2\varepsilon_r^2} \quad \text{[the exciton binding energy]} \\ \varphi_x^0(\mathbf{r}) = \dfrac{1}{\sqrt{\pi a_x^3}} e^{-|\mathbf{r}|/a_x} \quad \text{where } a_x = \dfrac{\hbar^2\varepsilon_r}{\mu e^2} \quad \text{[the exciton radius]} \end{cases}$$

The exciton in bulk materials (VII)

- Let us summarize : The lowest electron-hole pair energy and wavefunction are :

$$\begin{cases} \varepsilon = \varepsilon_g + \varepsilon_m^0 - \varepsilon_x^0 = \varepsilon_g - \varepsilon_x^0 \text{ where } \varepsilon_x^0 = \dfrac{\mu e^4}{2\hbar^2 \varepsilon_r^2} \text{ is the exciton binding energy,} \\ \psi(\mathbf{R},\mathbf{r}) \propto e^{-|\mathbf{r}|/a_x} \text{ where } a_x = \dfrac{\hbar^2 \varepsilon_r}{\mu e^2} \text{ is the exciton radius.} \end{cases}$$

Alternatively,

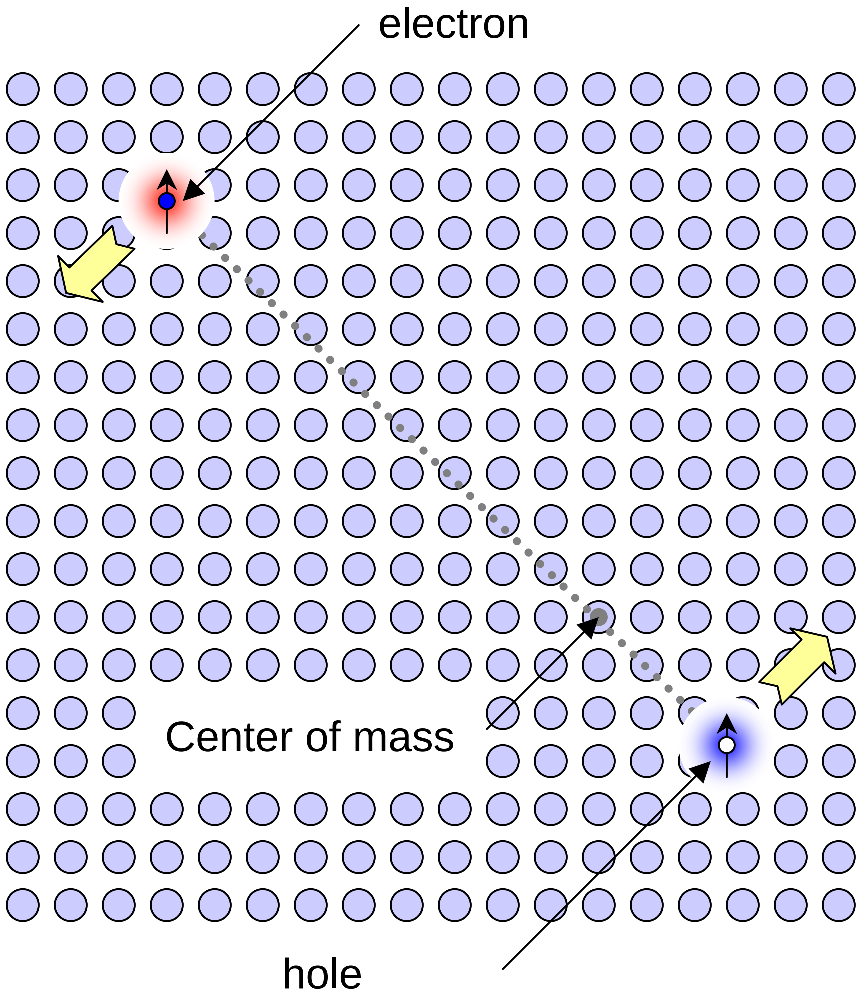
$$\psi(\mathbf{r}_e,\mathbf{r}_h) \propto e^{-|\mathbf{r}_e - \mathbf{r}_h|/a_x}$$

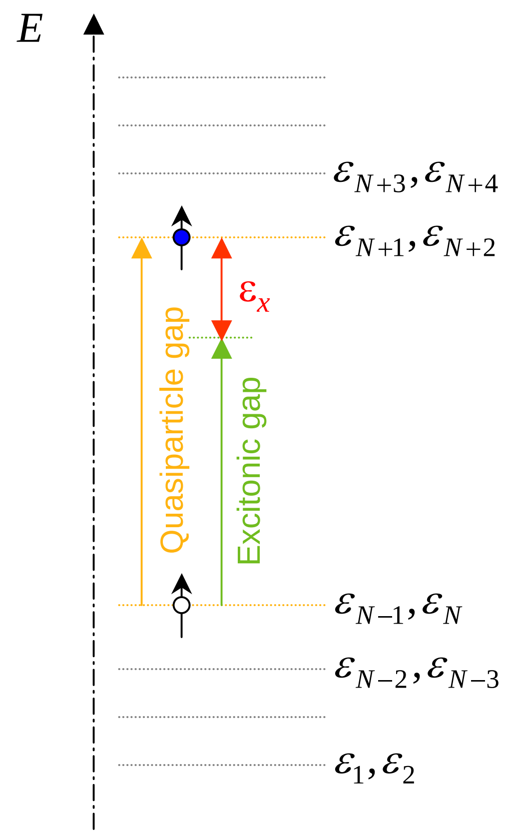
This wavefunction describes a bound electron-hole pair freely moving in the solid.

- **Application** : The exciton in GaAs.

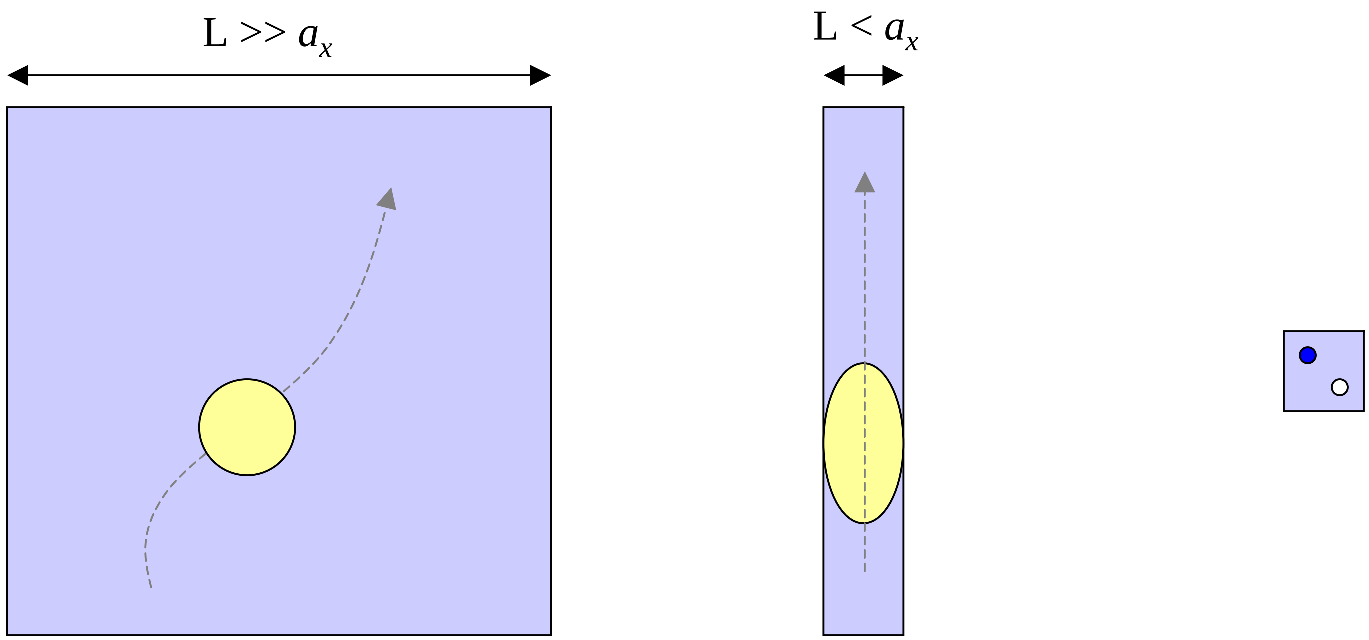
$$\begin{cases} m_e^* = 0.067 m_0 \\ m_e^* = 0.45 m_0 \\ \varepsilon_r = 11 \end{cases} \Rightarrow \mu^* = 0.06 m_0, \varepsilon_x^0 = 6.7 \text{ meV and } a_x = 9.7 \text{ nm}$$

The exciton in bulk materials (VIII)





Confining the exciton

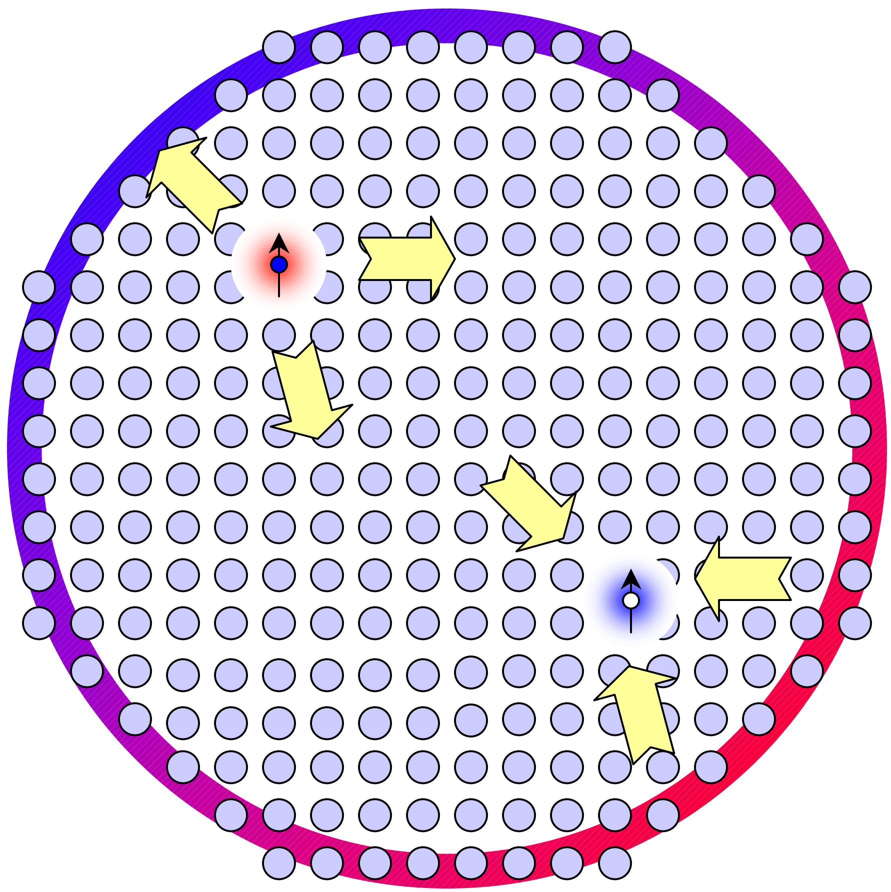


Center of mass confinement | Laterally squeezed exciton | Single-particle confinement

- When all the dimensions of the system become significantly lower than the bulk exciton radius a_x, the Coulomb interaction can not efficiently couple any more the motion of the electron and hole because their kinetic energy is too high. Thus,

$$\varphi(\mathbf{r}_e, \mathbf{r}_h) \approx \varphi_e(\mathbf{r}_e)\varphi_h(\mathbf{r}_h)$$ [Uncorrelated electron-hole pair]

The exciton in nanocrystals (I)



- In a nanocrystal, the electron interacts with the hole and its cloud of screening charge, including the image charges at the surface of the nanocrystal. The effective electron-hole interaction is thus :

$$W(\mathbf{r},\mathbf{r'}) = W_b(\mathbf{r},\mathbf{r'}) + W_s(\mathbf{r},\mathbf{r'})$$

where $W_b(\mathbf{r},\mathbf{r'}) = -e^2/\varepsilon_{in}\,|\,\mathbf{r}-\mathbf{r'}\,|$ and $W_s(\mathbf{r},\mathbf{r'})$ is the interaction with the surface image charges.

The exciton in nanocrystals (II)

- Since the diameter of the nanocrystals is usually much lower than the bulk exciton radius a_x, we may deal with the electron-hole attraction using first-order perturbation theory, which amounts to assume :

$$\varphi(\mathbf{r}_e, \mathbf{r}_h) \approx \varphi_e(\mathbf{r}_e)\varphi_h(\mathbf{r}_h)$$ [Uncorrelated electron-hole pair]

The exciton binding energy then reads :

$$\begin{aligned}\varepsilon_x &= \langle\varphi|W|\varphi\rangle \\ &= \int d^3r \int d^3r' \varphi_e(\mathbf{r})\varphi_h(\mathbf{r}')W(\mathbf{r},\mathbf{r}')\varphi_e(\mathbf{r})\varphi_h(\mathbf{r}') \\ &= \int d^3r \int d^3r' |\varphi_e(\mathbf{r})|^2 W(\mathbf{r},\mathbf{r}')|\varphi_h(\mathbf{r}')|^2\end{aligned}$$

Using again an effective mass ansatz for the wavefunctions $\varphi_e(\mathbf{r})$ and $\varphi_h(\mathbf{r})$:

$$\varphi(r) = \frac{1}{\sqrt{2\pi R}}\frac{1}{r}\sin\left[\frac{\pi}{R}r\right] \text{ if } r < R \text{ and } \varphi(r) = 0 \text{ if } r > R$$

as well as:

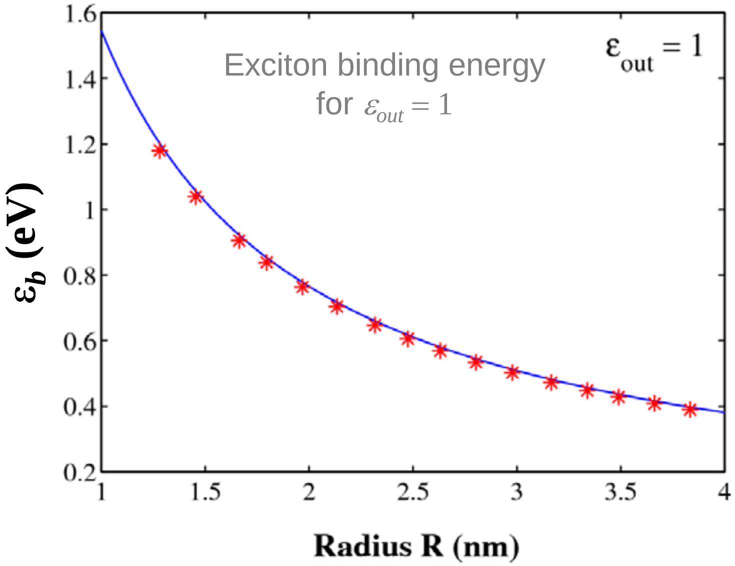
$$W(\mathbf{r},\mathbf{r}') = -\frac{e^2}{\varepsilon_{in}|\mathbf{r}-\mathbf{r}'|} - e^2\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_{in}-\varepsilon_{out})|\mathbf{r}|^n|\mathbf{r}'|^n P_n(\cos\theta)}{\varepsilon_{in}[\varepsilon_{out}+n(\varepsilon_{in}+\varepsilon_{out})]R^{2n+1}} \text{ if } r < R \text{ and } r' < R$$

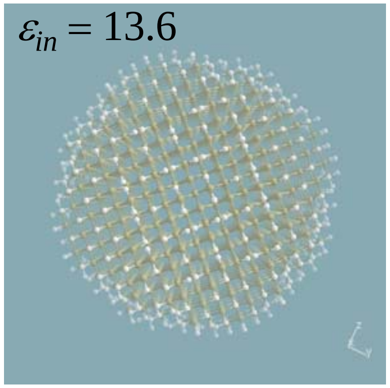
The exciton in nanocrystals (III)

- We finally end up with :

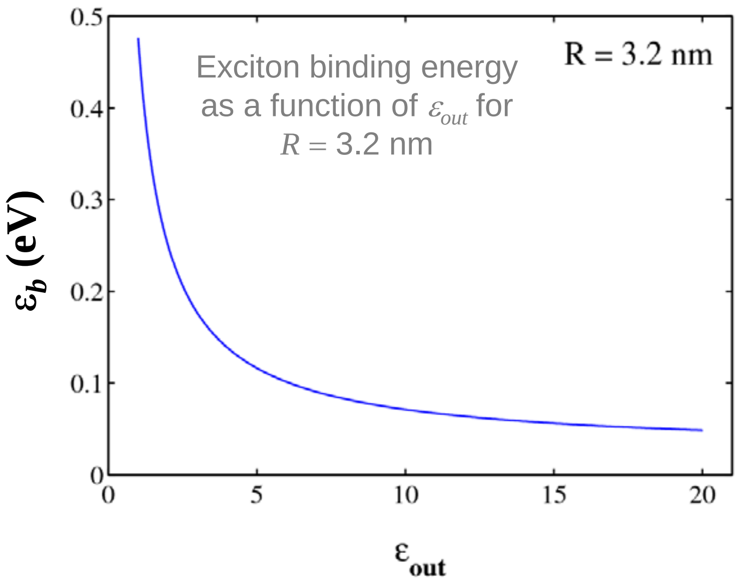
$$\varepsilon_x = \left(\frac{1}{\varepsilon_{out}} + \frac{0.79}{\varepsilon_{in}}\right)\frac{e^2}{R}$$

Application : InAs nanocrystals





$$\varepsilon_x = \left(\frac{1}{\varepsilon_{out}} + \frac{0.79}{\varepsilon_{in}} \right) \frac{e^2}{R}$$



From the tight-binding to the optical gap (I)

- Let :

$$\begin{cases} \varphi_e(\mathbf{r}) \text{ and } \varepsilon_e \text{ be the lowest electron wavefunction and energy} \\ \varphi_h(\mathbf{r}) \text{ and } \varepsilon_h \text{ be the highest hole wavefunction and energy} \end{cases}$$

… without self-energy potential. The first-order self-energy corrections read :

$$\begin{cases} E_c = \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle \\ E_h = \varepsilon_h - \langle \varphi_h | \Sigma | \varphi_h \rangle \end{cases} \quad \text{where } \Sigma(\mathbf{r}) = \Sigma_e(\mathbf{r}) = -\Sigma_h(\mathbf{r})$$

while the first-order excitonic correction read :

$$\varepsilon_x = \int d^3r \int d^3r' |\varphi_e(\mathbf{r})|^2 W(\mathbf{r},\mathbf{r}') |\varphi_h(\mathbf{r}')|^2$$

Using effective mass wavefunctions one gets :

$$\begin{cases} \langle \varphi_e | \Sigma | \varphi_e \rangle \approx \langle \varphi_h | \Sigma | \varphi_h \rangle \approx \dfrac{1}{2}\left(\dfrac{1}{\varepsilon_{out}} - \dfrac{1}{\varepsilon_{in}}\right)\dfrac{e^2}{R} + 0.47\dfrac{e^2}{\varepsilon_{in} R}\left(\dfrac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}}\right) \\ \varepsilon_x = \left(\dfrac{1}{\varepsilon_{out}} + \dfrac{0.79}{\varepsilon_{in}}\right)\dfrac{e^2}{R} \end{cases}$$

From the tight-binding to the optical gap (II)

- The optical gap is thus :

$$\begin{aligned} h\nu &= E_e - E_h - \varepsilon_b \\ &= \varepsilon_e + \langle \varphi_e | \Sigma | \varphi_e \rangle - \left(\varepsilon_h + \langle \varphi_h | \Sigma | \varphi_h \rangle \right) - \varepsilon_x \\ &= \varepsilon_e - \varepsilon_h + 2 \langle \varphi | \Sigma | \varphi \rangle - \varepsilon_x \\ &= \varepsilon_e - \varepsilon_h + \frac{1.79 e^2}{\varepsilon_{in} R} - \frac{0.94 e^2}{\varepsilon_{in} R} \left(\frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + \varepsilon_{out}} \right) \end{aligned}$$

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