Dissociation of Vertical Semiconductor Diatomic Artificial Molecules

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(Received 10 May 2001; published 18 July 2001)

We investigate the dissociation of few-electron circular vertical semiconductor double quantum dot artificial molecules at 0 T as a function of interdot distance. A slight mismatch introduced in the fabrication of the artificial molecules from nominally identical constituent quantum wells induces localization by offsetting the energy levels in the quantum dots by up to 2 meV, and this plays a crucial role in the appearance of the addition energy spectra as a function of coupling strength particularly in the weak coupling limit.

DOI: 10.1103/PhysRevLett.87.066801 PACS numbers: 73.21.–b, 36.40.Ei, 71.15.Mb, 85.35.Be

Semiconductor quantum dots (QD's) are widely considered as artificial atoms, and are uniquely suited to study fundamental electron-electron interactions and quantum effects [1]. There are many analogies with "natural" atoms. One of the most appealing is the capability of forming molecules. Indeed, systems composed of two QD's, artificial quantum molecules (QM's), coupled either laterally or vertically, have recently been investigated experimentally [2,3] and theoretically [4–7]. Nevertheless, the direct observation of a systematic change in the addition energy spectra for few-electron (number of electrons, $N < 13$) QM's as a function of interdot coupling has not been reported, and calculations of QM properties widely assume *a priori* that the constituent QD's are identical [4–6]. Special transistors incorporating QM's [8] made by vertically coupling two well defined and highly symmetrical QD's [9] are ideally suited to observe the former and test the latter.

In this Letter we present experimental and theoretical addition energy spectra characterizing the dissociation of slightly asymmetric vertical diatomic QM's on going from the strong to the weak coupling limits that correspond to small and large interdot distances, b, respectively. We also show that spectra calculated for symmetric diatomic QM's resemble only those actually observed when the coupling is strong. The interpretation of our experimental results is based on the application of local-spin density-functional theory (LSDFT) [10–12]. It follows the development of the method thoroughly described in Ref. [12], which includes finite thickness effects of the dots, and uses a relaxation method to solve the partial differential equations arising from a high order discretization of the Kohn-Sham equations on a spatial mesh in cylindrical coordinates [13]. Axial symmetry is imposed, and the exchange-correlation energy has been taken from Perdew and Zunger [10].

The molecules we study are formed by coupling, quantum mechanically and electrostatically, two QD's which individually can show clear atomiclike features [8,9]. For the materials we typically use, the energy splitting between the bonding and antibonding sets of single particle (sp) molecular states, Δ_{SAS}, can be varied from about 3.5 meV for $b = 2.5$ nm (strong coupling) to about 0.1 meV for $b = 7.5$ nm (weak coupling) [8]. This is expected to have a dramatic effect on the electronic properties of QM's [5–7,12]. Figure 1 shows (a) a schematic diagram of a submicron circular mesa, diameter D, containing two vertically coupled QD's, and (b) a scanning electron micrograph of a typical mesa after gate metal deposition. The starting material, a special triple barrier resonant tunneling structure, and the processing recipe are described elsewhere [8,14]. Current I_d flows through the two QD's, separated by the central barrier of thickness b, between the substrate contact and grounded top contact in response to voltage V_d applied to the substrate, and gate voltage V_g. The structures are cooled to about 100 mK and no magnetic field is applied.

To analyze the experiments we have modeled the QM by two axially symmetric QD's. The QM is confined in the radial direction by a harmonic oscillator potential $m\omega^2 r^2/2$ of strength $\hbar\omega = 5$ meV (a realistic lateral confinement energy for a single QD in the few electron limit [9,15]), and in the axial (z) direction by a double

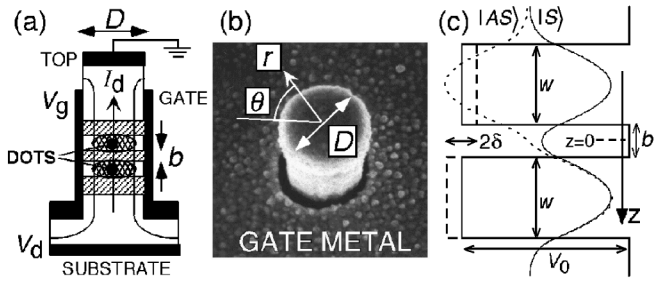

FIG. 1. Schematic diagrams of (a) mesa containing two vertically coupled quantum dots and (c) double quantum well structure, and (b) scanning electron micrograph of a typical circular mesa.

quantum well structure whose wells are of the same width w, and have depths $V_0 \pm \delta$, with $\delta \ll V_0$ [16]. Figure 1(c) schematically shows the double quantum well structure and its unperturbed bonding and antibonding sp wave functions. We have taken $V_0 = 225$ meV and $w = 12$ nm, which are appropriate for the actual experimental devices. If δ is set to zero, the artificial molecule is symmetric ("homonuclear" diatomic QM); otherwise, it is asymmetric ("heteronuclear" diatomic QM). In the calculations here, δ is 0, or is set to a realistic value of 0.5 or 1 meV [17]. In the homonuclear case Δ_{SAS} is well reproduced by the law $\Delta_{SAS}(b) = \Delta_0 e^{-b/b_0}$ with $b_0 = 1.68$ nm, and $\Delta_0 = 19.1$ meV. It is easy to check that in the weak coupling limit 2δ is approximately the energy splitting between the bonding and antibonding sp states which would be almost degenerate if δ is 0. For this reason we call the mismatch (offset) the quantity 2δ.

Figure 2(a) shows calculated addition energy spectra, $\Delta_2(N) = U(N+1) - 2U(N) + U(N-1)$, for homonuclear QM's with realistic values of b conveniently normalized as $\Delta_2(N)/\Delta_2(2)$. $U(N)$ is the total energy of the N-electron system. $\Delta_2(N)$ can reveal a wealth of information about the energy required to place an extra electron into a QD or QM system [9,18]. For small $b(\Delta_{SAS} \gtrsim \hbar\omega)$ the spectrum of a few electron QM is rather similar to a single QD, at least for $N < 7$ [15]. At intermediate dot separation, the spectral pattern becomes more complex. However, a simple picture emerges at larger interdot distances when the molecule is about to dissociate. For example, at $b = 7.2$ nm strong peaks at $N = 2$, 4, 12, and a weaker peak at $N = 8$ appear that can be easily interpreted from the peaks appearing in the single QD spectrum. The peaks at $N = 4$ and 12 in the QM are a consequence of symmetric dissociation into two closed shell (magic) $N = 2$ and 6 QD's, respectively, whereas the peak at $N = 8$ corresponds to the dissociation of the QM into two identical stable QD's holding four electrons each filled according to Hund's first rule to give maximal spin [6,9]. The QM peak at $N = 2$ is related to the localization of one electron on each constituent dot, the two-electron state being a spin-singlet QM configuration.

Since the modeled QM is homonuclear, each sp wave function is shared 50%–50% between the two constituent QD's. Electrons are completely delocalized in the strong coupling limit. As b increases, Δ_{SAS} decreases and eventually bonding, $|S\rangle$, and antibonding, $|AS\rangle$, sp molecular states become quasidegenerate. Electron localization can thus be achieved combining these states as $(|S\rangle \pm |AS\rangle)/\sqrt{2}$.

We conclude from Fig. 2(a) that the fingerprint of a dissociating few-electron homonuclear diatomic QM is the appearance of peaks in $\Delta_2(N)$ at $N = 2$, 4, 8, and 12 [6]. This is a robust statement, as it stems from the well understood shell structure of a single QD. If we now compare this picture with the experimental spectra shown in Fig. 2(b), we are led to conclude that the experimental devices are not homonuclear, but heteronuclear QM's.

The origin of the mismatch is the difficulty in fabricating two perfectly identical constituent QD's in the QM's discussed here, even though all the starting materials

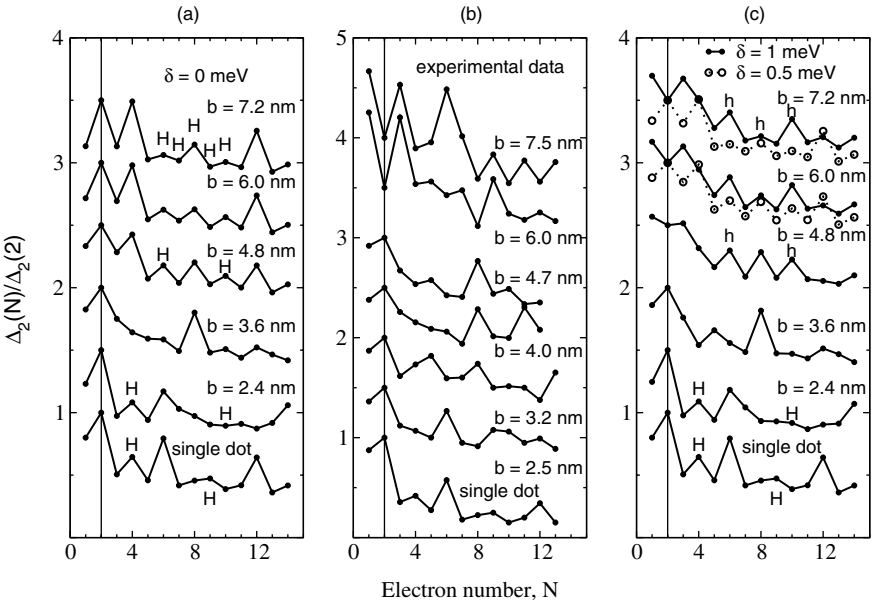

FIG. 2. (a) Calculated $\Delta_2(N)/\Delta_2(2)$ for homonuclear QM's with different interdot distances, b. Also shown is the calculated reference spectrum for a single QD. (b) Experimental QM addition energy spectra, $\Delta_2(N)/\Delta_2(2)$, for several interdot distances between 2.5 and 7.5 nm. Also shown is an experimental reference spectrum for a single QD [18]. (c) Same as panel (a) but for heteronuclear QM's obtained using a $2\delta = 2$ meV mismatch (dotted lines for $b = 6.0$ and 7.2 nm are for $2\delta = 1$ meV). In each panel the curves have been vertically offset so that at $N = 2$ they are equally separated by 0.5 units for clarity. All traces in panels (a) and (c) except 3.6 and 6.0 nm: $H(h)$ marks cases where we could clearly identify Hund's first rule like filling within single dot, or bonding or antibonding states (constituent dot states).

incorporate two nominally identical quantum wells. This mismatch can clearly influence the degree of delocalization-localization, and the consequences will depend on how big 2δ is in relation to Δ_{SAS} [7,19]. Elsewhere we will discuss how the effective value of Δ_{SAS} is measured, and the mismatch is determined for all values of b [17], so we merely note here that 2δ is typically 0.5 to 2 meV and nearly always with the upper QD (nearest top contact of mesa) states at higher energy than the corresponding lower QD states [see Fig. 1(c)].

Figure 2(b) shows experimental spectra, also normalized as $\Delta_2(N)/\Delta_2(2)$, for QM's with b between 2.5 and 7.5 nm, deduced accurately from peak spacings between Coulomb oscillations ($I_d - V_g$) measured by applying an arbitrarily small bias ($V_d < 100\ \mu V$). Likewise, also shown is a reference spectrum for a single QD [18]. The diameters of the mesas lie in the range of 0.5 to 0.6 μm, and while all mesas are circular, we cannot exclude the possibility that the QM's and QD's inside the mesas may actually be slightly noncircular, and that the confining potential is not perfectly parabolic as N increases [18,20]. We emphasize the following: (i) The spectrum for the most strongly coupled QM ($b = 2.5$ nm) resembles that of the QD up to the third shell ($N = 12$). (ii) For intermediate coupling ($b = 3.2$ to 4.7 nm), the QM spectra are quite different from the QD spectrum, and a fairly noticeable peak appears at $N = 8$. (iii) For weaker coupling ($b = 6.0$ and 7.5 nm) the spectra are different again, with prominent peaks at $N = 1$ and 3.

We confirmed the heteronuclear character of the QM's by performing LSDFT calculations with a 2 meV mismatch. The results are displayed in Fig. 2(c). For $b = 6.0$ and 7.2 nm, spectra for a 1 meV mismatch are also given. One-to-one comparison between theory and experiment of *absolute* values is not helpful, because the QM's (QD's) actually behave in a very complex way [15]. In particular, 2δ can vary from device to device, and probably it decreases with N [17]. Nonetheless, the overall agreement between theory and experiment of the general spectral shape is quite good, indicating the crucial role played by mismatch. In particular, the appearance of the spectra in the weak coupling limit for small N values is now correctly given, as well as the evolution with b of the peak appearing at $N = 8$ for intermediate coupling. A comparison between Figs. 2(a) and 2(c) reveals that for smaller values of b ($\lesssim$4.8 nm), for a reasonable choice of parameters (ω, δ), mismatch does not produce sizable effects. The reason is that the electrons are still rather delocalized, and distributed fairly evenly between the two dots. Exceptions to this substantial delocalization may arise only when both the constituent single QD states are magic, as discussed below, at intermediate coupling. For larger interdot distances, mismatch induces electron localization. The manner in which it happens is determined by the balance between interdot and intradot Coulomb repulsion, and by the degree of mismatch between the sp energy levels, and so is difficult to predict except in some trivial cases for certain model parameters (ω, δ). For example, a large mismatch compared to $\hbar\omega$ will cause the QD of depth $V_0 - \delta$ to eventually "go away empty."

Finally, still assuming perfect coherency, a deeper theoretical understanding of heteronuclear QM dissociation can now be gained from analysis of the evolution with b of the sp molecular wave functions. Thus, for each sp wave function $\phi_{nl\sigma}(r, z, \theta) = u_{nl\sigma}(r, z)e^{-il\theta}\chi_\sigma$ we introduce a z-probability distribution function defined as

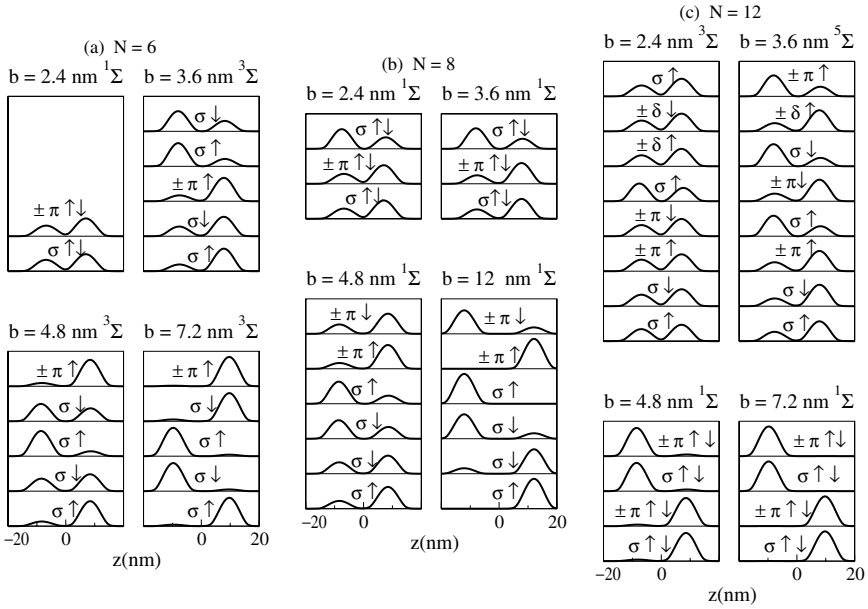

FIG. 3. Calculated probability distribution functions $\mathcal{P}(z)$ (arbitrary units) as a function of z for the heteronuclear $N = 6$, $N = 8$, and $N = 12$ QM's (a), (b), and (c) respectively, using a $2\delta = 2$ meV mismatch.

$$\mathcal{P}(z) \equiv 2\pi \int_0^\infty dr\, r[u(r,z)]^2. \quad (1)$$

Figure 3 shows $\mathcal{P}(z)$ for (a) $N = 6$, (b) $N = 8$, and (c) $N = 12$ (deeper well always in the $z > 0$ region), each for several values of b. States are labeled as $\sigma, \pm\pi, \pm\delta, \ldots$, depending on the $l = 0, \pm 1, \pm 2, \ldots$, sp angular momentum, and $\uparrow, \downarrow$ indicate the spins. In each subpanel, the probability functions are plotted, ordered from bottom to top, according to the increasing energies of the orbitals. For each b, the third component of the total spin and total orbital angular momentum of the ground state are also indicated by the standard spectroscopic notation $^{2S_z+1}|L_z|$ with $\Sigma, \Pi, \Delta, \ldots$, denoting $|L_z| = 0, 1, 2, \ldots$. We conclude the following: (i) QM's dissociate more easily for smaller values of b, if they yield magic number QD's, as is the case for $N = 12 \rightarrow 6 + 6$ for $b = 4.8$ nm [Fig. 3(c)] or $N = 4 \rightarrow 2 + 2$ (not shown), for example. (ii) Particularly for intermediate values of b, not all orbitals contribute equally to the QM bonding; i.e., the degree of hybridization is not the same for all QD sp orbitals. See, for example, the π and σ states in the $b = 4.8$ nm panel of Fig. 3(a). (iii) At larger b, dissociation can lead to Hund's first rule like filling in one of the QD's and full shell filling in the other dot. See, for example, the $b = 7.2$ nm panel in Fig. 3(a) for $N = 6$, which dissociates into $2 + 4$. The same happens for the $N = 10$ QM, which dissociates into $4 + 6$ (not shown). In other cases, dissociation leads to Hund's first rule like filling in each of the QD's, as shown in the $b = 12$ nm panel of Fig. 3(b) for $N = 8$, which breaks into $4 + 4$. In close analogy with natural molecules, atomic nuclei, or multiply charged simple metal clusters [21], homo and heteronuclear QM's choose preferred dissociation channels yielding the most stable QD configurations. (iv) Some configurations are extremely difficult to disentangle: even at very large b, there can still be orbitals contributing to the QM bonding. A good example of this is the $N = 8$ QM for $b = 12$ nm [Fig. 3(b)].

This work has been performed under Grants No. PB98-1247 and No. PB98-0124 from DGESIC, and No. 2000SGR-00024 from Generalitat of Catalunya, and partly funded by NEDO program (NTDP-98). We are grateful for the assistance of T. Honda with processing the samples, and for useful discussions with K. Ono and S. Sasaki.

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