Coulomb interaction in a quantum dot

Lin-Wang Wang

National Renewable Energy Laboratory, Golden, CO 80401

Abstract

One approximation is made to describe a M+1 electron many-body wavefunction by a M electron many-body wavefunction and a single electron wavefunction. Under this approximation, we have derived the Coulomb energy which relates the exciton energy $E_{exc}$ in a quantum dot with the quasiparticle band gap (defined as the difference between the ionization energy and the electron affinity), and the Coulomb energy which relates $E_{exc}$ with the single particle eigen values. We found that these two Coulomb energies are different. We have compared our results with the formulae used in different groups, which are proposed either ad hoc, or from the classical electrostatic point of view. We found important difference between our results and the classical formulae. Finally, under the above approximation, we provided an effective single particle Hamiltonian, which gives the quasiparticle band structure in a bulk system.

Keywords: quantum dot, screening, Coulomb interaction.
I. Introduction

The screened Coulomb interaction in a bulk semiconductor between an excited electron and a hole has been studied theoretically 30 years ago [1,2] from many body point of views. As a result of such theoretical analysis, the screening of the Coulomb interaction can be expressed using the dielectric response function of the bulk system. Recently, nanometer scale finite system has attracted a lot of research interests [3]. The confined excited electrons and holes within the finite systems have enhanced Coulomb interactions comparing to the bulk material [4]. However, there are different opinions about how to screen the Coulomb interactions in various cases. While the screening of the Coulomb interaction is clear when the electron is outside the nanostructure, it becomes clouded from a classical point of view when it enters the nanostructure. One problem is that the classical dielectric screening effects can already been partially represented by the single particle eigen energies. Thus combining the classical electrostatic model with the single particle Hamiltonian does not always provide a clear picture free from ambiguities. The more rigorous approach is to derive the single particle effective Hamiltonian and the screened Coulomb interaction from the many body Hamiltonian. However, the Feyman diagram technique used in the bulk study thirty years ago can not be directly applied to the finite system without complicated modifications of the Green’s functions according to the new quantum dot boundary conditions. In this article, we will present a derivation of the screened electron-hole Coulomb interaction in a nanosystem started from a many body Hamiltonian. Instead of basing on the Green’s functions, our derivation is based on many particle wavefunctions. We will restrict ourselves to the cases that the excited electrons and holes are strongly confined by a 0 dimension nanostructure (quantum dot). That means, the correlation between the excited electron and the hole can be ignored [5,6].

One of the earlier works on the quantum dot Coulomb interaction and its screening effects is given by L.E. Brus [7]. Using a classical model of the dielectric screening and a single particle Hamiltonian, Brus derived the change of electron affinity of a quantum dot (spherical, with radius R) relative to the bulk system:
\[ E_N - E_{N+1} = E_{\text{aff}}^{\text{bulk}} - \epsilon_e - \frac{1}{2R} \bar{P}'. \] (1)

Here \( E_M \) is the total energy of the quantum dot with \( M \) electrons. \( E_N \) is the neutral quantum dot. Thus \( E_N - E_{N+1} \) is the electron affinity of the quantum dot. \( E_{\text{aff}}^{\text{bulk}} \) is the electron affinity of the bulk. \( \epsilon_e \) is a single electron confinement energy in conduction band, which equals \( \frac{\pi^2}{2m_e^*R^2} \) under an effective mass model of electron effective mass \( m_e^* \). \( \frac{1}{2R} \bar{P}' \) is an electrostatic energy representing the interaction between the electron and its image charge produced by the quantum dot medium with dielectric constant \( \epsilon \). Similarly, for ionization energy, he has

\[ E_{N-1} - E_N = E_{\text{ion}}^{\text{bulk}} + \epsilon_h + \frac{1}{2R} \bar{P}'. \] (2)

Here \( \epsilon_h \) is the single hole confinement energy, which equals \( \frac{\pi^2}{2m_h^*R^2} \) under a single band effective mass model of hole effective mass \( m_h^* \). The last term in Eq(2) is the same as the last term in Eq(1). Then, using the conventional definition, the quasiparticle band gap \( E_y^{\text{qp}} \) equals the difference between the ionization energy the the electron affinity:

\[ E_y^{\text{qp}} \equiv E_{N+1} + E_{N-1} - 2E_N = E_{\text{ion}}^{\text{bulk}} + \epsilon_e + \epsilon_h + \frac{1}{R} \bar{P}'. \] (3)

Here, we have used the fact that the bulk band gap \( E_{\text{ion}}^{\text{bulk}} \) equals the difference between bulk ionization energy \( E_{\text{ion}}^{\text{bulk}} \) and the bulk electron affinity \( E_{\text{aff}}^{\text{bulk}} \). In this paper, we discuss only the cases where the quantum dot is surrounded by vacuum. Then if the dielectric constant of the quantum dot \( \epsilon \) is much larger than 1, we have (following Ref. [8]):

\[ \frac{1}{R} \bar{P}' = (1 - \frac{1}{\epsilon}) \frac{1}{R} + \frac{0.94}{\epsilon R} \left( \frac{\epsilon - 1}{\epsilon + 1} \right). \] (4)

In a second paper [9], Brus presented the result for the exciton energy \( E_{\text{exc}} \) in a quantum dot (which equals the photon energy needed to excite an electron from the valence band to the conduction band),
\[ E_{\text{exc}} = E_{g}^{\text{bulk}} + \epsilon_{e} + \epsilon_{h} - \frac{1.8}{\epsilon R} + \frac{0.94 (\epsilon - 1)}{\epsilon R (\epsilon + 1)}, \]

where \(-\frac{1.8}{\epsilon R}\) represents the direct Coulomb integral between the electron charge and hole charge, screened by \(\epsilon\), using the effective mass wavefunctions. The last term in Eq(5) is said to be the time averaged instantaneous dielectric energy while the classical particle moves around inside the quantum dot. Comparing Eq(3) to Eq(5), with the help of Eq(4), we have

\[ E_{\text{exc}} = E_{g}^{\text{qp}} - \frac{1.8}{\epsilon R} - (1 - \frac{1}{\epsilon}) \frac{1}{R}. \]

Note that, classically, the last term in Eq(6) represents the Coulomb interaction energy between a spherical charge density inside the quantum dot with its induced surface charge. The total of the last two terms in Eq(6) represents the electrostatic interaction between the confined bare electron charge density with a screened hole charge (i.e., the total charge density of the \(E_{N-1}\) system).

However, the above classical picture is not universally accepted. For example, in a recent paper of Ogut, et al. [10], the connection between \(E_{g}^{\text{qp}}\) and \(E_{\text{exc}}\) is not given by Eq(6), instead a simple Coulomb interaction \(-\frac{1.8}{\epsilon R}\) is used (in the effective mass limit):

\[ E_{\text{exc}} = E_{g}^{\text{qp}} - \frac{1.8}{\epsilon R}. \]

The difference between Eq(7) and Eq(6) is very large (up to 2 eV for \(R \sim 7\,\text{Å}\)), because there is an unscreened Coulomb interaction \(-1/R\) in the last term of Eq(6). Using Eq(7), Ogut et al. obtained an exciton energy \(E_{\text{exc}}\) much larger than the one obtained from the single particle empirical pseudopotential method (EPM) [11] (which is yield via Eq(5) but without its last term, and with \(\epsilon_{e}, \epsilon_{h}\) calculated via single particle EPM Hamiltonian). Based on this difference, they concluded that the empirical pseudopotential calculation is wrong because a size dependence of the GW selfenergy \(\Sigma\) is ignored. However, if Eq(6) instead of Eq(7) is used, one finds that the result from Ref. [10] is almost the same as the EPM result. Then their conclusion will be false and EPM calculation will be all right.
To settle the dispute between Eq(7) and Eq(6), and to test the other classical formulae [e.g, Eq(5)], it will be very useful to derive the above relationships from many body Hamiltonians. This will be provided in the rest of this paper. We found out that Eq(6) is correct instead of Eq(7), and Eq(5) is correct after deleting its last term.

II. The basic Formalism

In this section, we will derive our basic formula to be used in later sections. This formula is based on an approximation that the many-body wavefunction $\Phi_{M+1}$ of a M+1 electron system can be separated into one single particle wavefunction $\psi$ [i.e, $\psi_v$ (top of valence band state) or $\psi_c$ (bottom of conduction band state)] and the rest of the M particle wavefunction $\Phi_M$. More specifically, we have:

$$\Phi_{M+1}(x_1, x_2, \ldots, x_M, x_{M+1}) \equiv |\Phi_M \psi > \equiv \frac{1}{\sqrt{M+1}}[\Phi_M(x_1, x_2, \ldots, x_M)\psi(x_{M+1})$$

$$- \Phi_M(x_{M+1}, x_2, \ldots, x_M)\psi(x_1) \ldots - \Phi_M(x_1, x_2, \ldots, x_{M+1})\psi(x_M)].$$

(8)

Here, we have used $|\Phi_M \psi >$ to denote the break down of the total wavefunction $\Phi_{M+1}$ into $\Phi_M$ and $\psi$. $x \equiv (r, \sigma)$, and $r$ is the three dimensional Cartesian coordinate, and $\sigma$ is the spin index. Note that through the definition of Eq(8), $\Phi_{M+1}(x_1, x_2, \ldots, x_M, x_{M+1})$ is antisymmetric, provided $\Phi_M$ is antisymmetric. In general, $\Phi_M(x_1, x_2, \ldots, x_M)$ can be represented by a linear combination of different electron configurations (i.e, single slater determinates from a single particle orthogonal basis set including $\psi$). Any slater determinate which consists of $\psi$ will be eliminated in Eq(8) by the antisymmetry operation. Thus, it does not lose any generacity (in terms of variational degree of freedom for $\Phi_{M+1}$) to exclude the single particle orbital $\psi$ from the configurations of $\Phi_M(x_1, x_2, \ldots, x_M)$. In another word, we can restrict $\Phi_M(x_1, x_2, \ldots, x_M)$ to be orthogonal to $\psi(x)$, i.e,

$$\int \Phi_M(x_1, x_2, \ldots, x_M)\psi^*(x_1)d^3x_1 = 0.$$

(9)
This orthogonal condition is also called strong orthogonal condition [12,13]. Notice that, since we have not restrict any degree of freedom in $\Phi_{M+1}$ of Eq(8) by introducing Eq(9), Eq(9) should not be considered as an additional approximation. The approximation, if any, has already been made in Eq(8). By using Eq(8), we have neglected the correlation between the single particle state $\psi$ and the rest of the system $\Phi_M$. This is one approximate way to define an quasiparticle wavefunction $\psi(x_1)$ out of a many particle system. The approximation of Eq(8) has been called group function approximation [12,13], and has been used to study the effects (e.g, screening) of one group to another group. Thus, it is natural here to use it to describe the Coulomb screening effects of the background system ($\Phi_M$) to the quasiparticle (and exciton) system ($\psi$). Note that, Eq(8) goes beyond Hartree-Fock [14] approximation by retaining correlations within $\Phi_M$. Since our focus is to study the dielectric screening of the Coulomb interaction, which can already be described by Hartree Fock approximation, we expect Eq(8) to be adequate to represent the main physics of interest here. Similar approximations of Eq(8) has been used in the derivation of Extended Koopmans’ Theorem by Day, Smith, and Garrod [15], by Morrell, Parr and Levy [16], and by Kent, etal [17]. In Eq(8), one gets the wavefunction $\Phi_{M+1}$ of the M+1 electron system by adding one electron $\psi$ to the M electron wavefunction $\Phi_M$. Similary, one can get the M electron system wavefunction $\Phi_M$ by eliminating $\psi(x_1)$ from the M+1 electron wavefunction $\Phi_{M+1}$:

$$\Phi_M(x_1, x_2, ..., x_M) = \int \psi^*(x_{M+1})\Phi_{M+1}(x_1, x_2, ..., x_M, x_{M+1})d^3x_{M+1}. \quad (10)$$

Using the orthogonal condition Eq(9), one can derive Eq(10) from Eq(8). Equation (10) is also used in the derivation of the Extended Koopmans’ Theorem [15 17].

To appreciate the approximation embodied in Eq(8), we can take a look at the density matrix of the M+1 system. Under Eqs(8) and (9), $\rho_{M+1}(x, x') = \psi(x)\psi^*(x') + \rho_M(x, x')$, here $\rho_{M+1}$ and $\rho_M$ are the density matrix of the M+1 and M electron systems respectively. Besides, following the orthogonal condition of Eq(9), $\int \rho_M(x, x')\psi(x')d^3x' = 0$. As a result,
ψ(x) is a natural orbital of ρ_{M+1} with an occupation number of 1. As well known \[17\], the occupation numbers of the natural orbitals are usually less than 1, thus the Eq(8) is definitely an approximation. However, this approximation is similar to the approximations which use one single particle wavefunction to represent a quasiparticle in a many-body system. These include: the Hartree-Fock theory \[14\], empirical pseudopotential theory \[11\], the Kohn-Sham representation of the density functional theory \[20\] and in some extent the GW theory \[18\].

To include the correlation between ψ and Φ_M in Eq(8), one has to add in Eq(8) other configurations |Φ_M'ψ'\rangle. However, if the quasiparticle is represented by a unique single particle wavefunction ψ, then ψ' must be ψ. As a result, |Φ_Mψ⟩ + |Φ_M'ψ'⟩ = |Φ_M''ψ⟩, where Φ_M'' = Φ_M + Φ_M', and Eq(8) remains unchanged.

The Hamiltonian for the M+1 particle system can be written as

\[
H_{M+1} = -\frac{1}{2} \sum_{i=1}^{M+1} \nabla_i^2 + \sum_{i=1}^{M+1} V_{\text{ion}}(r_i) + \sum_{i \neq j}^{M+1} \frac{e^2}{|r_i - r_j|}.
\] (11)

Using Eq(11) and Eq(8), we can evaluate \(< Φ_{M+1}|H_{M+1}|Φ_{M+1}⟩\). After some algebras, it can be expressed as

\[
< Φ_{M+1}|H_{M+1}|Φ_{M+1}⟩ = E_ψ + < Φ_M|H_M|Φ_M >
+ \int ρ_M(r)V_{\text{coul}}^ψ(r)d^3r - \int V_{\text{ex}}^ψ(x,x')ρ_M(x,x')d^3xd^3x',
\] (12)

where \(H_M\) is just the \(H_{M+1}\) of Eq(11), but change the \(M+1\) to \(M\). \(E_ψ\) is defined as

\[
E_ψ = \int ψ(x) \left[ -\frac{1}{2} \nabla^2 + V_{\text{ion}}(r) \right] ψ^*(x)d^3x.
\] (13)

\(V_{\text{coul}}^ψ(r)\) is the Coulomb potential due to \(ψ\),

\[
V_{\text{coul}}^ψ(r) = \int \frac{e^2}{|r - r'|} |ψ(x')|^2d^3x',
\] (14)

\(ρ_M(r)\) is the total charge density of \(Φ_M\),
\[ \rho_M(r) = M \sum_\sigma \int |\Phi_M((r, \sigma), x_2, \ldots x_M)|^2 d^3 x_2 \ldots d^3 x_M. \]  

(15)

\[ V_{ex}^\psi(x, x') \]  
is the exchange nonlocal potential due to \( \psi \),

\[ V_{ex}^\psi(x, x') = \frac{e^2}{|r - r'|} \psi^*(x)\psi(x'), \]  

(16)

and \( \bar{\rho}_M(x, x') \) is the density matrix of \( \Phi_M \),

\[ \bar{\rho}_M(x, x') = M \int \Phi_M(x, x_2, \ldots x_M)\Phi_M^*(x', x_2, \ldots x_M) d^3 x_2 \ldots d^3 x_M. \]  

(17)

Note that \( \rho_M(r) = \sum_\sigma \bar{\rho}_M(r\sigma, r\sigma) \).

Equation (12) has been derived before as in the group function theory \[13\]. Under the assumption of the wavefunction \( \Phi_{M+1} \) of Eq(8), one can variationally minimize the total energy of Eq(12) with regard to \( \Phi_M \) and \( \psi \) under the constraint of Eq(9). Doing so, both \( \Phi_M \) and \( \psi \) can be solved selfconsistently from Eq(12). However, symmetries might need to be used to keep the \( \psi \) to be the desired single particle wavefunctions (i.e, the top of valence state and bottom of conduction state). Another approach is to calculate \( \psi \) from single particle Hamiltonians, e.g, quasi-particle GW method \[18\], or empirical pseudopotential method \[11\]. Later in Section IV, we will provide a new single particle Hamiltonian \( H_s \) [Eq(40)] to calculate \( \psi \). For a given \( \psi \), we can minimize Eq(12) with regard to \( \Phi_M \), thus get a many particle equation for \( \Phi_M \) under the perturbation of Coulomb potential \( V_{coul}^\psi(r) \) and the exchange potential \( V_{ex}^\psi(x, x') \).

III. Coulomb energy associated with the ionization energy and electron affinity

The exciton energy \( E_{exc} \) can be directly defined as \( E_N^* - E_N \). Here, \( E_N \) is the N electron ground state energy and \( E_N^* \) is the total energy of the N electron system which contains one exciton (i.e, an conduction band single particle state \( \psi_c \) is occupied and an valence
band single particle state $\psi_\nu$ is unoccupied). Then the Coulomb energy which connects $E_g^{qp}$ ($\equiv E_{N+1} + E_{N-1} - 2E_N$) with $E_{exc}$ is

$$E_{coul} \equiv E_{exc} - E_g^{qp} = (E_N^* - E_{N-1}) - (E_{N+1} - E_N), \quad (18)$$

where, $E_{N-1}$ and $E_{N+1}$ are the ground state energies of N-1 and N+1 electron systems. Note that in $E_N^*$, $E_N$, $E_{N-1}$ and $E_{N+1}$ systems, the ionic potential $V_{ion}(r)$ in Eq(11) is the same. The difference is the electron occupations. Using the approach outlined in the previous section, we will approximate the wavefunctions of the same. The difference is the electron occupations. Using the approach outlined in the previous section, we will approximate the wavefunctions of $E_N^*$, $E_N$, $E_{N-1}$ and $E_{N+1}$ systems as $|\Phi_{N-1}^c\psi_c\rangle$, $|\Phi_N^c\rangle$, $|\Phi_{N-1}^0\rangle$ and $|\Phi_N^c\psi_c\rangle$ respectively. Using the orthogonal conditions of Eq(9), and applying it equally to all the systems in Eq(18), we have $\Phi_{N-1}^c$, $\Phi_N^c$, $\Phi_{N-1}^0$ and $\Phi_N^c$ all orthogonal to $\psi_c$ [Eq(9), replacing $\psi$ by $\psi_c$, and $\Phi_M$ by these four wavefunctions]. In addition, $\Phi_{N-1}^c$ and $\Phi_{N-1}^0$ should be orthogonal to $\psi_\nu$ [Eq(9), replacing $\psi$ by $\psi_\nu$], so that a hole exists in these systems. Notice that, we have used the superscription “0” to indicate that the corresponding wavefunction $\Phi_M^0$ is a minimum energy variational solution of $< \Phi_M^0 | H_M | \Phi_M^0 >$. Similarly, the superscription “c” indicates that the corresponding wavefunction $\Phi_M^c$ is the variational solution of Eq(12) under the perturbation of $\psi_c$ [through $V_{coul}^{\psi_c}$ and $V_{exc}^{\psi_c}$]. Notice that, only in the strong confinement quantum dot size region [5], we can write $\Phi_N^*$ as $|\Phi_{N-1}^c\psi_c\rangle$ through Eq(8). In this size region, the electron and the hole are not correlated. As a result, we don’t have to write $\Phi_N^*$ as a summation of configurations $|\Phi_{N-1}^c\psi_c\rangle$ with different electron ($\psi_c$) and hole ($\psi_\nu$) wavefunctions. After the definitions of the wavefunctions, we can replace $E_N^*$, $E_N$, $E_{N-1}$ and $E_{N+1}$ by $\Phi_{N-1}^c | H_N | \Phi_{N-1}^c >$, $\Phi_N^c | H_N | \Phi_N^0 >$, $\Phi_{N-1}^0 | H_{N-1} | \Phi_{N-1}^0 >$ and $\Phi_N^c | H_{N+1} | \Phi_N^c >$, respectively. Using Eq(12), we have:

$$E_N^* - E_{N-1} = E_{\psi} + \Phi_{N-1}^c | H_{N-1} | \Phi_{N-1}^c > - \Phi_{N-1}^0 | H_{N-1} | \Phi_{N-1}^0 >$$

$$+ \int \rho_{N-1}^c(r)V_{coul}^{\psi_c}(r)d^3r - \int \rho_{N-1}^c(x, x')V_{exc}^{\psi_c}(x, x')d^3xd^3x', \quad (19)$$
and
\[ E_{N+1} - E_N = E_{\psi_e} + < \Phi_N^c | H_N | \Phi_N^c > - < \Phi_N^0 | H_N | \Phi_N^0 > \]
\[ + \int \rho_N^c(r)V_{\text{coul}}^\psi(r)d^3r - \int \rho_N^0(x,x')V_{\text{ex}}^\psi(x,x')d^3xd^3x'. \] (20)

The changes from \( \Phi_N^0 \) to \( \Phi_N^c \) can be described in first order by perturbation theory, under the external perturbation potentials \( V_{\text{coul}}^\psi(r) \) and \( V_{\text{ex}}^\psi \) in Eq(12). For a N-1 electron system, the energy changes from \( < \Phi_{N-1}^0 | H_{N-1} | \Phi_{N-1}^0 > \) to \( < \Phi_{N-1}^c | H_{N-1} | \Phi_{N-1}^c > \) in response to these perturbative potentials. The amplitude of this energy change is in the same order of the Coulomb interaction of the perturbation charge (\( \psi_e^2 \)) with the response charge of the system (which is also in the order of \( \psi_e^2 \)). In other words, \( \Delta E_{N-1} \equiv < \Phi_{N-1}^c | H_{N-1} | \Phi_{N-1}^c > - < \Phi_{N-1}^0 | H_{N-1} | \Phi_{N-1}^0 > \) scales as 1, instead of N. This is also evident from Eq(19). Note that \( E_N - E_{N-1} \) scales as 1. At the right hand side of Eq(19), combining the \( E_{\psi_e} \) term defined in Eq(13) with the \( \int \rho_{N-1}^c(r)V_{\text{coul}}^\psi(r)d^3r - \int \rho_{N-1}^c(x,x')V_{\text{ex}}^\psi(x,x')d^3xd^3x' \) term, one gets an energy similar to that of the Hartree Fock single particle eigen energy. Thus, this combined term also scales as 1. As a result, the \( \Delta E_{N-1} \) scales as 1. The same is true for \( \Delta E_N \equiv < \Phi_N^c | H_N | \Phi_N^c > - < \Phi_N^0 | H_N | \Phi_N^0 > \). The difference between \( \Delta E_{N-1} \) and \( \Delta E_N \) is the difference between N-1 and N electron system, which should scale as \( \Delta E_N/N \propto 1/N \). Thus, this difference is negligible comparing to the Coulomb energy \( E_{\text{coul}} \) which we are calculating. As a result, subtract Eq(20) from Eq(19), we have

\[ E_{\text{coul}} = \int [\rho_{N-1}^c(r) - \rho_N^c(r)]V_{\text{coul}}^\psi(r)d^3r \]
\[ - \int [\rho_{N-1}^c(x,x') - \rho_N^c(x,x')]V_{\text{ex}}^\psi(x,x')d^3xd^3x'. \] (21)

Further more, following the same perturbation argument, we have \( \rho_N^c(r) - \rho_N^0(r) \approx \rho_{N-1}^c(r) - \rho_{N-1}^0(r) \) and \( \rho_N^c(x,x') - \rho_N^0(x,x') \approx \rho_{N-1}^c(x,x') - \rho_{N-1}^0(x,x') \). Again, the approximation has an relative error \( \propto 1/N \), thus negligible. Then, we can change Eq(21) to

\[ E_{\text{coul}} = \int [\rho_{N-1}^0(r) - \rho_N^0(r)]V_{\text{coul}}^\psi(r)d^3r - \int [\rho_{N-1}^0(x,x') - \rho_N^0(x,x')]V_{\text{ex}}^\psi(x,x')d^3xd^3x'. \] (22)
This is our central result. Notice that, $\rho_{N-1}(r)$ is the total electron charge density of a N-1 electron system (containing one hole), and $\rho_N(r)$ is the total electron charge density of a N electron neutral system. Thus, $\rho^{srcv}(r) \equiv \rho_{N-1}(r) - \rho_{N}(r)$ is the screened hole charge (the bare hole charge plus the response screening charge) in the quantum dot. Note that

$$\int \rho^{srcv}(r) d^3r = -1.$$  \hspace{1cm} (23)

Thus, if we ignore the exchange interaction in Eq(22) (which is usually much smaller than the Hartree interaction), and express $V^\psi_{coul}(r)$ using Eq(14), we have

$$E_{exc} = E^{qp}_g + \int \frac{\rho^{srcv}(r_1) \rho_c(r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2$$  \hspace{1cm} (24)

where, $\rho_c(r) = \sum_\sigma |\psi_c(r\sigma)|^2$. In the case where phenomenological dielectric constant $\epsilon$ can be used to describe $\rho^{srcv}_v(r_1)$, we found that Eq(24) is in agreement with Eq(6), not Eq(7). More, explicitly, in that case we have

$$\rho^{srcv}_v(r) = -\frac{1}{\epsilon} \rho_v(r) \text{ for } r < R$$

$$= -(1 - \frac{1}{\epsilon}) \delta(r - R)/4\pi R^2 \text{ for } r \sim R$$

$$= 0 \text{ for } r > R,$$  \hspace{1cm} (25)

where $R$ is the quantum dot radius and $\rho_v(r) = \sum_\sigma |\psi_v(r\sigma)|^2$. Using the effective mass charge density $\rho_v(r) = \rho_c(r) = \sin^2(\pi r/R)/2\pi R^2$, we yield Eq(6) from Eq(24).

In the empirical electrostatic derivation of Eqs(1)-(2), it is not so clear whether the empirical single particle eigenvalues $\epsilon_e, \epsilon_h$ [in Eqs(1)-(2)] already include the effects of electrostatic energies. For example, when one electron is removed from the quantum dot, how to relate the single electron eigenvalue and classical electrostatic energy to the change of the total energy in the system is problematic [\textsuperscript{4,5}]. Here, deriving Eq(24) from the many-body wavefunctions, we do not have all these conceptional difficulties. That is the biggest advantage of the current derivation comparing to the classical empirical derivations [\textsuperscript{4,5}]. Notice
that, the dielectric constant $\epsilon$ is not derived here, unlike in the case of bulk exciton screening [2]. This, of course, doesn’t mean that we have no screening in our formalism. The dielectric screening of the Coulomb interaction is enclosed in $\rho^\text{src}_v$ of Eq(24) in our formula. We just didn’t derive the detail screening function in our formula (i.e, how to calculate $\rho^\text{src}_v$ from $\rho_v$ by a detail $\epsilon$ model). That is not the focus of our current study. In the cases of Eqs(6) and (7), the simple response model of Eq(25) is assumed. It is in this context, $\epsilon$ is used here, and Eq(6) is found to be correct.

IV. Coulomb energy associated with the single particle eigenvalues

Had proved Eq(6), now we like to test Eq(5). What important here is to define an effective single particle Hamiltonian, for which $\epsilon_v$ and $\epsilon_c$ are its conduction band minimum and valence band maximum eigen energies. Let’s start from the definition of the exciton energy: $E^\text{exc} = E^*_N - E_N$. Now, we will rewrite the N particle ground state wavefunction $\Phi^0_N$ of $E_N$ as $|\Phi^N_{N-1}\psi_v>$, with $\Phi^N_{N-1}$ being orthogonal to both $\psi_v$ and $\psi_c$. Using Eq(12), $E_N$ can be written as:

$$E_N - E_{\psi_v} = \langle \Phi^N_{N-1}|H_{N-1}|\Phi^N_{N-1} \rangle$$
$$+ \int \rho^N_{N-1}(r) V^{\psi_v}_\text{coul}(r) d^3r - \int \rho^N_{N-1}(x, x') V^{\psi_v}_\text{ex}(x, x') d^3xd^3x'. \quad (26)$$

Here, $E_{\psi_v}$ is evaluated from Eq(13). Similarly, like before, the exciton wavefunction can be expressed as $|\Phi^c_{N-1}\psi_c>$, with $\Phi^c_{N-1}$ being orthogonal to $\psi_v$ and $\psi_c$. Then, $E^*_N$ can be written as:

$$E^*_N - E_{\psi_c} = \langle \Phi^c_{N-1}|H_{N-1}|\Phi^c_{N-1} \rangle$$
$$+ \int \rho^c_{N-1}(r) V^{\psi_c}_\text{coul}(r) d^3r - \int \rho^c_{N-1}(x, x') V^{\psi_c}_\text{ex}(x, x') d^3xd^3x'. \quad (27)$$

Comparing Eq(27) with Eq(26), we find that we can obtain $\Phi^c_{N-1}$ from $\Phi^c_{N-1}$ by applying potentials $V^{\psi_c}_\text{coul} - V^{\psi_v}_\text{coul}$ and $V^{\psi_c}_\text{ex} - V^{\psi_v}_\text{ex}$ into Eq(26). More specifically we can define
\[
E(\beta) \equiv < \Phi_{N-1}^\beta | H_{eff}^\beta | \Phi_{N-1}^\beta > = \\
< \Phi_{N-1}^\beta | H_{N-1} + [(1 - \beta)V_{coul}^\psi_e + \beta V_{coul}^\psi_v] - [(1 - \beta)V_{ex}^\psi_e + \beta V_{ex}^\psi_v] | \Phi_{N-1}^\beta > . \tag{28}
\]

In Eq(28), \( \Phi_{N-1}^\beta \) is defined as the minimum energy variational solution of the Hamiltonian \( H_{eff}^\beta \), while subjected to orthogonal condition Eq(9) to \( \psi_c \) and \( \psi_v \). Using Eq(26) and Eq(27), we have \( E(\beta = 0) = E_N - E_{\psi_v} \) and \( E(\beta = 1) = E_N^* - E_{\psi_v}^* \). Now, using the “adiabatic integration technique”, we have

\[
E(\beta = 1) = E(\beta = 0) + \int_0^1 \frac{\partial E(\beta)}{\partial \beta} d\beta. \tag{29}
\]

Note, in Eq(28), \( \Phi_{N-1}^\beta \) is the variational solution of \( H_{eff}^\beta \), as a result,

\[
< \frac{\partial \Phi_{N-1}^\beta}{\partial \beta} | H_{eff}^\beta | \Phi_{N-1}^\beta > = < \Phi_{N-1}^\beta | H_{eff}^\beta | \frac{\partial \Phi_{N-1}^\beta}{\partial \beta} > = 0. \tag{30}
\]

Then, we have

\[
E(\beta = 1) = E(\beta = 0) + \int_0^1 \left\{ \int \rho_{N-1}^\beta (r) \left[ V_{coul}^\psi_e (r) - V_{coul}^\psi_v (r) \right] d^3r \\
- \int \tilde{\rho}_{N-1}^\beta (x, x') \left[ V_{ex}^\psi_e (x, x') - V_{ex}^\psi_v (x, x') \right] d^3x d^3x' \right\} d\beta. \tag{31}
\]

\( \rho_{N-1}^\beta \) and \( \tilde{\rho}_{N-1}^\beta \) are the density and density matrix of the N-1 electron system under the perturbation of \( \beta [V_{coul}^\psi_e - V_{coul}^\psi_v] \) and \( \beta [V_{ex}^\psi_e - V_{ex}^\psi_v] \) (the nonperturbed values are \( \rho_{N-1}^0 \) and \( \tilde{\rho}_{N-1}^0 \)). These perturbative potentials are due to charge density \( \beta [|\psi_c(x)|^2 - |\psi_v(x)|^2] \) and density matrix \( \beta [\psi_c(x)\psi_c^*(x') - \psi_v(x)\psi_v^*(x')] \). Here, we will only consider cases where a phenomenological macroscopic dielectric constant \( \epsilon \) can be used to describe the response of the N-1 electron system to these perturbative charges. These perturbative charges can be considered as external to the N-1 electron system. Thus, under this phenomenological description, the N-1 electron charges can be expressed as
\[
\rho_{N-1}^\beta(r) = \rho_{N-1}^\beta(r) + \beta\left(\frac{1}{\epsilon} - 1\right) \sum_\sigma |\psi_c(r, \sigma)|^2 - |\psi_v(r, \sigma)|^2
\]  
(32)

\[
\rho_{N-1}^\beta(x, x') = \rho_{N-1}^\beta(x, x') + \beta\left(\frac{1}{\epsilon} - 1\right) [\psi_c(x)\psi_c^*(x') - \psi_v(x)\psi_v^*(x')]
\]  
(33)

Note that, \(\rho_{N-1}^\beta(r) = \sum_\sigma \rho_{N-1}^\beta[(r, \sigma), (r, \sigma)]\), thus the dielectric constant \(\epsilon\) used to describe the response of \(\rho_{N-1}^\beta(r)\) [Eq(32)] and \(\rho_{N-1}^\beta(x, x')\) [Eq(33)] must be the same. Also notice that, the dielectric constant \(\epsilon\) used in Eqs(32),(33) is consistent with the conventional definition of \(\epsilon\), and there is no surface response charge as in Eq(25) because the net charge of \(\sum_\sigma |\psi_c(r, \sigma)|^2 - |\psi_v(r, \sigma)|^2\) is zero. Now, substitute Eqs(32)-(33) into Eq(31), carry out the \(\beta\) integration, we have:

\[
E^*_N - E_{\psi_c} = E_N - E_{\psi_v} + \int \{\rho_{N-1}^\beta(r) + \frac{1}{2}\left(\frac{1}{\epsilon} - 1\right) \sum_\sigma |\psi_c(r, \sigma)|^2 - |\psi_v(r, \sigma)|^2\} [V_{\text{coul}}^{\psi_c}(r) - V_{\text{coul}}^{\psi_v}(r)] d^3r
+ \int \{\rho_{N-1}^\beta(x, x') + \frac{1}{2}\left(\frac{1}{\epsilon} - 1\right) [\psi_c(x)\psi_c^*(x') - \psi_v(x)\psi_v^*(x')]\} [V_{\text{ex}}^{\psi_c}(x, x') - V_{\text{ex}}^{\psi_v}(x, x')] d^3xd^3x'.
\]  
(34)

Note that \(\rho_N^0(r) = \rho_{N-1}^\beta(r) + \sum_\sigma |\psi_v(r, \sigma)|^2\) and \(\rho_N^0(x, x') = \rho_{N-1}^\beta(x, x') + \psi_v(x)\psi_v^*(x')\), where \(\rho_N^0(r)\) and \(\rho_N^0(x, x')\) are the neutral system N electron ground state charge density and density matrix. Using this relations, and \(E_{\text{exc}} = E^*_N - E_N\), we can derive from Eq(34) that:

\[
E_{\text{exc}} = E_{\psi_c} - E_{\psi_v} + \int \rho_N^0(r)[V_{\text{coul}}^{\psi_v}(r) - V_{\text{coul}}^{\psi_v}(r)] d^3r - \int \rho_N^0(x, x')[V_{\text{ex}}^{\psi_v}(x, x') - V_{\text{ex}}^{\psi_v}(x, x')] d^3xd^3x'
- \frac{1}{\epsilon} \int \frac{|\psi_c(x)|^2|\psi_c(x')|^2}{|r - r'|} d^3xd^3x' + \frac{1}{\epsilon} \int \frac{\psi_v(x)\psi_v^*(x')\psi_v^*(x')}{|r - r'|} d^3xd^3x'.
\]  
(35)

Similar to Eqs(14) and (16), we can now define Coulomb and exchange potentials due to the N electron ground state charge density \(\rho_N^0(r)\) and density matrix \(\rho_N^0(x, x')\):

\[
V_{\text{coul}}^N(r) = \int \frac{1}{|r - r'|} \rho_N^0(r') d^3r'
\]  
(36)

\[
V_{\text{ex}}^N(x, x') = \frac{1}{|r - r'|} \rho_N^0(x, x')
\]  
(37)
Then, we can defined a effective single particle Hamiltonian $H_s$:

$$\epsilon_\psi \equiv \langle \psi | H_s | \psi \rangle = \int \psi^*(x) \left\{ \delta(x-x') \left[ -\frac{1}{2} \nabla^2 + V_{\text{ion}}(r) + V_{\text{coul}}^N(r) \right] - V_{\text{ex}}^N(x, x') \right\} \psi(x') d^3x d^3x'. \tag{38}$$

Using Eq(38), and Eqs(14),(16), the first part of Eq(35) can be simplified, and it leads to

$$E_{\text{exc}} = \epsilon_{\psi_c} - \epsilon_{\psi_v} - \frac{1}{\epsilon} \int \frac{|\psi_v(x)|^2|\psi_c(x')|^2}{|r - r'|} d^3x d^3x'$$

$$+ \frac{1}{\epsilon} \int \frac{\psi_c(x)\psi_c(x)\psi_v^*(x')\psi_v^*(x')}{|r - r'|} d^3x d^3x', \tag{39}$$

where $\epsilon_{\psi_c}$ and $\epsilon_{\psi_v}$ are the eigenvalues of the bottom of conduction band and top of valence band of the effective single particle Hamiltonian $H_s$ in Eq(38). This concludes our major result for this section.

Comparing Eq(39) to Eq(5), we notice that: (1) The bulk band gap $E_g^{\text{bulk}}$ in Eq(5) has been absorbed in the definition of the single particle eigen values $\epsilon_{\psi_c}$ and $\epsilon_{\psi_v}$. (2) The last term in Eq(5), which represents the classical instantaneous dielectric energy, does not exist in the current result. It is thus quite plausible that this term should not exist in Eq(4) either, which affects the electron affinity [Eq(1)], ionization energy [Eq(2)] and quasi-particle energy [Eq(3)].

Equation (39) confirms the conventional way to calculate the exciton energy via the single particle eigen values, e.g, as in the empirical pseudopotential approach \[11\]. Both the Hartree Coulomb interaction and the exchange interaction exist in Eq(39). Interestingly, following the assumption of Eqs(32)-(33), the exchange interaction is screened in Eq(39) just like the Coulomb interaction. This might shed some light on the long standing controversy about whether the exchange interaction should be screened \[1, 2, 19\] [notice also the second term in Eq(22)]. Also important here is that we have provided a definition of an effective single particle Hamiltonian $H_s$ in Eq(38) using the N electron charge density and density matrix. Equation (38) is like the variational equation obtained from Eq(12) for a given
$\Phi_M$. The difference is that, here, the same $\Phi_N$ is used for both $\psi_v$ and $\psi_c$. This $H_s$ can be compared with the conventional single particle Hamiltonians e.g., EPM [11], local density approximation (LDA) [20], quasi-particle GW calculation [18] and Hartree-Fock equation [14]. $H_s$ is almost the same as the Hartree-Fock equation, but that the uncorrelated HF exchange potential $V_{ex,HF}^N(x,x') = \frac{1}{|r-r'|} \sum_{i \in occ} \psi_i(x)\psi_i^*(x')$ has been changed to the correlated exchange potential $V_{ex}^N(x,x')$ of Eq(37). According to Eq(39), the eigenvalues of $H_s$ should provide the band structure (at least the band gap) of a bulk system. This remains to be tested.

Equations (6), (24) and Eq(39) represent two different approaches to calculate the exciton energy in a nanostructure. In the paper of Ogut et al [10], the first approach is taken. Unfortunately, Eq(7) instead of Eq(6) was used. If Eq(6) were used, the result of Ogut et al would be very close (within $\sim 0.1$ eV) to the results obtained via EPM calculations [11] and Eq(39) (a constant 0.68 eV Si LDA band gap correction needs to be added to $E_{qp,g,LDA}(R)$ in order to get this good agreement).

V. Numerical test of the formulae

Using local density approximation method, Ogut, et al [10] have calculated the $E_{N+1} - E_{N-1} - 2E_N$ and the single particle Kohn-Sham eigenvalues. If we approximate the Kohn-Sham eigenvalue as the single particle energies $\epsilon_{\psi_c}(\equiv \epsilon_c)$ and $\epsilon_{\psi_v}(\equiv \epsilon_v)$ given by Eq(38), then we have an good case to test our equations (24) and (39). According to Eqs(24) and (39), we have (ignoring the exchange interactions)

$$\Sigma \equiv (E_{N+1} - E_{N-1} - 2E_N) - (\epsilon_c - \epsilon_v) = (1 - \frac{1}{\epsilon(R)}) \frac{1}{R}$$

(40)

We have used the same symbol $\Sigma$ in Eq(40) as in Ref. [10], although we do not mean that it is the GW “selfenergy” as claimed in Ref. [10]. According to Eq(40), $\Sigma$ is simply an electrostatic energy between the electron charge and its induced surface charge. Although
there is a well known LDA error for the band gap energy, this error exists in both \((E_{N+1} + E_{N-1} - 2E_N)\) and \((\epsilon_c - \epsilon_v)\), thus should be cancelled. As a result, Eq(40) should still be valid for LDA calculations.

In Fig.1, the quantity \((E_{N+1} + E_{N-1} - 2E_N) - (\epsilon_c - \epsilon_v)\) is plotted as a function of \(1/R\). This quantity is compared with \((1 - 1/\epsilon(R))^R\). The agreement is quite good. Here, \(\epsilon(R)\) is a function of the quantum dot radius \(R\). This function is calculated in Ref. [21], and can be expressed as \(\epsilon(R) = 1 + (11.4 - 1)/(1 + (\alpha/R)^l)\). Here, we have used \(\epsilon(R)\) which corresponds to the total polarizibility of the quantum dot (\(\epsilon_s\) in Ref. [21]), i.e, \(\alpha = 4.25\,\AA\) and \(l = 1.25\). Of course, the agreement of Eq(40) depends on how good is the phenomenological macroscopic description of the quantum dot screening [Eq(25)]. There is no reason to believe that Eq(25) is exact for a small quantum dot. After considered all these uncertainties, the agreement in Fig.1 is quite good.

Notice that, the LDA Kohn-Sham single particle band gap \(\epsilon_c - \epsilon_v\) is almost the same (within 0.1 eV) as the single particle band gap calculated from empirical pseudopotential after a 0.68 eV band gap correction is added to LDA result. This can be confirmed by taken the data from Ref. [10] and Ref. [11]. It has also been confirmed separately by Delley etal in Ref. [22]. Then, using the good agreement between LDA \((E_{N+1} + E_{N-1} - 2E_N) - (\epsilon_c - \epsilon_v)\) and \((1 - 1/\epsilon(R))/R\) as shown in Fig.1, we know that the exciton energy \(E_{exc}\) calculated from LDA quasiparticle energy through Eq(6) [plus 0.68 eV correction], should be the same as \(E_{exc}\) calculated from empirical pseudopotential single particle eigen values through Eq(40) [11].

VI. Conclusions

One approximation [Eq(8)] to the many-body wavefunction is presented. This approximation allows us to define a single particle wavefunction in a many-body system. This approximation is more accurate than the Hartree-Fock Slater determinate for the many-
body wavefunction. Under this approximation, we have derived the Coulomb energy needed to relate the quasiparticle energy \( E_{qp} \) to the exciton energy \( E_{exc} \) (= the optical transition energy) [Eqs(22),(24)]. In the limit where the phenomenological description of the dielectric screening is valid, we found that the correct formula for this Coulomb energy is Eq(6), not Eq(7). We also derived the Coulomb energy which relates the single particle eigen values with the \( E_{exc} \) [Eq(39)]. We found that the classical instantaneous dielectric energy in the last term of Eq(5) does not exist in our currently derived formula [Eq(39)]. Under the assumption of Eqs(32)-(33), we found that the exchange interaction in Eq(39) is screened as for the Hartree interaction. Using Eq(24) and Eq(39) respectively, we found that the optical transition energy obtained from the LDA \( E_{qp} \) (plus the LDA band gap correction), is almost the same as the result obtained from the EPM single particle eigen values. Thus, the conclusion made in Ref. [14], that EPM misses the change of selfenergy with size \( R \), is incorrect. Finally, we presented an effective single particle Hamiltonian \( H_s \) [Eq(38)], which under the assumption of Eq(8), provides the band structure of a bulk system. Further testing of Eq(38) is needed.

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FIGURES

FIG. 1. The LDA calculated \((E_{N+1} + E_{N-1} - 2E_N) - (\epsilon_c - \epsilon_v)\) compared with the surface polarization Coulomb interaction \((1 - 1/\epsilon(R))/R\).
\[ A(\frac{-1}{R})^2 \times (E_{N+1} + E_{N-1} - 2E_N) - (\epsilon_c - \epsilon_v) \]

\[ (1 - \frac{1}{\epsilon(R)}) \times \frac{1}{R} \]

Fig.1, Wang, et al.