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The carrier "antibinding" in quantum dots: a charge separation effect

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Abstract. We show that the carrier "antibinding" observed recently in semiconductor quantum dots, i.e., the fact that the ground state energy of two electron-hole pairs goes above twice the ground-state energy of one pair, can entirely be assigned to a charge separation effect, whatever its origin. In the absence of external electric field, this charge separation comes from different "spreading-out" of the electron and hole wavefunctions linked to the finite height of the barriers. When the dot size shrinks, the two-pair energy always stays below when the barriers are infinite. On the opposite, because barriers are less efficient for small dots, the energy of two-pairs in a dot with finite barriers, ends by behaving like the one in bulk, i.e., by going above twice the one-pair energy when the pairs get too close. For a full understanding of this "antibinding" effect, we have also reconsidered the case of one pair plus one carrier. We find that, while the carriers just have to spread out of the dot differently for the "antibinding" of two-pairs to appear, this "antibinding" for one pair plus one carrier only appears if this carrier is the one which spreads out the less. In addition a remarkable sum rule exists between the "binding energies" of two pairs and of one pair plus one carrier.

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A very large amount of works are still devoted to the study of semiconductor quantum dots because of their possible applications in nanotechnology. The fundamental aspects of these quantum dots are however now essentially understood [1]: when a few carriers of mass m are confined in a box of characteristic size R, their kinetic energy is of the order of $\hbar^2/mR^2$, while their Coulomb energy is order of e^2/R; so that, if the box size is small compared to $\hbar^2/me^2$ (the so-called "strong-confinement regime"), Coulomb effects play a minor role — even if the absolute value of the Coulomb energy in a dot is larger than the usual one in bulk, for the carriers are closer. This is why the physics of quantum dots is essentially a one-body physics, driven by confinement: besides small energy shifts and level splittings, many-body effects in a dot are not expected to be of great interest in these confined systems.

Recently, however, a rather surprising "antibinding" effect has been observed in these dots: if one measures the lowest energy of two electron-hole pairs in the strong confinement regime, one finds that it goes from below to above twice the ground state energy of one-pair, when the dot size decreases (see Refs. [2–5] and references therein). Let us stress that this is not really an "antibinding" effect because the carriers always stay bound to the dot due to the strong confinement. A two-pair energy above twice one-pair is however surprising at first because we are used to biexciton always having an energy below twice the exciton energy. This actually comes from the fact that, in extended systems, the excitons can move freely; so that, to decrease their energy, they adjust their distance at an optimum value D^* which results from the competition between the kinetic energy they lose and the Coulomb energy they gain when they get closer.

The same argument may actually lead to think that the observed "antibinding" is in fact just normal! Indeed, if the particles get closer than D^*, which is what happens in small dots, the energy of two-pairs in bulk should start to rise because of the kinetic contribution. It should thus end by getting above twice the energy of one exciton. Consequently, it may appear as reasonable to find a

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two-pair "antibinding" when the dot size decreases, the pairs ending by being too close.

This way of thinking is actually incorrect: in a dot, the carriers are forced to stay together, at a given distance, by confinement. They have no choice! The kinetic energy necessary to stay so close, is actually paid once we put the carriers in the box. When comparing the energy of two pairs to twice the energy of one pair, we are thus left with the Coulomb parts only. As the dipolar attraction between electron-hole pairs makes their Coulomb contributions to the energy always negative, this should lead to a two-pair energy always below twice the energy of one pair, in contradiction with the experimental data.

The purpose of this paper is to show that the energy of two pairs going above twice the energy of one pair can entirely be assigned to charge separation, whatever its origin. It must be pointed out that such a charge separation exists even in the absence of an external electric field. It results from a "spreading-out" effect which increases when the dots shrink. The pairs, forced to stay closer than their optimum distance D^*, would love to get out of the box, in order to behave like free pairs in a bulk sample. This is of course impossible if the barrier height is really infinite: for such a barrier, the two-pair energy always stays below twice one-pair. However, for finite barriers, the carriers can partly escape from the dot and experience a subtle interplay between Coulomb interaction and confinement, i.e., interaction with the continuum linked to the environment of the dot [6]; consequently, the price in kinetic energy needed to put a carrier inside the dot is not really constant but depends on the dot size, through a *barrier-dependent* term.

In confined systems, what is really important is not so much the absolute value of the barrier height, but its relative value compared to the characteristic energy of the dot, namely $\hbar^2/mR^2$. This led us to introduce [7] the dimensionless parameter ν_i which characterizes a barrier of height V_i for a carrier of mass m_i trapped in a spherical dot of radius R. This parameter is defined as

$$V_i = \frac{\nu_i^2 \hbar^2}{2 m_i R^2}. \tag{1}$$

While ν_i is always infinite when V_i is infinite, it goes to zero for finite V_i when the dot shrinks: a dot size reduction makes a given barrier less and less efficient to prevent the carriers from spreading-out.

The purpose of this work is to show that the charge separation between the electron and the hole of a dot leads, just by itself, to a two-pair energy going above twice the one-pair energy. The analytical results presented here are very general, and apply to quantum dots of *any geometry* within the strong confinement regime: to use them for a particular experiment, one just has to introduce the specific carrier wave functions of the dot in the relevant quantities given in equations (2, 11, 13). For the purpose of illustration, the numerical results given here correspond to a model spherical dot. In order to fully control the physics of this phenomenon, we have also reconsidered analytically the case of one pair plus one carrier [9]. Even without electric field, the energy of one pair plus one hole ends by going above the energy of one pair plus the energy of one hole if — but only if — the electron spreads out more than the hole, while in the case of two pairs, the electron and hole just have to spread out *differently*, for the "antibinding" to appear.

General background on a few carriers in quantum dot

One carrier, electron *(e)*, or hole *(h)*, trapped in a dot, is characterized by a quantum number n_i, with $i = (e, h)$, its energy and wave function being $\epsilon_{n_i}^{(i)}$ and $\varphi_{n_i}^{(i)}(\mathbf{r})$. If we put more than one carrier in a dot, they feel each other by Coulomb interactions — and possibly by Pauli exclusion, if their spins are identical. The Coulomb potential in a confined geometry is characterized by a set of matrix elements $V^{(ij)}_{n_i' m_j' m_j n_i}$ between electrons, between holes and between electrons and holes, defined as

$$V^{(ij)}_{n_i' m_j' m_j n_i} = \int d^3\mathbf{r}\, d^3\mathbf{r}'\, \varphi_{n_i'}^{(i)\,*}(\mathbf{r})\, \varphi_{m_j'}^{(j)\,*}(\mathbf{r}') \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, \varphi_{m_j}^{(j)}(\mathbf{r}')\, \varphi_{n_i}^{(i)}(\mathbf{r}). \tag{2}$$

In small enough dots, it is well-known that the energy of a few carriers is dominated by the kinetic contribution, and so that the Coulomb interactions can be treated as a perturbation [1,8]. Up to second order, the ground state energy of one electron-hole pair thus reads as

$$\mathcal{E}_{\bar{0}}^{(eh)} = \epsilon_0^{(e)} + \epsilon_0^{(h)} - V_{0000}^{(eh)} + W^{(eh)} + \cdots \tag{3}$$

where 0 is the ground state quantum number, the second order Coulomb term $W^{(i,j)}$ being

$$W^{(ij)} = \sum_{(n_i, m_j) \neq (0,0)} \frac{|V^{(ij)}_{n_i m_j 00}|^2}{\epsilon_0^{(i)} + \epsilon_0^{(j)} - \epsilon_{n_i}^{(i)} - \epsilon_{m_j}^{(j)}}. \tag{4}$$

In the same way, the ground state energy of one pair plus one carrier $i = (e, h)$, with different spins, reads

$$E_0^{(ehi)} = \epsilon_0^{(e)} + \epsilon_0^{(h)} + \epsilon_0^{(i)} + V_{0000}^{(ii)} - 2\, V_{0000}^{(eh)} + W^{(ii)} + 2\, W^{(eh)} \tag{5}$$

while the ground state energy of two pairs with different spins is given by

$$E_0^{(eehh)} = 2\,\epsilon_0^{(e)} + 2\,\epsilon_0^{(h)} + V_{0000}^{(ee)} + V_{0000}^{(hh)} - 4\, V_{0000}^{(eh)} + W^{(ee)} + W^{(hh)} + 4\, W^{(eh)} + \cdots \tag{6}$$

The Coulomb expansions of the carrier energies given above are valid when the dot size is small, more precisely when the dimensionless parameter r_d, characterizing a dot of volume Ω, defined as

$$\Omega = \frac{4}{3}\pi r_d^3 a_X^3 \tag{7}$$

is small compared to 1, $a_X = \hbar^2/\mu e^2$ being the Bohr radius with $\mu^{-1} = m_e^{-1} + m_h^{-1}$. (For spherical dot, r_d is just the dot radius in Bohr units). The Coulomb expansions (3-6), valid for small dots, in fact correspond to a small r_d expansion.

Equations (3, 6) allow to obtain the lowest energies of one pair, two pairs and one pair plus one carrier for *any dot shape and barrier height*, up to second order in Coulomb interaction: to get them, we just need to first determine the free carrier eigenstates, $\epsilon_{n_i}^{(i)}$ and $\varphi_{n_i}^{(i)}(\mathbf{r})$ (see e.g. [2,3,6]), and then to use these wave functions in the $V^{(ij)}$ Coulomb matrix elements defined in equation (2).

For the purpose of illustration, we here consider a *model spherical dots with infinite barriers*. The problem is quite simple in the case of spherical dots because the free carrier eigenstates are then analytically known, the ground state energy being given by

$$\epsilon_0^{(i)} = \frac{\pi^2}{r_d^2}\frac{\mu}{m_i}\,R_X \tag{8}$$

with $R_X = \hbar^2/2\,\mu\,a_X^2$. As the wave functions $\varphi_{n_i}^{(i)}(\mathbf{r})$ for infinite barriers do not depend on mass, the $V^{(ij)}_{n_i' m_j' m_j n_i}$'s do not depend on (i,j), the one between ground states being equal to $V_{0000}^{(ij)} \simeq 3.57\,R_X/r_d$. This makes all the second order Coulomb terms $W^{(ij)}$ also equal for equal electron and hole masses - while they differ for $m_e \neq m_h$.

Consequently, in the case of spherical dots with infinite barriers, we find the following energy expansions:

$$\begin{aligned}
\mathcal{E}_0^{(eh)} &= R_X\left[\frac{\pi^2}{r_d^2} - \frac{3.57}{r_d} - c^{(eh)}(m_e,m_h) + \mathcal{O}(r_d)\right]\\
E_0^{(ehi)} &= R_X\left[\frac{\pi^2}{r_d^2}\left(1+\frac{\mu}{m_e}\right) - \frac{3.57}{r_d}\right.\\
&\qquad\left. - c^{(ehi)}(m_e,m_h) + \mathcal{O}(r_d)\right]\\
E_0^{(eehh)} &= 2\,R_X\left[\frac{\pi^2}{r_d^2} - \frac{3.57}{r_d} - c^{(eehh)}(m_e,m_h) + \mathcal{O}(r_d)\right].
\end{aligned} \tag{9}$$

For $m_e = m_h$, all the W's are equal to $(-\gamma\,R_X)$ with $\gamma = 0.133$ so that $c^{(eh)} = \gamma$, while $c^{(ehi)} = c^{(eehh)} = 3\,\gamma$ (Note that $E_0^{(eehh)}$ has a factor 2 in front). For different electron and hole masses, more precisely, in the particular case of $m_e = 0.0665$ and $m_h = 0.340$, which corresponds to pure $GaAs$, these quantities become $c^{(eh)} = 0.182$, $c^{(ehh)} = 0.772$, $c^{(ehe)} = 0.444$ while $c^{(eehh)} = 0.608$ (The first 20 electron and 20 hole levels were taken into account to achieve convergence of these sums).

Carrier "binding" energy

The "binding" energy $\Delta^{(ehi)}$ of one pair plus one carrier $i = (e,h)$ can be defined as

$$\begin{aligned}
-\Delta^{(ehi)} &= E_0^{(ehi)} - \mathcal{E}_0^{(eh)} - \epsilon_0^{(i)}\\
&= \delta_1^{(ehi)} + \delta_2^{(ehi)} + \cdots
\end{aligned} \tag{10}$$

Using equations (3, 5), we find that the second order term is just $\delta_2^{(ehi)} = W^{(eh)} + W^{(ii)}$ while the first order term can be rewritten [9], using the definition of $V_{0000}^{(ij)}$ given in equation (2), as

$$\delta_1^{(ehi)} = \int d\mathbf{r}\,d\mathbf{r}'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,n_i(\mathbf{r})\;|\varphi_0^{(i)}(\mathbf{r}')|^2 \tag{11}$$

where $n_i(\mathbf{r}) = n(\mathbf{r}) = |\varphi_0^{(h)}(\mathbf{r})|^2 - |\varphi_0^{(e)}(\mathbf{r})|^2$ for $i = h$ and $n_i(\mathbf{r}) = -n(\mathbf{r})$ for $i = e$.

In the same way, the "binding" energy of two pairs can be defined as

$$\begin{aligned}
-\Delta^{(eehh)} &= E_0^{(eehh)} - 2\,\mathcal{E}_0^{(eh)}\\
&= \delta_1^{(eehh)} + \delta_2^{(eehh)} + \cdots
\end{aligned} \tag{12}$$

When using equations (3,6), the second order term is just $\delta_2^{(eehh)} = W^{(ee)} + W^{(hh)} + 2\,W^{(eh)}$ while the first order term now reads

$$\delta_1^{(eehh)} = \int d\mathbf{r}\,d\mathbf{r}'\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,n(\mathbf{r})\,n(\mathbf{r}'). \tag{13}$$

From equations (11, 13) and the definitions of the δ's, it is easy to check that a remarkable sum rule exists between the "binding energies" of two pairs and of one pair plus one carrier:

$$\begin{aligned}
\delta_1^{(eehh)} &= \delta_1^{(ehe)} + \delta_1^{(ehh)}\\
\delta_2^{(eehh)} &= \delta_2^{(ehe)} + \delta_2^{(ehh)}.
\end{aligned} \tag{14}$$

Let us stress that equations (11, 13) as well as equation (14) are completely general, i.e., they *do not rely on any specific assumption for the dot geometry nor on a possibly non-zero electric field*. From equations (11, 13) we already see that the first order Coulomb terms of these "binding" energies reduce to zero if $n(\mathbf{r}) = 0$ everywhere, i.e., if the dot has a local carrier neutrality.

Dot with local carrier neutrality

Local carrier neutrality implies the absence of any external electric field which tends to tear apart opposite charges. We also need to assume infinite barriers or, possibly, carriers spreading out of the dot identically, for their wave functions to be the same.

For $n(\mathbf{r}) = 0$, the first order terms, $\delta_1^{(ehi)}$ and $\delta_1^{(eehh)}$ reduce to zero [10]. If we now turn to the second order

terms, $\delta_2^{(ehi)}$ and $\delta_2^{(eehh)}$, we see that they are both negative, for all the W's are negative, the sum they contain being taken over excited states. These second order terms, which are the dominant ones in small dots in the absence of first order terms, make the two binding energies $\Delta^{(ehi)}$ and $\Delta^{(eehh)}$ positive (for the latter case, see [8]). We conclude that, in a small dot with infinite barrier, two-pairs, and one-pair plus one carrier, are always below the "dissociated" configuration, i.e., twice one-pair or one-pair and one carrier.

Dot with local charge separation

For non-zero electric fields, or for finite barriers and different masses, i.e., different (m_i, V_i), the two types of carriers generally have different wave functions, so that $n(\mathbf{r})$ differs from zero. Due to $e^2/|\mathbf{r}-\mathbf{r}'|$, the integrals of $\delta_1^{(ehi)}$ and $\delta_1^{(eehh)}$, in equations (11, 13), are dominated by the $\mathbf{r} \simeq \mathbf{r}'$ domain. As for such $(\mathbf{r}, \mathbf{r}')$, we have $n(\mathbf{r})\, n(\mathbf{r}') \simeq [n(\mathbf{r})]^2$, so that the integrand of $\delta_1^{(eehh)}$ is positive in the relevant part of the integral, whatever the sign of $n(\mathbf{r})$, making $\delta_1^{(eehh)}$ always positive.

If we turn to $\delta_1^{(ehi)}$, we see that, due to the additional $|\varphi_0^{(i)}(\mathbf{r})|^2$, the important part of the integral given in equation (11), is now the one for $\mathbf{r} \leq R$. Consequently, the sign of $\delta_1^{(ehi)}$ is controlled by the sign of $n_i(\mathbf{r})$ inside the dot. As the electron is usually the carrier which spreads out the more, the hole wave function in the dot is larger than the electron one, for the wave functions are normalized. This leads to $n(\mathbf{r})$ essentially positive in the dot, making $\delta_1^{(ehh)}$ positive and $\delta_1^{(ehe)}$ negative.

When the first and second order terms are both negative, as for (ehe), the carrier "binding" energy is unambiguously positive, even for extremely small dots. On the opposite, when the first order term is positive, as for $(eehh)$ and (ehh), this first order term — even if it is very small, i.e., if the electron and hole nearly have the same wave function — must end by being the dominant Coulomb contribution when the dot shrinks. Consequently, the carrier "binding" energy, positive for intermediate dot sizes — as it is then dominated by the second order Coulomb term — must turn negative when the dot shrinks, in qualitative agreement with experimental data [2,3]. Therefore the phenomenon of competition between first and second order Coulomb contributions drives the cross-over between binding and antibinding. In [10] we find a numerical calculation up to second order in the Coulomb interaction illustrating ideally our argument. One even notices that our sum rule (14) is accurately verified by Figure 2 of [10] in most of the size range (namely above $r = 90$ A). Unfortunately in the antibinding region, below $r = 90$ A, a small discrepancy appears, probably due to limitations in the calculation of the second order term. Nevertheless the overall numerical result of Figure 2 beautifully confirms the findings of our analytical theory.

To conclude we state our main thesis which says that, in order to find an "antibinding" for two-electron-hole pairs, we just need $n(\mathbf{r}) \neq 0$, i.e., a carrier local non-neutrality, while to find such an "antibinding" for one-pair plus one carrier, we need an excess charge inside the dot of the same sign than the additional carrier. This conclusion fully agree with experimental data [11–13].

Link with the carrier spreading-out

Let us end this work by taking again for an illustration, a quantum dot with a spherical geometry, and show how we can relate the dot size for the cross-over from "binding" to "antibinding" of $(eehh)$ and (ehh), to one of the important physical quantities for carriers in dots, namely their spreading-out lengths.

In a previous communication [7], we have shown that the energies of a particle with mass m_i in a spherical dot of radius R and barrier height V_i, are given by $\alpha_i^2 \hbar^2/2m_i R^2 \equiv \alpha_i^2\, R_X(\pi^2/r_d^2)(\mu/m_i)$. The α_i's for states with $l = 0$ symmetry fulfil $\nu_i = \alpha_i/\sin(\alpha_i)$, where ν_i is the parameter defined in equation (1). In the large ν_i limit, i.e., for large V_i, this leads to $\alpha_i \sim \pi/(1+\nu_i^{-1})$ for the ground state; so that the spatial extension d_i of this ground state, defined as $E_i = \hbar^2/2m_i d_i^2$, varies with the effective barrier height ν_i as $d_i \simeq R\,(1+\nu_i^{-1})$. Note that, as expected, d_i is just equal to R for infinite barriers, i.e., for infinite ν_i.

We now use this result in the "binding" energy first order terms, equations (11, 13): since, due to dimensional arguments, $|\varphi^{(i)}|^2 \simeq 1/d_i^3$, the first order term $\delta_1^{(eehh)}$, given in equation (13), can be estimated as

$$\delta_1^{(eehh)} \simeq R^3 R^3 \frac{e^2}{R}\left(\frac{1}{d_h^3}-\frac{1}{d_e^3}\right)^2 \simeq \frac{e^2\,(d_e-d_h)^2}{R^3} \simeq \frac{e^2\,(\nu_e^{-1}-\nu_h^{-1})^2}{R^3} \qquad (15)$$

while the same argument leads to

$$\delta_1^{(ehh)} \simeq \frac{e^2\,(\nu_e^{-1}-\nu_h^{-1})}{R} \qquad (16)$$

with a similar result for $\delta_1^{(ehe)}$.

We now define the characteristic length l_i over which a carrier m_i spreads out of a material having a barrier V_i, as

$$V_i = \frac{\hbar^2}{2m_i l_i^2}. \qquad (17)$$

(Note that this l_i is inversely proportional to $\sqrt{m_i V_i}$, while it is exactly 0 for infinite barrier.) Following part I, the second order Coulomb term is of the order of $(-e^2/a_X)$, so that, from the definition of ν_i given in equation (1) — in which enters the dot radius — we obtain a cross-over radius from "binding" to "antibinding" which behaves as

$$R^{(eehh)} \simeq \sqrt[3]{a_X(l_e-l_h)^2} \qquad (18)$$

$$R^{(ehi)} \simeq \sum_{j=(e,h)} \Theta(l_j-l_i)\sqrt{a_X(l_j-l_i)} \qquad (19)$$

where $\Theta(x)$ is the step function. This gives a finite cross-over radius for $(eehh)$ whatever (l_e, l_h) are, while the one for (ehi) depends on the sign of $(l_e - l_h)$. For $l_e - l_h > 0$, which is the most usual situation, the cross-over radius for (ehh) is finite while the one for (ehe) is zero, i.e., no cross-over takes place when the dot is negatively charged.

Equations (18, 19) also show that when the barriers are very high, the spreading-out lengths l_i are very small, so that the cross-over radii are very small. For usual barrier heights, however, the l_i's are of the order of the Bohr radius a_X, making the cross-over radii also of the order of a_X. In order to fit a particular experiment, it is possible to get precise values of these cross-overs by going back to the expressions of the energies given in equations (3–6), the purpose of this last part being just to get *a physical understanding of this cross-over by establishing its physical link with the carrier spreading-out lengths*.

One should not however conclude in all cases that charge separation increases when the quantum dot size diminishes. For example in wurtzite-type GaN/AlGaN heterostructures, where piezoelectricity or spontaneous polarization are prominent effects, charge separation effects may increase with the quantum dot size [14], therefore the behaviour of "binding energies" with the box size may be strongly affected.

Comparison with other approaches

A number of authors have made very complex calculations of 3D wave functions (accounting for the details of the confinement potential resulting from the inhomogeneous strain, band mixing, and the piezoelectric potential), and subsequently have carried out configuration-interaction calculation of the biexciton binding energy. Although it is not our purpose here to include such effects, our approach is able fully exploit the results of any such complex 3D numerical single particle wave functions: the contrast lies in the analysis of the results. An evaluation of equation (12) with such wave functions allows to firmly assess the exact size limit for the validity of the strong confinement regime: for that, we just have to compare the level shifts of the two approaches. More important, equation (12) also allows to assess the relative magnitude of the first and second order Coulomb contributions for different dot sizes. Note that in the second order contribution, can also enter a nearby continuum of states. Finally, a numerical evaluation of equation (13) allows *to prove* that charge separation is already of importance at first order, and being actually the *main cause* for the antibinding of two pairs.

Let us now show how the results presented here, which are completely general, would actually bring useful insights in the understanding of specific experiments.

We focus on references [2,3] where the transition from binding and antibinding is systematically studied, both experimentally and numerically. These authors find a qualitative agreement with experiments when the aspect ratio is varied, but not the dot size. Their results also show that, in the two-pair ground state of the largest dot, namely 20 nm, there is still a relatively small mixing with the other excited states due to the Coulomb interaction, showing in this way that, in smaller dots, the strong confinement regime is certainly reached. The antibinding is then attributed to a number of combined effects such as "3D confinement, quenching correlations and exchange, and causing local charge separation", without precise evaluation of their relative importance, this relative importance being however crucial for physical understanding.

In order to show how we can analyze the results of the numerical approaches within our procedure, let us focus on the calculation presented in [2]. In this work, the authors do not vary the dot size to understand the transition to antibinding — which is the physically relevant parameter — but vary the number of confined states they include in the sums — which only is a mathematically relevant parameter. Indeed, their numerical procedure is (i) *to fix the dot size at 13 nm* and (ii) *to vary the number of bound states taken into account* in the calculation, between 1 and 3. From our approach, it is clear that there are fundamental flaws in this procedure: indeed, the confinement energy and the first and second order Coulomb contributions all have *a different*, but crucial, *dot size dependence* (see e.g. the explicit r_d dependence in Eq. (6)) these dependences having nothing to do with the possible variation of the number of confined states included in the numerical calculation. The latter procedure amounts to only change the magnitude of the second order terms, *without any size effect*.

A refined set of calculations is presented in reference [3] where the previous criticism do not fully apply. Indeed the authors convincingly show that a complex CI calculation reproduces the trend of the experiments when one truly varies the QD size. They attribute the crossing to "correlation" (which we here simply call "second order corrections"). The authors of reference [3] check that the number of excited hole bound states affect the crossing, while the electrons do not. We agree and think that this is a natural result of the smaller hole level spacing. However besides the convergence check we feel again that it is difficult to draw definitive *physical* conclusions about the actual number of bound states from this artificial procedure. In particular we note that there are also in principle contributions from the continuum, and when a higher bound state "disappears", it merges in the continuum, however it is not obvious to guess how much this effect increases the contribution of the continuum.

The "Quantum Confined Stark Effect" on one and two-pair states in small dots has also been investigated in two different sets of experiments namely, random local field [12], or external field [15]. Both show that the binding energy of two-pairs decreases with the external electric field strength at the dot position. Such a behaviour is in perfect agreement with our discussion concerning the importance, the sign and magnitude of the first order term (13) in small dots, as a function of charge separation.

Experiments [11–13], involving the states of one pair plus one carrier (the so-called "charged excitons"), with possibly an additional external field [12,13], show that, in small dots, the binding energy is of opposite sign for

the two types of excess charge, and that the trend to "antibind" is enhanced by the field for both types of excess charge. The authors explain it qualitatively by saying that the electric field tends to tear apart opposite charges and keep together identical charges, so that the repulsive Coulomb interactions are wining over the attractive ones when the field increases. This first explanation is fully intuitive. Our equation (11) shines new light on this problem because it demonstrates that, in the end, it is just this exact integral involving only the charge separation, evaluated with single-particle wavefunctions, that matters to understand the behaviour of the "binding energy".

Conclusion

We have shown, in very general terms, that the two-pair ground state energy, in strongly confined quantum dots, can possibly go above twice the energy of one-pair due to a single physical quantity: the local charge separation. Our conclusion holds independently of the physical origin of the charge separation, which can be complex and internal (e.g. due to piezoelectric fields resulting from strain), or external (e.g. applied electric fields). Even in the absence of electric field, local charge separation can be induced by finite barrier heights, the carriers spreading out of the dot differently. Only the precise value of the cross-over is influenced by the complicated geometry of real dots. It is attributed to a competition effect between the first and second order Coulomb contributions. While such an "antibinding" always exists for two-pairs, it only exists for one-pair plus one carrier if the additional carrier is the one which spreads out the less. For illustration, we have, in the case of spherical dots, related the radius of the cross-over from "binding" to "antibinding" to the typical carrier spreading-out lengths induced by the finite dot barriers. As a by-product we have also found a remarkable sum rule for the "binding energies" of two pairs and one pair plus one carrier. Finally, we have shown how our approach can be used to analyse the results of complex numerical calculations of two-pair states in realistic dot geometry, and how it allows to reinterpret a variety of experimental data in strongly confined quantum dots.

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