Temperature dependent empirical pseudopotential theory for self-assembled quantum dots

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Received 24 July 2012, in final form 20 September 2012
Published 26 October 2012
Online at stacks.iop.org/JPhysCM/24/475302

Abstract
We develop a temperature dependent empirical pseudopotential theory to study the electronic and optical properties of self-assembled quantum dots (QDs) at finite temperature. The theory takes the effects of both lattice expansion and lattice vibration into account. We apply the theory to InAs/GaAs QDs. For the unstrained InAs/GaAs heterostructure, the conduction band offset increases whereas the valence band offset decreases with increasing temperature, and there is a type-I to type-II transition at approximately 135 K. Yet, for InAs/GaAs QDs, the holes are still localized in the QDs even at room temperature, because the large lattice mismatch between InAs and GaAs greatly enhances the valence band offset. The single-particle energy levels in the QDs show a strong temperature dependence due to the change of confinement potentials. Because of the changes of the band offsets, the electron wavefunctions confined in QDs increase by about 1–5%, whereas the hole wavefunctions decrease by about 30–40% when the temperature increases from 0 to 300 K. The calculated recombination energies of excitons, biexcitons and charged excitons show red shifts with increasing temperature which are in excellent agreement with available experimental data.

(Some figures may appear in colour only in the online journal)

1. Introduction
During the past two decades, enormous progress has been achieved in understanding the electronic and optical properties of self-assembled quantum dots (QDs), both through theory and through experiments, stimulated by their potential applications in QD lasers at room temperature \[1–3\], and as qubits and quantum photon emitters at low temperature \[4–8\]. For the former applications, it generally requires high density and highly uniform QDs. The QD laser has been demonstrated with a much lower threshold current \(J_c\) and much higher material and differential gains as compared to semiconductor quantum well lasers \[9\]. For the latter applications, the preparation of single QDs is crucial. A number of methods have demonstrated the feasibility to isolate a single QD from a QDs ensemble \[10–13\]. Rabi oscillation of excitons and charged excitons \[14, 15\] in a single QD have been observed experimentally, showing that the charge and spin quantum states in a single QD can be coherently controlled via optical methods. Single QDs have also been demonstrated experimentally as a source of single photons and entangled photopairs \[7, 16\], which is much brighter \[17\] than the traditional parameter-down entangled photon source \[18, 19\]. These experimental achievements pave the way for future applications of QDs in quantum computation.

On the other hand, the development of the atomistic theories, including the empirical pseudopotential method \[20–22\] and the tight-binding models \[23–25\] provides a deep insight into the electronic and optical properties of self-assembled QDs. The atomistic theories of QDs not only give results that agree well with experiments \[26–29\], but also greatly improve
our understanding of the properties of QDs. The atomistic models capture the correct point group symmetry of the QDs, which is missing in the continuum model. Therefore they can give a correct interpretation of some subtle properties of QDs, e.g., fine structure splitting (FSS) [30], and light polarization of excitons [31]. Unfortunately, so far all the theories of QDs have been restricted to zero temperature.

Temperature is a very important degree of freedom in experiments to tune the electronic and optical properties of QDs, besides strain [32], electric field [33] and magnetic field [34]. For example, in the QD-cavity system, the temperature is generally used to tune the resonance between the QDs and the cavity in order to achieve strong coupling between the two quantum systems [35–38]. The temperature dependent optical spectra of (single and ensemble) QDs have been investigated intensively in experiments in the past decades [10–12, 14, 15, 39–41]. New physics, for example, the formation of excitonic polarons [40, 42, 43] due to strong coupling between excitons and optical phonons, may be found in QDs at high temperature. However, a theoretical understanding of the temperature effects in QDs is still missing. Therefore, to facilitate the future device applications of QDs, the development of a temperature dependent theory is not only of theoretical interest, but also of practical importance.

In this work, we develop such a temperature dependent atomistic pseudopotential theory to study the electronic and optical properties of QDs at finite temperature. We take the effects of both lattice expansion and lattice vibration into account. The latter is done by introducing a temperature dependent dynamical Debye–Waller factor to the structure factor. We first examine the temperature dependent electronic structures of bulk InAs and GaAs, and then apply the theory to investigate the electronic and optical properties of self-assembled InAs/GaAs QDs. The calculated temperature dependent photoluminescence (PL) spectra of QDs are in excellent agreement with available experimental data.

The rest of the paper is organized as follows. In section 2 we introduce the temperature dependent empirical pseudopotential method (TDEPM). In section 3, we study the electronic structures of bulk InAs, GaAs using TDEPM, including the energy band gaps and band offsets, etc. We present the temperature dependent band offsets for InAs/GaAs QDs in section 4.1 and the single-particle energy levels and wavefunctions of InAs/GaAs QDs in section 4.2. We discuss the temperature dependent optical spectra of InAs/GaAs QDs in section 4.3, and summarize in section 5.

2. Methodology

To study the electronic and optical properties of the semiconductors at finite temperature, we introduce temperature dependent pseudopotentials in the single-particle Hamiltonian,

$$\hat{H} = -\frac{1}{2}\nabla^2 + \sum_{\alpha n} \hat{v}_\alpha (\mathbf{r} - \mathbf{R}_{\alpha n}, \epsilon, T),$$

(1)

where $\hat{v}_\alpha (\mathbf{r}, \epsilon, T)$ is the strain dependent screened empirical pseudopotential for an atom of type $\alpha$ and atom index $n$ at temperature $T$. $\mathbf{R}_{\alpha n}$ is the optimized atom position from the valence force field (VFF) method [44, 45]. In a strained lattice, the atomic potential is assumed to have the form

$$v_\alpha (\mathbf{r}, \epsilon, T) = v_\alpha (\mathbf{r}, T)[1 + \gamma_\alpha \text{Tr}(\epsilon(\mathbf{r}))],$$

(2)

where Tr$(\epsilon(\mathbf{r}))$ is the local hydrostatic strain at $\mathbf{r}$. $\gamma_\alpha$ is fitted to the deformation potentials of the bulk materials.

The effects of lattice vibration can be taken into account using Brooks–Yu theory [46, 47], which has been applied to study the energy gap of bulk materials in the context of pseudopotentials [48–51]. The total atomic potential at temperature $T$, which is the sum of all atomic potentials $\hat{v}_\alpha (\mathbf{r}, \epsilon, T)$, can be written as

$$V(\mathbf{r}, T) = \sum_\mathbf{q} \sum_\alpha v_\alpha (\mathbf{q}) S_\alpha (\mathbf{q}) \text{e}^{i\mathbf{q}\cdot\mathbf{r}}_T,$$

(3)

where $\mathbf{q}$ is the reciprocal lattice vector. $v_\alpha (\mathbf{q})$ is the Fourier transform of the screened atomic potential at zero temperature, which takes the form [52]

$$v_\alpha (\mathbf{q}) = \frac{\alpha_0 (\mathbf{q}^2 - \alpha_1)}{\alpha_2 \epsilon^{2\alpha_3} - 1},$$

(4)

where $q = |\mathbf{q}|$, and the parameters $\alpha_0, \alpha_1, \alpha_2, \alpha_3$ are fitted to the bulk properties of InAs and GaAs, including the band gaps, band offsets, effective masses, etc. $\langle S_\alpha (\mathbf{q}) \rangle_T$ is the averaged structure factor over all the phonon configurations at temperature $T$,

$$\langle S_\alpha (\mathbf{q}) \rangle_T = \left\langle \sum_n e^{-i\mathbf{q}\cdot\mathbf{R}_{\alpha n}} \right\rangle_T .$$

(5)

Assuming $\mathbf{R}_{\alpha n} = \mathbf{R}_{\alpha n}^0 + \mathbf{u}_\alpha$, where $\mathbf{u}_\alpha$ is the amplitude of the phonon mode. For any $\mathbf{q}$, we have

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_\alpha} \rangle_T = e^{-\frac{1}{2}(\mathbf{q}\cdot\mathbf{u}_\alpha)^2} T,$$

(6)

using Wick’s theorem [53]. Therefore, the temperature effects on the atomic potentials are equivalent to considering a temperature dependent structure factor,

$$\langle S_\alpha (\mathbf{q}) \rangle_T = \sum_n e^{-i\mathbf{q}\cdot\mathbf{R}_{\alpha n}^0} e^{-W_\alpha (\mathbf{q}, T)},$$

(7)

in equation (3), where $W_\alpha (\mathbf{q}, T)$ is the dynamical Debye–Waller factor for the $\alpha$-th element,

$$2W_\alpha (\mathbf{q}, T) = \langle (\mathbf{q} \cdot \mathbf{u}_\alpha)^2 \rangle_T .$$

(8)

For simplicity, we assume the system to be isotropic, then we have

$$W_\alpha (\mathbf{q}, T) = \frac{1}{6} |\mathbf{q}|^2 \langle u_{\alpha n}^2 \rangle,$$

(9)

where $\langle u_{\alpha n}^2 \rangle$ is the total mean-square displacement for an atom of type $\alpha$ at temperature $T$, including the contribution from acoustic (A) and optical (O) phonons,

$$\langle u_{\alpha n}^2 \rangle = \langle u_{\alpha n}^2 \rangle_A + \langle u_{\alpha n}^2 \rangle_O .$$

(10)
We use the Debye model for acoustic phonons,

\[
(u^2)_A = \int_0^{\omega_D} g(\omega) \frac{h}{N M \omega} \left( \frac{1}{e^{\hbar \omega/k_B T} - 1} + \frac{1}{2} \right) d\omega
= a_4 \left[ \left( \frac{T}{\theta_B} \right)^2 \int_0^{\frac{T}{\theta_B}} x e^x - 1 dx + 1 \right],
\]

where \(a_4 = 9h/2M \theta_D\), and \(\theta_B = h\omega_D / k_B\) is the Debye temperature. The second term in the bracket is from zero-point quantum fluctuation, which can be absorbed to the zero-temperature pseudopotentials. At high temperature, the acoustic phonon displacement \((u^2)_A \propto T\), whereas in the low-temperature limit, \((u^2)_A \propto T^2\). For the optical phonons, the average displacement can be written as

\[
(u^2)_O = \frac{\alpha_5}{e^{\hbar \omega_D / k_B T} - 1}.
\]

where \(\omega_D\) is the frequency of the optical phonon. We neglect the dispersion of optical phonons here. Generally, the contribution of the optical phonon could be significant only at high temperature [54]. Although \(\alpha_4\) and \(\alpha_5\) can be calculated directly using the parameters of bulk materials, the approximations made during the derivations of equations (11) and (12) can introduce some errors to the energy gap of semiconductors at finite temperature. To overcome this problem, we treat \(\alpha_4\) and \(\alpha_5\) as fitting parameters, which are fitted to the temperature dependent band structures in combination with the zero-temperature empirical pseudopotentials. Therefore, the dynamical Debye–Waller factors might be different from the real physical Debye–Waller factors of the system.

To determine the temperature dependent pseudopotential, we first determine the pseudopotential parameters \(\alpha_0 - \alpha_3\) and \(\gamma\) at zero temperature by fitting them to the electronic structures of bulk materials, including the effective mass, and energies of the high symmetry \(\Gamma\), X and L points, etc. The target values and fitted values for GaAs and InAs are compared in table 1, and are in good agreement. The parameters \(\alpha_0 - \alpha_3\) and \(\gamma\) are presented in table 2. With these parameters at hand, we then determine the values of \(\alpha_4\) and \(\alpha_5\) by fitting them to the temperature dependent energy gap of bulk materials, which can be described well by the empirical Varshni formula [56, 57],

\[
\Delta E_g(T) = \frac{c_1 T^2}{T + c_2},
\]

where \(c_1\) and \(c_2\) are the Varshni parameters. For GaAs, \(c_1 = 0.5405\) meV K\(^{-1}\) and \(c_2 = 204\) K, and for InAs, \(c_1 = 0.276\) meV K\(^{-1}\) and \(c_2 = 93\) K [56]. The fitted parameters for \(\alpha_4\) and \(\alpha_5\) are summarized in table 3.

We apply the temperature dependent pseudopotential theory to the self-assembled QDs. We consider InGaAs QDs embedded in the centre of a 60 \(\times\) 60 \(\times\) 60 GaAs 8-atom unit cell. A periodic boundary condition is used to obtain the single-particle energy levels. The single-particle Hamiltonian (1) can be solved by expanding the wavefunctions into a linear combination of Bloch bands (LCBB) [22],

\[
\psi_i = \sum_{n, k, \lambda} c_{n, k, \lambda, i} \psi_{n, k, \lambda, T},
\]

where \(\psi_{\lambda, i} = \text{the bulk Bloch bands with orbital } n \text{ and wavevector } \lambda \text{ close to } \Gamma \text{ point at finite temperature } T\), and \(\lambda = (\text{InAs, GaAs})\). The experimental lattice constants for InAs and GaAs at a given temperature [55] are given as input to construct the Bloch basis. At each temperature, we relax the dot + matrix structure using the VFF method to get the atomic position \(R_{n, a}(T)\). The VFF parameters at a given temperature can be obtained from the temperature dependent elastic constants of InAs and GaAs [58, 59]. We find that including the temperature dependence of the VFF parameters (except the bond lengths) does not affect the results much.

Due to the spatial confinement, the carriers in the QDs have strong Coulomb interactions. The many-particle Hamiltonian reads as

\[
H = \sum_i \epsilon_i \psi_i^\dagger \psi_i + \frac{1}{2} \sum_{ijkl} \Gamma^{i\ell}_{j\ell'} \psi_i^\dagger \psi_j^\dagger \psi_{j'} \psi_{i'},
\]

where \(\psi_i = c_i \psi_i^0(T)\) is the field operator corresponding single-particle energy \(\epsilon_i\); \(\Gamma^{i\ell}_{j\ell'}\) are the Coulomb integrals,

\[
\Gamma^{i\ell}_{j\ell'} = \oint dr dr' \frac{\psi_{\ell'}^+ (r) \psi_{\ell'}^0 (r') \psi_i^0 (r)}{\epsilon (r - r') + |r - r'|}.
\]

Here, \(\epsilon (r - r')\) is the screened dielectric function [60]. The many-particle Hamiltonian is solved using a configuration interaction method [61], where the many-particle wavefunctions are expanded on the Slater determinants constructed from the 12 electron levels and 12 hole levels at given temperatures, which converge the results very well. This method has been successfully applied to studying the electronic and optical properties of InAs/GaAs QDs and the obtained results are in very good agreement with the experimental observations [26, 28, 29, 52].
### Table 2. Fitted pseudopotential parameters for InAs/GaAs in equations (2) and (4). A plane-wave cut-off of 5 Ry is used.

| Parameters | Ga (GaAs) | As (GaAs) | In (InAs) | As (InAs) |
|------------|-----------|-----------|-----------|-----------|
| $\alpha_0$ | 476 845.70| 11.9753   | 771.3695  | 26.8882   |
| $\alpha_1$ | 1.9102    | 3.0181    | 1.6443    | 2.9716    |
| $\alpha_2$ | 22 909.50 | 1.1098    | 18.1342   | 1.2437    |
| $\alpha_3$ | 0.1900    | 0.2453    | 0.3940    | 0.4276    |
| $\gamma_0$ | 2.5215    | 0.0       | 2.1531    | 0.0       |
| $\gamma_{\alpha}$ | 0.1035   | 0.0976    | 0.5973    | 0.0976    |

### Table 3. Debye temperatures [55], the optical phonon energies and the fitted $\alpha_4$, $\alpha_5$ parameters for GaAs and InAs.

| Bulk     | $\theta_D$ (K) | $\omega_0$ (meV) | $\alpha_4$ | $\alpha_5$ | $\alpha_4$ | $\alpha_5$ |
|----------|-----------------|------------------|-------------|-------------|-------------|-------------|
| GaAs     | 344             | 35.36            | 0.3024      | 0.0786      | 0.0128      | 0.0084      |
| InAs     | 247             | 29.6             | 0.1014      | 0.0984      | 0.0130      | 0.0084      |

### 3. TDEPM for bulk materials

We first test our method for bulk materials. Figure 1 depicts typical band structures of GaAs and InAs at $T = 0$, 150, 300 K. The overall band structures are quite similar to those at zero temperature even at rather high temperature (300 K). However, the energies of high-symmetry $k$-points $\Gamma$, $X$, and $L$ have a different response to the temperature. In principle, all the energies of these $k$-points should be taken as the target values to determine the values of $\alpha_4$ and $\alpha_5$. Unfortunately, the experimental data of the energies of these $k$-points at finite temperature are not available, therefore, tentatively, we fit the potentials only to the temperature dependent energy gaps at the $\Gamma$ point. The potentials can be improved by fitting to the energies of more $k$-points in the future.

We present in figure 2 the change of energy gap $\Delta E_g$ as a function of temperature for GaAs. The filled circles are the data recommended by [56], whereas the solid line is calculated from TDEPM. The fitting error is less than 0.2 meV in the whole temperature range. The dashed line is the change of energy gap of GaAs taking into account only lattice vibration, whereas the dotted line is the result with only lattice expansion. As we see, to accurately describe the red shift of the band gap with respect to temperature, both the lattice expansion and lattice vibration have to be taken into account in the theory. These results agree with the results obtained from the temperature dependent tight-binding method by Pour et al [62]. Similar features are also found for InAs using the parameters given in table 3.

The conduction band offset ($\Delta E_c$) and valence band offset ($\Delta E_v$) between InAs and GaAs, defined as

$$\Delta E_c = E^{\text{CBM}}_{\Gamma} \text{(GaAs)} - E^{\text{CBM}}_{\Gamma} \text{(InAs)},$$

$$\Delta E_v = E^{\text{VBM}}_{\Gamma} \text{(InAs)} - E^{\text{VBM}}_{\Gamma} \text{(GaAs)},$$

are very important to the electronic structures of the InAs/GaAs heterostructures, because they are important for the confinement of electron and hole in InAs/GaAs QDs. We show the change of CBM and VBM of InAs and GaAs with temperature in figure 3(a), and the temperature dependent band offsets between InAs and GaAs in figure 3(b). We find:

(i) The CBM and VBM of GaAs change much more than their counterparts in InAs.
(ii) The VBM generally changes much more than the CBM. At high temperature ($T > 100$ K), CBM and VBM change approximately linearly with respect to temperature. The changes of the band offsets with respect to the temperature
Figure 2. The red shift of band gap as a function of temperature for GaAs. The filled circles represent the data recommended by [56]. The dashed line is the result calculated from TDEPM with only lattice vibration whereas the dotted line is the result with only lattice expansion. The solid line is from TDEPM taking account of both lattice vibration and lattice expansion.

Figure 3. (a) Changes of CBM and VBM as functions of temperature for InAs and GaAs bulk materials. (b) The valence band offset and the conduction band offset (inset) between InAs and GaAs as functions of temperature.

Table 4. The alloy composition and size of the lens-shaped In$_x$Ga$_{1-x}$As/GaAs QDs used in this work.

| QD  | $x$  | Base (nm) | Height (nm) |
|-----|------|-----------|-------------|
| QD-A| 1.0  | 25        | 3.5         |
| QD-B| 0.6  | 25        | 3.5         |
| QD-C| 0.7  | 25        | 3.5         |
| QD-D| 0.8  | 25        | 3.5         |
| QD-E| 1.0  | 25        | 5.5         |
| QD-F| 0.6  | 25        | 5.5         |
| QD-G| 0.7  | 25        | 5.5         |
| QD-H| 0.8  | 25        | 5.5         |
| QD-I| 0.6  | 20        | 6.0         |

4. TDEPM for InAs/GaAs QDs

In section 3, we studied the temperature dependent electronic structures of bulk InAs and GaAs. The band offsets between InAs and GaAs are greatly modified due to the temperature effects and there is a type-I to type-II transition in the hypothetically unstrained InAs/GaAs heterostructure. The change of band offsets will significantly change the corresponding electronic and optical properties in QDs. However, the temperature dependent properties are more complicated in QDs because of the strain effects. In this section, we investigate the temperature dependent electronic and optical properties of InAs/GaAs QDS using TDEPM. We study QDs with different sizes and alloy compositions. The alloy compositions of selected lens-shaped QDs are presented in table 4. In most of the cases, we use QD-A to illustrate the main physics. The results of other QDs will also be presented for comparison.

4.1. Temperature dependent band offset

We first investigate the strained band offsets in InAs/GaAs QDs, which is crucial for the electronic and optical properties of QDs. In previous works, [63, 64] the Bir–Pikus model is used to obtain the strain-modified band profiles. However, the temperature dependent parameters for the Bir–Pikus model are generally unavailable. Therefore, we calculate the band profiles directly using the TDEPM. After the lattice relaxations for the dot system, we construct the 8-atom unit cell according to the local strain, and then calculate the
band structures using the TDEPM. Typical band offsets in InAs/GaAs dots along the [100] direction at $T = 150$ K are compared to those of zero temperature in figure 4(a). We see that the overall profiles of the heavy hole (HH) and light hole (LH) and spin–orbit (SO) bands are still quite similar at the two temperatures. The SO band is lower than the HH and LH by about 400 meV in the matrix and is greatly enhanced in the dot materials. The degeneracy of the HH and LH bands is lifted because of the biaxial strain [63, 65]. The strained band offsets of CBM and VBM in the centre of the InAs/GaAs QDs are presented in figure 4(b) in the temperature range of 0–300 K. For electrons, the confinement is enhanced with increasing temperature, whereas for holes, the confinement decreases from 320 to 180 meV. However, unlike the bulk materials, even at high temperature, $\Delta E_v$ is always positive, indicating that the hole is always localized in the QDs. The change of the band offsets greatly modifies the electronic and optical properties of QDs, as shall be discussed below.

4.2. Temperature dependent single particle levels and wavefunctions

The evolution of single particle energy levels as functions of temperature is illustrated in figure 5. We show the results for QD-A here. Similar features are also found for all other QDs. We show all confined electron states, and the highest 20 hole states. Because of the enhancement of confinement potential for electrons, more states are confined in the dots with increasing temperature. The labels of $e_i$($h_i$) represent the energy levels of electrons (holes) in ascending (descending) order. One can also use angular momentum $s$, $p$, $d$, etc to label the wavefunctions. For instance, the states $e_0$ and $h_0$ can be labelled as $s$ and the $e_{1,2}$ ($h_{1,2}$) states are usually labelled by $p_{1,2}$, etc.

The $s$–$p$ energy level spacing is shown in figure 6, which is defined as

$$\delta \epsilon_{sp} = \left| \frac{\epsilon_{p_1} + \epsilon_{p_2}}{2} - \epsilon_s \right|$$

for both electrons and holes. Because of the increase of confinement potential, the electron $s$–$p$ level spacing increases
Figure 6. The single-particle s–p level energy spacings as functions of temperature for electrons and holes in the InAs/GaAs QDs.

Figure 7. The single particle p-orbit energy splittings as functions of temperature for electrons and holes in InAs/GaAs QDs.

with increasing temperature. In contrast, for holes, the energy level spacing decreases with increasing temperature due to the decrease of the hole confinement potential. For QD-A, we find that the level spacing of electrons increases from 64 to 70 meV when the temperature increases from 0 to 300 K. For holes, the energy difference decreases from 11 to about 1 meV. The change of level spacings in QDs may be measured from PL emission spectra.

The p-orbit splitting is another important quantity for the single particle levels, which is defined as:

$$\delta \epsilon_{pp} = |\epsilon_{p1} - \epsilon_{p2}|.$$

If the QDs have $C_{4v}$ or $T_d$ symmetry, the p-orbit splitting is exactly zero. However, for real QDs, the highest symmetry is $C_{2v}$, and in alloyed QDs, the symmetry is $C_1$, the splitting is nonzero. The results of the p-orbit splitting are presented in figure 7 for different types of QDs. For QD-A and QD-E, the electron p-orbit splittings are almost independent of temperature, whereas for other two types of QDs the p-orbit splittings slightly increase with increasing temperature. The results for holes are very different from those for electrons, as shown in figure 7(b). Because the hole level spacings are very small and the anti-crossing between the hole levels may occur when increasing the temperature, the p-level splittings are not monotonic functions of the temperature. At high temperature, the p-level spacing may even exceed the s–p level spacing, which will never happen for electrons. The p-orbit splitting can be measured experimentally via pump-probe spectroscopy [66, 67].

We also calculate the single-particle energy levels including the first- and second-order piezoelectric effects [68]. We find that the first-order piezoelectricity has considerable effects on the electron/hole single particle energies. However, the second-order piezoelectricity tends to compensate the first-order effects, and the overall effects are small. This can be seen in figure 8, where we compare the p-orbit splitting without piezoelectricity, with first-order and with both first- and second-order piezoelectricity as functions of temperature.

The change of confinement potentials may also change the shapes of the wavefunctions. We present the squared envelope wavefunctions of electrons and holes at $T = 0$, 100 and 300 K in figure 9 for QD-A. The number in the lower
right corner of each small panel represents the percentage of the density confined in the QDs. For $e_0, e_1, e_2$, we find that the confined densities increase by about 1%–2%, whereas for the higher states, the confined densities may increase by about 4%–5%. Although the electron squared wavefunctions confined in QDs slightly increase, their overall shapes hardly change. In contrast, for holes, the confined densities reduce dramatically when the temperature increases. For instance, the confined density decreases from 88.8% to 52.4% for $h_0$ when the temperature increases from 0 to 300 K. For $h_5$, the confined density decreases from 76.8% to 44.7%. The shapes of the envelope functions for holes also change dramatically. For instance, the $h_0$ state is Gaussian-like at low temperature, but at high temperature there is a node at the centre of the wavefunction. This change of the wavefunction is due to the enhancement of the interfacial effect in the QDs, because the confinement is very small for holes at high temperature. At low temperature only the tall QDs have such interfacial hole states [63, 64]. The change of the wavefunctions with respect to temperature can be measured experimentally using magnetotunneling spectroscopy [69, 70].

Figure 9. The squared envelope wavefunctions of the confined electron and hole states at $T = 0, 100$ and 300 K. The number in the lower right corner of each small panel represents the percentage of the state densities confined in the QDs.

4.3. Temperature dependent PL emission spectrum

In this section, we investigate the temperature dependence of the optical spectra of InAs/GaAs QDs. The PL intensity of exciton $\chi$ is calculated from transition dipole matrix elements between the initial and final states,

$$I^{(\chi)}(\omega, T; \chi) = \sum_{if} |M^{(\chi)}_{if}(\omega)|^2 P_i(T; \chi) \delta(\omega - \omega_{if}(\chi)).$$  (19)

Here $P_i(T; \chi)$ is the occupation number of the initial state $|\Psi_i\rangle$. The transition dipole matrix element $M^{(\chi)}_{if}$ between the initial state $|\Psi_i\rangle$ and final state $|\Psi_f\rangle$ is [71]

$$M^{(\chi)}_{if}(\chi) = \langle \Psi_f(\chi) | \hat{e} \cdot \mathbf{p} | \Psi_i(\chi) \rangle,$$  (20)

where $\hat{e}$ is the polarization vector of the radial field and $\mathbf{p}$ is the dipole momentum. The optical spectra of single InAs/GaAs QD have been measured at low temperature [10–12, 14, 15, 39]. The highest measuring temperature as far as we know is up to 100 K, performed by Ortner et al [39]. At higher temperature, the signal to noise ratio may become very low and the single QD emission is usually hard to detect. However, for QDs ensemble, the emissions from QDs can be resolved even at room temperature [72]. Therefore in this work, we study the optical spectra of QDs up to 300 K. It has been observed that the PL intensities drop dramatically above 200 K, due to holes tunnelling out the QDs [72]. This is consistent with our results that the valence band offsets of InAs/GaAs QDs decrease with increasing temperature, and therefore holes may tunnel out of dots more easily. Adding
Al into the surrounding matrix will significantly increase the valence band offsets, and therefore helps the PL to maintain its intensity up towards room temperature [72].

Figure 10 depicts the normalized PL emission spectra of QD-A from 0 to 300 K. We assume that all the initial states are occupied with equal probability. The energy difference between S and P shell emission can be approximated by the sum of the s–p single-particle energy level spacings of electrons and holes, i.e.

$$\Delta E_{SP} \approx \delta \epsilon_e^{sp} + \delta \epsilon_h^{sp}.$$  

Although the change of level spacing in figure 6 cannot be directly measured from PL emission spectra, the sum of them can be measured. The energy difference between S and P shells for QD-A is 80 meV at zero temperature, and reduces to 72.5 meV at 300 K.

Figure 11 depicts the temperature dependent energies of the primary exciton, biexciton and charged excitons for dots A, C, E, G. All the energies of exciton complexes show red shifts as the temperature increases. For all dots, we find that the red shifts of the exciton complexes emission lines can be fitted very well using the Varshni formula, with the fitting errors generally less than 1 meV. The fitting errors are slightly larger than that for the bulk materials (<0.2 meV), but much smaller than the total red shift of the emission line, which is about 100 meV. This suggests that the red shift of the emission energies is proportional to $T^2$ at low temperature. The values of the Varshni parameters are summarized in table 5. These parameters are very different from those of bulk InAs, GaAs, and also vary from dot to dot.

![Figure 10. Temperature dependent PL emission spectra of QD-A. The emission lines are broadened by 0.5 meV with a Lorentz function. The intensity of the spectra is normalized by the occupation number of the initial states.](image1)

![Figure 11. The red shifts of emission lines of (a) X, (b) XX, and (c) X⁻ and (d) X⁺ as functions of temperature. The symbols are the results calculated from TDEPM, whereas the solid lines are the fitted results using the Varshni formula.](image2)
Table 5. Fitted Varshni parameters for different QDs. $E_0$ is the energy at zero temperature in units of eV. The Varshni parameters, $c_1$ is in unit of meV K$^{-1}$ and $c_2$ is in unit of K. The geometry and alloy composition of the QDs are listed in table 4.

| QD | $E_0$ (meV) | $c_1$ (meV K$^{-1}$) | $c_2$ (K) | $E_0$ (meV) | $c_1$ (meV K$^{-1}$) | $c_2$ (K) | $E_0$ (meV) | $c_1$ (meV K$^{-1}$) | $c_2$ (K) | $E_0$ (meV) | $c_1$ (meV K$^{-1}$) | $c_2$ (K) |
|----|-------------|----------------------|----------|-------------|----------------------|----------|-------------|----------------------|----------|-------------|----------------------|----------|
| A  | 1.006       | 0.486                | 151      | 1.004       | 0.458                | 138      | 1.005       | 0.445                | 140      | 1.003       | 0.505                | 156      |
| B  | 1.260       | 0.458                | 232      | 1.259       | 0.450                | 218      | 1.257       | 0.446                | 220      | 1.261       | 0.461                | 218      |
| C  | 1.202       | 0.442                | 188      | 1.201       | 0.436                | 181      | 1.199       | 0.427                | 182      | 1.202       | 0.449                | 184      |
| D  | 1.111       | 0.436                | 157      | 1.139       | 0.428                | 151      | 1.139       | 0.406                | 141      | 1.140       | 0.450                | 162      |
| E  | 0.971       | 0.717                | 181      | 0.973       | 0.711                | 193      | 0.977       | 0.715                | 195      | 0.966       | 0.718                | 182      |
| F  | 1.232       | 0.496                | 188      | 1.231       | 0.485                | 183      | 1.231       | 0.484                | 190      | 1.231       | 0.499                | 184      |
| G  | 1.172       | 0.502                | 166      | 1.170       | 0.486                | 159      | 1.172       | 0.480                | 160      | 1.169       | 0.511                | 167      |
| H  | 1.109       | 0.540                | 164      | 1.108       | 0.515                | 155      | 1.110       | 0.506                | 153      | 1.105       | 0.542                | 161      |
| I  | 1.244       | 0.444                | 146      | 1.242       | 0.437                | 144      | 1.243       | 0.431                | 148      | 1.242       | 0.458                | 147      |

QDs have been investigated by Ortner et al [39] from $T = 0$ K to $T = 100$ K. In figure 12(a), we compare our theoretical results (QD-B, QD-F, QD-I) with the available experimental data [39] for the In$_{0.6}$Ga$_{0.4}$As/GaAs QDs. The red shift of the emission line of the exciton agrees well with QD-B (less than 1 meV). In the inset of figure 12, we present the exciton energies as a functions of temperature, which also show excellent agreement. The red shift of exciton energy in [39] can be described well by the Varshni formula using $c_1 = 0.4419$ meV K$^{-1}$ and $c_2 = 221.77$ K, with an error less than 1 meV. This is also in a good agreement with the theoretical values for QD-B given in table 5. It seems odd that QD-I has the most similar geometry to the experimental QDs, and yet the agreement is less well. However, note that the geometry of the experimental dot was measured before capping and it is well known that the dot geometry change dramatically after capping. Therefore, one could not make a direct comparison.

In figure 12(b), we compare the theoretical results of QD-A and QD-C with the experimental results for a QDs ensemble measured by Yeo et al [41] where the peak energy of the S-shell is chosen as the exciton emission lines at each temperature. For QDs ensemble, the S-shell can be resolved well even at room temperature. We see that the red shifts of QDs ensemble $A_2$ and $A_3$ agree well with the theoretical prediction of QD-A. Moreover, the exciton energy of $A_2$ and $A_3$ at zero temperature is around 1.02–1.03 eV, also agree well with the exciton energy of QD-A listed in table 5.

We note that some experiments [73] suggest that the red shift of the exciton energies proportional to $T^4$ [74, 75], instead of $T^2$ as suggested by TDEPM at very low temperature ($T < 10$ K). The discrepancy may come from two reasons. First, it is because we do not have highly accurate temperature dependent band gaps to fit at very low temperature at the present stage. It may also partly come from the approximations we made in deriving the temperature dependent pseudopotentials. Nevertheless, in this temperature range, the change of exciton energies is very small, and the difference between the experimental values and the theory is very subtle.

We also calculate the FSS and the polarization of the mono-exciton at finite temperatures. We find that the FSS and the polarization are generally insensitive to the temperature. For example, the change of FSS is usually less than 1 µeV, and the change of polarization is less than 5° when increasing the temperature from 0 to 100 K. This result suggests that the FSS cannot been tuned using temperature effect.
5. Summary and conclusions

We develop a temperature dependent empirical pseudopotential theory, and apply it to study the electronic and optical properties of self-assembled InAs/GaAs quantum dots (QDs) at finite temperature. The theory takes the effects of both lattice expansion and lattice vibration into account. The pseudopotentials correctly reproduce the temperature dependent band gap of bulk III–V semiconductors such as InAs, and GaAs, etc. We find that for the unstrained InAs/GaAs heterostructure, the conduction band offset increases whereas the valence band offsets decrease with increasing temperature, and there is a type-I to type-II transition at approximately 135 K. Yet, for InAs/GaAs QDs, the holes are still localized in the QDs even at room temperature because the large lattice mismatch between InAs and GaAs greatly enhances the valence band offset. The single particle energy levels in the QDs show a strong temperature dependence due to the change of confinement potentials. As a consequence, more electron states are confined at higher temperature. Because of the changes of the band offsets, the electron wavefunctions confined in QDs increase by about 1%–5%, whereas the hole wavefunctions decrease by about 30%–40% when the temperature increases from 0 to 300 K. The calculated recombination energies of exciton, biexciton and charged excitons show red shifts with increasing temperature. We expect the theory can facilitate the future device applications of QDs.

Acknowledgments

LH acknowledges the support from the Chinese National Fundamental Research Programme 2011CB921200, National Natural Science Funds for Distinguished Young Scholars and the Fundamental Research Funds for the Central Universities No. WK2470000006.

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