Pressure effects on neutral and charged excitons in self-assembled InGaAs/GaAs quantum dots

Gustavo A. Narvaez, Gabriel Bester, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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By combining an atomistic pseudopotential method with the configuration interaction approach, we predict the pressure dependence of the binding energies of neutral and charged excitons: \( X^0 \) (neutral monoexciton), \( X^- \) and \( X^+ \) (charged trions), and \( XX^0 \) (biexciton) in lens-shaped, self-assembled In\(_{0.6}\)Ga\(_{0.4}\)As/GaAs quantum dots. We predict that (i) with applied pressure the binding energy of \( X^0 \) and \( X^+ \) increases and that of \( X^- \) decreases, whereas the binding energy of \( XX^0 \) is nearly pressure independent. (ii) Correlations have a small effect in the binding energy of \( X^0 \), whereas they largely determine the binding energy of \( X^- \), \( X^+ \) and \( XX^0 \). (iii) Correlations depend weakly on pressure; thus, the pressure dependence of the binding energies can be understood within the Hartree-Fock approximation and it is controlled by the pressure dependence of the direct Coulomb integrals \( J \). Our results in (i) can thus be explained by noting that holes are more localized than electrons, so the Coulomb energies obey \( J^{(hh)} > J^{(eh)} > J^{(ee)} \).

The energetics of excitons reflects a balance between single-particle energy levels \( E^{(c)} \) and \( E^{(h)} \) of electrons \( (e) \) and holes \( (h) \) in the system, and the many-particle carrier-carrier interactions, resulting from electron-hole Coulomb and exchange interactions. The variation of excitonic energies under pressure naturally reflects the corresponding variations in single- vs many-particle energies. Of particular interest are the pressure variations of excitons confined to nanosize dimensions such as in quantum dots. Unlike the case of excitons in higher-dimensional systems, where binding and its pressure dependence reflects mostly many-particle (correlation) effects, in zero-dimensional (0D) systems where the geometric dimensions are smaller than the excitonic radius, binding of neutral and charged excitons results from an interesting interplay between single-particle and many-particle effects. Here, we use a realistic description of both single-particle and many-body effects in self-assembled In\(_{0.6}\)Ga\(_{0.4}\)As/GaAs quantum dots, showing how pressure affects the different components of exciton binding. We distinguish the neutral monoexciton \( X^0 \) (one \( e \), one \( h \)), from the neutral biexciton \( XX^0 \) (two \( e \), two \( h \)), positive trion \( X^+ \) (one \( e \), two \( h \)) and negative trion \( X^- \) (two \( e \), one \( h \)). While the effect of pressure on \( X^0 \) has been measured, to the best of our knowledge, the optical spectroscopy of \( X^- \), \( X^+ \) and \( XX^0 \) under pressure has not yet been reported. For these reasons, we provide definite predictions of the pressure effects. Each of the \( q \)-charged excitons has a spectrum of levels \( \{ \nu \} \), of which the lowest is termed the “ground state of \( \chi^q \) (\( \chi = X, XX \)). This spectrum is usually expressed by expanding the many-body excitonic states \( |\Psi(\chi^q)\rangle \) via a set of Slater determinants \( |\Phi(\chi^q)\rangle \). The latter are constructed from single-particle electron and hole states and accommodate as many carriers as are present in \( \chi^q \). The single-particle states are solutions to the effective Schrödinger equation

\[
\left\{ -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{R}) + V_{\text{scr}}(\mathbf{R}) \right\} \psi_i = E^{(c)} \psi_i, \tag{1}
\]

where \( V_{\text{ext}}(\mathbf{R}) \) is the external (pseudo) potential (due to the ion-ion or ion-electron interaction) and \( V_{\text{scr}}(\mathbf{R}) \) is the screening response to such external potentials. The effect of pressure or strain is encoded in the ion-ion geometry

\[
H = \sum_i E^{(c)}_i c_i \mathbf{c}_i^\dagger - \sum_j E^{(h)}_j h_j \mathbf{h}_j^\dagger + \frac{1}{2} \sum_{ijkl} J^{(ee)}_{ijkl} c_i \mathbf{c}_j^\dagger c_k \mathbf{c}_l^\dagger c_l + \frac{1}{2} \sum_{ijkl} J^{(hh)}_{ijkl} h_i \mathbf{h}_j^\dagger h_k \mathbf{h}_l^\dagger + \frac{1}{2} \sum_{ijkl} \left[ J^{(eh)}_{ijkl} - K^{(eh)}_{ijkl} \right] \mathbf{c}_i \mathbf{c}_j^\dagger \mathbf{h}_k \mathbf{h}_l^\dagger, \tag{2}
\]

where \( c_i^\dagger (c_i) \) and \( h_j^\dagger (h_j) \) create (destroy) an electron in the single-particle state \( \psi_i^{(c)} \) and a hole in \( \psi_j^{(h)} \), respectively. In Eq. \( \mathbf{2} \), the Coulomb and electron-hole exchange matrix elements are given, respectively, by

\[
J^{(\nu \nu)}_{ijkl} = \int \int d\mathbf{R} d\mathbf{R}' \left| \frac{\psi^{(\nu)}_i(\mathbf{R}) \psi^{(\nu)}_j(\mathbf{R}') \psi^{(\nu)}_k(\mathbf{R}') \psi^{(\nu)}_l(\mathbf{R})}{\epsilon(\mathbf{R}, \mathbf{R}') |\mathbf{R} - \mathbf{R}'|} \right|, \tag{3}
\]
Here, $\epsilon(R, R')$ is a phenomenological, microscopic dielectric function that screens the Coulomb and exchange interactions, and in this work we have adopted the $\epsilon(R, R')$ proposed by Resta. The diagonal elements $j^{(\mu \mu')}_{ij}$ of Eq. (3) are the familiar electron-electron $(\mu \mu' = ee)$, hole-hole $(\mu \mu' = hh)$ and electron-hole $(\mu \mu' = eh)$ direct Coulomb integrals. The electron-electron and hole-hole exchange integrals are given by $J^{(ee)}_{ij}$ and $J^{(hh)}_{ij}$, respectively. Solving the single-particle Eq. (4) for a given dot yields the wavefunctions $\psi_i$, which are used to construct the Slater determinants $|\Phi(\chi^q)\rangle$ for $\chi^q$ and solve the many-particle, configuration interaction (CI) problem [Eq. (2)]. This gives the total (ground-state) energy $E_C(1)$ of exciton $\chi^q$, as well as excitonic excited states.

The binding energy of the excitonic complexes are defined as

$$
\Delta_{CI}(X^0) = \left[ E^{(e)}_0 - E^{(h)}_0 \right] - E_C(1)(X^0)
$$

$$
\Delta_{CI}(X^-) = \left[ - E^{(e)}_0 + E_C(1)(X^-) \right] - E_C(1)(X^-)
$$

$$
\Delta_{CI}(X^+) = \left[ - E^{(h)}_0 + E_C(1)(X^+) \right] - E_C(1)(X^+)
$$

$$
\Delta_{CI}(X^0) = 2E_C(1)(X^0) - E_C(1)(X^0).
$$

In a simplified Hartree-Fock approximation and neglecting the electron-hole exchange $K_{00;00}$ (whose magnitude is of the order of a few to hundreds of $\mu eV$), we have

$$
\Delta_{HF}(X^0) = J^{(eh)}_{00}
$$

$$
\Delta_{HF}(X^-) = J^{(eh)}_{00} - J^{(ee)}_{00}
$$

$$
\Delta_{HF}(X^+) = J^{(eh)}_{00} - J^{(hh)}_{00}
$$

$$
\Delta_{HF}(X^0) = 2J^{(eh)}_{00} - [J^{(ee)}_{00} + J^{(hh)}_{00}]
$$

where $N$ is the number of primary cells in the simulation supercell that contains the quantum dot and GaAs matrix. The many-body configuration-interaction (CI) expansion is taken over all the Slater determinants $|\Phi(\chi^q)\rangle$ generated within a set of 12 electron and 20 hole single-particle, confined states.

**Direct-Coulomb vs correlation contributions to binding.**—Table II shows the CI-calculated binding energies $\Delta_{CI}(\chi^q)$ as well as its decomposition [Eq. (6)] into Hartree-Fock $\Delta_{HF}(\chi^q)$ and correlation $\delta(\chi^q)$ contributions. We see that (i) the binding energy of the neutral monoexciton $X^0$ is constituted primarily by HF energy with only 6% being due to correlation. This is in contrast with $X^0$ in bulk semiconductors where $\delta(X^0)$ dominates over $\Delta_{HF}(X^0)$.

(ii) For $X^-$, $X^+$ and $XX^0$ the HF and correlation contributions to binding are comparable. Specifically, while $X^-$ is bound (positive $\Delta$) already in HF, here $X^+$ and $XX^0$ are unbound in HF, but become bound by correlation. (iii) For each excitonic complex, the magnitude of the correlations depends weakly on pressure.

In this work, we consider a lens-shaped (base diameter $b = 252\, \text{Å}$ and height $h = 35\, \text{Å}$) In$_{0.5}$Ga$_{0.5}$As/GaAs quantum dot and study how the excitonic binding energies $\Delta_{CI}(\chi^q)$ depend on pressure (well below the $\Gamma_1 c - X_0 c$ crossover). We then analyze this dependence in terms of the pressure dependence of (i) Coulomb integrals $J^{(\mu \mu')}_{00}$ and (ii) correlation energies $\delta(\chi^q)$. In Eq. (7), we use a screened pseudopotential expressed as a superposition of screened atomic pseudopotentials

$$
V_{ext}(R) + V_{scr}(R) = V_{SO} + \sum_i \sum_\alpha v_\alpha [R - R_i^{(\alpha)}; \text{Tr}(\tilde{\varepsilon})],
$$

where $V_{SO}$ is a non-local spin-orbit pseudopotential $v_\alpha$ is a screened pseudopotential for atom of type $\alpha$ that depends on strain; and $R_i^{(\alpha)}$ is the vector position of atom $n$ of type $\alpha$ after the atomic positions within the simulation supercell (quantum dot+GaAs-matrix) have been relaxed, using a valence force field in order to minimize the elastic energy of the nanostructure. The explicit dependence of $v_\alpha$ on strain transfers to the electronic Hamiltonian the information on atomic displacements. $v_\alpha$ has been fitted to bulk properties of GaAs and InAs, including bulk band structures, experimental deformation potentials and effective masses, as well as LDA-determined band offsets. Equation (7) is solved in a basis of linear combination of Bloch bands $\{u^{(M)}_{nk}(R, \tilde{\varepsilon})\}$ with band index $n$ and wave vector $k$ of material $M$ (=GaAs, InAs) strained to $\tilde{\varepsilon}$. Thus,

$$
\psi_i(R) = \sum_M \sum_{n,k} C_i^{(M)} \frac{1}{\sqrt{N}} u^{(M)}_{nk}(R, \tilde{\varepsilon}) e^{i k \cdot R},
$$
TABLE I: Comparison of Hartree-Fock (HF) and many-body configuration-interaction (CI) binding energies (in meV), and verification of the “sum rule” \( \Delta_{HF}(X^0) + \Delta_{HF}(X^+) \) for different pressures. For each excitonic complex \( \chi^0 \), we present the CI binding energy \( \Delta_{CI}(\chi^0) \) as a sum of the Hartree-Fock binding energy \( \Delta_{HF}(\chi^0) \) and correlation-energy component \( \delta(\chi^0) = \Delta_{CI}(\chi^0) - \Delta_{HF}(\chi^0) \).

| Quantity | 0.2 GPa | 0.8 GPa | 1.3 GPa | 1.8 GPa | 2.4 GPa |
|----------|---------|---------|---------|---------|---------|
| \( \Delta_{CI}(X^0) \) | 20.8 + 1.3 | 21.1 + 1.4 | 21.3 + 1.4 | 21.6 + 1.5 | 21.9 + 1.5 |
| \( \Delta_{CI}(X^+) \) | 1.2 + 1.3 | 1.0 + 1.4 | 0.8 + 1.5 | 0.6 + 1.6 | 0.5 + 1.6 |
| \( \Delta_{CI}(X^{00}) \) | -1.8 + 2.4 | -1.5 + 2.3 | -1.2 + 2.3 | -0.9 + 2.2 | -0.7 + 2.2 |
| \( \Delta_{CI}(X^{00}) \) | -0.6 + 2.0 | -0.4 + 2.0 | -0.3 + 2.0 | -0.3 + 2.0 | -0.2 + 2.0 |
| \( \Delta_{CI}(X^0) + \Delta_{CI}(X^+) \) | 3.1 | 3.2 | 3.4 | 3.5 | 3.6 |
| Sum rule | -0.6 | -0.5 | -0.4 | -0.3 | -0.2 |

Pressure dependence.—Figure 1 shows the dependence on pressure of (a) the binding energies \( \Delta_{CI}(\chi^0) \), (b) Coulomb energies \( J_{00}^{(ee)} \), \( J_{00}^{(eh)} \), and \( J_{00}^{(hh)} \), and (c) correlation energies \( \delta(\chi^0) \). Pressure is represented by \( \Delta a/a_0 = (a - a_0)/a_0 \), where \( a \) and \( a_0 \) are the distorted and equilibrium lattice parameter of the GaAs matrix, respectively. The pressure values showed in the upper axis on Fig. 1(a) are calculated by using the equation of state \( P = (B_0/B_0')(V_0/V)^{B_0' - 1} \), where we take \( V_0/V = [1 + \text{Tr}(\tilde{\varepsilon})]^{-1} \) and calculate \( \text{Tr}(\tilde{\varepsilon}) \) in the GaAs matrix away from the dot. The calculation of \( \tilde{\varepsilon} = \tilde{\varepsilon}(\mathbf{R}) \) is performed using atomistic elasticity. We take \( B_0 = 74.7 \) GPa and \( B_0' = 4.67 \) as the GaAs bulk modulus and its derivative with respect to pressure, respectively. We see from Fig. 1 that the pressure dependence of the binding energy of the various excitons is different: (i) \( \Delta_{CI}(X^0) \) shows a small, nearly linear increase with pressure; changing about 7% in the studied pressure range. \( \Delta_{CI}(X^-) \) decreases slightly with increasing pressure, while \( \Delta_{CI}(X^+) \) increases significantly; at \( \Delta a/a_0 = -0.0087 \) (\( P = 2.4 \) GPa) it has increased by 160% compared to its value at \( \Delta a/a_0 = 0 \). Similar to the monoeexciton case, the binding energy of the biexciton depends only weakly on pressure, showing a small relative change as pressure reaches 2.4 GPa. (ii) Equation 6 shows that the binding has a HF part and a correlation part. Table I showed that the magnitude of the binding is decided by the HF part for \( X^0 \) and by both HF and correlation for \( X^- \), \( X^+ \), and \( X^{00} \). However, Fig. 1 shows that the pressure dependence is always decided by the HF contribution. (iii) The “sum rule” of Eq. 6 valid within HF is not valid at the CI level, quantitatively failing to predict the correct values of the biexciton binding energies. (iv) From (ii), we see that the trends of the binding energies with pressure are determined by \( J_{00}^{(eh)} \), \( J_{00}^{(ee)} \), and \( J_{00}^{(hh)} \). By calculating these integrals, we find that \( J_{00}^{(hh)} > J_{00}^{(eh)} > J_{00}^{(ee)} \) and the magnitude of \( J_{00}^{(eh)} \) and \( J_{00}^{(ee)} \) increase with a similar slope as pressure increases while \( J_{00}^{(hh)} \) remains nearly constant; see Fig. 1. This explains the decrease of \( \Delta_{CI}(X^-) \) and the increase of \( \Delta_{CI}(X^+) \) with applied pressure. Further, it also becomes clear why the binding energy of the biexciton remains nearly unchanged with changing pressure:

The similar rate of increase of \( J_{00}^{(ce)} \) and \( J_{00}^{(eh)} \) with pressure combined with the magnitude of \( J_{00}^{(hh)} \) leads to a weak pressure-dependent binding energy for \( X^{00} \).

Wavefunction localization with pressure.—To understand the trend \( J_{00}^{(hh)} > J_{00}^{(eh)} > J_{00}^{(ee)} \) and also that \( J_{00}^{(hh)} \) has the weakest pressure dependence, while \( J_{00}^{(ee)} \) has the strongest, Figure 2 shows the calculated wavefunctions...
for the electron ground state \( \psi_0^{(e)} \) and hole ground state \( \psi_0^{(h)} \) as a function of pressure. The isosurfaces enclose 75\% of the charge density, the in-plane contour plot is taken at 1 \( \text{nm} \) above the dot's base and the out-of-plane contour plot bisects the dot. We see that the electron is always more localized than the hole. In addition, the electron gets more localized as pressure is applied, while the localization of the hole remains nearly unchanged. The in-plane (parallel to the base) spatial extent of the electron does not change as much as the out-of-plane. In particular, Fig. 2 clearly shows that the spatial penetration of the electron wavefunction into the GaAs matrix decreases with applied pressure. The increased localization of the electron with pressure can be explained by the larger magnitude of the conduction-band edge (CBM) deformation potential of bulk GaAs with respect to that of bulk InAs \( \psi_0 \) which results in an increased electron confinement in the dot with pressure. In contrast, the similar magnitude of the valence-band edge (VBM) deformation potential of both bulk GaAs and InAs leads to small changes in hole confinement with pressure and, therefore, to small changes in localization.

**Single-particle and excitonic pressure coefficients.**— We calculate the linear pressure coefficient \( a \) by fitting the pressure dependence of the band gap to \( E_g(P) = E_g(0) + a P + b P^2 \). For the dot, at the single-particle (SP) level, we obtain \( a_{SP}^{(dot)} = 86.47 \text{(meV/GPa)} \), whereas the excitonic value is \( a_{SP}^{(X)}(0) = 85.79 \text{(meV/GPa)} \). The latter compares well with the values of 85 (meV/GPa), 80 (meV/GPa), and 82 (meV/GPa), observed in InAs/GaAs dots for the emission lines at 1.28 eV, 1.26 eV and 1.30 eV, respectively. For bulk GaAs, we obtain \( a^{(bulk)} = 105.86 \text{(meV/GPa)} \), which is within the range of observed values: 94-120 (meV/GPa) \( \text{[18-21]} \). Thus, the dot has a smaller linear pressure coefficient than bulk GaAs. In addition, it is interesting to inspect how the VBM and CBM contribute to the linear pressure coefficient of the band gap. By fitting the lattice-deformation (pressure) dependence of single-particle eigenvalues \( E_i(a) = E_i(0) + A_i(\Delta a/\Delta a_0) + B_i(\Delta a/\Delta a_0)^2 \), we find \( A_{VBM}^{(dot)} = -1.76 \text{eV} \) and \( A_{CBM}^{(dot)} = -22.49 \text{eV} \). For, bulk GaAs we find \( A_{VBM} = -3.74 \text{eV} \) and \( A_{CBM} = -27.23 \text{eV} \). We see that the band-gap response to the lattice distortion (pressure) is largely dominated by the changes in CBM. To reproduce this LDA-predicted behavior, it is necessary to have a pseudopotential that explicitly depends on strain, otherwise one gets a nearly pressure independent. (ii) The correlation-energy dependence of single-particle eigenvalues \( \mathcal{E}_i(a) = \mathcal{E}_i(0) + A_i(\Delta a/\Delta a_0) + B_i(\Delta a/\Delta a_0)^2 \), we find \( A_{VBM} = -0.46 \text{eV} \) and \( A_{CBM} = -11.72 \text{eV} \) and, consequently, VBM dominates the gap changes.

In summary, we have studied the effects of pressure on the binding energies of \( X^0, X^-, X^+ \) and \( XX^0 \). Our main findings are the following. (i) With applied pressure, the binding energy of \( X^0 \) and \( X^+ \) increases and that of \( X^- \) decreases, whereas the binding energy of \( XX^0 \) is nearly pressure independent. (ii) The correlation-energy component in the binding energy of \( X^0 \) is small, whereas it is large in \( X^-, X^+ \) and \( XX^0 \); indeed, correlation is fully responsible for binding the latter complexes. (iii) Correlations depend weakly on pressure. (iv) The pressure dependence of the binding energies is controlled by the pressure dependence of the direct Coulomb integrals. Further, the relative magnitude (order) of these direct integrals explains the relative magnitude (order) of the binding energies. (v) Pressure dependence of \( J_{00}^{(hh)}, J_{00}^{(eh)} \) and \( J_{00}^{(ee)} \) is explained by the changes of the LUMO and HOMO wavefunctions with pressure.

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1. R. S. Knox, *Theory of Excitons* (Academic Press, New York, 1963).
2. K. Cho, in *Excitons*, edited by K. Cho (Springer, New York, 1979), Chap. 2.
3. T. Takagahara, *Phase Transitions* 68, 281 (1999).
4. W. Chen, J. Z. Zhang, and A. G. Joly, J. Nanosci. Nanotech. 4, 919 (2004).
5. C. S. Menoni et al., Phys. Rev. Lett. 84, 4168 (2000).
6. R. W. Meulenberq and G. F. Strouse, Phys. Rev. B 66, 035317 (2002).
7. J. Li et al., J. Phys.: Condensed Matter 13, 2033 (2001).
8. B. S. Ma et al., J. Appl. Phys. 95, 933 (2004).
9 F. J. Manjón et al., phys. stat. sol. (b) 235, 496 (2003).
10 S. I. Rybchenko et al., Phys. Stat. Sol. (b) 241, 3257 (2003).
11 S. G. Lyapin et al., Phys. Stat. Sol. (b) 211, 79 (1999).
12 G. H. Li et al., J. Chem. Phys. Solids 56, 385 (1995).
13 I. E. Itskevich et al., Phys. Stat. Sol. (b) 211, 73 (1999).
14 A. J. Williamson and A. Zunger, Phys. Rev. B 58, 6724 (1998).
15 R. Resta, Phys. Rev. B 16, 2717 (1977).
16 A. Franceschetti, H. Fu, L. W. Wang, and A. Zunger, Phys. Rev. B 60, 1819 (1999).
17 M. Bayer et al., Phys. Rev. B 65 195315 (2002).
18 A. R. Goñi, K. Strössner, K. Syassen, and M. Cardona, Phys. Rev. B 36, 1581 (1987).
19 A. J. Williamson, L. W. Wang, and A. Zunger, Phys. Rev. B 62, 12963 (2000).
20 L.-W. Wang and A. Zunger, Phys. Rev. B 59, 15806 (1999).
21 B. Welber, M. Cardona, C. K. Kim, and S. Rodriguez, Phys. Rev. B 12, 5729 (1975).
22 C. Pryor et al., J. Appl. Phys. 83, 2548 (1998).
23 H. J. McSkimin, A. Jayaraman, and P. Andreatch, Jr., J. Appl. Phys. 38, 2362 (1967).
24 S.-H. Wei and A. Zunger, Phys. Rev. B 60, 5404 (1999).