

Excitonic and Quasiparticle Gaps in Si Nanocrystals

C. Delerue,* M. Lannoo, and G. Allan

*Institut d'Electronique et de Microelectronique du Nord, Département Institut Supérieur d'Electronique du Nord,
41 boulevard Vauban 59046 Lille Cédex, France*

(Received 18 June 1999)

We present calculations of the one- and two-particle excitations in silicon nanocrystals. The one-particle properties are handled in the *GW* approximation, and the excitonic gap is obtained from the Bethe-Salpeter equation. We develop a tight binding version of these methods to treat clusters up to 275 atoms. The self-energy and Coulomb corrections almost exactly cancel each other for crystallites with radius larger than 0.6 nm. The result of this cancellation is that one-particle calculations give quite accurate values for the excitonic gap of crystallites in the most studied range of sizes.

PACS numbers: 71.24.+q

One of the most challenging problems concerning semiconductor nanocrystals remains the accurate prediction of their excitonic energy gap. For silicon, a number of calculations of the independent particle gap ε_g^0 have been performed based either on empirical techniques (tight binding [1] or pseudopotentials [2]) or on the *ab initio* local density approximation (LDA) [3]. In the latter case, as LDA underestimates the bulk band gap, the results are usually shifted by the bulk correction. Interestingly, these corrected LDA band gaps are in quite good agreement with the best tight binding or pseudopotential results [3,4]. The second step has usually been to subtract from this value the screened direct electron-hole attraction. However the whole procedure is not clearly justified and conflicting points of view [5–7] have been expressed concerning its validity. The aim of this Letter is thus to clarify this problem. For this we express the excitonic gap $\varepsilon_g^{\text{exc}}$ as the difference between the quasiparticle gap $\varepsilon_g^{\text{qp}}$ (the difference between the separate electron and hole quasiparticle energies) and E_{coul} , the attractive interaction between these two quasiparticles.

$$\varepsilon_g^{\text{exc}} = \varepsilon_g^{\text{qp}} - E_{\text{coul}} = \varepsilon_g^0 + \delta\Sigma - E_{\text{coul}}, \quad (1)$$

where $\varepsilon_g^{\text{qp}}$ is written as the sum of the independent particle value ε_g^0 and a self-energy correction $\delta\Sigma$. The main result of the present work is that there is strong cancellation between the two large quantities $\delta\Sigma - \delta\Sigma_b$ (where $\delta\Sigma_b$ is the bulk value) and E_{coul} , such that $\varepsilon_g^{\text{exc}} \approx \varepsilon_g^0 + \delta\Sigma_b$. This justifies why the above-mentioned single particle calculations should yield accurate results. We also show that $\delta\Sigma$ and E_{coul} are dominated to a large extent by classical electrostatic contributions.

To perform these calculations, we proceed in two steps: (i) We calculate the separate electron and hole quasiparticle energies via the *GW* method [8], and (ii) we determine the attractive Coulomb interaction between these quasiparticles by resolution of the Bethe-Salpeter equation. Similar work has already been achieved with success from an *ab initio* point of view for bulk semiconductors [9], Na_4 clusters [10], and small silicon clusters saturated by hydrogen atoms (up to $\text{Si}_{14}\text{H}_{20}$) [11]. However the computation is very time consuming and cannot be extended to

nanocrystals. This is why we have chosen here a tight binding formulation which allows one to treat easily nanocrystals with a diameter up to 2.2 nm and will help to clarify the situation concerning the gap.

We first determine the self-energy correction $\delta\Sigma$ to the gap using the *GW* approximation [8] of the self-energy operator Σ which works well for bulk semiconductors [12]. Σ is given by [13]

$$\begin{aligned} \Sigma(\mathbf{r}, \mathbf{r}', \omega) = & - \sum_k \psi_k(\mathbf{r}) \psi_k^*(\mathbf{r}') \\ & \times \left[n_k W(\mathbf{r}, \mathbf{r}', \varepsilon_k - \omega) \right. \\ & \left. + \frac{1}{\pi} \int \frac{\text{Im}W(\mathbf{r}, \mathbf{r}', \omega')}{\omega - \varepsilon_k - \omega' + i\delta} d\omega' \right], \end{aligned} \quad (2)$$

where the ψ_k are the eigenstates of the one-particle equations of energy ε_k . $W(\mathbf{r}, \mathbf{r}', \omega)$ is the dynamically screened electron-electron interaction, equal to $\int \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) V(\mathbf{r}'', \mathbf{r}', \omega) d\mathbf{r}''$, where V is the bare Coulomb interaction, and ε^{-1} is the inverse frequency dependent dielectric function. We have shown recently that tight binding is an efficient way to calculate ε^{-1} even for large silicon crystallites [14], and we apply it here to simplify the *GW* calculation. The eigenstates ψ_k are defined in an atomic basis composed of one *s* and three *p* orbitals for each silicon atom. Because of the neglect of terms involving overlaps of different atomic orbitals, the main advantage of the tight binding method is that all the functions and operators (e.g., ε^{-1} , V) are defined by matrices at discrete values of \mathbf{r} (\mathbf{r}') corresponding to the atomic positions \mathbf{R}_i , the size of the matrices being equal to the number of atoms in the system. The matrix of W is equal to the product of the matrices of ε^{-1} and V . ε itself is equal to $I - VP$, where P is the polarizability matrix [14]. Σ is thus also defined by a matrix which can be calculated from Eq. (2).

The previous discussion shows that tight binding allows us to get information on the self-energy operator Σ .

However what we really want is, starting from a given independent particle Hamiltonian h , to get the corresponding self-energy correction $\delta\Sigma$. Calling ν_{xc} the exchange-correlation part of h , $\delta\Sigma$ can be expressed to first order in perturbation as [15]

$$\delta\Sigma = \langle \psi_c | \Sigma(\varepsilon_c) - \nu_{xc} | \psi_c \rangle - \langle \psi_v | \Sigma(\varepsilon_v) - \nu_{xc} | \psi_v \rangle, \quad (3)$$

where ψ_c, ψ_v are the eigenstates of energy $\varepsilon_c, \varepsilon_v$ corresponding, respectively, to the lowest unoccupied and highest occupied orbitals of the cluster (LUMO and HOMO). Our main problem here is then to calculate ν_{xc} . The most natural method is to start from the tight binding Hamiltonian $h = h_{TB}$. The corresponding $\nu_{xc} = (\nu_{xc})_{TB}$ is simply transferred without change from the bulk to the cluster case. It thus represents the best approximation to Σ_b , the bulk self-energy. We thus get the simple recipe that $\delta\Sigma$ can be obtained by replacing $(\nu_{xc})_{TB}$ by $\Sigma_b(\varepsilon_{cb})$ in the first term of Eq. (3) and by $\Sigma_b(\varepsilon_{vb})$ in the last one, where ε_{cb} and ε_{vb} are the bulk values. The corresponding results are given in Fig. 1 as a function of the cluster radius $R = 3a^3N/32\pi$, where a is the bulk lattice constant, and N is the number of silicon atoms.

For obvious reasons one might also want to get $\delta\Sigma$ starting from *ab initio* LDA calculations, i.e., using in (3) Σ deduced from tight binding with the corresponding $(\nu_{xc})_{LDA}$. In this case it is more difficult to determine $\Sigma - (\nu_{xc})_{LDA}$ since a central difficulty in tight binding comes from the use of a minimal basis set, so that the completeness relation $\sum_k \psi_k(\mathbf{r})\psi_k^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ is not verified. The consequence is that the short range part of Σ (when $\mathbf{r} \rightarrow \mathbf{r}'$) is not correctly described [15], and it is precisely this part which is well approximated by $(\nu_{xc})_{LDA}$ [16]. We have

thus calculated $\Sigma - (\nu_{xc})_{LDA}$ by two distinct methods: (1) Following the arguments of Ref. [16] we consider that the short range part of Σ corresponds to $(\nu_{xc})_{LDA}$ so that the matrix $\Sigma - (\nu_{xc})_{LDA}$ is simply equal to Σ in which the diagonal terms are removed; (2) following Ref. [15] we replace $(\nu_{xc})_{LDA}$ by the self-energy operator Σ^h of the homogeneous electron gas with the same electron density. The matrix elements of Σ^h are also calculated in tight binding. The homogeneous gas is described using a simple Thomas-Fermi model, where the matrix P of the polarizability which defines ε is diagonal. Each diagonal term of P is equal to $N(\varepsilon_F)$, the density of states per atomic volume at the Fermi level of the free electron gas (we use for the atomic volume of silicon the bulk silicon value and for hydrogen a spherical volume of radius 1 Å).

We use the tight binding parametrization of Ref. [17] which includes interactions up to third-nearest neighbors and three center terms. For bulk silicon, this allows one to get a quite good band structure over a large energy range and a correct dielectric function (e.g., static dielectric constant = 11.05). For hydrogen atoms, we include only nearest neighbors Si-H interactions and we fit the tight binding parameters on the LDA electronic structure of SiH₄. One then calculates $\delta\Sigma$. The frequency dependence of ε is completely evaluated and there is no free parameter in the calculation. The self-energy corrections to LDA calculated for bulk Si ($\delta\Sigma_b$) are, respectively, 0.41 eV and 0.75 eV with the first and second methods, to compare with an average difference of ~ 0.65 eV between experimental and LDA gaps [12] (the full tight binding one is zero by construction). In Fig. 1 we plot $\delta\Sigma - \delta\Sigma_b$ calculated for nanocrystals containing up to 275 Si atoms. In spite of their differences, the three approaches give very similar results, especially for $R > 0.6$ nm. For smaller clusters, the results become more scattered, in particular, those obtained with the second method to calculate $\Sigma - (\nu_{xc})_{LDA}$ tend to differ slightly from the others. We attribute this to the increasing importance of the hydrogen terminations, where our approximations are less justified.

We now show that the main contribution to $\delta\Sigma - \delta\Sigma_b$ is actually a classical electrostatic effect [18]: When one puts an extra electron (or hole) at site \mathbf{r} into a nanocrystal, the electronic relaxation (screening) induces charges at the surface and the extra particle interacts with this self-image charge distribution leading to a self-polarization energy $E_{pol}(\mathbf{r})$ as discussed in Ref. [18]. We can then average this quantity over the cluster with a statistical weight $|\psi(\mathbf{r})|^2$, where ψ is the particle wave function. The total result Σ_{pol} is obtained in this way for the separate addition of one electron plus a hole into the cluster. An excellent approximation is obtained by using an effective mass wave function $\psi(\mathbf{r}) \propto \sin(kr)/r$ which leads to [18]

$$\Sigma_{pol} \approx \left(1 - \frac{1}{\varepsilon(R)}\right) \frac{e^2}{R} + 0.94 \frac{e^2}{\varepsilon(R)R} \left(\frac{\varepsilon(R) - 1}{\varepsilon(R) + 1}\right), \quad (4)$$

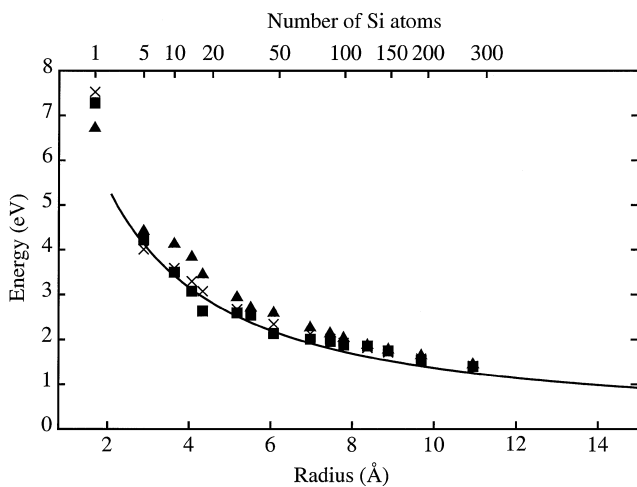


FIG. 1. Variation versus size of the self-energy correction ($\delta\Sigma - \delta\Sigma_b$) in Si nanocrystals (■: full tight binding; ×: first LDA method; ▲: second LDA method). Continuous line: classical electrostatic energy [Σ_{pol} , Eq. (4)] for the separate addition of an electron and a hole in a nanocrystal.

where $\varepsilon(R)$ is an effective dielectric constant defined for each crystallite which depends on its radius R , because the polarizability decreases when the band gap opens [18]. We see in Fig. 1 that $\delta\Sigma - \delta\Sigma_b$ is well given by Σ_{pol} . Recently, Ögüt *et al.* [5] have proposed to calculate the self-energy directly from LDA $[(\delta\Sigma)_{\text{LDA}} = (\varepsilon_g^{\text{qp}})_{\text{LDA}} - (\varepsilon_g^0)_{\text{LDA}}]$ using $(\varepsilon_g^{\text{qp}})_{\text{LDA}} = E(n+1) + E(n-1) - 2E(n)$, where $E(n)$ is the LDA total energy of the n -electron neutral cluster. As already shown in Ref. [7], the values of $(\delta\Sigma)_{\text{LDA}}$ calculated in Ref. [5] are equal to Σ_{pol} within 0.1 eV, i.e., LDA contains the self-polarization term but is unable to produce the ν_{xc} discontinuity across the gap for the bulk [6]. We conclude that $\varepsilon_g^{\text{qp}} \approx (\varepsilon_g^{\text{qp}})_{\text{LDA}} + \delta\Sigma_b$ holds in a large range of cluster sizes.

We now calculate the excitonic gap $\varepsilon_g^{\text{exc}}$ by solving the Bethe-Salpeter equation for the two-particle Green's functions [19–21]. We follow the same procedure as Ref. [11], writing the triplet excitons:

$$(\varepsilon_n^{\text{qp}} - \varepsilon_m^{\text{qp}})A_{mn} + \sum_{m'n'} K_{mn,m'n'}^d(\Omega)A_{m'n} = \Omega A_{mn}, \quad (5)$$

where A_{mn} is the coefficient of the expansion of the total wave function in a Slater determinantal basis corresponding to the single particle excitation of an electron in state ψ_n (energy $\varepsilon_n^{\text{qp}}$) and a hole in state ψ_m (energy $\varepsilon_m^{\text{qp}}$). $\varepsilon_n^{\text{qp}}$ and $\varepsilon_m^{\text{qp}}$ are known from the GW calculations, while K^d is the effective direct electron-hole interaction matrix which can be expressed as

$$K_{mn,m'n'}^d(\Omega) = \int dr dr' \psi_n^*(r) \psi_{n'}(r) \psi_m^*(r') \psi_{m'}(r') \frac{i}{2\pi} \int d\omega e^{-i\omega t} W(r, r', \omega) \times [(\Omega + \omega - \varepsilon_n^{\text{qp}} + \varepsilon_m^{\text{qp}} + i0^+)^{-1} + (\Omega + \omega - \varepsilon_n^{\text{qp}} + \varepsilon_{m'}^{\text{qp}} + i0^+)^{-1}]. \quad (6)$$

As for GW we calculate these matrix elements in a tight binding framework. For the frequency dependence of (6) we make use of a single plasmon pole approximation together with a first order expansion of the correction with respect to the static approximation, in a way similar to [11]. We then diagonalize the matrix equation (5), increasing the number of electron-hole states till convergence is reached (this usually requires ~ 10 electron and hole states). The lowest eigenvalue obtained in this way thus corresponds to the triplet exciton gap $\varepsilon_g^{\text{exc}}$. The corresponding results are given in Fig. 2. However, for reasons which will become clear later, we have preferred to plot E_{coul} versus size, taken from (1) as the difference $\varepsilon_g^{\text{qp}} - \varepsilon_g^{\text{exc}}$. We also compare the computed E_{coul} with the result of the classical electrostatic argument of [18], where the effective interaction for the electron and hole at distance r_{e-h} is the sum of two terms: a direct screened interaction $e^2/\varepsilon(R)r_{e-h}$ plus the interaction of one particle with the polarization charge induced by the other [18]. Taking the average of this with respect to the electron and hole distribution in the effective mass approximation gives $[0.79/\varepsilon(R) + 1](e^2/R)$ which we plot in Fig. 2. The values for E_{coul} are well approximated by the classical law, even if this latter tends to be too large for a small cluster, where the influence of the boundary conditions becomes important (the effective mass approximation as used underestimates the radius R of the crystallite resulting in an overestimation of E_{coul}).

We also plot in Fig. 2 the difference $(\delta\Sigma - \delta\Sigma_b) - E_{\text{coul}}$ for our two extreme values of $\delta\Sigma - \delta\Sigma_b$, and we compare with the same quantity obtained from the full *ab initio* GW calculation [11] for SiH_4 , Si_5H_{12} , $\text{Si}_{10}\text{H}_{16}$, and $\text{Si}_{14}\text{H}_{20}$. Our values fall in the same range as the *ab initio* values, especially those arising from the second LDA model. A striking feature displayed by Fig. 2 is that

the quantities E_{coul} and $\delta\Sigma - \delta\Sigma_b$, while being pretty large, compensate each other to a large degree and, for clusters with $R > 0.6$ nm, the two quantities are practically identical so that their contributions to the excitonic gap cancel each other. From Eq. (1) one thus gets

$$\varepsilon_g^{\text{exc}} \approx \varepsilon_g^0 + \delta\Sigma_b. \quad (7)$$

This means that $\varepsilon_g^{\text{exc}}$ is directly given by the single particle gap $(\varepsilon_g^0)_{\text{TB}}$ in full tight binding (where $\delta\Sigma_b = 0$) and $(\varepsilon_g^0)_{\text{LDA}} + 0.65$ eV in local density calculations. This result not only justifies the use of single particle calculations to get the excitonic gap but also explains the agreement

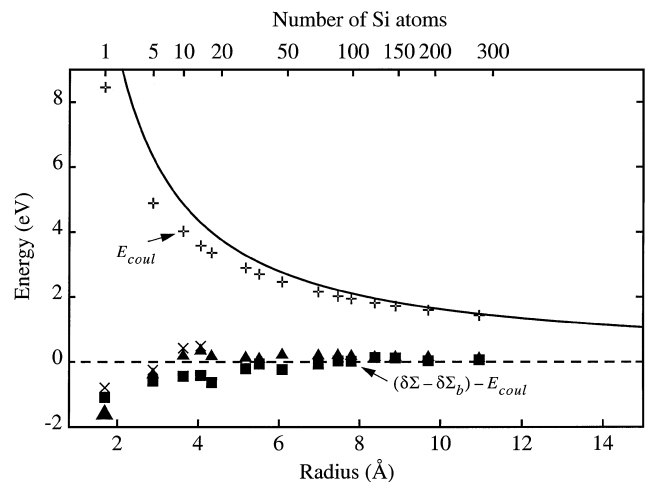


FIG. 2. Exciton Coulomb energy (E_{coul}) versus size in Si nanocrystals (✦: full GW + Bethe-Salpeter calculation; continuous line: classical electrostatics calculation with effective mass wave functions). Difference between the self-energy correction $\delta\Sigma - \delta\Sigma_b$ and E_{coul} (■: present calculations, full tight binding; ▲: present calculations, second LDA approximation; ✕: *ab initio* results of Ref. [11]).

between empirical and LDA results once these are shifted by the bulk correction 0.65 eV [3]. Of course, the cancellation is not strictly exact but for $R > 0.6$ nm it is verified to better than 0.2 eV in Fig. 2. One can also notice that Eq. (7) is likely to hold true to some extent for other semiconductor crystallites. We have checked that this is indeed the case for Ge and even for C for which, at $R = 0.8$ nm the deviation from perfect cancellation is 0.8 eV still small compared to the gap value (~ 12 eV in this case).

An important point to consider is the accuracy of our tight binding predictions. We believe that the most important source of errors is the short range contribution in the GW part. In this regard one measure of the uncertainty in our calculations is the dispersion of our results for $\delta\Sigma - \delta\Sigma_b$ between the three approximations used to include this short range term. The corresponding error is ± 0.2 eV at $R = 0.6$ nm but decreases very rapidly with size to become practically negligible at $R = 0.8$ nm. Another interesting point is illustrated in Fig. 2 which shows that our results with the Thomas-Fermi approximation (second LDA model) agree well with the *ab initio* calculations for small crystallites. As they also provide a fairly accurate bulk value $\delta\Sigma_b = 0.75$ eV this certainly means that they must remain practically exact over the whole range of sizes, strengthening the conclusion concerning the cancellation between $\delta\Sigma - \delta\Sigma_b$ and E_{coul} . Finally we also obtain the same cancellation effect using another inferior tight binding parametrization of bulk silicon [22] or even when using other boundary conditions with no hydrogen terminations, the sp^3 dangling bonds at the surfaces being simply removed from the tight binding basis.

In conclusion we have calculated the excitonic gap of silicon crystallites from the most accurate methods available (*GW* + Bethe-Salpeter equation). We have used a tight binding formulation which allows one to handle large clusters (with radius up to 1.1 nm). Our central result is that for crystallites with radius larger than 0.6 nm there is cancellation between the change in self-energy correction with respect to the bulk and the Coulomb term. This means that the lowest excitonic energy is correctly predicted by simple one-particle theories like LDA with the bulk correction for the gap or the best semiempirical tight binding or pseudopotential calculations.

The Institut d'Electronique et de Microélectronique du Nord is UMR 8520 of CNRS.

*Email address: delerue@isen.fr

- [1] J. P. Proot, C. Delerue, and G. Allan, Appl. Phys. Lett. **61**, 1948 (1992); C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **48**, 11024 (1993).
- [2] Lin-Wang Wang and A. Zunger, J. Phys. Chem. **98**, 2158 (1994).
- [3] B. Delley and E. F. Steigmeier, Phys. Rev. B **47**, 1397 (1993); Appl. Phys. Lett. **67**, 2370 (1995).
- [4] M. Lannoo, G. Allan, and C. Delerue, in *Structural and Optical Properties of Porous Silicon Nanostructures*, edited by G. Amato, C. Delerue, and H.-J. von Bardeleben (Gordon and Breach, Amsterdam, 1997), p. 187.
- [5] S. Ögüt, J. R. Chelikowsky, and S. G. Louie, Phys. Rev. Lett. **79**, 1770 (1997).
- [6] R. W. Godby and I. D. White, Phys. Rev. Lett. **80**, 3161 (1998).
- [7] A. Franceschetti, L. W. Wang, and A. Zunger, Phys. Rev. Lett. **83**, 1269 (1999).
- [8] L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.
- [9] S. Albrecht, G. Onida, and L. Reining, Phys. Rev. B **55**, 10278 (1997).
- [10] G. Onida, L. Reining, R. W. Godby, R. DelSole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
- [11] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. **80**, 3320 (1998).
- [12] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **34**, 5390 (1986); R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10159 (1988).
- [13] M. Lannoo, M. Schlüter, and L. J. Sham, Phys. Rev. B **32**, 3890 (1985).
- [14] C. Delerue, M. Lannoo, and G. Allan, Phys. Rev. B **56**, 15306 (1997).
- [15] F. Bechstedt and R. Del Sole, Phys. Rev. B **38**, 7710 (1988).
- [16] F. Gygi and A. Baldereschi, Phys. Rev. Lett. **62**, 2160 (1989).
- [17] C. Tserbak, H. M. Polatoglou, and G. Theodorou, Phys. Rev. B **47**, 7104 (1993).
- [18] M. Lannoo, C. Delerue, and G. Allan, Phys. Rev. Lett. **74**, 3415 (1995).
- [19] P. Nozières, *Theory of Interacting Fermi Systems* (Benjamin, New York, 1964).
- [20] L. J. Sham and T. M. Rice, Phys. Rev. **144**, 708 (1966).
- [21] G. Strinati, Phys. Rev. B **29**, 5718 (1984).
- [22] J. Van der Rest and P. Pêcheur, J. Phys. Chem. Solids **45**, 563 (1984).