Supporting Information

Loosening quantum confinement: Observation of real conductivity in semiconductor nanoparticles smaller than the Bohr radius

Ronald Ulbricht, Joep J.H. Pijpers

FOM Institute AMOLF, Amsterdam, Science Park 104, 1098 XG Amsterdam, Netherlands

Esther Groeneveld, Rolf Koole, Celso de Mello Donega, Daniel Vanmaekelbergh

Utrecht University, P.O. Box 80000, 3508 TA Utrecht, Netherlands

Christophe Delerue, Guy Allan

IEMN - Dept. ISEN, 41 boulevard Vauban, 59046 Lille Cedex, France

M. Bonn*,

FOM Institute AMOLF, Amsterdam, Science Park 104, 1098 XG Amsterdam, Netherlands,

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

Germany

*: Corresponding author: e-mail: bonn@mpip-mainz.mpg.de

Methods

Synthesis

Colloidal CdTe nanoparticles with radii ranging from 3 to 8 nm were prepared by a modified SILAR procedure using smaller CdTe nanoparticles as seeds. Nanoparticles with radius smaller than 5 nm were grown from 3.5 nm diameter CdTe nanocrystals [1], while nanoparticles with radius larger than 5 nm were grown from 10 nm diameter CdTe nanocrystals.

CdTe nanocrystal seeds with 3.5 nm diameter.

Chemicals. Dimethylcadmium (99.9%) was purchased from ARC Technologies. Tellurium (99.999%, < 250 μm) was purchased from Heraeus. Dodecylamine (DDA, 98%), Tri-octylphosphine (TOP, 90%), methanol and chloroform were purchased from Aldrich. Before use, DDA was degassed and dried under vacuum at 100ºC for several hours.

Synthesis of DDA capped CdTe QDs [2]. In a three necked flask 10 g of dry DDA and 7 mL of TOP were heated to 50°C. To this solution 0.22 g (1.54 mmol) $Cd(Me)_2$ in 7 mL of TOP and 0.16 g (1.25 mmol) Te powder were added. The reaction mixture was heated to 200ºC under vigorous stirring and kept at this temperature for 4 h.

CdTe nanocrystal seeds with 10 nm diameter.

Chemicals: Octadecylamine (ODA, ≥90%) was purchased from Fluka. Tributylphosphine (TBP, 99%) and Tetradecylphosphonic acid (TDPA, min 97%) were purchased from Bunschwig and STREM Chemicals, respectively. 1-Octadecene (ODE, tech. grade, 90%) and trioctylphosphine (TOP, tech. grade ≥ 90%) were purchased from Aldrich. Cadmium acetate dihydrate ($Cd(Ac)_2.2H_2O$, 99.99+%) and tellurium powder (99.999%, ≤250 micron) were purchased from Chempur. Anhydrous toluene, anhydrous hexane, anhydrous methanol, and anhydrous acetone were purchased from Sigma-Aldrich. All reagents were used as purchased with the exception of ODE and ODA. Before use, ODE and ODA were dried and degassed under vacuum (3 h at 120°C).

Stock solutions: A stock solution of Cd-TDPA precursor was made by heating a mixture containing 1.76 g (7.08 mmol) $Cd(Ac)_2 2H_2O$, 4.34 g TDPA and 10.61 mL (8.37 g) of ODE to 300 °C under N_2 atmosphere. After completion of the reaction (colorless solution was obtained) the temperature was lowered to ~170 °C and the solution was degassed under vacuum. Finally, 12.9 mL (10.18 g) ODE and 2 mL (1.66 g) TOP were added. The stock

solution of the Te precursor was made by dissolving 0.31 g (2.41 mmol) Te in 5.70 g (7.04 mL) TBP in a glove-box under nitrogen (< 5 ppm O_2 and H_2O).

Synthesis of TDPA capped CdTe QDs [3]. The synthesis was performed in a glove-box under nitrogen (< 5 ppm O_2 and H_2O). 0.4 g of Cd-TDPA stock solution and 3.6 g ODE were loaded in a reaction flask and heated to 300 °C. At this temperature a mixture of 0.5 g Te-Stock and 1.5 g (1.9 mL) ODE was swiftly injected under stirring. The temperature was allowed to cool to ~270 °C and kept constant. A 1 mL aliquot (sample 1, ~1mL) was taken 10 min after the Te injection. The synthesis was continued 12 min after the injection of Te by alternate dropwise additions of Cd-TDPA and Te stock, which are referred to as addition cycles. Every addition cycle took about 3 min, and was started by 10 drops of Cd-TDPA precursor solution, followed by alternate additions of Cd-TDPA and Te stock (10 drops at a time) until the total intended volume had been added. The precursors were allowed to react for 12 min after each addition cycle. In the first four addition cycles 0.26 g Te stock, and a mixture of 0.31 g Cd-TDPA stock and 0.35 g ODE were added. From addition cycle five to eight 0.5 g Te stock, and a mixture of 0.43 g Cd-TDPA stock and 0.17 g ODE were added. In the final addition cycle 1 g Te stock, and 0.36 g Cd-TDPA stock were added. The mixture of Cd-TDPA stock solution and ODE was pre-heated to 250 °C and added as a hot solution, whereas the Te-TBP stock was kept at ambient temperature. Aliquots of ~1mL were taken from the reaction mixture 3 min before the start of every addition cycle. The synthesis temperature was lowered to 250 °C after the second addition cycle. The synthesis was stopped by removing the heating mantle 18 min after completion of the final addition cycle.

Purification of the crude reaction mixture consisted of a hexane/methanol extraction in order to remove unreacted Cd precursors. Extraction was performed by mixing a solution of the crude reaction mixture in anhydrous hexane, and anhydrous methanol (1:1:1 volume ratio). The colored top layer containing the nanocrystals was removed and the nanocrystals were precipitated by adding anhydrous acetone (1:1 volume ratio). The sediment was isolated by centrifugation (3000 rpm, 15 min), and redissolved in anhydrous toluene (or in ODE if they were to be used as seeds).

Preparation of CdTe nanoparticles with radius smaller than 5 nm from 3.5 nm diameter seeds [1].

Briefly, the CdTe nanocrystal seeds were purified once by adding methanol to the crude reaction mixture (3:1 volume ratio), followed by centrifugation and redispersion of the precipitate in a mixture of ODE and octadecylamine (ODA) (4 mL ODE; 1.5 g ODA, and 0.1

μmol seeds). Subsequently, pre-calculated volumes of a precursor solution (0.1 M Cd oleate in ODE and 0.1 M Trioctylphosphine-Te in ODE) were slowly added (1 monolayer of Cd or Te at a time), while keeping the temperature constant at 220 °C. Each monolayer was allowed to grow for 10-15 minutes before the next precursor solution was added.

Preparation of CdTe nanoparticles with radius larger than 5 nm from 10 nm diameter seeds.

Chemicals. Cadmium acetate dihydrate ($Cd(Ac)_2xH_2O$, 99.99+%), octadecene (ODE, tech. grade 90%), and oleic acid (tech. grade 90%) were purchased from Sigma-Aldrich. Trioctylphosphine (TOP, tech. grade $\geq$ 90%) and octadecylamine (ODA, $\geq$90%) were purchased from Fluka. Tellurium powder (99.999%, $\leq$250 micron) was purchased from Hereaus. Anhydrous toluene, anhydrous hexane, anhydrous methanol, and anhydrous acetone were all purchased from Sigma-Aldrich.

Stock solutions: Stock solution of 0.093 M Cd-Oleate in ODE was made by heating 0.926 g $Cd(Ac)_22H_2O$ with 2.92 mL oleic acid in 37.05 mL ODE to 100 °C under N_2 atmosphere for 1h. Subsequently this Cd-stock solution was dried and degassed under vacuum (2 h at 100°C). A stock solution of 0.1M Te in TOP and ODE (TOP:ODE, 1:9 volume ratio) was prepared by dissolving 0.514 g Te powder in 4 mL TOP and 36 mL ODE under N_2 atmosphere.

Synthesis: The synthesis was performed in a glove-box under nitrogen (< 5 ppm O_2 and H_2O). ODA (0.81 g), ODE (1.5 mL), and 1.3 mL of CdTe nanocrystal stock solution in ODE (37.5×10^{-9} mol of CdTe nanocrystal seeds) were loaded in a reaction flask and heated to 230 °C. The amount of Cd and Te needed for an additional layers was calculated based on CdTe wurtzite structure in which the average thickness of one monolayer is 0.375 nm.. During the synthesis alternate additions of Cd and Te stock solutions were performed (each during ~2 min). Before every Cd stock solution addition, aliquots (0.5 mL) from the reaction mixture were taken. The synthesis was started by the addition of Cd stock solution of the first monolayer. Each monolayer was allowed to grow for 30 minutes before the next precursor solution was added. After the third monolayer the waiting time was increased to 45 min. The synthesis was finished after the addition of fourteen monolayers.

Purification and size selection procedure. The purification procedure consisted of precipitating the nanoparticles from a solution of the crude reaction mixture in toluene (1:1 volume ratio) by adding anhydrous methanol. The sediment was isolated by centrifugation (3000 rpm, 15 min) and redissolved in anhydrous toluene. By using post-preparative size

selective precipitation, ensembles of monodisperse (5 - 7% standard deviation) spherical CdTe nanoparticles ranging from 10.5 to 15.7 nm diameter were isolated from the reaction mixture.

Characterization

Absorption spectra were measured on a double beam Perkin-Elmer Lambda 16 UV/Vis spectrometer (scan rate: 1 nm/s). Emission spectra were recorded by using a Princeton Instrument Liquid N_2–cooled CCD-detector and a 0.25 m Acton Research monochromator (150 lines/mm grating blazed at 550 nm). The excitation wavelength was selected from a 450 W Xe lamp by a double-grating monochromator (0.22 m, SPEX 1680). All measurements were performed at room temperature under N_2 atmosphere. Samples for optical measurements were prepared by directly dissolving the crude reaction mixture in anhydrous toluene under nitrogen. All measurements were carried out on samples with a low optical density (≤0.2 at 300 nm). Transmission electron microscopy was performed on a Tecnai20F (FEI) microscope equipped with a Field Emission Gun, a Gatan 694 CCD camera and an EDAX spectrometer. The microscope was operated at 200kV. Samples for TEM imaging were prepared by dipping a carbon coated polymer film copper grid (300 mesh) into a toluene solution of purified nanocrystals. The excess liquid was removed by blotting with filter paper.
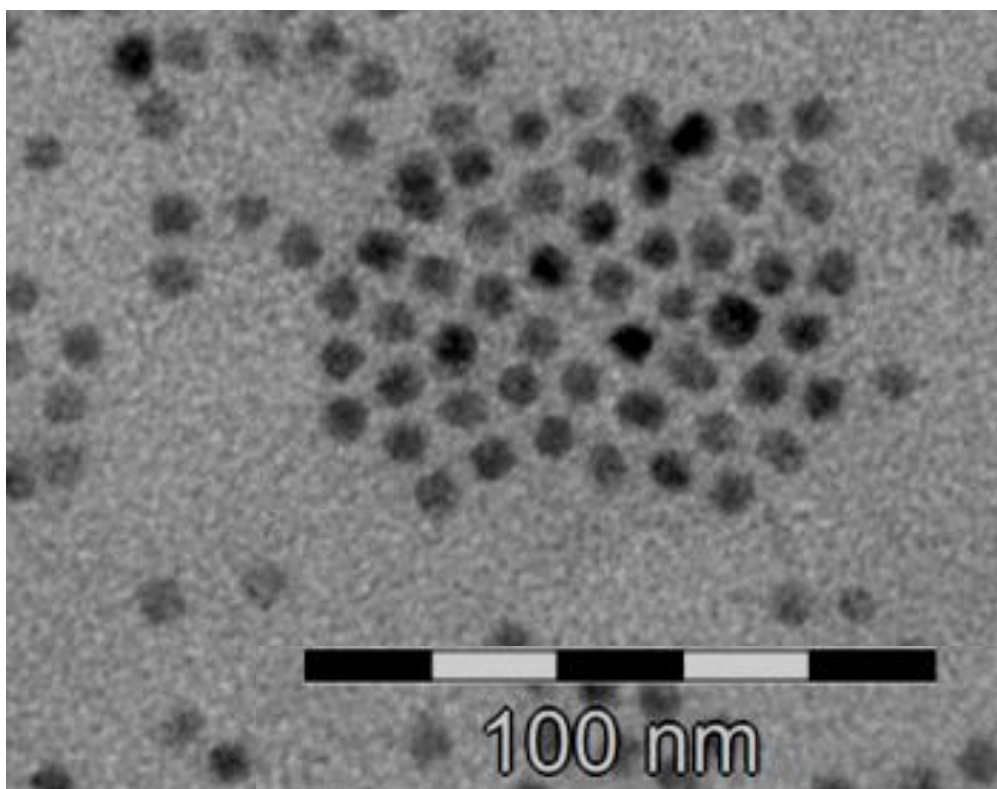
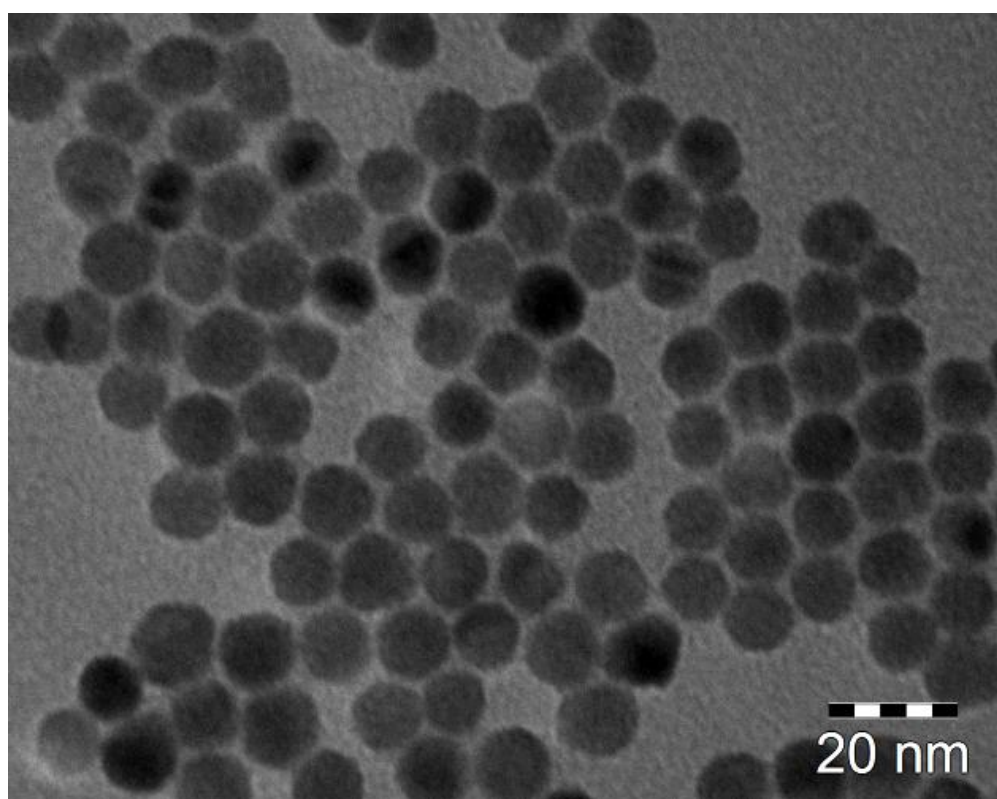Fig S1. TEM image of CdTe nanoparticles with a mean diameter of 6.1 nm (±0.6 nm)

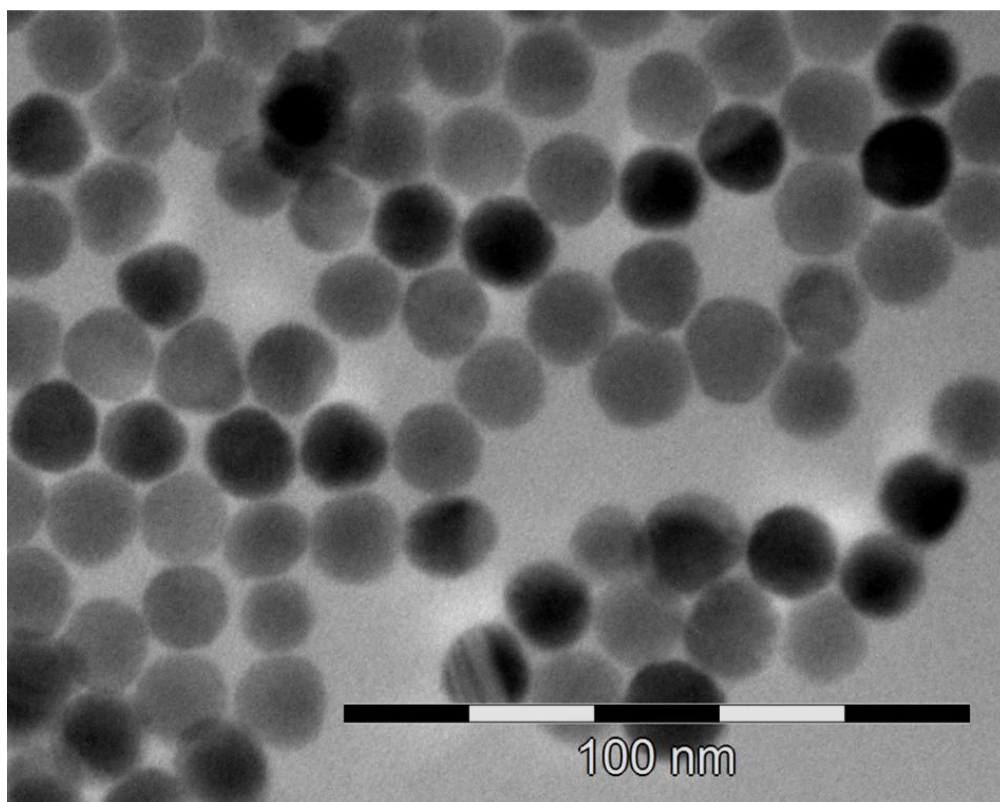Fig. S2. TEM image of CdTe nanoparticles with a mean diameter of 10.7 nm (±1.0 nm)

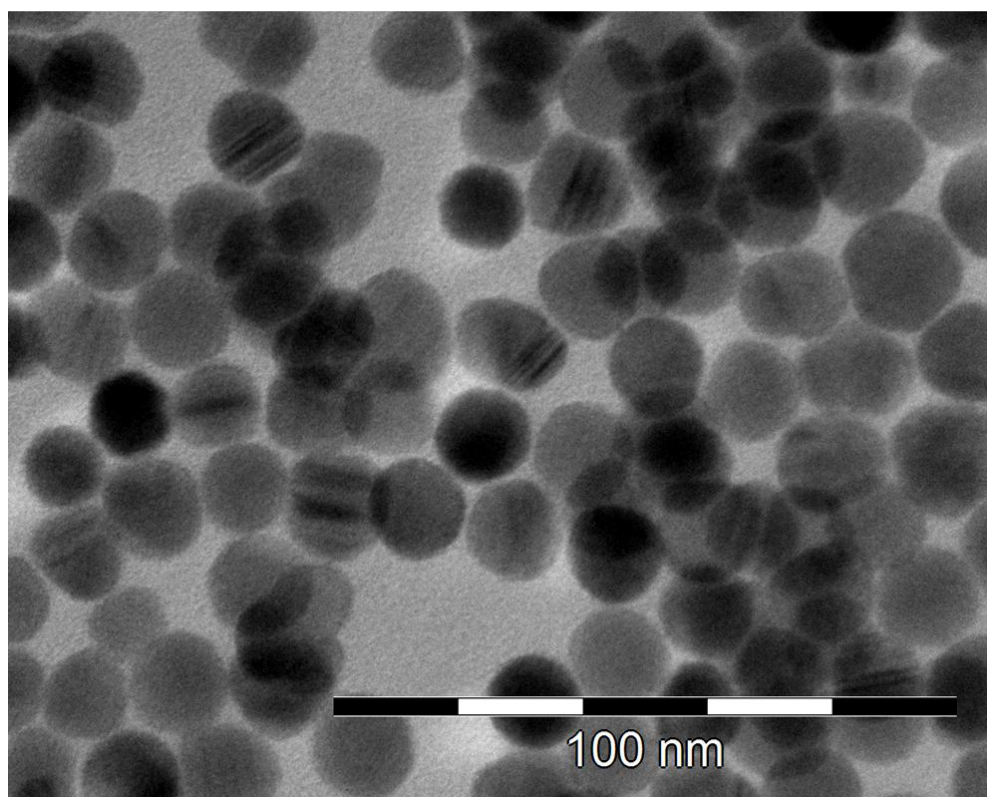Fig. S3. TEM image of CdTe nanoparticles with a mean diameter of 14.0 nm (±1.0 nm)

Fig. S4 TEM image of CdTe nanoparticles with a mean diameter of 15.11 nm (±1.2 nm)

Tight-binding calculations

The objective is to calculate the change in the polarizability of a QD after a single excitation. Since experiments are performed at room temperature, it is not sufficient to consider that the QD is in its lowest energy exciton states, many exciton states must be considered.

Principle of the calculation

The excitonic states of the QD are calculated using a Configuration Interaction (CI) method as described below. The excitonic states of energy E_i are denoted Ψ^i_{exc} (the zero of energy corresponding to the QD is its ground states, i.e., without exciton). Assuming that the external electric field is a small perturbation, the polarizabilty of the exciton is given by:

$$
\alpha(h\nu) = -e^2 F^2 \sum_{i,j} \left| \left\langle \Psi^i_{\text{exc}} \mid \sum_n \mathbf{e}.\mathbf{r}_n \mid \Psi^j_{\text{exc}} \right\rangle \right|^2
$$
$$
\times \frac{f_i - f_j}{h\nu - (E_j - E_i) + i\eta} \tag{1}
$$

where $h\nu$ is the photon energy, $\mathbf{e}$ is the polarization vector, F is the local-field factor, $\mathbf{r}_n$ represents the position of the electron n, f_i is the thermal occupancy of the exciton state Ψ^i_{exc}, and η is the broadening which accounts for the coupling to phonons (or eventually other mechanisms). $\sum_n$ is a sum over all the electrons of the system, $\left\langle \Psi^i_{\text{exc}} \mid \sum_n \mathbf{e}.\mathbf{r}_n \mid \Psi^j_{\text{exc}} \right\rangle$ is the dipolar matrix element between two excitonic states.

Configuration Interaction

The ground state $|O>$ of the QD corresponds to filled valence states and empty conduction states. We consider a basis of electron-hole pair (eh) states ψ_{vc} corresponding to the excitation of an electron from a valence state v to a conduction state c. In a basis of single-particle states (those obtained in tight-binding), each eh state is a Slater determinant. With respect to the Slater determinant $|O>$, the single-particle state v has been replaced by the single-particle state c.

In CI, the excitonic states are defined as linear combinations of the eh states:

$$
\Psi^i_{\text{exc}} = \sum_{vc} a^i_{cv} \psi_{vc}. \tag{2}
$$

To solve the problem, we must write the matrix of the Hamiltonian in the basis of the eh states and we must diagonalize it. The energies E_i are the eigenvalues. The matrix element between two eh states ψ_{vc} and $\psi_{v'c'}$ are

$$\langle \psi_{vc} \mid H \mid \psi_{v'c'} \rangle = ([\varepsilon_c + \Sigma_c] - [\varepsilon_v + \Sigma_v])\delta_{cc'}\delta_{vv'}$$
$$- \int c^*(\mathbf{x}_1)v^*(\mathbf{x}_2)V_{coul}(\mathbf{r}_1,\mathbf{r}_2)c'(\mathbf{x}_1)v'(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$$
$$+ \int c^*(\mathbf{x}_1)v^*(\mathbf{x}_2)V_{exch}(\mathbf{r}_1,\mathbf{r}_2)v'(\mathbf{x}_1)c'(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 \qquad (3)$$

where $\mathbf{x}_1 \equiv (\mathbf{r}_1, \xi_1)$ in which ξ_1 represents the spin variable of the particle 1. The second line is the Coulomb term, the third one is the exchange one. $V_{coul}(\mathbf{r}_1,\mathbf{r}_2)$ describes the energy potential of a charge $+e$ at $\mathbf{r}_1$ induced by a charge $+e$ at $\mathbf{r}_2$:

$$V_{coul}(\mathbf{r}_1,\mathbf{r}_2) = \int \epsilon^{-1}(\mathbf{r}_1,\mathbf{r})\frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}d\mathbf{r} \qquad (4)$$

in which $\epsilon^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ is the generalized dielectric constant (here taken in the static limit). We assume that $V_{exch} = V_{coul}$.

The term Σ_c (Σ_v) represents the self-energy of the electron (hole) coming from the interaction of the electron with the polarization charges induced at the dielectric interfaces (or surfaces) by its own presence:

$$\Sigma_c = \frac{1}{2}\int |c(\mathbf{r}_1)|^2 \lim_{\mathbf{r}_2 \to \mathbf{r}_1}\left(V_{coul}(\mathbf{r}_1,\mathbf{r}_2) - \frac{e^2}{\epsilon_{in}|\mathbf{r}_1 - \mathbf{r}_2|}\right)d\mathbf{r}_1 \qquad (5)$$

where ϵ_{in} is the dielectric constant of the material at the position $\mathbf{r}_1$. In the case of a spherical QD, V_{coul} is easily obtained assuming a dielectric sphere of dielectric constant ϵ_{in} in a medium of dielectric constant ϵ_{out} (the solvent for example).

Optical matrix elements in CI

The optical matrix elements in CI are given by:

$$\left\langle \Psi_{exc}^{i} \,|\, \sum_{n} \mathbf{e}.\mathbf{r}_n \,|\, \Psi_{exc}^{j} \right\rangle = \sum_{v,c \neq c'} a_{vc'}^{*} a_{vc} < c' \,|\, \mathbf{e}.\mathbf{r} \,|\, c >$$

$$+ \sum_{c,v \neq v'} a_{v'c}^{*} a_{vc} < v \,|\, \mathbf{e}.\mathbf{r} \,|\, v' > \tag{6}$$

The single-particle dipolar matrix elements $< c' \,|\, \mathbf{e}.\mathbf{r} \,|\, c >$ and $< v \,|\, \mathbf{e}.\mathbf{r} \,|\, v' >$ are easily calculated in tight-binding.

References

[1] de Mello Donegá, C.; and Koole, R., *J. Phys. Chem. C*, **2009**, *113*, 6511.

[2] Wuister, S. F.; de Mello Donegá, C.; Meijerink, A. *J. Am. Chem. Soc.* **2004,** 126, 10397.

[3] Yu, W. W.; Wang, Y. A.; Peng, X.; *Chem. Mater.* **2003** *15* , 22, 4300.