CMTH-Vvedensky-3

A group-theoretical treatment of first-order perturbations of potential boundaries in semiconducting nanocrystals

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1   Layperson's summary

Breaking the Symmetry, or, When Crystals Are Almost Perfect

The title of the layperson's summary: "Breaking the Symmetry, or, When Crystals Are Almost Perfect". It will focus firstly on the role of symmetries in selection rules and secondly on the overlap decomposition as a quantifier of what we mean by *approximate*. Technicalities such as double groups or growth of QDs shall be omitted for brevity (although [3] will be discussed as a motivator for the perturbative approach).

2   Abstract

In this project, we investigate the photonic properties of quantum dots employing a group-theoretical description of first-order perturbation theory. Experimental data from polarisation resolved photoluminiscence spectroscopy are investigated using the theory of exciton complexes and group theory. The major features of the spectral diagrams can be labelled by exciton state transitions immediately by considering the total angular momentum coupling of these exciton complexes. These major features also exhibit splitting caused by crystallographic symmetry breaking. The transitions between said energy levels are subject to symmetry selection rules, and we attempt to quantify the rates of these transitions by considering approximate symmetries. A list of other effects that may cause symmetry elevation is stated and reviewed.

3   Contents

4   Introduction

Firstly, a historical context of the problem and a brief literature review (namely [1]). Secondly, a brief review of [3] as a *de facto* solution to symmetry elevation, and then motivating the need for a perturbative analysis under strain and imperfect growth, which favour the three pyramid-defined directions out of the six grown. Thirdly, a list of proposed solutions, with the first one, a perturbative model of a low-symmetry Hamiltonian being mathematically explored and quantified.

5   Discussions of theory employed

5.1   The InGaAs pyramidal quantum dot

A brief description of the growth process as employed by Karlsson, Pelucchi etc. A discussion of [3] and its arguments for the true shape. A review of effects that alter the shape (and hence the symmetry) of a quantum dot, including strain and other mechanical effects.

5.2   Exciton complexes and double groups

A theoretical description of exciton complexes, the decomposition of their wavefunctions into a periodic function and an envelope function, and a model of the enevlope function's "effective Hamiltonian" as a box (of a non-rectangular shape) potential with particles interacting via Coulomb interaction and magnetic momenta interaction (here we justify a first-quantization approach by asserting non-relativistic effective speeds). Total angular momentum is shown to be a good quantum number and its treatment within the full rotoinversion $SU(2) \otimes C_i$ group is described.
NOTES:

- In the semi-classical tight-binding model, we consider excited fermions in the nanocrystal as "particles in a box", confined to a spatial domain in which they move freely, and the effects of the atomic structure on the free particles are encoded in the effective mass parameter.

- We can use the effective mass formulation because the nanocrystals are big enough to have a band-structure (cite Dresselhaus).

- The full wavefunction $\Psi(\vec{r})$ is decomposed into an envelope function $\Upsilon(\vec{r})$ and a periodic function $U(\vec{r})$, where $U(\vec{r} - \vec{r}_n) = U(\vec{r})$. Therefore

$$\Psi(\vec{r}) = \Upsilon(\vec{r}) U(\vec{r})$$

and therefore the character of the wavefunction under a rotation $\hat{R}$ is

$$\chi^{(\Psi(\vec{r}))}\left(\hat{R}\right) = \chi^{(\Upsilon(\vec{r}))}\left(\hat{R}\right) \chi^{(U(\vec{r}))}\left(\hat{R}\right)$$

  Due to energy constraints, we expect the envelop functions to be dominated by the ground state levels, which transform according to the identity irrep. The character of the periodic function is then given by taking the toal angular momentum eigenstate j and subduing it into the spatial point group of the quantum dot (which governs also the boundary conditions of the envelope function).

- Luttinger-Kohn model to justify free-electrons and effective masses at the Γ point (only there!!!!!).

TEXT

The physical phenomenon which is subject to our study is photoluminiscence. Since this mechanism does not have the QDs in a laboratory ensemble interact or "communicate", we can formulate a theoretical model of photoluminiscence on a singular QD. An external electromagnetic field in the form of a light-beam interacts with the QD in a non-resonant way (as for not to favour a single excited state), which promotes electrons into the conduction band and holes into the valence bands (since there are typically two valence bands at the band edge, which touch at Γ). The population of excited electrons and different characteristics of holes is called an exciton complex. Exciton complexes decay into lower-occupancy exciton complexes via electron-hole recombination, which produces bright emission lines in the photoluminiscence spectrum. These lines are sharp and occur at fixed frequencies corresponding to the energy level differences, and the theoretical description of their spectrum is the ultimate goal of this work.

In the Karlsson *et al.* system, the light-beam is a laser with a spot size of $1\,\mu\mathrm{m}$, power in the range 25–$750\,\mathrm{nW}$, and wavelength of $532\,\mathrm{nm}$. The semiconductor nanocrystal has a direct band-gap at Γ. The excitons with resolvable emissions have low occupancy numbers (3 or fewer of any of the three fermions–electrons, light holes, and heavy holes). Since the number of fermions excited on a single band is smaller than the number of states available on the band by many orders of magnitude (GIVE ROUGH ESTIMATE), we approximate the exciton complexes as living on Γ, i.e. each excited fermion having zero crystal momentum.

Clearly, the phenomenon of photoluminiscence and its behaviour is wholly described by the specific wavefunctions of the exciton complexes. However, finding the wavefunctions and the matrix elements of interaction operators is a near-impossible task and is not viable to make predictions about the spectrum of the quantum dot. However, we can make multiple very strong qualitative predictions (mainly regarding degeneracies of energy levels and selection rules) by using purely symmetry arguments, using the formalism of group theory. To employ group theory, we must first identify the physical symmetries of our quantum dot.

5.2.1   Envelope function method

The following approach is informed by that developed by Burt (1999), [4]. Let us consider a QD with a single excited electron which is promoted to the conduction band (the following easily generalises to holes promoted to valence bands). Disregarding the spin component of its wavefunction for simplicity, we decompose the electron's spatial wavefunction $\Psi\left(\vec{r}\right)$ into plane-waves:

$$\Psi\left(\vec{r}\right) = \int \mathrm{d}\vec{k}\,\tilde{\Psi}\left(\vec{k}\right)\exp\left\{i\vec{k}\cdot\vec{r}\right\} \tag{1}$$

where $\tilde{\Psi}\left(\vec{k}\right)$ is the Fourier transform of $\Psi\left(\vec{r}\right)$. We now decompose the integral domain into the first Brillouin zone (B.Z.) summed over the set of reciprocal lattice vectors G:

$$\Psi\left(\vec{r}\right) = \sum_{\vec{g}\in G}\int_{\vec{k}\in 1\text{st B.Z.}} \mathrm{d}\vec{k}\,\tilde{\Psi}\left(\vec{k}+\vec{g}\right)\exp\left\{i\left(\vec{k}+\vec{g}\right)\cdot\vec{r}\right\} \tag{2}$$

Note that G is equivalent to the set of wave-vectors of plane waves periodic on the Bravais lattice. Therefore, we can choose a set of basis functions $U_n(\vec{r})$ periodic on the Bravais lattice like so:

$$U_n(\vec{r}) = \sum_{\vec{g} \in G} u_n(\vec{g}) \exp\{i\vec{g} \cdot \vec{r}\} \tag{3}$$

$$U_n(\vec{r} + \vec{r}_B) = \sum_{\vec{g} \in G} u_n(\vec{g}) \exp\{i\vec{g} \cdot \vec{r}\} \exp\{i\vec{g} \cdot \vec{r}_B\} = U_n(\vec{r}) \tag{4}$$

where $\vec{r}_B \in R$ is a lattice vector and $u_n(\vec{g})$ are the coefficients of the decomposition of U_n into reciprocal lattice plane waves, typically chosen such that U_n are orthonormal. Then, inverting this decomposition, we obtain

$$\exp\{i\vec{g} \cdot r\} = \sum_n u_n(\vec{g})^* U_n(\vec{r}) \tag{5}$$

which allows us to decompose the original wavefunction into a sum of the orthonormal basis vectors U_n and their envelope functions Υ_n:

$$\Psi(\vec{r}) = \sum_n \Upsilon_n(\vec{r}) U_n(\vec{r}) \tag{6}$$

$$\Upsilon_n(\vec{r}) = \sum_{\vec{g} \in G} \int_{\vec{k} \in \text{B.Z.}} d\vec{k}\, u_n(\vec{g})^* \tilde{\Psi}\left(\vec{k} + \vec{g}\right) \exp\left\{i\vec{k} \cdot \vec{r}\right\} \tag{7}$$

Now, we choose $U_n(\vec{r})$ to represent the band-edge wavestates in the bulk structure. Using a tight-binding model with spin-orbit coupling, these wavestates can be labelled by three quantum numbers: total angular momentum j, its projection onto the z-axis j_z, and the orbital energy excitation ε_n, which we assume to be in the ground state in our system due to energy occupancy statistics (as we expect the population of states other than in the ground state to be negligible for a low-power light-source). Furthermore, the quantum number j is determined by the orbital angular momentum l, which is given by the electron configuration in each specific band, and the spin $s = 1/2$ determined for electrons and electron holes by their fundamental properties.

Photonic nanostructures can, on a small scale, cease to posses a standard band-structure, instead featuring e.g. flat bands. Dresselhaus *et al.* (2007) quotes the number of Bravais lattice cells below which this occurs to be in the order of 10^2 [5, p. 213]. Our QDs have volumes typically higher than $100\,\text{nm}^3$ [2, p. 2], which corresponds to the number of unit cells in the order of 10^3. Hence we can reasonably expect our system to posses a band structure. This has two consequences to our envelope function model:

1. The envelope function $\Upsilon(\vec{r})$ is varying slowly enough for it to have an approximately defined crystal momentum. As discussed in 5.2, we assume $k \approx 0$.

2. The wavefunction $\Psi(\vec{r})$ of a single excited fermion approximately corresponds to a single state on the excited band of the infinite bulk crystal band structure. In other words, there exists a basis vector U_n such that for all other basis vectors $U_m, m \neq n$, their contribution to the wavefunction is negligible.

Labelling the single contributing basis vector by the quantum numbers l, s, j, j_z, we can express the wavefunction of a single excited fermion as

$$\langle \vec{r}|\Psi\rangle = \Upsilon(\vec{r}) \langle \vec{r}|l, s = 1/2, j, j_z\rangle \tag{8}$$

where $|l, s = 1/2, j, j_z\rangle$ are the usual spinor spherical harmonics which include the spinor part of the wavefunction, as treated e.g. in Biedenharn, Louck (1981) [6].

5.2.2 Symmetry arguments and group theory

Outline what group theory tells us.

5.2.3 Total angular momentum and double groups

here I elaborate on j

5.3 Photoluminiscence spectrum and evidence of symmetry elevation

6 Results

6.1 Treatment of parity

The theoretical treatment of parity under l and j-coupling is shown. The program AReTDoG as an implementation of this and its agreement with [1] is discussed.

6.2 Symmetry suppression theory

The first-order perturbation treatment of selection rules and its applicability to low-to-high symmetry systems is shown.

7 Discussion of results

7.1 Symmetry suppression in pyramidal quantum dots

The suppression theory in 6.2 is discussed in the context of the quantum dots grown in the mode described in 5.1. The limiting symmetry of the nanocrystallic structure is shown. The effects of strain and other causes of perturbation are discussed. The C_{3v} probing for the $X_{\bar{1},1}$ transition is discussed and explanations are offered.

7.2 Other hypothetical causes of symmetry elevation

This section serves to enumerate another effects we have identified which might cause symmetry breaking or potential elevation in QDs. These include band-mixing effects and electron gas models. Since they are not mathematically developed, my goal is to identify specifically the aspects of these hypotheses that might for a basis for a change of symmetry. I also discuss why the interplay between these effects can be neglected, as that would constitute second-order effects (and I justify this claim by qualitative arguments).

8   Conclusions

The importance of [3] on the entire research community in the context of symmetry elevation is discussed. The treatment of parity and symmetry suppression theory are described in the perspective of their generality and other areas where they may be useful are identified. The implications of the parity treatment are discussed. I conclude that [3] is a satisfactory explanation for symmetry elevation, with our symmetry suppression theory justifying the dismissal of small perturbations, e.g. by mechanical means.

9   Acknowledgements

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10 Bibliography

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