

Novel Scaling Laws for Band Gaps of Quantum Dots

Xihong Peng,¹ Surya Ganti,² Pradeep Sharma,^{3,4,*} Azar Alizadeh,²
 Saroj Nayak,¹ and Sanat Kumar⁵

¹Department of Physics, Applied Physics and Astronomy, ⁵Department of Chemical and Biological Engineering,
 Rensselaer Polytechnic Institute, Troy, NY, 12180, USA

²General Electric Global Research Center, Niskayuna, NY 12309, USA

³Department of Mechanical Engineering, ⁴Department of Physics, University of Houston,
 Houston, TX 77204-4006, USA

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We present new scaling laws that govern coupled mechanical deformation and opto-electronic properties (band gap) of quantum dots. Our theoretical work on quantum dots, confirmed via electronic structure calculation based on density functional theory indicates that novel size effects in band gap (above and beyond the well studied quantum confinement, electrostatic interaction and mechanical strain coupling) become operative in the 1–5 nm size range. These new coupled size-effects illustrated for Silicon clusters arise out of the size-dependency of the mechanical strain which has traditionally been ignored and devoid in classical continuum field theories (and what is typically employed by most current studies of strain-quantum dot coupling). The surface energies which induce the aforementioned size-effect are themselves found to be size-dependent for extremely small cluster size and peak within a very narrow cluster size range (0.6–2 nm).

Keywords: Quantum Dots, Strain, Size-Effect, Surface Energy, Scaling Laws.

While a fairly sophisticated and involved mathematical rendition of quantum dot band gap calculation is possible, a fairly simple picture of the appropriate scaling laws emerges upon analysis of a spherical quantum dot within a single-band effective mass approximation:^{1,2}

$$E_g(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2m^* R^2} - \frac{1.786e^2}{\epsilon_r R} + 0.284E_{Ry} \quad (1)$$

Here, $E_g(R)$ is the quantum dot band gap as a function of radius, $E_g(\infty)$ is the bulk band gap, E_{Ry} is the constant Rydberg energy for the bulk semiconductor, ϵ_r is the effective dielectric constant while other parameters have their usual significance. Equation (1) exemplifies the well-known quantum confinement induced scaling of $1/R^2$ and also the presence of a $(-1/R)$ scaling due to electrostatic effects. Indeed experimental evidence^{3–6} typically indicates a $1/R^n$ scaling with $1 < n < 2$. Electrostatic interactions ($-1/R$ scaling) and other physical causes are often considered responsible for the deviation from the “idealized” quantum confinement of $n = 2$. The breakdown of

the effective mass theory for extremely small dots (on which Eq. (1) is predicated) is also partly responsible for observed deviation from $n = 2$. Size is routinely employed to tailor the band gap and the consequent optoelectronic characteristics of quantum dots.⁷ Mechanical strain is yet another factor that is frequently utilized for tailoring the band gap.^{7,8} In a simplistic picture (ignoring complications like anisotropy etc.) one may simply add a term $a\epsilon_{kk}$ to the right side of Eq. (1) to account for strain induced changes. Here “ a ” is the effective deformation potential constant and ϵ_{kk} is the trace of the strain tensor. A key point to note is that in existing works (e.g., Refs. [9–14]) strain is always computed using traditional continuum mechanics, which is intrinsically size-independent i.e., regardless of whether the quantum dot dimensions are in kilometers or nanometers, as long as scaling is self-similar, the same strain state is predicted. In other words, scaling exponent (n) of band gap due to strain-induced effect predicated on classical continuum elasticity is zero.^{15–17}

In this letter we show that while the latter statement is true for “large” quantum dots, a new scaling law emerges

*Author to whom correspondence should be addressed.

in the size-range of 1–10 nm due to (in violation of classical continuum mechanics) the size-dependence of strain in the aforementioned size range. The physical cause of this size-dependency of strain is due to the involvement of surface or interface energies at the nanoscale due to a large surface-to-volume ratio explicitly modifying classical elasticity to include absolute size.¹⁸ While we argue using simple analytical expressions that size-dependent strain induces a (+1/*R*) scaling, the focus of this letter is on numerical density function theory (DFT) simulations of Si clusters that seek to illustrate the impact of surface energy induced strains. Our parameter free DFT calculations avoid several deficiencies of the more empirical and coarse-grained effective mass approach. We point out at the outset that direct *ab initio* simulations of quantum dots, for the purpose of ascertaining scaling laws associated with their optoelectronic properties, have also been carried out by other researchers (see for example, Refs. [19, 20]). Why have these works not noticed the afore-mentioned additional scaling effects considering that in principle these effects should be automatically incorporated in their atomic simulations? The key point to note is that all conventional simulations that are reported in the literature constrain the surface atoms to remain configurationally fixed thus effectively precluding the manifestation of influence of surface energies on strain. In the simplest possible picture, for the case of un-embedded quantum dots where there is no apparent source of strain (i.e., no lattice mismatch), the effect of surface tension is excluded. In the case of embedded quantum dots, the correction to the lattice mismatch induced strain due to interfacial tension and elasticity is excluded. This form of simulations where surface atoms are not allowed to relax is primarily employed for savings in computational time with the unfortunate consequence of effectively voiding the strain induced scaling. For example, the DFT computation time for a surface relaxed cluster Si₅₉H₆₀ is 1694 minutes while the time for the same cluster without atomic relaxation is 125 minutes.²¹

In earlier works we have derived simple expressions that modify the strain in an embedded (spherical) quantum dot incorporating surface/interface energetic effects:^{15–17}

$$\varepsilon_{rr} = \underbrace{\frac{3K_{\text{QD}}\varepsilon_m - 2\tau_o/R}{4\mu_M + 3K_{\text{QD}} - 2K_I/R}}_{\text{Embedded}}; \quad (2)$$

$$\varepsilon_{rr} = - \underbrace{\frac{1}{3K_{\text{QD}} - 2K_s/R}}_{\text{Un-embedded}} \left(\frac{2\tau_o}{R} \right)$$

Here ε_m is the lattice mismatch strain, while τ_o is the surface or interfacial tension. K is the hydrostatic modulus and μ is the shear modulus where the subscripts “QD” and “M” indicate “quantum dot” and “matrix” respectively. K_s and K_I are the surface and interface elastic modulus respectively (and are typically only significant for

high strains). Note that the mismatch strain must be subtracted from Eq. (2) before employing in band structure calculations. Both the expressions in Eq. (2) are for an isotropic elastic quantum dot and for the embedded case, the quantum dot is assumed to be surrounded by an infinite isotropic solid admitting a certain lattice mismatch strain. More realistic scenarios where anisotropic effects, piezoelectric coupling and other complications are included can be dealt with numerically. We simply emphasize that the exceedingly simple expressions in Eq. (2) provide a splendid illustration of the surface-energy induced size-effect in strain without delving into the aforementioned only-numerically-tractable complications. Finally, we note that even for the unembedded case, there is a strain present due to free surface tension and surface elasticity.

Evidently for large radius of quantum dots ($R \rightarrow \infty$) or zero surface energy, the result in Eq. (2) reverts to well known classical results for spherical quantum dots used by several authors (e.g., see Yang and Sturms⁹). The asymptotic (1/*R*) scaling of the size-dependent strain and hence the quantum dot band gap is readily apparent from for both embedded as well as free-standing cases.

It is also instructive to reconcile, at least qualitatively, our analytical results with available experimental data in the literature. A host of explanations have been advanced to explain the departure of the scaling exponent $1 < n < 2$ from $n = 2$. We have already indicated that electrostatic interactions are one possible explanation that can potentially account for such a departure. The other is the errors due to the breakdown of effective mass approach. We have collected some of the experimental data (from various sources) in Figure 1 for two unembedded quantum dot systems (InP and Si) and performed a curve fit with respect to size. Instead of attempting to determine “*n*” we have isolated the “1/*R*²” and “1/*R*” terms. We obtain (for both InP and Si) a positive coefficient for the 1/*R* term. Electrostatic interactions invariably predict a negative coefficient thus possibly suggesting an additional positive +1/*R* term. Recall that size-dependent strain induced scaling (which is compressive) results in a positive coefficient for 1/*R* dependence. Thus these experimental results are encouraging and suggestive although, unfortunately not conclusive since the fitting process is prone to errors and uncertainties. The latter fact provides further motivation for the numerical DFT simulations the results of which are the main object of this letter.

We now proceed to present a test of the assertions and implications of Eq. (2) through DFT calculations of unembedded Si clusters of various sizes. We note here the work of Delley²⁰ who performed such a study without incorporating the surface effects outlined in Eq. (2). The surface atoms were configurationally fixed in his analysis thus excluding the scaling effect we predict.

In our pseudo-potential DFT calculations, the starting clusters were truncated spherically from bulk silicon with

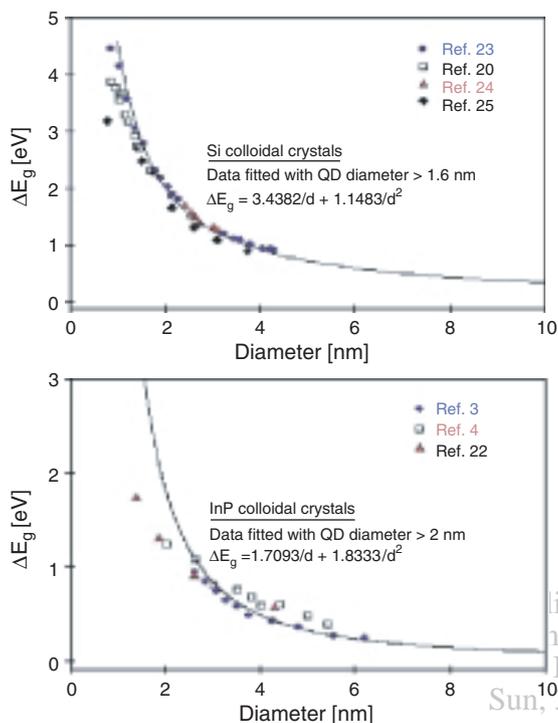


Fig. 1. Suggestive literature evidence.^{3,4,20,22–25} This collection of results obtained from the literature is meant to emphasize the deviation of band gap scaling from $n = 2$.

lattice constant $a = 5.461$ angstroms. The latter is the DFT optimized value of the bulk silicon. The spherical clusters were centered at a silicon atom. To retain the tetrahedral configuration of silicon (refer to Fig. 2), all the dangling bonds of the surface silicon atoms were terminated by hydrogen at initial bond length of 1.47 angstroms. The clusters were varied from Si_5H_{12} to $\text{Si}_{239}\text{H}_{196}$ (i.e., from 5.8 Å to 21.0 Å). We have used plane wave energy cutoff of 300 eV and an energy convergence criterion of 1.0×10^{-5} was used for the self-consistent scheme. The calculations were performed using VASP²⁸ and the conjugate gradient method was used for energy minimization. The energy gap of the cluster was computed from the difference between the eigenvalues of highest occupied

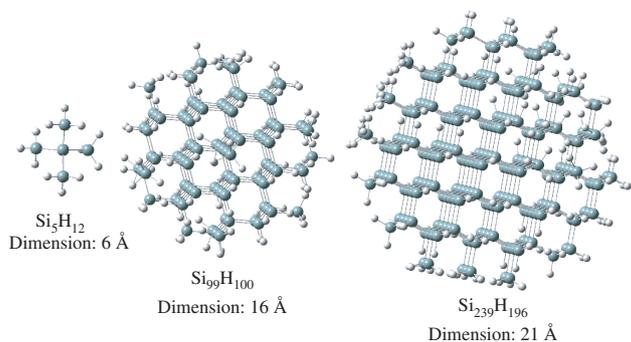


Fig. 2. Snapshots of various sized Si clusters used in the DFT simulations.

Table I. Silicon clusters in present study. N_{Si} is the number of silicon atoms in a specific cluster. N_{H} is the number of hydrogen atoms needed to passivate the surface silicon atoms. X -coordination ($x = 1, 2, 3, 4$) columns present the number of silicon atoms which connect other x silicon atoms and have 4- x dangling bond which then terminated by hydrogen. The diameter of the cluster is related to the number of silicon atoms through “ $a(0.75N/\pi)^{1/3}$ ” where “ a ” is the lattice constant of 5.461 angstroms.

N_{Si}	N_{H}	4-coord.	3-coord.	2-coord.	1-coord.	Diameter (Å)
1	4	0	0	0	0	3.4
5	12	1	0	0	4	5.8
17	36	5	0	0	12	8.7
29	36	5	12	12	0	10.4
35	36	5	24	6	0	11.1
47	60	17	12	6	12	12.2
59	60	17	24	18	0	13.2
71	84	29	12	18	12	14.0
87	76	35	28	24	0	15.0
99	100	47	16	24	12	15.7
123	100	59	28	36	0	16.8
147	100	71	52	24	0	17.9
159	124	83	40	24	12	18.4
191	148	99	52	24	16	19.5
239	196	135	40	36	28	21.0

molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

The characteristics of the various sized cluster are summarized in Table I. The surface atoms were allowed to relax to their equilibrium state thus triggering the strain in Eq. (2). Our main results are depicted in Figure 3 where we plot the band gap as a function of cluster size and compare with Delley-like²⁰ unrelaxed cluster study. As already anticipated from Eq. (2) we note a significant shift in band gap at small sizes where surface energy induced strains make their presence felt. A somewhat surprising result that emerges from Figure 3, not indicated by Eq. (2) is that this scaling effect disappears for extremely small sizes!

A maximum band gap shift of nearly 0.51 eV is observed at a cluster size of 17 atoms. Plausible explanations for the disappearance of this new scaling effect at

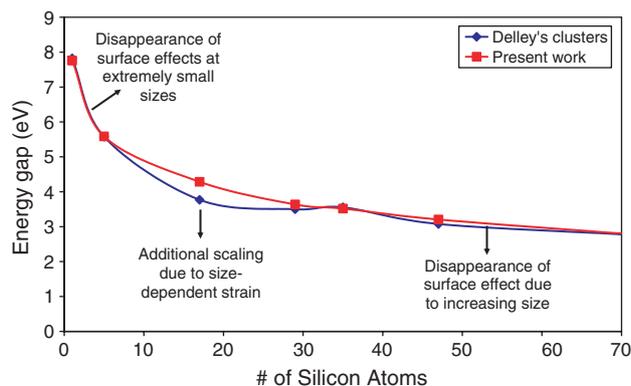


Fig. 3. Comparison of the present work incorporating the size-dependent strain due to surfaces and Delley's results. Figure 3 shows our implementation of Delley's²⁰ study.

sizes below 17 atoms appear to suggest that surface energy parameterized by surface tension and surface elastic modulus must itself be size-dependent i.e.,

$$\{\tau_o, K_s\} \propto \frac{\{\tau_o, K_s\} \text{ at "large" size}}{1+k/R} \quad (3)$$

Where “k” is a constant and presumably has the significance of the so-called Tolman’s length invoked for fluid drops. Obviously, as $R \rightarrow 0$, the surface energy smoothly vanishes explaining the disappearance of concerned scaling effect at extremely small sizes. Physically and in hindsight, this is easy to justify. The continuum field concept of surface energy, tension and surface elastic modulus signify the difference between the surface atom properties with the corresponding ones in the bulk (due to different coordination number, charge distribution, bond length etc.)²⁶ However, at extremely small size where only few atoms remain, this difference and the distinction between surface and bulk atoms becomes very tenuous or in other words, the continuum notions of surface energy (if we insist on using them) must become zero.

A more mechanistic explanation for Eq. (3) appears from unexpected quarters. Mindlin²⁷ showed that elasticity theory when extended to incorporate 2nd gradients of strain (the classical simply depends on the strain itself) automatically incorporates surface tensions and surface elasticity phenomenon. His solution of an isolated liquid drop in equilibrium roughly reproduces Eq. (3). Straightforward considerations of his work (details of which are beyond the scope of the present letter), indicate that a similar result is expected for solids thus providing a field theoretic basis for Eq. (3). There is thus the tantalizing implication that at very small sizes, one may be permitted to use the 2nd strain gradient elasticity theory (appropriately coupled to say effective mass band gap theory) to phenomenologically capture the size-effects we observed in our DFT simulations. For the simple case of a spherical quantum dot discussed in Eq. (2), we anticipate an expression of the form:

$$E_g(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2m^* R^2} - \frac{1.786e^2}{\epsilon_r R} + 0.284E_{Ry} + \underbrace{\frac{a}{3K_{QD} - 2K_s/(R+k)} \left(\frac{2\tau_o}{R} \right) \left(\frac{1}{1+k/R} \right)}_{\text{new scaling due to surface effects}} \quad (4)$$

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