Mathematical modeling of semiconductor quantum dots based on the nonparabolic effective-mass approximation

Abstract
Within the effective mass and nonparabolic band theory, a general framework of mathematical models and numerical methods is developed for theoretical studies of semiconductor quantum dots. It includes single-electron models and many-electron models of Hartree-Fock, configuration interaction, and current-spin density functional theory approaches. These models result in nonlinear eigenvalue problems from a suitable discretization. Cubic and quintic Jacobi-Davidson methods of block or nonblock version are then presented for calculating the wanted eigenvalues that are clustered in the interior of the spectrum and may have small gaps and degeneracy. These are challenging issues arising from modeling a great variety of semiconductor nanostructures fabricated by advanced technology in semiconductor industry and science. Generic algorithms for many-electron simulations under this framework are also provided. Numerical results obtained within this framework are summarized to three eminent aspects, namely, accuracy of models, physical novelty, and effectivity of nonlinear eigensolvers. Concerning numerical accuracy, important details related to experimental data are also addressed.

Keywords
Quantum dots • electronic structure • quantum models • nonlinear eigenproblems • Jacobi-Davidson method.

PACS: 73.21.La, 73.23.Hk, 78.67.Hc
MSC: 65N06, 65F15
© Versita sp. z o.o.

1. Introduction

Semiconductor quantum dots (QDs) are man-made nanostructures that typically consist of $10^3$ to $10^9$ atoms with equivalent number of electrons [52]. They are used to confine free electrons ranging from single to several hundreds in all three space dimensions and hence regarded as artificial atoms for their quantum analogies to natural atoms but with controllable spectrum of energies for adding or removing electrons [2, 44, 52]. Rapid and far-reaching advances in understanding their electronic structure [70], transport phenomena [85], optical properties and quantum spin properties [32] etc. have been achieved significantly since the term 'quantum dot' was coined in 1988 [69]. Researchers have studied QDs in a wide range of applications from transistors [26], lasers [8], solar cells [50], biological imaging [40], medical diagnostics [60], to quantum computing [56].

On the other hand, a hierarchy of theories in solid state physics from Schrödinger, Bloch, Kronig-Penny, Wannier, Hartree–Fock, Slater, Thomas–Fermi, to Kohn–Sham have been applied to develop a great deal of mathematical models.
from tight-binding [18, 46, 47], configuration interaction [12, 13, 21, 59, 67, 72, 81, 82], density functional theory (DFT) [41, 55, 75, 84], multiband [64, 68, 79], to one-band [4, 15, 22, 23, 29, 34, 51, 54, 74, 88, 89, 95] to study QD systems. No attempt is made in this article to review or compare vast results published in the literature of QD modeling. For comprehensive reviews in this aspect, we refer to [1, 5, 9, 10, 46, 47, 58, 62, 70, 91, 96] for more references.

We survey instead a class of one-band envelope-function models that are based on the nonparabolic dispersion and effective-mass approximation. These models are formulated in a framework setting for single-electron and many-electron QD simulations. Hartree-Fock (HF), configuration interaction (CI), and Kohn-Sham (KS) theories are used to develop the many-electron models. It is obvious that many-body QD simulations using HF, CI, or KS approach based on a full scale of multiband structures are much more complicated in implementation and computationally expensive than those of one-band structures.

Generic algorithms concerning numerical solution of eigenvalue problems, calculation of Coulomb integrals, and simulation procedures are also provided. The most salient part of this framework is a particular type of nonlinear eigenvalue problems for which the wanted eigenvalues are clustered in the interior of the spectrum that in turn lies in the complex plane. Moreover, the eigenvalues may have very small gaps or even be degenerate. These issues are in fact major challenges in the development of state-of-the-art eigensolvers for modeling large scale nano-systems [87]. Nonlinear Jacobi-Davidson methods of both nonblock and block type are presented here in template style for tackling these problems and for motivating future studies. There are many other important issues such as linear scaling of KS or HF calculations [28], multiscale and multiphysics modeling [58, 62], parallel implementation [46], and various diagonalization methods for many-body simulations [53] etc. that will not be addressed here.

Numerical results obtained by our group within this framework are summarized into three examples in terms of accuracy of models [13, 34, 55], physical novelty [55, 88, 89, 95], and effectiveness of nonlinear eigensolvers [36–38, 55, 92]. The examples together with important details related to experimental data provide a synthetic view on how to perform many-electron QD simulations with advanced nonlinear eigensolvers.

Considering fundamental impacts on nanoscale science, engineering, and technology by powerful and rapidly advancing simulation tools that go hand in hand with experimental developments, it is worthwhile to mention research software packages such as nextnano [9], NEMO [46, 47], and QUANTUM ESPRESSO [27] to name just a few that are available to public access. All these packages are more general than ours in application, modeling, numerical, and complexity aspects. Nevertheless, our eigensolvers, an essential kernel of QD simulators, are rather effective for certain QD models and may be useful to the QD software development community. We shall integrate our solvers into a more user friendly package for the community in the future as a supplemental material to the present paper.

The remaining part of the paper is organized as follows. We begin with single-electron models in Section 2 on which the general framework is built. Many-electron models using HF, CI, and DFT approaches are then formulated in Section 3. Numerical methods for nonlinear eigenproblems and simulation algorithms are presented in Section 4 where physical and mathematical results are also given. We then make some concluding remarks in Section 5.

2. Single-Electron Models

In a bulk crystal of semiconductor material, the Hamiltonian for a noninteracting electron moving in a periodic potential \( V(r) \) is

\[
H_0 = -\frac{\hbar^2}{2m_0} \nabla^2 + V,
\]

(1)

where \( \hbar \) is the reduced Planck constant, \( m_0 \) is the free electron mass, and \( \nabla \) stands for the spatial gradient operator. For a given value of the crystal momentum \( p = \hbar k = -i\hbar \nabla \) where \( k \) is the Bloch wave vector, there are many discrete energies \( \varepsilon_{nk} \) labeled by the band index \( n \) that an electron may have. For many electronic properties of semiconductor, we are only interested in a small \( k = |k| \) range around some extrema of the band structure of \( \varepsilon_{nk} \) instead of the whole Brillouin zone. By the Bloch theory [5], the original Hamiltonian (1) can be transformed to the \( k \cdot p \) Hamiltonian

\[
H_{kp} = -\frac{\hbar^2}{2m_0} \nabla^2 + \frac{\hbar k \cdot p}{m_0} + \frac{\hbar^2 k^2}{2m_0} + V
\]

(2)

that is defined in the smaller first Brillouin zone. By composing multiple bands to one band, we can further simplify the Hamiltonian to an effective-mass approximation

\[
H_e = -\frac{\hbar^2}{2m^*} \nabla^2 + V_e(r),
\]

(3)
where the effective mass is usually assumed to satisfy the parabolic dispersion relation

$$\varepsilon_k = \hbar^2 k^2 / 2m^*. \tag{4}$$

For a given $k$, the lighter electrons in effective mass $m^*$ would have larger kinetic energy rendering that the energy band gap $E_g$ and the spin–orbit split energy $\Delta$ cannot be neglected in the dispersion relation. Kane [43] analyzed the $\varepsilon_n k$ relation beyond the quadratic approximation and presented a nonparabolic dispersion theory that includes these characteristic energies intrinsic to semiconductors. By this theory, the effective mass of electrons in an InAs QD embedded in the GaAs matrix, for example, can be defined more accurately as [17]

$$\frac{1}{m(r, \varepsilon)} = \frac{\hbar^2}{2m^*} \left[ \frac{2}{\varepsilon + E_g(r)} - \frac{1}{\varepsilon + E_g(r) - V_c(r) + \Delta(r)} \right]. \tag{5}$$

where the confinement potential

$$V_c(r) = \begin{cases} 0 & \text{in } \Omega_{\text{InAs}} \\ V_0 & \text{in } \Omega_{\text{GaAs}} \end{cases} \tag{6}$$

is induced by a discontinuity of conduction-band edges of InAs and GaAs. Note that the effective mass of an electron depends not only on its spatial location $r$ but also on its energy $\varepsilon$. Here the spatial domain of the QD model is denoted by $\Omega = \Omega_{\text{InAs}} \cup \Omega_{\text{GaAs}} \subset \mathbb{R}^3$. A scanning tunneling microscope image of an InAs QD on GaAs presented in [39] is replicated in Fig. 1 as an illustration of a typical simulation geometry of a QD model.

It should be noted that the electronic dispersion relations of narrow gap materials like InAs calculated by the Kane model coincide remarkably well with that by the empirical tight-binding method [5]. Compared with the parabolic band approximation, significant effects due to nonparabolicity have been shown in both experimental and theoretical studies on various physical properties of semiconductor heterostructures [11, 15, 17, 23, 29, 34, 45, 51, 54, 55, 61] [68, 73, 74, 84, 88, 89, 94, 97]. We also remark that the confinement potential should be modified by a cumulative potential of band gap deformations due to strain and piezoelectric effects inside a QD for more realistic modeling.

One of interesting applications of QDs is to exploit their unique electronic, magnetic, and optical properties for the development of optoelectronic devices as a promising candidate in optical quantum information technology [12]. For this kind of magneto–optical studies, the Hamiltonian should include effects of an external magnetic field $B$ and the spin–orbit interaction and assumes the following form

$$H_i = -\hbar \left( \frac{1}{2m(r, \varepsilon)} \right) \nabla + U(r) \tag{7}$$

$$\nabla = -ih \nabla + eA(r), U(r) = V_c(r) + V_B(r), \quad V_B(r) = \frac{\mu_B}{2} g(r, \varepsilon) \sigma \cdot B,$$

$$g(r, \varepsilon) = 2 \left[ 1 - \frac{m_0}{m(r, \varepsilon)} \left( \frac{\Delta(r)}{\varepsilon + E_g(r)} + 2\Delta(r) \right) \right].$$
Mathematical modeling of semiconductor quantum dots

where $\Pi$ denotes the electron momentum operator, $e$ is the proton charge, $A(r)$ is the vector potential induced by the magnetic field $B$, $\mu_B$ is the Bohr magneton, $g(r,\epsilon)$ is the Landé factor, and $\sigma$ denotes the Pauli spin matrices.

The single-electron QD model problem under consideration is hence to seek the wave function $\phi(r)$ and energy $\epsilon$ satisfying the effective-mass Schrödinger equation

$$H_0 \phi = \epsilon \phi$$

(8)

and the interface conditions

$$[\phi] = 0 \quad \text{and} \quad \frac{1}{m(r,\epsilon)} \nabla \phi \cdot n = 0,$$

(9)

where $[\phi]$ denotes the jump of $\phi$ across the interface $\Gamma$ between two materials, i.e. $\Gamma = \overline{\Omega_{\text{left}}} \cap \overline{\Omega_{\text{right}}}$, and $n$ is an outward normal unit vector on $\Gamma$. Suitable boundary conditions of the Dirichlet type for $\phi$ should also be prescribed on the boundary $\partial \Omega$ of $\Omega$.

3. Many-Electron Models

Our discussion on many-electron QD models is strictly within the above effective-mass approximation theory which allows us to model conduction electrons and holes in a QD as a decoupled interacting system from their background environment that may consist of millions of atoms in crystalline structure. To describe a system of $N$ electrons in a QD under the influence of the Coulomb interaction, we write the total Hamiltonian $H$ as a sum of single-particle operators $H_i$ and two-body operators $V_{ij}$ as

$$H = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i<j} V_{ij},$$

(10)

$$H_i = H_i(r_i), \quad V_{ij} = \frac{1}{D(r_i)|r_i - r_j|}, \quad D(r_i) = \frac{4\pi \epsilon_0 \epsilon(r_i)}{e^2},$$

where the single-electron Hamiltonian $H_i(r_i)$ is defined by (7) for the $i$th electron, $\epsilon_0$ is the vacuum permittivity, and $\epsilon(r_i)$ is the dielectric constant of two III-V compounds. For the sake of simplicity in exposition, the mutual interaction between the electrons in the system is taken to be purely Coulombic.

3.1. Hartree-Fock Approach

The Hartree-Fock approach postulates that the many-electron wave function $\Psi$ of $N$ interacting electrons in a QD system can be written as a single Slater determinant

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1,\sigma_1) & \psi_2(r_1,\sigma_1) & \cdots & \psi_N(r_1,\sigma_1) \\ \psi_1(r_2,\sigma_2) & \psi_2(r_2,\sigma_2) & \cdots & \psi_N(r_2,\sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_N,\sigma_N) & \psi_2(r_N,\sigma_N) & \cdots & \psi_N(r_N,\sigma_N) \end{vmatrix}$$

(11)

of spin-orbitals $\psi_i(r,\sigma_j) = \psi_i(r) \chi_i(\sigma_j)$ so that the Pauli principle is fulfilled. Here, $\psi_i(r_j)$ represents the $i$th one-electron wave function (space orbital) occupied by the $j$th electron whose spin state is $\chi_i(\sigma_j) = \delta_{ij}$ or $\delta_{i,1-j}$ where $\delta_{ij}$ is the Kronecker delta of the two integers $k$ and $l$. The spin variable $\sigma_j$ takes a value of either $+1$ for spin-up or $-1$ for spin-down. This antisymmetric representation of the electronic wave function enables us to include quantum mechanical effects of correlation and exchange in the QD system.

Denoting the coordinates $r_j,\sigma_j$ by the shorthand notation $j$, the complete expectation value of the Hamiltonian (10) in an antisymmetrized state (11) is

$$\langle \Psi | H | \Psi \rangle = \sum_i \sum_j \int d\tau_j \psi_i^*(j) \left( \frac{-1}{2m(r_j,\epsilon_j)} \right) \Pi^2 \psi_j(j) + U(r_j) |\psi_j(j)|^2$$

- NanoMNTA · Vol. 1 · 2012 · 58–79-
\[
\sum_{j} \sum_{j', i} \int dr_i dr_j \frac{1}{D(r_i)} \nabla_{r_i} \cdot \left[ \frac{1}{|r_i - r_j|} \right] \left[ \left| \psi_j(i) \right|^2 \left| \psi_j(i) \right|^2 - \psi_j^*(j) \psi_j^*(i) \psi_j(j) \psi_j(i) \right],
\]
(12)

where the energy level \( \epsilon_j \) of the \( j \)th orbital is obtained by solving the Hartree-Fock equation

\[
H \psi_j(r) + J \psi_j(r) + K \psi_j(r) = \epsilon_j \psi_j(r)
\]
(13)

in which the mass \( m(r, \epsilon_j) \) depends on the unknown energy. The Coulomb operator \( J \) and the exchange operator \( K \) are defined as

\[
J \psi_j(r) = \psi_j(r) \sum_i \int dr_i \frac{|\psi_i(r_i)|^2}{D(r_i) |r - r_i|},
\]
(14)

\[
K \psi_j(r) = -\sum_i \delta_{i,j} \psi_i(r) \int dr_i \frac{\psi_i^*(r_i) \psi_j(r_i)}{D(r_i) |r - r_i|}.
\]
(15)

Note that the integration is taken over the bounded domain \( \Omega \).

### 3.2. Configuration Interaction Approach

The configuration interaction is a more accurate theory than the Hartree-Fock theory in which the wave function is expressed as a linear combination of Slater determinants so that the instantaneous Coulomb correlation of electrons is taken into account.

From single-particle picture to many-particle picture for QDs, we follow the theoretical framework developed by Pietiläinen and Chakraborty in [67]. The wave functions \( \phi_i \) of (8) are chosen to form a single-particle basis set

\[
B_i = \{|\phi_i| = |i\rangle : i = 1, 2, \cdots, N_i\}
\]
(16)

with \( N_i \) being the total number of single-particle states undertaken. The larger \( N_i \) the more accurate many-electron wave function can be obtained. However, it is finite since the number of energy levels in a QD is finite due to the confinement potential (6). This is fundamental difference between the present approach and that in [67] where a parabolic confinement of QDs is used and hence their \( N_i \) is theoretically unbounded. Consequently, the number of basis functions (of the associated Laguerre polynomial) required by their approach is of the order of million in implementation. Nevertheless, accuracy of our approach is controlled not only by \( N_i \) but also by the number of grid points used in, for instance, the finite difference approximation of (8).

From this set, a basis \( B_N \) for \( N \) interacting electrons in a QD can be constructed as a direct antisymmetrized product of \( B_i \) of the form

\[
B_N = A \bigotimes_{i=1}^{N} B_i = \{|L_i| : i = 1, 2, \cdots, N_m\},
\]
(17)

where \( A \) denotes the antisymmetrization operator for the Slater determinant as (11) and \( N_m = \binom{N}{N_i} \) the binomial coefficient of \( N_i \) and \( N \). More specifically, the many-electron basis functions \( |L_i\rangle \) are Slater determinants defined as

\[
|L_\ell \rangle = A \left[ |l_\ell_1\rangle \otimes |l_\ell_2\rangle \cdots \otimes |l_\ell_N\rangle \right]

= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{i_1}(r_1) & \phi_{i_2}(r_1) & \cdots & \phi_{i_N}(r_1) \\ \phi_{i_1}(r_2) & \phi_{i_2}(r_2) & \cdots & \phi_{i_N}(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{i_1}(r_N) & \phi_{i_2}(r_N) & \cdots & \phi_{i_N}(r_N) \end{vmatrix}
\]
(18)

in which the spin variable is omitted for simplicity. The states of the interacting system are then expressed by the superposition of the non-interacting states (17) as

\[
|\Psi\rangle = \sum_{i=1}^{N_m} c_i |L_\ell\rangle,
\]
(19)
where the unknown coefficients $c_i$ are sought by minimizing the energy functional

$$\langle \Psi | \hat{H} | \Psi \rangle$$

(20)

with respect to $c_i$ subject to the normalization condition

$$\langle \Psi | \Psi \rangle = 1.$$  

(21)

As an example, we illustrate the above formalism by considering a simple two-electron system as follows:

$$N = 2, N_i = 3, B_1 = \{ | \phi_i \rangle : l = 1, 2, 3 \}, N_m = C_2^3 = \frac{3!}{2!1!} = 3,$$

(22)

$$B_2 = A \bigotimes_{q=1}^2 B_1 = \{ | L_i \rangle : i = 1, 2, 3 \},$$

(23)

$$| L_1 \rangle = | l_1; l_2 \rangle = \frac{1}{\sqrt{2}} \left| \begin{array}{cc} \phi_1 (r_1) & \phi_2 (r_1) \\ \phi_1 (r_2) & \phi_2 (r_2) \end{array} \right|,$$

$$| L_2 \rangle = | l_1; l_3 \rangle = \frac{1}{\sqrt{2}} \left| \begin{array}{cc} \phi_1 (r_1) & \phi_3 (r_1) \\ \phi_1 (r_2) & \phi_3 (r_2) \end{array} \right|,$$

$$| L_3 \rangle = | l_2; l_3 \rangle = \frac{1}{\sqrt{2}} \left| \begin{array}{cc} \phi_2 (r_1) & \phi_3 (r_1) \\ \phi_2 (r_2) & \phi_3 (r_2) \end{array} \right|.$$

(24)

$$| \Psi \rangle = \sum_{j=1}^3 c_j | L_j \rangle.$$  

Using the method of Lagrange multipliers, the minimization of (25) subject to (26) yields

$$\frac{\partial}{\partial c_i} \{ \langle \Psi | \hat{H} | \Psi \rangle - \varepsilon \langle \Psi | \Psi \rangle \} = 0, i = 1, 2, 3,$$

(27)

$$\frac{\partial}{\partial c_i} \langle \Psi | \hat{H} | \Psi \rangle = \int \int dr_1 dr_2 \left( \sum_{j=1}^3 c_j | L_j \rangle \right)^* \hat{H} \left( \sum_{j=1}^3 c_j | L_j \rangle \right),$$

(28)

$$\frac{\partial}{\partial c_i} \varepsilon \langle \Psi | \Psi \rangle = 2 \varepsilon \sum_{j=1}^3 c_j \int \int dr_1 dr_2 | L_j \rangle^* | L_j \rangle,$$

(29)
\[ H_{ij} = \langle L_i | \mathcal{H} | L_j \rangle = \left( L_i | H_1 + H_2 + \frac{1}{2} V_{12} | L_j \right) \],

\[ \langle L_2 | H_1 | L_3 \rangle = \int \int dr_1 dr_2 L_2^* H_1 L_3 \]
\[ = \frac{1}{2} \int \int dr_1 dr_2 [\phi_1^* (r_1) \phi_1^* (r_2) - \phi_1^* (r_2) \phi_1^* (r_1)] H_1 \]
\[ [\phi_2 (r_1) \phi_2 (r_2) - \phi_2 (r_2) \phi_2 (r_1)] \]
\[ = \frac{1}{2} \int \int dr_1 dr_2 [\phi_3^* (r_1) \phi_3^* (r_2) - \phi_3^* (r_2) \phi_3^* (r_1)] \]
\[ [\phi_3 (r_2) H_1 \phi_2 (r_3) - \phi_3 (r_2) H_1 \phi_3 (r_3)] , \]  

\[ \langle L_2 | H_2 | L_3 \rangle = \frac{1}{2} \int \int dr_1 dr_2 [\phi_2^* (r_1) \phi_2^* (r_2) - \phi_2^* (r_2) \phi_2^* (r_1)] \]
\[ [\phi_2 (r_1) H_2 \phi_3 (r_2) - \phi_3 (r_1) H_2 \phi_2 (r_2)] , \]  

\[ \langle L_3 | \frac{1}{2} V_{12} | L_3 \rangle = \frac{1}{4} \int \int dr_1 dr_2 [\phi_1^* (r_1) \phi_1^* (r_2) - \phi_1^* (r_2) \phi_1^* (r_1)] \]
\[ \frac{1}{|r_1 - r_2|} [\phi_2 (r_1) \phi_3 (r_2) - \phi_2 (r_2) \phi_3 (r_1)] , \]

\[ \left[ \begin{array}{ccc}
H_{11} & H_{12} & H_{13} \\
H_{21} & H_{22} & H_{23} \\
H_{31} & H_{32} & H_{33}
\end{array} \right]
\left[ \begin{array}{c}
\epsilon_1 \\
\epsilon_2 \\
\epsilon_3
\end{array} \right] = \epsilon \left[ \begin{array}{c}
\epsilon_1 \\
\epsilon_2 \\
\epsilon_3
\end{array} \right]. \]  

Therefore, the total energy of \( N \) electrons in the QD can be obtained by diagonalizing the linear eigenvalue problem

\[ \sum_{j=1}^{N_e} (H_{ij} - \epsilon \delta_{ij}) \epsilon_j = 0, \]

where the eigenvectors \( \mathbf{c} = [\epsilon_1 \epsilon_2 \cdots \epsilon_{N_e}]^T \) are expansion coefficients and the eigenvalues \( \epsilon \) are corresponding energies of the interacting system. The finite confinement potential leads to a finite number of localized states as well as to energetically higher delocalized states. When the influence of the delocalized states on the discrete QD spectrum is neglected, the eigenvalue problem (35) has a finite dimension and can be solved without further approximations.

There is another more accurate CI approach. Instead of using the single-electron wave functions \( \phi_i \) calculated from (8), we can also use the single-electron Hartree–Fock orbitals \( \psi_i \) obtained from (13) to form the basis set \( B_j \) as (16). It is very expensive in numerical implementation due to the following numerical problems:

(I) We have two nonlinear problems for this approach. The first one is the nonlinear eigenvalue problem originated from the nonparabolic mass \( m(r, \epsilon_j) \) in (13). This problem is the main focus in Section 4, which is also unavoidable for the simpler CI approach. The second nonlinear problem is associated with the nonlinear dependence of the HF orbital \( \psi_i \) on the Coulomb and exchange integrals (14)-(15).

(II) Computation of the Coulomb and exchange integrals is the bottleneck of Hartree–Fock simulations. These integrals are calculated only once for the simpler approach as illustrated by (33) and (34) whereas, for the expensive approach, they are repeatedly evaluated in an iterative and alternating process between solving (13) and updating (14)-(15) until self-consistent wave function and potential are found.
3.3. Density Functional Approach

The density functional theory developed by Hohenberg, Kohn, and Sham [33, 49] is perhaps the most successful quantum mechanical method in reducing the computational complexity to investigate the electronic structure of many-body systems in physics and chemistry within tolerable computer time and accuracy. Vignale and Rasolt [86] extended DFT to the current-spin DFT (CSDFT) by including gauge fields in the energy functional. It has been widely used for modeling QDs in magnetic fields [41, 70, 75].

The crux of DFT is that the electron density of a many-electron system contains almost all essential material properties of the system that otherwise should be calculated from a many-electron wave function. Kohn and Sham proposed using single-electron wave functions to define the electron density. In this formalism, the kinetic energy of electrons can be captured more successfully not only by the density but also by its gradients. In CSDFT, the electron density is decomposed into the spin-up ( \( \sigma = \uparrow \) ) and spin-down ( \( \sigma = \downarrow \) ) components

\[
\rho(\mathbf{r}) = \rho^\uparrow(\mathbf{r}) + \rho^\downarrow(\mathbf{r})
\]

that satisfy the constraint \( \int \rho^\sigma(\mathbf{r})d\mathbf{r} = N^\sigma \) with \( N^\uparrow = (N + 2S)/2 \) and \( N^\downarrow = (N - 2S)/2 \) where \( S \) is the total spin of these \( N \) electrons [70]. Let \( \psi_{i\sigma} \) be the single-electron wave function of an electron occupying the \( j\sigma \) state such that

\[
\rho^\sigma(\mathbf{r}) = \sum_j |\psi_{j\sigma}|^2, \quad \rho^\uparrow(\mathbf{r}) = \sum_j |\psi_{j\uparrow}|^2, \quad \rho^\downarrow(\mathbf{r}) = \sum_j |\psi_{j\downarrow}|^2.
\]

The ground state energy of the system is a variational functional of the density defined as

\[
E(\rho) = T(\rho) + E_B(\rho) + \int \rho(\mathbf{r})\left[V_c(\mathbf{r}) + \frac{1}{2}V_s(\mathbf{r})\right]d\mathbf{r} + E_{XC}(\rho).
\]

Minimization of this functional by varying \( \psi_{i\sigma} = \phi_{i\sigma}(\mathbf{r})\chi_j(\sigma) \) under the above constraint yields the Kohn-Sham equation

\[
\mathcal{H}_{KS}^\sigma \psi_{i\sigma} = \epsilon_{i\sigma} \psi_{i\sigma}, \quad j = 1, \cdots, \lfloor N/2 \rfloor
\]

with the KS Hamiltonian

\[
\mathcal{H}_{KS}^\sigma = -\frac{1}{2m} \left[ \frac{\nabla}{\nabla} \left( \frac{1}{\mathbf{r} - \mathbf{r}'} \right) \right] + V_B(\mathbf{r}) + V_c(\mathbf{r}) + V_s(\mathbf{r}) + V_{XC}(\mathbf{r}),
\]

where

\[
T(\rho) = \sum_{j,\sigma} \left\langle \psi_{j\sigma} \left| \frac{1}{2m(\mathbf{r},\epsilon_{j\sigma})} \right| \psi_{j\sigma} \right\rangle
\]

is the kinetic energy of the electrons,

\[
V_s(\mathbf{r}) = \frac{1}{D(\mathbf{r})} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
\]

is the Hartree potential,

\[
V_{XC}(\mathbf{r}) = \frac{\delta [\rho \epsilon_{XC}(\rho, \gamma)]}{\delta \rho^\sigma} - \frac{j_\rho}{\rho} \cdot A_{XC}
\]

is the exchange-correlation potential, and \( \lceil \cdot \rceil \) is the ceiling function symbol. Here

\[
j_\rho(\mathbf{r}) = -\frac{i\hbar e}{2m} \sum_{j,\sigma} \left[ \psi_{j\sigma}^*(\mathbf{r}) \nabla \psi_{j\sigma}(\mathbf{r}) - \psi_{j\sigma}(\mathbf{r}) \nabla \psi_{j\sigma}^*(\mathbf{r}) \right]
\]
is the paramagnetic current density and

\[ A_{\text{XC}} = \frac{1}{\rho} \left( \frac{\partial}{\partial y} \frac{\delta [\rho \varepsilon_{\text{XC}}(\rho, \zeta)]}{\delta \zeta} - \frac{\partial}{\partial x} \frac{\delta [\rho \varepsilon_{\text{XC}}(\rho, \zeta)]}{\delta \zeta} \right) \]  

(45)

is the exchange-correlation vector potential assuming that the external magnetic field \( \mathbf{B} \) is directed along the \( z \)-axis.

For the exchange-correlation energy functional \( \varepsilon_{\text{XC}} \), we adopt the form developed by Perdew and Wang [65] as

\[ \varepsilon_{\text{XC}}(\rho, \zeta) = \varepsilon_X(r_s, \zeta) + \varepsilon_C(r_s, \zeta) \]  

(46)

with

\[ \varepsilon_X(r_s, \zeta) = -\frac{3}{4\pi r_s} \left[ \frac{9\pi}{4} \right]^{1/3} \left[ \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}}{2} \right], \]  

(47)

\[ \varepsilon_C(r_s, \zeta) = \varepsilon_C(r_s, 0) + \alpha_C(r_s) \frac{f(\zeta)}{\int \rho(0)} (1 - \zeta^4) \]

\[ + \left[ \varepsilon_C(r_s, 1) - \varepsilon_C(r_s, 0) \right] f(\zeta) \zeta^4, \]  

(48)

where \( \zeta = \left( \rho^1(r) - \rho^2(r) \right) / \rho(r) \) is the relative spin polarization, \( r_s = \left( \frac{3}{4\pi \rho} \right)^{1/3} \) is the Wigner-Seitz radius, and the functions \( f(\zeta), \varepsilon_C(r_s, 0), \varepsilon_C(r_s, 1) \) and \( -\alpha_C(r_s) \) are given in [65].

In numerical implementation, it is useful to break the KS Hamiltonian into separate components as

\[ \mathcal{H}^\rho_{\text{KS}} = \mathcal{T}_S + \mathcal{T}_B + \mathcal{V}_B + \mathcal{V}_C + \mathcal{V}_{\text{int}} + \mathcal{V}_X + \mathcal{V}_C \]  

(49)

with the kinetic energy of each single electron being further split into

\[ \langle \mathcal{T}_S \rangle = -\frac{\hbar^2}{2m} \int_\Omega \psi^*_\sigma \nabla^2 \psi_\sigma \, dr \quad \text{and} \quad \langle \mathcal{T}_B \rangle = \frac{e^2}{2m} \int_\Omega \psi^*_\sigma A^2 \psi_\sigma \, dr. \]  

(50)

Other energy terms are similarly defined. Note that \( \mathcal{V}_{\text{int}}, \mathcal{V}_X, \) and \( \mathcal{V}_C \) depend self-consistently on the density \( \rho \).

The total energy of that electron is then evaluated according to the formula

\[ E_{\rho\sigma} = \langle \mathcal{T}_S \rangle + \langle \mathcal{T}_B \rangle + \langle \mathcal{V}_B \rangle + \langle \mathcal{V}_C \rangle + \frac{1}{2} \langle \mathcal{V}_{\text{int}} \rangle + E_X + E_C. \]  

(51)

Accuracy of the exchange energies can be verified by the ratio of \( \frac{1}{2} \langle \mathcal{V}_{\text{int}} \rangle \) to the absolute value of \( E_X \), which is about 2 for two-electron atoms [35]. It has been theoretically shown in [24] that this ratio is exactly equal to 2 for a two-electron model for which the exchange-correlation energy and potential can be determined exactly in an external harmonic potential. The total energy of the \( N \) electrons is therefore the sum of these individual energies.

4. Numerical Methods

For semiconductor QD models with hard-wall confinement potential, real-space discretization methods such as the finite difference or finite element method are more suitable for numerical approximation. The potential profile makes essential difference between natural and artificial atomic systems in implementation. Since conduction electrons in a QD system are not confined to any specific nucleus of natural atom, the widely used basis functions in computational quantum chemistry such as Slater-type orbitals and Gaussian functions for the calculation of Coulomb integrals are not feasible for QD simulations. Therefore, we shall only consider the finite difference method and numerical basis functions in the following discussion. As mentioned above, we are only concerned with the nonlinear eigenvalue problem and the calculation of Coulomb and exchange integrals among many important issues in realistic simulations.
4.1. Nonlinear Eigenvalue Problems

Due to the nonparabolic effective mass (5), a finite difference discretization of (8) and (9) with the magnetic field \( B = 0 \) yields a cubic eigenvalue problem of the form

\[
A(\lambda)x = \left( A_0 + \lambda A_1 + \lambda^2 A_2 + \lambda^3 A_3 \right)x = 0,
\]

(52)

where an unknown eigenpair \((\lambda, x)\) is an approximate solution of \((\epsilon_i, \phi_i)\) of (2.8) for some energy level \( l \) at grid points \( r_j \in \Omega \), i.e., the eigenvalue \( \lambda \approx \epsilon_i \) and \( x_j \approx \phi_i(r_j) \) with \( x_j \) being the \( j \)th component of the eigenvector \( x \). If (5) is rewritten as

\[
\frac{1}{m(r, \epsilon)} = \frac{1}{m(r, \lambda)} = \frac{c\lambda + d}{(\lambda + a)(\lambda + b)}
\]

(53)

with the constants \( a, b, c, \) and \( d \) being simplified from the physical parameters in (5), it can be seen that the matrix \( A_0 \) is a combination of two matrices corresponding to the kinetic and potential terms in (7) together with the gradient interface condition in (9), \( A_1 \) is related to all three terms in (8), \( A_2 \) is from the potential term and the right-hand side of (8), and \( A_3 \) is an identity matrix from the right-hand side. Note that the Landé factor \( g(r, \epsilon) \) in (7) will make the nonlinear eigenvalue problem even further to the fifth order if \( B \neq 0 \).

The cubic or quintic eigenvalue problem belongs to a more general family of polynomial eigenvalue problems [3]. A variety of numerical methods [36–38, 90, 92] have been developed for solving this type of problems in recent years due to their interesting mathematical and physical features.

The cubic eigenproblem (52) can be transformed to the generalized linear eigenvalue problem

\[
\begin{bmatrix}
0 & I & 0 \\
0 & 0 & I \\
A_0 & A_1 & A_2
\end{bmatrix}
\begin{bmatrix}
x \\
\lambda x \\
\lambda^2 x
\end{bmatrix}
= \lambda
\begin{bmatrix}
I & 0 & 0 \\
0 & I & I \\
0 & 0 & -A_3
\end{bmatrix}
\begin{bmatrix}
x \\
\lambda x \\
\lambda^2 x
\end{bmatrix}
\]

(54)

This enlarged problem can be solved by various well-known methods such as the Lanczos or Arnoldi method. However, disadvantages of such an approach still exist. First of all, the order of the matrix is tripled and its condition number may increase drastically since the set of admissible perturbations for (54) is larger than that of (52) [83]. Secondly, the performance of these methods may be reduced for the enlarged problem in terms of convergence and accuracy. Thirdly, Lanczos and Arnoldi methods require the use of the shift-and-invert technique for such a large sparse eigenvalue problem since the desired eigenpairs are located in the interior of the spectrum of the problem. Consequently, the computational cost for solving linear system is excessive.

It can also be transformed to a fixed-point problem

\[
F(\lambda)x = \mu G(\lambda)x
\]

(55)

with, for instance,

\[
F(\lambda) = -A_1 + \lambda A_2 + \lambda^2 A_3, \ G(\lambda) = A_0, \text{ and } \mu = \frac{1}{\lambda}.
\]

There are of course other choices for \( F(\lambda) \) and \( G(\lambda) \) [37]. A general algorithm for solving (55) consists of the following two steps:

Step 1. Solve \( F(\lambda_i)x = \mu G(\lambda_i)x \) by an eigensolver for the maximum eigenpair \((\mu_{\text{max}}, x_{\text{max}})\) with \( \lambda_i \) being given.

Step 2. Update \( i = i + 1; \lambda_i = 1/\mu_{\text{max}} \), where \( \lambda_0 \) is an initial guess value. Go to Step 1 until convergence.

Again there are many methods that can be used to implement the eigensolver. If \( \lambda_i \) is close to a desired eigenvalue, Step 1 can be accelerated by Newton’s method, namely, by solving the correction equation

\[
A(\lambda_i)x = \mu A'(\lambda_i)x
\]

(56)

for the minimum eigenpair \((\mu_{\text{min}}, x_{\text{min}})\) with an update \( \lambda_{i+1} = \lambda_i - \mu_{\text{min}} \) instead of solving (55). Here \( A'(\lambda) \) is the derivative of \( A(\lambda) \) at \( \lambda_i \).

There is another type of subspace methods such as the nonlinear Arnoldi and Jacobi-Davidson (JD) method for solving (52) [38, 90]. A Jacobi-Davidson algorithm generally consists of the following steps.

**Algorithm 1.** A Cubic Jacobi-Davidson Method.
(1) Choose an $n \times m$ initial orthonormal matrix $V$ (a subspace) where $n$ is the matrix size of (52) and $m < < n$.

(2) Form smaller matrices $W_i = A_i V$ and $M_i = V^* W_i$ for $i = 0, 1, 2, 3$.

(3) Solve the smaller cubic eigenproblem

\[
(M_0 + \theta M_1 + \theta^2 M_2 + \theta^3 M_3) y = 0 \tag{57}
\]

for $(\theta, y)$ so that the Ritz pair $(\theta, z = V y) \approx (\lambda, x)$ is the wanted eigenpair.

(4) Solve approximately the correction equation

\[
\left( I - \frac{pz^*}{z^* p} \right) A(\theta) (I - zz^*) t = -r \tag{58}
\]

for $t \perp z$, where $r = A(\theta) z$ is the residual and $p = A'(\theta) z$.

(5) Expand $V = [V, t]$. Go to Step (2) until convergence or go to Step (1) for a restart.

Since the matrix size of the projected eigenproblem (57) is much smaller than that of (52), its transformation to a linear problem like (54) is now computationally feasible, which can then be solved by, for example, the QR method. Of course, there are other alternatives for solving the subspace eigenproblem. The correction equation (58) is originated from Jacobi’s idea. It is the most computationally demanding part in a JD algorithm for large matrix systems and thus should be solved via some efficient preconditioner such as SSOR [38]. Nevertheless, it has been demonstrated in [7] that JD is highly sensitive to preconditioning and can display an irregular convergence behavior. It takes the form of $K t = r$ for the Arnoldi method [90] with $K$ being a preconditioner such that $K \approx A(\sigma)$ and $\sigma$ is a pole close to a wanted eigenvalue.

In addition to fundamental problems associated with these two basic principles of JD methods [77, 78], several numerical issues on (52) that arise from the physical properties of QDs need to be addressed. The wanted eigenvalues are embedded in the interior of the eigenvalue spectrum in the complex plane, i.e. $(\lambda, x) \in \mathbb{C} \times \mathbb{C}^n$, may be clustered with small gaps, and may have multiplicity larger than one [37].

For seeking multiple eigenpairs, it is well known that a combination of JD and implicit deflation techniques based on the Schur form can lead to effective algorithms for linear eigenproblems. However, the Schur form is in general undefined for a cubic matrix pencil and hence the use of explicit deflation schemes is inevitable. In cases that two consecutive eigenvalues are close to each other, the explicit deflation scheme specific to linear eigenproblems may not be stable due to ill-conditioned deflation matrices.

More specifically, let $(\Lambda, V_F) \in \mathbb{R}^{\times r} \times \mathbb{R}^{\times r}$ be an eigenmatrix of $A(\Lambda)$ with $V_F^T V_F = I$, i.e. let $r$ eigenpairs be already found and hence

\[
A(\Lambda) V_F = A_0 V_F + A_1 V_F \Lambda + A_2 V_F \Lambda^2 + A_3 V_F \Lambda^3 = 0. \tag{59}
\]

We then deflate $\Lambda$ to infinity by defining a new deflated cubic eigenproblem as

\[
\tilde{A}(\lambda) x = \left( \Lambda_0 + \lambda \Lambda_1 + \lambda^2 \Lambda_2 + \lambda^3 \Lambda_3 \right) x = 0,
\]

\[
\tilde{\Lambda}_0 = A_0 \tag{60}
\]

\[
\tilde{\Lambda}_1 = A_1 - \left( A_1 V_F V_F^T + A_2 V_F \Lambda V_F^T + A_3 V_F \Lambda^2 V_F^T \right),
\]

\[
\tilde{\Lambda}_2 = A_2 - \left( A_2 V_F V_F^T + A_1 V_F \Lambda V_F^T \right),
\]

\[
\tilde{\Lambda}_3 = A_3 - A_3 V_F V_F^T.
\]

By (59) and (60), it can be shown that [38]

\[
A(\theta) = \tilde{A}(\theta) T(\theta), \quad T(\theta) = I - \theta V_F \Lambda^{-1} V_F^T, \tag{61}
\]
where \( \theta \notin \sigma(\Lambda) \) the spectrum of \( \Lambda \).

The matrix \( T(\theta) \) is called the deflation transformation matrix which may be ill-conditioned if \( \theta \) is very close to any computed eigenvalue in \( \sigma(\Lambda) \). This means that a direct replacement of \( A(\lambda) \) by \( \tilde{A}(\lambda) \) in Algorithm 1 for calculating the next eigenpair may incur instability or even divergence. Note that this kind of situation occurs inevitably for many-electron QD systems since the energy difference between spin-up and spin-down electrons (two eigenvalues) occupying the same orbital state is very small and approaches zero as the magnetic field \( B \) tends to zero.

Moreover, the computational cost for solving the deflated problem becomes more expensive as \( V_F \) gets larger. Therefore, a key factor to develop robust and efficient JD methods for QD models is to solve the correction equation (58) not only approximately but also indirectly. For this, a more convenient formulation for (58) is

\[
A(\theta)t = -r + \alpha p
\]

from which one can have various ways for calculating the ‘stepping length’ \( \alpha \), for instance [38, 78],

\[
\alpha = \frac{z^T K^{-1} r}{z^T K^{-1} p},
\]

where \( K \) is a preconditioner of \( A(\theta) \). With this preconditioner, the correction equation (58) is replaced by

\[
Kt = -r + \alpha p, \ p = \left[A'(\theta) - \tilde{A}'(\theta) T(\theta)\right] z
\]

for the next eigenpair.

Block eigensolvers are commonly used in many-body simulations in computational quantum chemistry and physics [87, 93]. They are more efficient than nonblock methods for calculating multiple or clustered eigenvalues that are essentially originated from the interaction Hamiltonian of many-body systems. Moreover, they allow parallelism and efficient use of local memory [16, 25, 30, 48, 87, 98, 99]. A block method is more suitable for many-electron QD models since degeneracies and small gaps of eigenvalues cause slow convergence in the deflation procedure. For the DFT model (39) with the magnetic field \( B \neq 0 \), the block Davidson method of Crouzeix, Philippe, and Sadkane [16] can be generalized to a block JD method as follows.

Algorithm 2. A Quintic Block Jacobi–Davidson Method.

(1) Choose an \( n \times m \) initial orthonormal matrix \( V \) where \( n \) is the matrix size of the quintic eigenproblem

\[
A(\lambda)x = \left( A_0 + \lambda A_1 + \lambda^2 A_2 + \lambda^3 A_3 + \lambda^4 A_4 + \lambda^5 A_5 \right) x = 0
\]

(65)

corresponding to the \( N \)-electron KS equation (39) and \( m = \lceil N/2 \rceil \) for both spin-up and spin-down states \((m << n)\).

(2) Form smaller matrices \( W_i = A_i V \) and \( M_i = V^* W_i \) for \( i = 0, 1, \cdots, 5 \).

(3) For \( j = 1, 2, \cdots, m \),

(3a) solve the smaller quintic eigenproblem

\[
\left( M_0 + \theta_j M_1 + \theta_j^2 M_2 + \theta_j^3 M_3 + \theta_j^4 M_4 + \theta_j^5 M_5 \right) y_j = 0
\]

for \((\theta_j, y_j)\) so that the Ritz pair \((\theta_j, z_j = V y_j) \approx (\lambda_j, x_j)\) is the wanted eigenpair,

(3b) solve the preconditioned correction equation

\[
Kt = -r + \alpha p,
\]

\[
r = A(\theta_j) z_j, \ \alpha = \frac{z_j^T K^{-1} r}{z_j^T K^{-1} p}, \ p = A(\theta_j) z_j, \ t \perp z_j, \text{ and}
\]
(3c) expand $V = [V, t]$.

(4) Go to Step (2) until convergence or go to Step (1) for a restart.

This is a general algorithm of a solution procedure for this kind of large and complicated nonlinear eigenproblems. There are of course many details missing in the algorithm such as restarting strategy, rank deficiency, adaptive block sizes, numerical schemes for the subspace problem (66), effective preconditioners, and variants of the correction equation that may affect the overall performance of the algorithm.

For the CI approach, the basic step is to construct numerically the single-electron basis functions $\phi_i$ in (16). With $B \neq 0$, one can apply either Algorithm 1 or 2 to the single-electron model (8) with a corresponding quintic eigenproblem. Again many details concerning the accuracy and efficiency of the construction and computation of the basis set remain to be investigated.

4.2. Evaluation of Coulomb Integrals

We now give a brief discussion on the calculation of Coulomb and exchange integrals in many-electron models. Since the many-electron basis functions $|L\rangle$ in (18) lead to a Slater determinant of single-electron basis functions $\phi_i$ that have been approximated via a JD algorithm which in turn renders a set of orthonormal eigenvectors, the matrix elements like (31) and (32) only involve the single-electron Hamiltonians $H_1$ and $H_2$ and hence their discrete forms are simply diagonal matrix elements associated with the products of the eigenvectors. In other words, the computationally demanding terms in the matrix elements $H_{ij}$ in (35) are those of Coulomb integrals like (33) for which we use the following generic four-center two-electron repulsion formula

$$\langle 12|V_c|34 \rangle = \int\int_\Omega d' r' \phi_1^*(r) \phi_2^*(r') \frac{1}{D(r)|r-r'|} \phi_3^*(r) \phi_4^*(r'),$$

(68)

where $V_c$ denotes the two-body Coulomb operator and $\phi_i(r), i = 1, 2, 3, 4$, represent any arbitrary four single-electron functions.

For real space approximation, we define a potential-like function

$$V_{24}(r) = \frac{1}{D(r)} \int_\Omega \phi_3^*(r') \phi_4^*(r') \frac{r-r'}{r'.}$$

(69)

that can be obtained by solving the Poisson equation

$$-\nabla \cdot D(r) \nabla V_{24}(r) = \phi_{24}(r), \quad \phi_{24}(r) = \phi_3^*(r) \phi_4^*(r).$$

(70)

Again a finite difference approximation of (70) and (9) results in a matrix system

$$Ax = b,$$

(71)

where $A$ is an $n \times n$ matrix that corresponds to the left-hand side of (70) and is different from $A(\lambda)$, $b$ corresponds to $\phi_{24}(r)$, and $x_j \approx V_{24}(r_j)$ with $x_j$ being the $j$th component of the unknown vector $x$. The literature on the development of fast Poisson solvers is vast, see e.g. [14, 31, 71]. Note that, for DFT approach, the Hartree potential (42) can also be calculated by means of the Poisson equation

$$-\nabla \cdot D(r) \nabla V_{H}(r) = \rho(r).$$

(72)

We summarize our discussion on numerical methods for many-electron QD simulations in the following two general algorithms via CI and DFT approaches.

Mathematical modeling of semiconductor quantum dots

Fig 2. A cross section of an InAs/GaAs QD in nano meters.

(1) Solve the single-electron model (8) in discrete form (52) by Algorithm 1 or 2 for $N_s$ basis functions in (16).

(2) Form an $N_m \times N_m$ interaction matrix $H = [H_{ij}]$ as in (35) with $N_m = C_N^{N_e}$ by

(2a) calculating diagonal elements $H_{ii}$ via the inner product of eigenvectors in correspondence to (31), and
(2b) calculating mixing elements $H_{ij}$ via solving (71) in correspondence to (33) by a suitable Poisson solver.

(3) Solve the eigenproblem as (34) for the total energy $\varepsilon$ and wave function $\Psi$ (19) of the $N$ electrons by a suitable eigensolver.


(1) Set $V_{ii} = V_{XC} = 0$ and solve the KS equation (39) in discrete form (66) by Algorithm 2 with $\sigma = \uparrow$ and then $\sigma = \downarrow$ to get $\psi_{j\sigma}$ for $j = 1, \ldots, [N/2]$.

(2) Evaluate all electron energies $E_{j\sigma}$ by (51) and go to the next step until a self-consistent convergence is reached.

(3) Update the electron densities $\rho^\uparrow, \rho^\downarrow, \rho$ in (36) and (37) with new $\psi_{j\sigma}$.

(3a) Solve (72) in discrete form (71) for a new $V_{ii}$ by a suitable Poisson solver.

(3b) Solve the KS equation (39) by Algorithm 2 for new $\psi_{j\sigma}$ and then go to Step (2).

4.3. Physical and Mathematical Results

The main purpose of this section is to present novel physical and mathematical results obtained in the past years under this framework albeit its simplification and approximation in energy band structures [13, 34, 37, 38, 54, 55, 88, 89, 92, 95]. For conciseness, we summarize our results to three noteworthy aspects.

A. Accuracy of Models. We first present results that are verified with experimental data to show the correctness of our QD models. We consider an InAs/GaAs QD as shown in Fig. 1 where a 2D cross section is depicted in Fig. 2. The finite confinement potential is $V_c = 0.77$ eV and the effective potential acting upon the quantum dot volume is $V_e = 0.482$ eV [22] to account the strain and piezoelectric effects. In order to verify the accuracy of the CSDFT model (39), numerical results are presented in an analogous way to that of [22] where the CV experimental data of [61] were extracted for numerical studies.

All numerical values of the parameters used in this paper are listed in Table 1.

In Fig. 3, the capacitance-gate-voltage trace from [61] is shown. The peaks correspond to the occupation of the s-shell ($E_0$) and p-shell ($E_1$) energy levels by tunneled electrons with an increasing number of electrons, i.e., $N = 1, 2, \ldots, 6$. As mentioned in [61], the trace has been scaled by a multiplication factor (within about 30% accuracy)
**Table 1.** Numerical values of the parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (InAs)</td>
<td>( 1.20311 \times 10^{-28} )</td>
<td></td>
</tr>
<tr>
<td>( \rho ) (GaAs)</td>
<td>( 1.25614 \times 10^{-28} )</td>
<td></td>
</tr>
<tr>
<td>( m_0 )</td>
<td>( 9.10956 \times 10^{-31} ) kg</td>
<td></td>
</tr>
<tr>
<td>( E_g ) (InAs)</td>
<td>( 0.421 ) eV</td>
<td></td>
</tr>
<tr>
<td>( E_g ) (GaAs)</td>
<td>( 1.52 ) eV</td>
<td></td>
</tr>
<tr>
<td>( \Delta ) (InAs)</td>
<td>( 0.48 ) eV</td>
<td></td>
</tr>
<tr>
<td>( \Delta ) (GaAs)</td>
<td>( 0.34 ) eV</td>
<td></td>
</tr>
<tr>
<td>( V_c )</td>
<td>( 0.77 ) eV</td>
<td></td>
</tr>
<tr>
<td>( \epsilon_0 )</td>
<td>( 8.854187 \times 10^{-12} ) F/m</td>
<td></td>
</tr>
<tr>
<td>( \epsilon_{\text{InAs}} )</td>
<td>12.2</td>
<td></td>
</tr>
<tr>
<td>( \epsilon_{\text{GaAs}} )</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td>( \mu_0 )</td>
<td>( 9.2741 \times 10^{-24} ) J/T</td>
<td></td>
</tr>
</tbody>
</table>

**Fig 3.** The capacitance-gate-voltage trace where the capacitance is in arbitrary units. The peaks correspond to the occupation of the s and p energy shells by tunneled electrons. The arrows with \( E_0, E_1, E_2 \) indicate the s, p, and d levels, respectively, obtained by the CV spectroscopy data [61]. Our results are denoted by \( \tilde{E}_0, \tilde{E}_1, \tilde{E}_2 \).

and is offset for clarity. Note that at zero magnetic field the peak corresponding to the d-shell (\( E_2 \)) level is not present in [61]. Since the precise values of these levels are not given in both [61] and [22], the experimental values \( E_0 = 0.59, E_1 = 0.642, \) and \( E_2 = 0.69 \) eV are approximated by inspecting the data shown in the figures in [22]. Our numerical results of the corresponding peak energies are \( \tilde{E}_0 = 0.608, \tilde{E}_1 = 0.65, \) and \( \tilde{E}_2 = 0.701 \) that show good agreement with the experimental results. Moreover, there are two small sub-peaks in the s peak and four in the p peak, which indicate small variations in total energy of the system as electrons are added to the QD one by one. Our capacitance profile also shows these variations and is consistent with the experimental profile.

We next compare the results obtained by parabolic and nonparabolic CSDFT methods for the 6-electron system in a magnetic field to show the importance of nonparabolic effect with respect to the magnetic field. In Fig. 4, the solid lines represent the results of the s, p, and d shells with various magnetic fields by the nonparabolic method while the dashed lines correspond to the parabolic method. We find that the nonparabolic effect is more pronounced in many-electron...
system than in single-electron system. For example, for the p-shell levels at $B = 20 \, \text{T}$ in Fig. 4, the Zeeman splitting of the parabolic case is $\Delta E = 70 \, \text{meV}$ which is much wider than $\Delta E = 47 \, \text{meV}$ of the nonparabolic case. By inspecting the results of [22], the splitting for the nonparabolic single-electron model is $\Delta E = 42 \, \text{meV}$. Obviously, the nonparabolic band effect is more important for the many-electron models than single ones. Note that the upper energy levels of the d-shell electron are not present in the figures of [22]. Furthermore, the energy level of the spin-down d-shell electron at $B = 20 \, \text{T}$ obtained by the nonparabolic method is $E_{2\downarrow} = 0.758 \, \text{eV}$ which is still within the confinement potential well. It is, however, out of the confinement for the parabolic case.

B. Quantum Entanglement. There is significant interest in quantum information processing based on Fermionic qubits using semiconducting materials [6, 19, 20, 42, 63]. One of the proposals in this approach is to exploit electronic interactions of coupled quantum dots that form an artificial molecule (QDM) [6, 20, 63]. In QDM, one can adjust the inter-dot distance and through that to control coupling between electronic states localized in different dots. The ability to control coherent coupling between quantum dots may open possibility for designing quantum logic gates [6, 63].

The inter-dot distance control is an example of a static approach to the gate design. Another possibility to control dynamically the coupling lies in application of external fields [42].

We demonstrate a theoretical model of quantum entanglement in a triple-dot artificial molecule via dynamic control of magnetic or electric field. The QDM is a vertical stack of three InAs dots with two different sizes embedded in GaAs as depicted in Fig. 5 where the radius, thickness, and separation of each dot are indicated by coordinates in nano meters. These QD dimensions are commensurable with those of [63] where a transmission electron micrograph of a QDM sample is illustrated. The magnetic field $B$ is applied in the $z$-axis and the electric field is controlled by changing the voltage $V_g$ of a circular Schottky gate surrounding the central dot as shown in blue in Fig. 5. The red part represents an insulator.

We study the electronic configuration of $N = 6$ electrons confined in the QDM under these two fields by using the CSDFT approach.

The entanglement is posited under two different field conditions. Case 1: $V_g = 0 \, \text{V}$ and $B = 0$ to $15 \, \text{T}$. The left panel of Fig. 6 consists of three frames in which the configuration of 6 electrons in QDM with $B = 0$ is illustrated. Each frame represents a contour of the wave function of 2 electron (spin-up and spin-down). These three frames indicate that all 6 electrons are located in the central dot. We denote this 6-electron state in the QDM by $|0\rangle$. The right panel of the figure corresponds to $B = 15 \, \text{T}$. Each dot of the QDM contains two electrons as shown by the contour in each
Fig 5. A radial cross-section of three vertically aligned InAs quantum dots (a QDM) embedded in GaAs.

Fig 6. Case 1. $V_g = 0$ V. Left panel: $B = 0$. Each frame represents the contour of the wave function of two electrons (spin-up and -down). All 6 electrons are in the central dot. Right panel: $B = 15$ T. Each dot contains two electrons.

These results show that we may be able to control electrons in a QDM by varying the magnetic field so that an entangled state $\alpha \langle 0 \rangle + \beta \langle 1 \rangle$ with $\alpha \neq 0$ and $\beta \neq 0$ for quantum computing can be established. Similar results are found for Case 2: $V_g = 3$ V and $B = 0$ to 15 T as shown in Fig. 7.

C. Effectivity of Eigensolvers. Experimental implementations of quantum information processing with semiconductor QDs require the measurement accuracy of energy spectrum be as small as in the order of tens of $\mu$eV. For example, the spectral resolution of a $N_2$-cooled Si-CCD camera is 80 $\mu$eV for detecting the optical emission of a QD exciton by a continuous wave laser in the study of the excitonic transitions of QDs [66]. On the other end, theoretical implementations in, for instance, our DFT model setting, require the numerical accuracy of the correlation energy be in
Mathematical modeling of semiconductor quantum dots

Fig 7. Case 2. $V_g = 3$ V. Left panel: $B = 0$. All 6 electrons are in the central dot. Right panel: $B = 15$ T. Each dot contains two electrons.

the order of tenths of $\mu$eV. These precision requirements make the development of effective and efficient eigensolvers for modeling and simulation of many-body QDs very challenging especially in the situation of clustered, small gaps, and interior eigenvalue spectrum of interest.

We report numerical evidence of the effectiveness of nonlinear Jacobi-Davidson solvers developed within the above general algorithmic framework. For the same 6-electron QDM model of Fig. 5 at $B = 15$ T, various energy terms (defined in (51)) of the lowest 6 energy states denoted by $q = \{n, l, a\}$ are given in Table 2, where $n$ and $l$ are the principal and angular momentum quantum number, respectively. The essential physics of this study, namely the state change of electrons in QDM under the influence of magnetic field as illustrated in the right panel in Fig. 6, can also be simulated by the simpler single-electron model (3). However, the numerics of the computed energies is quite different from that of the many-electron model (39) as shown in the second ($E_n^2$) and third ($E_n^3$) row in Table 2. The single-electron model yields degenerate states such as $\{2, 0, +1\}$ and $\{3, 0, +1\}$ which obviously are incorrect. The energy spacing between these two states is 126 $\mu$eV but their difference in exchange–correlation energy is only 0.4 $\mu$eV indicating that the quintic block Jacobi-Davidson method is quite effective.

5. Conclusions

A general framework for modeling and simulation of semiconductor quantum dots (QDs) is proposed. It includes single-electron models and many-electron models of Hartree–Fock, configuration interaction, and current-spin density functional theory approaches. All these models are based on the nonparabolic effective–mass approximation and result in cubic or quintic eigenvalue problems by a suitable discretization method. Nonlinear Jacobi–Davidson (JD) methods are then presented for solving these types of polynomial eigenproblems for which the wanted eigenvalues are clustered, having small gaps, and located in the interior of the spectrum. These challenging issues on mathematical modeling and numerical methods for QD simulations are direct consequences of rapid advances in semiconductor technology in recent years. Generic algorithms involving JD and Poisson solvers for many-electron simulations are also presented. Eminent numerical results in terms of accuracy of models, quantum entanglement demonstration, and effectiveness of eigensolvers, obtained under this general framework are also provided for a possible motivation in future developments of more realistic and efficient simulation tools for QD studies along with advanced experimental methods.
Table 2. Energies in eV of 6-electron QDM model at \( B = 15 \). \( E_q^* \) and \( E_q \) are calculated by the single-electron and 6-electron DFT models, respectively.

<table>
<thead>
<tr>
<th>( q )</th>
<th>{1.0, +1}</th>
<th>{2.0, +1}</th>
<th>{3.0, +1}</th>
<th>{1.0, -1}</th>
<th>{2.0, -1}</th>
<th>{3.0, -1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_q^* )</td>
<td>0.103250</td>
<td>0.134668</td>
<td>0.134668</td>
<td>0.114840</td>
<td>0.146072</td>
<td>0.146072</td>
</tr>
<tr>
<td>( E_q )</td>
<td>0.113092</td>
<td>0.146387</td>
<td>0.147649</td>
<td>0.120784</td>
<td>0.153012</td>
<td>0.154220</td>
</tr>
<tr>
<td>( \langle T_s \rangle )</td>
<td>0.078144</td>
<td>0.114168</td>
<td>0.113827</td>
<td>0.077302</td>
<td>0.113209</td>
<td>0.112880</td>
</tr>
<tr>
<td>( \langle T_A \rangle )</td>
<td>0.008975</td>
<td>0.002510</td>
<td>0.002499</td>
<td>0.008889</td>
<td>0.002484</td>
<td>0.002473</td>
</tr>
<tr>
<td>( \langle V_r \rangle )</td>
<td>0.017801</td>
<td>0.021184</td>
<td>0.021067</td>
<td>0.017713</td>
<td>0.021108</td>
<td>0.020994</td>
</tr>
<tr>
<td>( E_B )</td>
<td>-0.004436</td>
<td>-0.003913</td>
<td>-0.003877</td>
<td>0.004325</td>
<td>0.003832</td>
<td>0.003798</td>
</tr>
<tr>
<td>( \frac{1}{2} \langle V_{1h} \rangle )</td>
<td>0.021932</td>
<td>0.026358</td>
<td>0.028058</td>
<td>0.021925</td>
<td>0.026359</td>
<td>0.028059</td>
</tr>
<tr>
<td>( E_X )</td>
<td>-0.008884</td>
<td>-0.013414</td>
<td>-0.013418</td>
<td>-0.008877</td>
<td>-0.013419</td>
<td>-0.013422</td>
</tr>
<tr>
<td>( E_C )</td>
<td>-0.000441</td>
<td>-0.000506</td>
<td>-0.000506</td>
<td>-0.000493</td>
<td>-0.000562</td>
<td>-0.000562</td>
</tr>
</tbody>
</table>

Acknowledgments

This work was supported by National Science Council of Taiwan under Grant 99-2115-M-134-004-MY3. The author would like to thank the referees for their valuable comments on the manuscript.

References

[43] A. V. Knyazev, Toward the optimal preconditioned eigensolver: Locally optimal block preconditioned conjugate


