# Hidden quasisymmetry in the optical absorption of quantum dot nanorings

Ioan Bâldea* and Lorenz S. Cederbaum

*Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229,*
*D-69120 Heidelberg, Germany*

We report numerical results demonstrating the existence of a hidden dynamical quasisymmetry in the optical absorption of finite nanorings consisting of metallic quantum dots described by means of the extended Hubbard model for closed shells, causing, out of a multitude of transitions allowed by spatial symmetry, all but one to be practically forbidden. We show that, by shining only a part of the nanoring, one can get more information than by irradiating the whole nanoring, and suggest that experimentalists apply this method to measure optical absorption spectra.

PACS number(s): 78.67.Hc, 73.21.La, 73.63.Kv, 85.35.Be

## I. INTRODUCTION

Recent nanoscience techniques allow a bridging between molecules and solids by assembling metallic or semiconducting quantum dots (QDs) in "artificial" molecules or solids with tunable properties. In isolated QDs, electrons move within a length scale of a few nanometers and possess a discrete spectrum, similar to atomic orbitals (AOs) of ordinary atoms.[1] In QD arrays, the overlap of the wave functions for electrons of adjacent QDs is significant, and a small fraction of electrons become delocalized over the whole nanostructure, analogous to $\pi$ electrons in molecules or conduction electrons in solids. However, an important difference exists. In molecules or solids, the physical parameters are fixed (or almost fixed). By contrast, the electronic properties of the QD nanoarrays can be smoothly *tuned* in wide ranges by changing parameters that can be easily controlled experimentally, like dot diameter ($2R$), interdot spacing ($D$),[2] or gate voltages.[3]

Because of their tunable properties, assemblies of QDs represent ideal systems for studying effects of strong electron correlations. We shall show that electron correlations can indeed be very strong for QDs assembled in a nanoring. Unless the QDs are nearly touching, the exact ground state has a (very) small overlap with the self-consistent-field (SCF) ground state, and this also holds for the excited states.

Optical properties are among the most useful and widely studied properties of nanosystems.[4] The most important result reported in this paper is that, in spite of strong correlations, the optical absorption of the nanorings consists practically of a single spectral line (monochromatic spectrum). This statement is based on exact numerical diagonalization results for finite rings. In addition to this, we discuss qualitative differences between optical absorption on QD nanorings and ordinary molecules. Recently, we proposed a different method to conduct experiments on ionization in nanorings,[5] hardly conceivable in molecular physics. In this paper, we shall show that applying this method to measure the optical absorption is even more interesting than for ionization: as demonstrated in Sec. V, it allows to get more information on the excited states.

In order to emphasize the realistic character of the conclusion emerging from the present study, we shall employ parameter values for already fabricated silver QDs (Ref. 2) that are by now well documented from earlier studies.[5–10] Individual QDs can be characterized by the on-site Coulomb repulsion energy $U$ (related to self-elastance, or Coulomb blockade) and the energy of (valence) electrons $\epsilon$. QDs are coupled by electron tunneling (resonance integral $t_0$) and Coulomb interaction $V$ (related to the mutual elastance). Basically, $U$ and $\epsilon$ depend on $R$, whereas $t_0$ and $V$ depend on $D$.

## II. MODEL

As done for similar systems,[7,9–11] each QD will be modeled by a single AO, and to describe the nanoring with $N$ QDs containing $N$ valence electrons (half-filling), we shall employ an extended Hubbard Hamiltonian[12]

$$H = -t_0 \sum_{l=1}^{N} \sum_{\sigma=\uparrow,\downarrow} (a_{l,\sigma}^\dagger a_{l+1,\sigma} + a_{l+1,\sigma}^\dagger a_{l,\sigma})$$
$$+ \sum_{l=1}^{N} (\epsilon \hat{n}_l + U\hat{n}_{l,\uparrow}\hat{n}_{l,\downarrow} + V\hat{n}_l \hat{n}_{l+1}), \quad (1)$$

where $a$ ($a^\dagger$) denotes creation (annihilation) operators for electrons in AOs, $\hat{n}_{l,\sigma} \equiv a_{l,\sigma}^\dagger a_{l,\sigma}$ and $\hat{n}_l \equiv \hat{n}_{l,\uparrow} + \hat{n}_{l,\downarrow}$.

In the fabrication of the nanoarrays of Ag QDs, Heath *et al.* succeeded in obtaining a very narrow size distribution ($\sim 3\% - 5\%$).[2] This legitimates the assumtion of dot ($l$-) independent parameters made in Eq. (1). For departures from this idealized case, see the end of Sec. IV. The analysis of the model parameters $t_0$, $U$, and $V$ has been presented earlier[5,7,10] and will not be repeated here. We only remind that the practically continuous variation of $d \equiv D/(2R)$ in the range $1.1 \lesssim d \lesssim 1.85$ achieved by the Langmuir technique[2] allows a wide tuning of the hopping integral $t_0$ [$\propto \exp(-5.5d)$].

Our main interest here is on the optical absorption. The absorption coefficient in the ground state $|G\rangle$ of a nanoring lying in the $(x, y)$ plane irradiated by a laser field linearly polarized along the $j$ direction ($j = x, y$) reads

$$\alpha_j(\omega) = \rho^{-2}\omega \sum_{\gamma \in E_{1u}} \sum_{\lambda=1,2} |\langle \Psi_{\gamma,\lambda}|\mu_j|G\rangle|^2 \delta(\omega - \varepsilon_\gamma + \varepsilon_0), \quad (2)$$

where $\mu_{x,y}$ are the components of the dipole operator

$$\boldsymbol{\mu} = -|e|\rho \sum_l \hat{n}_l \left[ \hat{\mathbf{x}} \cos\left(\frac{2\pi l}{N}\right) + \hat{\mathbf{y}} \sin\left(\frac{2\pi l}{N}\right) \right], \qquad (3)$$

$e$ and $\rho = (D/2)\sin(\pi/N)$ denote elementary charge and ring radius, respectively. The components $(\mu_x, \mu_y)$ transform according to the two-dimensional irreducible representation $E_{1u}$, and therefore, only eigenstates with $E_{1u}$ symmetry contribute to the sum (2). Symmetry reasons also imply that the oscillator strengths summed for each pair of degenerate $E_{1u}$ states $\lambda = 1, 2$ are equal, and one can omit therefore the subscript $j$ in Eq. (2). This implies that there is no difference between linearly, circularly polarized or nonpolarized light, unlike in the case of high harmonic generation (see, e.g., Ref. 9).

For later purposes, besides the AO representation in terms of operators $a_{l,\sigma}$, it is also helpful to express the dipole momentum in terms of molecular orbital (MO) operators $c_{p,\sigma} = (1/\sqrt{N})\Sigma_l a_{l,\sigma} \exp(-2\pi p l i/N)$

$$\mu_x = -\frac{|e|\rho}{2} \sum_{p,\sigma} (c_{p+1,\sigma}^\dagger c_{p,\sigma} + c_{p,\sigma}^\dagger c_{p+1,\sigma}),$$

$$\mu_y = \frac{i|e|\rho}{2} \sum_{p,\sigma} (c_{p+1,\sigma}^\dagger c_{p,\sigma} - c_{p,\sigma}^\dagger c_{p+1,\sigma}). \qquad (4)$$

## III. GROUND-STATE CORRELATIONS

The Langmuir technique employed experimentally[2] allows a wide tuning of the hopping integral and thereby a practically continuous change between two limiting cases. In one limit, that of sufficiently distant QDs, electron tunneling is inefficient. The lowest energy is achieved by localized electrons that avoid double occupancy of the same QD, since otherwise the energy penalty, the on-site Coulomb repulsion energy $U$, is higher than the interdot Coulomb interaction $V$. In the other limit, corresponding to almost touching QDs ($d \gtrsim 1$), in the ground state $|G\rangle$ the (valence) electrons are completely delocalized over the whole nanostructure due to efficient tunneling between neighboring QDs. In this limit, correlations are practically absent and the single-particle description (SCF) is very good. Let us denote the ground state in the former limit by $\Psi_{loc}$ and that in the latter limit by $\Psi_{del}(\approx \Psi_{SCF})$. The curves for various properties of the neutral ground state exhibit a dependence on $d$, smoothly interpolating between the limits of perfect delocalization and perfect localization discussed above.

For illustration, we present in Fig. 1(a) the quantities

$$w_k = |\langle G|\Psi_k\rangle|^2, \qquad (5)$$

($k = del, loc$) for six- and ten-QD nanorings.[13–15] One sees that the SCF approximation provides a very good description of the exact ground state for $d \gtrsim 1$, but completely fails for distant QDs (say $d > 1.5$), where the localized picture becomes quite appropriate. The same physical picture emerges from the analysis of the curves in Fig. 1(b) for the numbers of electrons $n_{MO} \rightarrow \langle G|c_{p,\sigma}^\dagger c_{p,\sigma}|G\rangle$ per spin direction for the molecular orbitals possessing well-defined symmetries of the
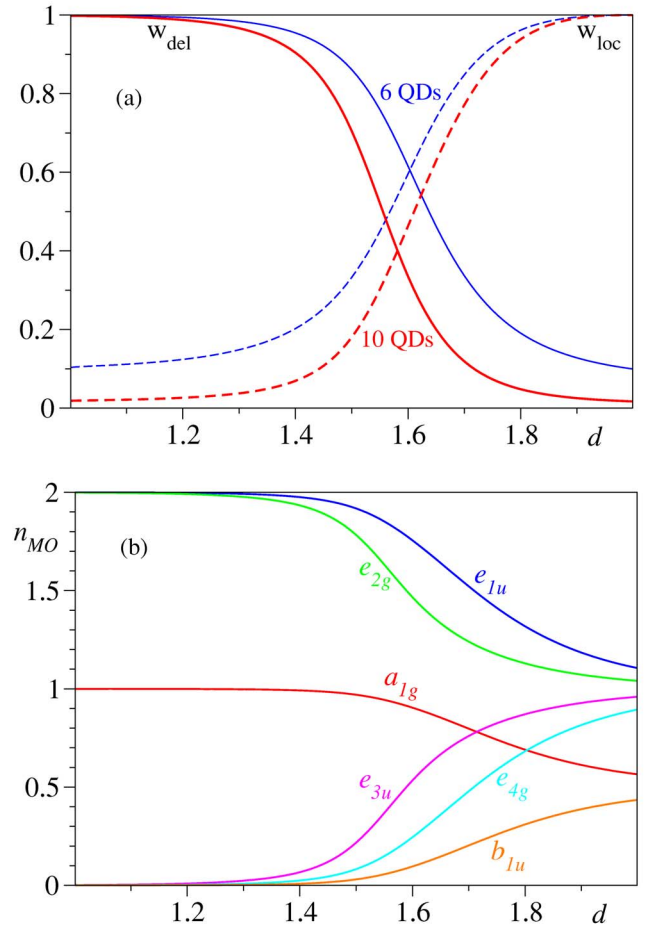


FIG. 1. (Color online) Ground-state properties versus interdot spacing $d$: (a) the weights $w_{del}$ and $w_{loc}$ corresponding to perfectly delocalized (SCF) and localized electrons (solid and dashed lines, respectively) in the neutral ground state of a nanoring with six and ten QDs. (b) Populations of MOs (symmetry indicated in the figure) for ten-QD nanorings. (Ref. 16)

point group $D_{10h}$.[16] As visible in Fig. 1(b), for almost touching QDs ($d \gtrsim 1$), the populations $n_{MO}$ tend to the SCF values 1 and 2 (for one- and two-dimensional irreducible representations, respectively) for the orbitals below the Fermi level and zero, otherwise. For large $d$ ($t_0 \ll V < U/2$), the electrons are practically localized, one electron at each QD. The MOs become practically degenerate and none is empty. Without summing over spatially degenerate MOs, all MO occupancies are equal.

## IV. HIDDEN SYMMETRY IN OPTICAL ABSORPTION

Let us now switch to optical absorption. Our results for spectral intensities are presented in logarithmic scale in Fig. 2. The SCF spectrum consists of exactly one line of nonvanishing intensity [upper curves of Figs. 2(a) and 2(b)] that strongly decreases with increasing $d$. Only highest occupied molecular orbital–lowest unoccupied molecular orbital transitions contribute to absorption within the single-particle picture, see Eqs. (4).
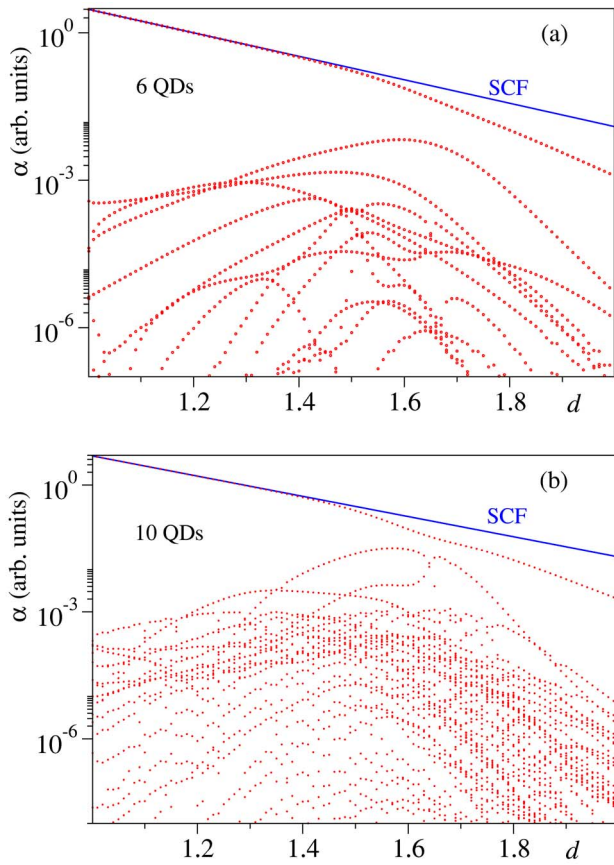
FIG. 2. (Color online) Spectral intensities for six- and ten-QD nanorings. Note the logarithmic scale.



FIG. 3. (Color online) MO populations of the lowest $E_{1u}$ eigenstate for ten-QD nanorings (Ref. 16.

Figure 1 revealed that the single-particle description worsens gradually with increasing $d$. Because the ground state $|G\rangle$ is an $A_{1g}$ singlet for all $d$'s, in principle, all excited singlet $E_{1u}$ eigenstates contribute to optical absorption [Eq. (2)]. Out of the 924 eigenstates for six-QD nanorings, 175 are singlet states, and out of these, there are 54 states of $E_{1u}$ symmetry.[17] For ten-QD nanorings, there are 184 756 eigenstates; out of these, 19 404 are singlet states and thousands thereof possess $E_{1u}$ symmetry. One should therefore expect that for larger $d$ values, with the dramatical increase of the part played by electron correlations, more and more transitions allowed by spatial symmetry acquire spectral intensity.

The intriguing and most important result we report here is that, despite the strong correlations, a single optical transition from the ground state continues to remain significant with increasing $d$. To rephrase, our numerical results demonstrate the existence of a *hidden dynamical quasisymmetry* in the optical absorption of nanorings consisting of QDs, causing, out of a multitude of transitions allowed by spatial symmetry, all but one to be practically forbidden. We called this a quasisymmetry because it is not a true symmetry: as visible in the *logarithmic* plot of Fig. 2, although very small, the intensities of the transitions to the higher $E_{1u}$ eigenstates exhibit a regular $d$ dependence and are definitely nonvanishing; they are many orders of magnitude larger than inherent numerical inaccuracies. This quasisymmetry holds in very broad parameter ranges.[18] To the best of our knowledge, such
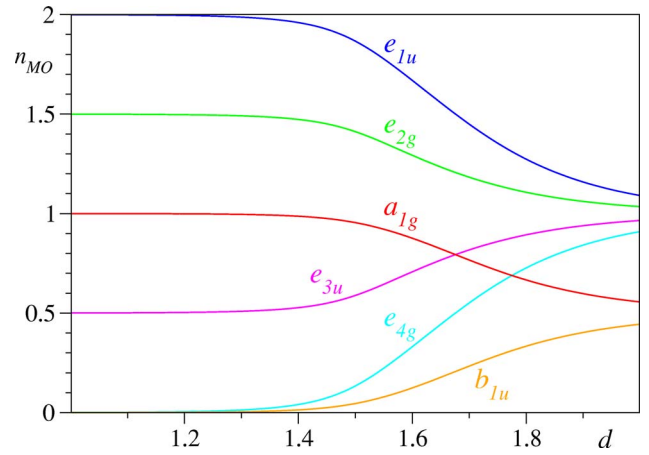
a symmetry has not been discussed so far in the literature. It is quite different from the previously discussed hidden symmetries in the optical absorption of an isolated QD with degenerate shells.[19]

It is difficult to put forward an explanation for this hidden quasisymmetry by conciliating the existence of the strong correlations with the extreme simplicity of the optical absorption. The correlations are really very strong. In the MO-basis, the expansion of the exact ground state $|G\rangle$ of the six-QD nanoring contains 68 Slater determinants; some of them form linear combinations consisting of 2, 4, and 8 terms with equal weights, forming 22 distinct linear combinations, corresponding to the total number of 22 $A_{1g}$ eigenstates. Practically, all these $A_{1g}$ configurations contribute to $|G\rangle$ and, excepting for $d \gtrsim 1$, there exists no dominant contribution from a certain state to this expansion.

In the attempt to understand this paradoxical behavior, we have monitored the properties of the various $E_{1u}$ excited states. Results for the MO occupations, shown in Fig. 3, for the lowest $E_{1u}$ excitation (that significantly contributes to absorption) are typical. They indicate that electron correlations on $E_{1u}$ excitations above $d \approx 1.5$ are also very strong, comparable to the ground-state correlations. This makes the extreme simplicity of the absorption spectrum even more intriguing.

Let us ask whether this hidden quasisymmetry is robust against symmetry-breaking factors, e.g., spread in size $\delta R$ and interdot spacing $\delta D$, affecting $\epsilon$ and $t_0$. Our extensive calculations show that this disorder causes a splitting between several transitions that become allowed. However, most spectral intensity remains concentrated in a very narrow range $\delta\omega$. For instance, for ten-QD rings and $\bar{d}=1.5$, a spread of $\delta R/\bar{R} \approx 2\%$ and $\delta D/\bar{D} \approx 1\%$ give 90% of absorption signal within $\delta\omega \simeq 4$ meV, which is small compared to the excitation energy $\omega = 212$ meV. Consequently, a weak disorder [comparable to that ($\sim 3\%$) achieved in the fabricated nanostructures, see end of Ref. 2] does not affect our conclusion.

## V. EFFECT OF PARTIAL COVERING

In ordinary molecules, the photon interacts with the *whole* molecule, and absorption normally means a transition of an
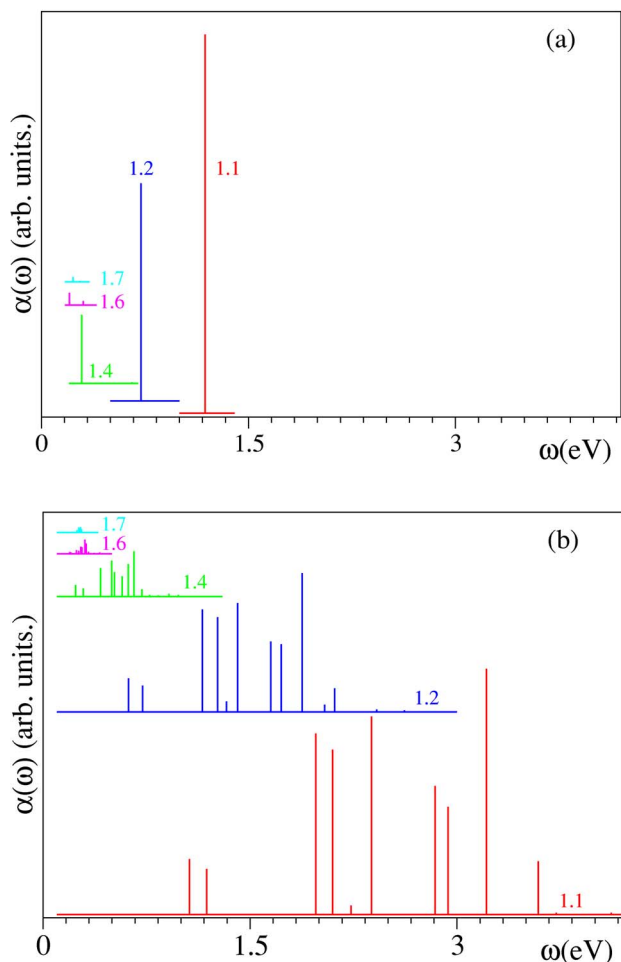
FIG. 4. (Color online) Optical absorption spectra for ten-QD nanorings by irradiating (a) the entire ring and (b) only one QD computed at $d=1.1$, 1.2, 1.4, 1.6, and 1.7.

nanosystem and then only the remaining part (as a limiting case, an *individual* QD) is subjected to radiation.[5] This is just another way to destroy the symmetry, not that of the system itself, but by the manner in which one can conduct an optical absorption experiment in QD nanorings, a method hardly conceivable in ordinary molecules. This latter method has been proposed by us in Ref. [5]. There, it has been merely discussed as a tool to relate the ionization process of lowest energy with the localization-delocalization transition observed experimentally.[2]

Optical absorption and ionization are quite different phenomena. Recording optical absorption spectra by using the method of partial covering provides information richer than by irradiating the whole ring. This conclusion emerges from our calculations performed for the case where only one or a few QDs are irradiated. For illustration, results for the case where all but one QD are covered are presented in Fig. 4. As seen in Fig. 4(b), the spectra do not remain monochromatic any longer. Out of the $E_{1u}$ eigenstates, only the first gives nonvanishing contribution to absorption, as in the case where the whole ring is irradiated. However, there are additional lines due to transition to states of other symmetries, since the radiation field lowers the symmetry from $D_{N,h}$ to $C_{2v}$. Moreover, the $E_{1u}$ transition even ceases to be the most intense in the spectrum [compare with Fig. 4(a)]. To conclude, by irradiating only a part of the nanoring, one can target more states, so more information can be extracted than when irradiating the entire nanosystem. One should emphasize that this holds in general, since the above argument is based on general symmetry considerations.

## VI. CONCLUSION

In conclusion, we have presented results demonstrating that optical absorption by nanorings is extremely selective, and we related this practical monochromaticity to a hidden quasisymmetry characterizing finite nanorings described by the extended Hubbard model in very broad parameter ranges. Therefore, we believe that, in addition to the Ag QDs considered here, other structures of already fabricated semiconducting nanorings with equidistant barriers[3] deserve similar interest. The physical properties of these systems could also be widely and easily tuned by varying the gate voltage. By employing well-established parameter values for Ag QDs, we wanted to emphasize that the present predictions have a pretension to be realistic and hope to stimulate further experimental work on nanosystems.

## ACKNOWLEDGMENT

electron from a certain lower molecular orbital to a higher one. In many molecules, correlations play only a reduced role. This is the case of the ground state of the $\pi$-electron molecules of benzene ($C_6H_6$) and (planar) cyclodecatriene ($C_{10}H_{10}$), which are counterparts of the six-QD and ten-QD rings discussed above. For these molecules, quantum chemical calculations yield values of $w_{del}\approx 96\%$ and $w_{del}\approx 92\%$, respectively.[20] There is an additional important difference between the QD nanorings considered here and molecules. In the former, the parameters can be tuned continuously by varying $d$, and one can smoothly go from weak to strong correlations. Above, we have considered absorption processes of nanorings of the type just described, and they occur if the radiation flux spreads over the whole system. However, unlike in molecules, one can alternatively cover a part of the

*Permanent address: NILPRP, ISS, RO 077125 Bucharest. Electronic address: ioan@pci.uni-heidelberg.de

[1] M. A. Kastner, Phys. Today **46** (1), 24 (1996).

[2] J. R. Heath, C. M. Knobler, and D. V. Leff, J. Phys. Chem. B **101**, 189 (1997); C. P. Collier, R. J. Saykally, J. J. Shiang, S. E. Henrichs, and J. R. Heath, Science **277**, 1978 (1997); G. Markovich, C. P. Collier, and J. R. Heath, Phys. Rev. Lett. **80**, 3807 (1998); J. J. Shiang, J. R. Heath, C. P. Collier, and R. J. Saykally, J. Phys. Chem. B **102**, 3425 (1998); G. Medeiros-Ribeiro, D. A. A. Ohlberg, R. S. Williams, and J. R. Heath, Phys. Rev. B **59**, 1633 (1999); K. C. Beverly, J. F. Shampaio, and J. R. Heath, J. Phys. Chem. B **106**, 2131 (2002).

[3] A. Fuhrer, S. Lüscher, T. Ihn, T. Heinzel, K. Ensslin, W. Wegscheider, and M. Bichler, Nature (London) **413**, 822 (2001); D. Granados and J. M. Garcia, Appl. Phys. Lett. **82**, 2401 (2003); X. Y. Kong, Y. Ding, R. Yang, and Z. L. Wang, Science **303**, 1348 (2003).

[4] *Nano-Optoelectronics*, edited by M. Grundmann (Springer Verlag, Berlin, 2002); U. Woggon, *Optical Properties of Semiconductor Quantum Dots* (Springer Verlag, Berlin, 2003).

[5] I. Bâldea and L. S. Cederbaum, Phys. Rev. Lett. **89**, 133003 (2002).

[6] F. Remacle, C. P. Collier, G. Markovich, J. R. Heath, U. Banin, and R. D. Levine, J. Phys. Chem. B **102**, 7727 (1998).

[7] F. Remacle and R. D. Levine, J. Am. Chem. Soc. **122**, 4048 (2000).

[8] F. Remacle and R. D. Levine, Nano Lett. **2**, 697 (2002).

[9] I. Bâldea, A. K. Gupta, L. S. Cederbaum, and N. Moiseyev, Phys. Rev. B **69**, 245311 (2004).

[10] I. Bâldea, H. Köppel, and L. S. Cederbaum, Phys. Rev. B **69**, 075307 (2004).

[11] I. Bâldea, H. Köppel, and L. S. Cederbaum, Phys. Rev. B **55**, 1481 (1997); Eur. Phys. J. B **20**, 289 (2001); Phys. Rev. B **63**, 155308 (2001).

[12] Realistic *ab initio* calculations [B. B. Smith and A. J. Nozik, Nano Lett. **1**, 36 (2001)] as well as accounting for a number of different electronic properties of Ag QD arrays (Refs. 5–8) show that such a simple approximation is reasonable.

[13] One should note that, in general, $\langle \Psi_{del} | \Psi_{loc} \rangle \neq 0$ and, therefore, the sum $w_{del} + w_{loc}$ can be larger than 1.

[14] We restrict ourselves here to six- and ten-QD rings, since they belong to the simpler case of anti-Hückel closed-shell systems. See, e. g., Ref. 11.

[15] For six QDs, all eigenstates can be easily obtained by straightforward numerical exact diagonalization. For ten QDs, a threefold run of Lanczos algorithm allows us to compute the ground state as well as the absorption *line* spectra, not only their envelopes; see Refs. 10 and 11.

[16] The MOs transforming according to the one-dimensional irreps $a_{1g}$ and $b_{1u}$ have $p=0$ and $N/2$, respectively, those transforming according to two-dimensional irreps ($e_{2n-1,u}$ or $e_{2n,g}$) (having $p = \pm 2n-1$ or $p = \pm 2n$) are degenerate and their population summed.

[17] For six QDs, the particle-hole symmetry further reduces the number of $E_{1u}$ states that may contribute to 32. (Ref. 9).

[18] This conclusion also holds, e.g., by doubling $U$ and/or $V$ from their values deduced from the Ag QDs considered, or by setting $V=0$ (i.e., restricted Hubbard model). It applies to a very broad region of the phase diagram $0 < U/(4t_0) < 20$, $0 \leq V/(4t_0) < 10$.

[19] M. Bayer, O. Stern, P. Hawrylak, S. Fafard, and A. Forchel, Nature (London) **405**, 923 (2000); P. Hawrylak, Solid State Commun. **127**, 793 (2003).

[20] I. Bâldea (unpublished).