Quantum-Dots

Effective Mass Approximation:

Assume for an electron in a spherical Q.D. all band-effects are contained in the form of the effective mass of the electron in the bulk-material. (Brus paper).

Conduction band:

Bulk effective mass:

$$\frac{1}{m_e^*} = \frac{1}{m_e} + \frac{2P^2}{3\hbar^2}\left(\frac{2}{E_g} + \frac{1}{E_g+\Delta}\right). \quad (i)$$

$$\left[\frac{\hat{p}^2}{2m_e^*} + V(r)\right]\Psi_{ne} = (E_{ne} - E_g)\Psi_{ne} \quad (ii)$$

with $V(r) = \begin{cases} 0 & r < R \\ \infty & r > R \end{cases}$

$$\Rightarrow \Psi_{n^e \ell^e m^e}(r,\theta,\varphi) = A_{n^e\ell^e}\, j_{n^e\ell^e}\left(\alpha_{n^e\ell^e}\frac{r}{R}\right) Y_{\ell^e}^{m^e}(\theta,\varphi).$$

where $A_{n^e\ell^e} = \left[\int_0^R j_\ell\left(\alpha_{n^e\ell^e}\frac{r}{R}\right) j_\ell\left(\alpha_{n^e\ell^e}\frac{r}{R}\right) r^2\, dr\right]^{-\frac{1}{2}}$.

(iii)

& $E^{c}_{n\ell} = E_g + \dfrac{\hbar^2 \alpha^2_{n^c \ell^c}}{2 m^*_e R^2}$. (iv)

Valence Bands: (4-band, with spin degeneracy)

$\dfrac{1}{m_{v_1}^*} = \dfrac{1}{m_e}$; $\dfrac{1}{m^*_{v_2}} = \dfrac{1}{m_e} - \dfrac{4P^2}{3\hbar^2 E_g}$. (v)

Equivalently, $m_{v_1}^* = \dfrac{m_e}{\gamma' - 2\gamma}$; $m^*_{v_2} = \dfrac{m_e}{\gamma' + 2\gamma}$, using Luttinger-Kohn parameters.

$\Psi_{n^v, \ell^v, m^v} = A_{n^v \ell^v}\, j_{\ell^v}\left(\alpha_{n^v \ell^v} \dfrac{r}{R}\right) Y^{m^v}_{\ell^v}(\theta, \varphi)$ (vi)

$E^{v_1}_{n\ell} = -\dfrac{\hbar^2 \alpha^2_{n\ell}}{2 m^*_{v_1} R^2}$; $E^{v_2}_{n\ell} = -\dfrac{\hbar^2 \alpha^2_{n\ell}}{2 m^*_{v_2} R^2}$

$v = v_1, v_2$ (vii)

Transition dipole Moments (Gas-Phase)

$\langle n^v \ell^v m^v | (-e\, r \sin\theta \cos\varphi | n^c \ell^c m^c \rangle$ (vii)

$= -e A_{n^c \ell^c} A_{n^v \ell^v} \left[\int_0^R j_{\ell^v}\left(\alpha_{n^v \ell^v} \dfrac{r}{R}\right) j_{\ell^c}\left(\alpha_{n^c \ell^c} \dfrac{r}{R}\right) r^3\, dr \right] \ldots$

$\ldots \left[\int_0^{2\pi}\int_0^{\pi} Y^{*m^v}_{\ell^v} Y^{m^c}_{\ell^c} \sin^2\theta \cos\varphi \, d\theta\, d\varphi \right]$

Noting: $\sin\theta\cos\varphi = \frac{x}{r} = \sqrt{\frac{2\pi}{3}}\left(Y_1^{-1} - Y_1^{1}\right)$

$$\int_0^{2\pi}\int_0^{\pi} Y^{*\,m^v}_{l^v}\, Y^{m^c}_{l^c} \sin\theta\cos\varphi \, d\theta\, d\varphi$$

$$= \left[\int_0^{2\pi}\int_0^{\pi} Y^{*\,m^v}_{l^v}\, Y^{m^c}_{l^c}\, Y_1^{-1} \sin\theta\, d\theta\, d\varphi\right] - \left[\int_0^{2\pi}\int_0^{\pi} Y^{*\,m^v}_{l^v}\, Y^{m^c}_{l^c}\, Y_1^{1} \sin\theta\, d\theta\, d\varphi\right] \ldots$$

$$\ldots \sqrt{\frac{2\pi}{3}}$$

$$= \sqrt{\frac{3(2l^c+1)}{4\pi(2l^v+1)}}\sqrt{\frac{2\pi}{3}}\left(C^{l^c\,1\,l^v}_{0\,0\,0}\left(C^{l^c\,1\,l^v}_{m^c\,1\,m^v} - C^{l^c\,1\,l^v}_{m^c\,-1\,m^v}\right)\right).$$

Thus,

(vii)

$$= eA_{n^c l^c}A_{n^v l^v}\left[\int_0^R j_{l^v}\!\left(\alpha_{n^v l^v}\frac{r}{R}\right) j_{l^c}\!\left(\alpha_{n^c l^c}\frac{r}{R}\right) r^3\, dr\right] \ldots$$

$$\ldots \sqrt{\frac{3(2l^c+1)}{4\pi(2l^v+1)}}\sqrt{\frac{2\pi}{3}}\left(C^{l^c\,1\,l^v}_{0\,0\,0}\left(C^{l^c\,1\,l^v}_{m^c\,1\,m^v} - C^{l^c\,1\,l^v}_{m^c\,-1\,m^v}\right)\right)$$

Similarly, with $\sin\theta\sin\varphi = \frac{y}{r} = i\sqrt{\frac{2\pi}{3}}\left(Y_1^{-1} + Y_1^{1}\right)$

$$\int_0^{2\pi}\int_0^{\pi} Y^{*\,m^v}_{l^v}\, Y^{m^c}_{l^c} \sin\theta\sin\varphi\, d\theta\, d\varphi$$

$$= i\sqrt{\frac{3(2l^c+1)}{4\pi(2l^v+1)}}\sqrt{\frac{2\pi}{3}}\left(C^{l^c\,1\,l^v}_{0\,0\,0}\left(C^{l^c\,1\,l^v}_{m^c\,1\,m^v} + C^{l^c\,1\,l^v}_{m^c\,-1\,m^v}\right)\right)$$

Making

$$\langle n^c l^c m^c | (-er \sin\theta \sin\varphi) | n^v l^v m^v \rangle$$

$$= i A_{n^c l^c} A_{n^v l^v} \left[\int_0^R j_{l^c}\left(\alpha_{n^c l^c} \frac{r}{R}\right) j_{l^v}\left(\alpha_{n^v l^v} \frac{r}{R}\right) \ldots r^3 dr \right] \sqrt{\frac{3(2l^c+1)}{4\pi(2l^v+1)}} \sqrt{\frac{2\pi}{3}} \ldots$$

$$\ldots \left(C^{l^c 1 l^v}_{0\,0\,0} \left(C^{l^c 1 l^v}_{m^c 1 m^v} + C^{l^c 1 l^v}_{m^c -1 m^v} \right) \right)$$

(viii)

Finally, with $\frac{z}{r} = 2\sqrt{\frac{\pi}{3}}\, Y_1^0(\theta, \varphi)$

$$\langle n^c l^c m^c | (-er \cos\theta) | n^v l^v m^v \rangle$$

$$= A_{n^c l^c} A_{n^v l^v} \left[\int_0^R j_{l^c}\left(\alpha_{n^c l^c} \frac{r}{R}\right) j_{l^v}\left(\alpha_{n^v l^v} \frac{r}{R}\right) r^3 dr \right] \ldots$$

$$\ldots \sqrt{\frac{3(2l^c+1)}{4\pi(2l^v+1)}}\, 2\sqrt{\frac{\pi}{3}}\, C^{l^c 1 l^v}_{0\,0\,0}\, C^{l^c 1 l^v}_{m^c 0 m^v}$$

...(ix)

where $V = V_1, V_2$

Simplification of radial integrals:

$$\int_0^R j_{\ell c}\left(\alpha_{n\nu\ell c}\frac{r}{R}\right) j_{\ell c}\left(\alpha_{nc\ell c}\frac{r}{R}\right) r^3 dr$$

$$= R^4 \int_0^1 j_{\ell c}(\alpha_{n\nu\ell c}\bar{r}) j_{\ell c}(\alpha_{nc\ell c}\bar{r})\,\bar{r}^3 d\bar{r}, \ldots \text{etc.}$$

$$\int_0^R \left(j_{\ell c}\left(\alpha_{nc\ell c}\frac{r}{R}\right)\right)^2 r^2 dr$$

$$= R^3 \int_0^1 \left(j_{\ell c}(\alpha_{nc\ell c}\bar{r})\right)^2 \bar{r}^2 d\bar{r}$$

$$= \frac{R^3}{2}\left[j_{\ell c+1}(\alpha_{nc\ell c})\right]^2, \ldots \text{etc.}$$

Some Simplifications:

$$C^{\ell^c \ell^v 1}_{0\,0\,0}\left[C^{\ell^c \ell^v 1}_{m^c\, m^v\, 1} + C^{\ell^c \ell^v 1}_{m^c\, m^v\, -1}\right]$$

$$= 2C^{\ell^c \ell^c 1}_{0\,0\,0}\left(C^{\ell^c \ell^c 1}_{m^c\, 1-m^c\, 1} + C^{\ell^c \ell^c 1}_{m^c\, -(1+m^c)\, -1}\right) + \dots$$

$$\dots + 2C^{\ell^c\, \ell^c-1\, 1}_{0\,0\,0}\left(C^{\ell^c\, \ell^c-1\, 1}_{m^c\, 1-m^c\, 1} + C^{\ell^c\, \ell^c-1\, 1}_{m^c\, -(1+m^c)\, -1}\right).$$

$$\ell^c > 0,\ m^c > 0.$$

Similarly,

$$C^{\ell^c \ell^v 1}_{0\,0\,0}\left(C^{\ell^c \ell^v 1}_{m^c\, m^v\, 1} - C^{\ell^c \ell^v 1}_{m^c\, m^v\, -1}\right)$$

$$= 2C^{\ell^c \ell^c 1}_{0\,0\,0}\left(C^{\ell^c \ell^c 1}_{m^c\, 1-m^c\, 1} - C^{\ell^c \ell^c 1}_{m^c\, -(1+m^c)\, -1}\right) + 2C^{\ell^c\, \ell^c-1\, 1}_{0\,0\,0} \dots$$

$$\dots \cdot \left(C^{\ell^c\, \ell^c-1\, 1}_{m^c\, 1-m^c\, 1} - C^{\ell^c\, \ell^c-1\, 1}_{m^c\, -(1+m^c)\, -1}\right).$$

$$\& \quad C^{\ell^c \ell^v 1}_{0\,0\,0}\, C^{\ell^c \ell^v 1}_{m^c\, m^v\, 0}$$

$$= 2C^{\ell^c \ell^c 1}_{0\,0\,0}\, C^{\ell^c \ell^c 1}_{m^c\, -m^c\, 0} + 2C^{\ell^c\, \ell^c-1\, 1}_{0\,0\,0}\, C^{\ell^c\, \ell^c-1\, 1}_{m^c\, -m^c\, 0}.$$

$\therefore$ Consistent with selection rules of electric-dipole operator, $|\ell_c - \ell_v| = 0, 1$.

Gas-Phase Polarizability Tensor:

The components of $\overleftrightarrow{\alpha}_0$ are calculated according to the formula:

$$\alpha_0^{ij} = \frac{1}{\hbar} \sum_{n^v, \ell^v, m^v} \sum_{n^c, \ell^c, m^c} \Bigg[\frac{\langle n^c \ell^c m^c | -e\hat{r}_i | n^{v'} \ell^{v'} m^{v'} \rangle \langle n^{v'} \ell^{v'} m^{v'} | -e\hat{r}_j | n^c \ell^c m^c \rangle}{E_{n^c \ell^c} - E_{n^{v'} \ell^{v'}}} \ldots$$

$$\ldots + \frac{\langle n^c \ell^c m^c | -e\hat{r}_i | n^{v2} \ell^{v2} m^{v2} \rangle \langle n^{v2} \ell^{v2} m^{v2} | -e\hat{r}_j | n^c \ell^c m^c \rangle}{E_{n^c \ell^c} - E_{n^{v2} \ell^{v2}}} \Bigg]$$

where $\sum_{n^v, \ell^v, m^v}$ is a summation over both $|n^{v'} \ell^{v'} m^{v'}\rangle$ & $|n^{v2} \ell^{v2} m^{v2}\rangle$ states, $\hat{r}_i$ & $\hat{r}_j$ are position operators. The sums can be just changed to ones just over n^c, ℓ^c, m^c, n^v using simplified T.D.M.-s (x)-(xii). The (i,j)-th component is ~~the~~ obtained in the basis-set convergence method.

Needed Calculations:

$$\langle n^c \ell^c m^c | \hat{x} | n^v \ell^v m^v \rangle$$

$$= \frac{2}{\sqrt{2}} A_{n^c\ell^c} A_{n^v\ell^c} \left[\int_0^R j_{\ell^c}\left(\alpha_{n^c\ell^c}\frac{r}{R}\right) j_{\ell^c}\left(\alpha_{n^v\ell^c}\frac{r}{R}\right) r^3 dr\right] C^{\ell^c \ell^c 1}_{0\,0\,0} \cdots$$

$$\cdots \left(C^{\ell^c \ell^c 1}_{m^c\, 1-m^c\, 1} + C^{\ell^c \ell^c 1}_{m^c\, -(1+m^c)\, -1}\right) + 2\sqrt{\frac{(2\ell^c+1)}{2(2\ell^c-1)}}\, A_{n^c\ell^c} A_{n^v\ell^c-1} C^{\ell^c\, \ell^c-1\, 1}_{0\,0\,0} \cdots$$

$$\cdots \left(C^{\ell^c\, \ell^c-1\, 1}_{m^c\, (1-m^c)\, 1} + C^{\ell^c\, \ell^c-1\, 1}_{m^c\, -(1+m^c)\, -1}\right) \left[\int_0^R j_{\ell^c}\left(\alpha_{n^c\ell^c}\frac{r}{R}\right) j_{\ell^c-1}\left(\alpha_{n^v\ell^c-1}\frac{r}{R}\right) \cdots\right.$$

$$\left.\cdots r^3 dr\right]$$

$$= X_{n^v, n^c, \ell^c, m^c} + X_{n^v, n^c, \ell^c-1, m^c} \cdots \text{(definitions)}.$$

$$\langle n^c \ell^c m^c | \hat{y} | n^v \ell^v m^v \rangle$$

$$= -i \left[\frac{2}{\sqrt{2}} A_{n^c\ell^c} A_{n^v\ell^c} \left[\int_0^R j_{\ell^c}\left(\alpha_{n^c\ell^c}\frac{r}{R}\right) j_{\ell^c}\left(\alpha_{n^v\ell^c}\frac{r}{R}\right) r^3 dr\right] C^{\ell^c \ell^c 1}_{0\,0\,0} \cdots\right.$$

$$\cdots \left(C^{\ell^c \ell^c 1}_{m^c\, 1-m^c\, 1} - C^{\ell^c \ell^c 1}_{m^c\, -(1+m^c)\, -1}\right) + 2\sqrt{\frac{(2\ell^c+1)}{2(2\ell^c-1)}}\, A_{n^c\ell^c} A_{n^v\ell^c-1} \cdots$$

$$\cdots \left[\int_0^R j_{\ell^c}\left(\alpha_{n^c\ell^c}\frac{r}{R}\right) j_{\ell^c}\left(\alpha_{n^c\ell^c-1}\frac{r}{R}\right) r^3 dr\right] C^{\ell^c\, \ell^c-1\, 1}_{0\,0\,0} \cdots$$

$$\left.\cdots \left(C^{\ell^c\, \ell^c-1\, 1}_{m^c\, 1-m^c\, 1} - C^{\ell^c \ell^c 1}_{m^c\, -(1+m^c)\, -1}\right)\right] = -i\left[Y_{n^v, n^c, \ell^c, m^c} + Y_{n^v, n^c, \ell^c-1, m^c}\right]$$

$$\langle n^c l^c m^c | \hat{z} | n^v l^v m^v \rangle$$

$$= 2 A_{n^c l^c} A_{n^v l^c} \left[\int_0^R j_{l^c}\left(\alpha_{n^c l^c} \frac{r}{R}\right) j_{l^c}\left(\alpha_{n^v l^c} \frac{r}{R}\right) r^3 dr \right] C^{l^c l^c 1}_{0\,0\,0} C^{l^c l^c 1}_{m^c\,-m^c\,0} \ldots$$

$$\ldots + 2 \sqrt{\frac{(2l^c+1)}{(2l^c-1)}} A_{n^c l^c} A_{n^v l^c-1} C^{l^c\, l^c-1\, 1}_{0\,0\,0} C^{l^c\, l^c-1\, 1}_{m^c\,-m^c\,0} \ldots$$

$$\ldots \left[\int_0^R j_{l^c}\left(\alpha_{n^c l^c} \frac{r}{R}\right) j_{l^c-1}\left(\alpha_{n^v l^c-1} \frac{r}{R}\right) r^3 dr \right]$$

$$= Z_{n^v, n^c, l^c, m^c} + Z_{n^v, n^c, l^c-1, m^c}.$$

<u>Polarizability Components:</u> (Next page)

α^0_{xx}

Using

$$\alpha^{\circ}_{xx}$$

$$= \frac{e^2}{\hbar} \sum_{n^v, n^c, l^c, m^c} \Bigg[X^2_{n^v, n^c, l^c, m^c} \left(\frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c}}{m_{v_1}^*} \right)} \cdots \right.$$

$$\cdots + \left. \frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c}}{m_{v_1}^*} \right)} \right) + X^2_{n^v, n^c, l^c-1, m^c} \left(\frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c-1}}{m_{v_1}^*} \right)} \right.$$

$$\cdots + \left. \frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c-1}}{m_{v_2}^*} \right)} \right) \Bigg]$$

Similar expressions for α°_{yy} & α°_{zz} with

$X^2_{n^v, n^c, l^c, m^c} \longrightarrow Y^2_{n^v, n^c, l^c, m^c} / Z^2_{n^v, n^c, l^c, m^c}$, etc.

$$\alpha^{\circ}_{xy}$$

$$= -\frac{ie^2}{\hbar} \sum_{n^v, n^c, l^c, m^c} \Bigg[X_{n^v, n^c, l^c, m^c} Y_{n^v, n^c, l^c, m^c} \left(\frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c}}{m_{v_1}^*} \right)} \cdots \right.$$

$$\cdots + \left. \frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} - \frac{\alpha^2_{n^v, l^c}}{m_{v_1}^*} \right)} \right) + X_{n^v, n^c, l^c-1, m^c} Y_{n^v, n^c, l^c-1, m^c} \cdots$$

$$\cdots \left(\frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c}}{m^*} \right)} + \frac{1}{E_g + \frac{\hbar^2}{2R^2}\left(\frac{\alpha^2_{n^c, l^c}}{m_c^*} + \frac{\alpha^2_{n^v, l^c}}{m_{v_2}^*} \right)} \right) \Bigg]$$

$\text{lh}\left(\alpha^{0}_{xz}\right)^{*} = \alpha^{0}_{xz} = \alpha^{0}_{zx}$.

$-i\, e^{2}/\hbar \sum_{n^{v}, n^{c}, \ell^{c}, m^{c}} [\,\cdot\;\cdot\;\cdot\,]$

α^{0}_{yz}.
