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A Chemical Bond Theory of Quantum Size Effects of Semiconductor Clusters

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Size dependence effects in semiconductor clusters have been a subject of extensive studies for the last two decades. However, it is still difficult to employ the existing theoretical models to give reliable results of energies for clusters in the *whole* nanometer region. Here we offer a new theoretical method for the quantum size effects based on the idea that the energy gap shift of the cluster arises from the sum of the surface effect shift and quantum effect shift parts. We express the effects through algebraic relations rather than through variational solutions of the wave equation, without the use of any special adjustable parameter. Results reveal for the first time that the shape of the energy gap shift curve is dominated by the surface energy shift. Our method can also predict quantitatively the size dependence of dielectric constant. The new theoretical findings in the ultrasmall (<1 nm) anatase TiO_2 and the silicon clusters cannot be explained using previous theories.

Introduction

Semiconductor clusters (or nanocrystals) have attracted considerable interest due to their potential use in the fields of nonlinear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics.[1−3] Most semiconducting clusters show size-dependence effects in the nanometer region. Along with the energy gap of the cluster, the photoluminescence can even be varied through the red to blue region of the visible spectrum. Thus, this allows scientists the unique opportunity to tune the electronic and chemical properties of a material simply by controlling its particle size. Theoretically, predicting accurately the spectra of clusters as a function of their size is one of the fundamental nanoscientific issues, and of utmost importance. First, the effective-mass models (EMA) based on the exciton confinement is empolyed to explain the blueshift of the optical gap.[4] However, this model is suitable only for very large nanocrystals. Although ab initio calculations appear to be a more desirable way to investigate the optical gaps of clusters,[5] for most nanosystems containing from a few thousands to 10^6 atoms, ab initio calculations are still too laborious to be practical. The intermediate approaches, such as the empirical tight-binding (ETBM)[6] or empirical pseudopotential (EPM) methods,[7] seem to be well established though some of the parameters are made to fit the experimental data.[3] But they can only treat thousand-atom electronic structure calculations. Furthermore, almost all existing theoretical calculations on clusters to date assume that interior-to-interior optical transitions dominate the optical properties, neglect surface effects, and effectively treat the crystal surface as a perfectly reflecting wall.[8] These weaknesses would lead to insufficient prediction for the spectra of clusters, hindering the understanding of novel properties. Our studies indicate that surface effects can be very important, especially for the smaller clusters. The interatomic bonding and the fraction of the under-coordinated atoms at the surface play the key roles in indicating why the behavior of a nanosolid differs from that of an isolated atom or its bulk phase. Here we establish a systematic method for solving the size-dependence effects of semiconductor clusters. In order to calculate readily the energy gap shifts for clusters of all size, we express the effects through algebraic relations rather than through variational solutions of the wave equation. It has been applied to the calculations of the energy gaps and the dielectric constants of the clusters.

Theoretical Analysis

In our opinions, the optical gap shift, basically arises from two types of size-dependent effects: surface effects which are related to the bonding and the fraction of atoms at the surface and quantum effects which show the reduction of the band structure into discrete quantum levels due to the limited atoms of the nanocrystals. Thus, the energy gap shift ΔE, which may be measured by the shift of absorption threshold

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of the nanocrystal with respect to that of the bulk, can be expressed as the sum of the surface effect shift $\Delta E^{\text{surface}}$ and the quantum effect shift ΔE^{kubo} parts:

$$\Delta E = \Delta E^{\text{kubo}} + \Delta E^{\text{surface}} \tag{1}$$

On a macroscopical scale, interaction of an infinite number of atomic orbitals within a crystal leads to a continuum of energy levels known as band. As the size gets smaller, even to a nanometer scale, the number of atomic orbitals which take part in conbination becomes less and less, and the band continuum becomes broken down to quantized energy levels. The gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) energy levels, which may be called the Kubo gap,[9] increases as the size of the nanoclusters decreases. Thus, the first term in eq 1 may also be called the Kubo energy shift, resulting from electrons that are confined inside a finite volume V. Ref 10 suggested an emprical expression for the Kubo energy shift: $\Delta E^{\text{kubo}} = 24/(DN_{\text{e}}^{1/3})$, where N_{e} is the valence electron density of the bonds, and D is diameter of nanoclusters. Accordingly, we propose a new expression as

$$\Delta E^{\text{kubo}} = (m_e e^4/2\hbar^2)(VN_{\text{e}})^{-1/3} \tag{2}$$

in which there is no adjustable parameter.

On the other hand, the termination of the lattice periodicity in the surface of nanoclusters not only creates a potential boundary but also reduces the coordination number of the surface atoms.[11] Here we define the atoms with an imperfect coordination number as the surface atoms. The bonding of atoms at the surface of a single nanocrystal is different from that of atoms inside that nanocluster. Therefore, from the chemical bond point of view, a nanocluster contains two different kinds of bonds: surface and inside bonds. Since the electron feels the effects of the nanocrystal boundaries in addition to the periodic potential, the surface energy shift part should be resolved into contributions from the two types of bonds, which may be expressed as

$$\Delta E^{\text{surface}} = F^{\text{surface}}(E_{\text{g}}{}^{\text{surface}} - E_{\text{g}}{}^{\text{bulk}}) \tag{3}$$

where F^{surface} is the fraction of surface bonds composing the nanocluster. $E_{\text{g}}{}^{\text{surface}}$ and $E_{\text{g}}{}^{\text{bulk}}$ represent the gap of the surface bond of the nanocluster and the bulk phase, respectively. Since Phillips' chemical bond theory has proved to be an elegant and simple means of obtaining the energy gaps of semiconductor crystals with reasonable accuracy[12,13] and is successfully applied to many aspects, especially those that are difficult to address by first principles technique,[14] here we will employ the bond theory to determine the variations of these energy gaps.

According to ref 15, for a binary compound, the Hamiltonian and the potential may be expressed as

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(\mathbf{r});$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}}[V_{\text{S}}(\mathbf{G})S_{\text{S}}(\mathbf{G}) + iV_{\text{A}}(\mathbf{G})S_{\text{A}}(\mathbf{G})]\exp(i\mathbf{G}\cdot\mathbf{r}) \tag{4}$$

Here **G** is a reciprocal lattice vector, $S_{\text{S}}(\mathbf{G})$ and $S_{\text{A}}(\mathbf{G})$ are the symmetric and antisymmetric structure factors, and $V_{\text{S}}(\mathbf{G})$ and $V_{\text{A}}(\mathbf{G})$ are the symmetric and antisymmetric form factors. The matrix elements of the Hamiltonian are expressed as $H_{11} = H_{22} = 0$, $H_{12} = H_{21}{}^{*} = E_{\text{h}} + iC$,[12] where, to first order in $V(\mathbf{r})$, the symmetric, homopolar part E_{h} arises from the real part of eq 4, and the antisymmetric, heteropolar part C arises from the imaginary part. Obviously, the energy gap E_{g} between the HOMO and LUMO energy levels may be given by $E_{\text{g}}^2 = E_{\text{h}}^2 + C^2$.[12]

In the case of a pure covalent Group IV clusters, such as nanodiamond and nanosilicon, E_{g} just equal to E_{h}, which can be expressed as a function of the bond length d,[12] $E_{\text{h}} = 39.74/d^{2.48}$, where d and E_{h} are in Å and eV, respectively.

We first calculate the energy shifts of the diamond cages with the structure of diamondoids, which are a unique form of diamond clusters. Their diamond cage structures allow unprecedented investigations about the evolution of solid-state properties as a function of size and shape. The smallest diamondoid is adamantane, and all further members, such as di-, tri-, tetra-, and pentamantane, are derived by adding one face-fused cage at a time to the preceding diamondoid structure.[16] As shown above, the bond length plays an important role in calculating the energy gaps. Here we take the bond length data of the bulk diamond as that of inside of the diamond clusters and take the bond length of the diamond cage with the structure of adamantine as the bond length of outside bonds of the diamond clusters, since the diamond cage with the structure of adamantine is composed of only surface carbon atoms.

In order to determine the bond length for outside and inside of diamond clusters, the geometry optimization by first principles for the bulk diamond and the diamond cage with the structure of adamantine was carried out. We carried out the first principles calculation using the generalized gradient approximation (GGA) approach by the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional of density functional theory (DFT) with the Material studio.[17] The calculations were performed by using an energy cutoff of 380 eV with the plane wave basis set. Brillouin zone (BZ) integration was performed using the special k-point Monkhorst–Pack sampling scheme. We employed the tool of build nanostructure in the Material studio[17] to build the clusters and further determined the number of surface atoms inside the atoms and the bond number at the surface of the clusters.

The optimized lattice constant of the diamond and the bond length of adamantine are 3.535 and 1.545 Å, respectively. The energy gap shifts calculated for dimond cages are

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Table 1. Experimental and Theoretical Energy Gap Shifts for the Carbon Cages with the Structure of Diamondoids and the Spherical Silicon Clusters of Different Sizes[a]

diamond cages	ΔE^{kubo}	$\Delta E^{\mathrm{surface}}$	ΔE	ΔE^{b}	D (silicon clusters)	ΔE^{kubo}	$\Delta E^{\mathrm{surface}}$	ΔE	ΔE^{c}
C_{10} (adamantine)	3.98	−0.31	3.67	3.71	23.1	1.24	0.02	1.26	1.30
C_{14} (diamantane)	3.55	−0.31	3.25	3.28	23.9	1.20	0.01	1.21	1.25
C_{16} (triamantane)	3.27	−0.28	2.99	3.01	24.3	1.18	0.02	1.20	1.15
C_{22} (1(2)3-tetramantane)	3.06	−0.25	2.81	2.87	25.0	1.12	0.01	1.13	1.12
C_{22} (123-tetramantane)	3.06	−0.27	2.79	–	26.8	1.09	0.01	1.10	1.00
C_{26}(1(2,3)4-pentamantane)	2.89	−0.21	2.69	2.66	30.4	0.95	0.01	0.96	0.94

[a] The diameter of the silicon clusters is D in Å, and the energy gap, ΔE, the kubo energy, ΔE^{kubo}, and the surface energy, $\Delta E^{\mathrm{surface}}$, shifts are in eV. [b] From ref 18. [c] From ref 19; ΔE is the difference between the experimental gap of clusters and the experimental gap of the bulk phase.

listed in Table 1. It is noted that although there are little errors for the bond lengths of crystals or nanocrystals calculated by DFT, which could affect the calculation results of energy gaps, it has only a minor effect on the change in energy gap, ΔE, due to counteraction of the errors. As we can see, the surface energy shifts of the diamond cage with the structure of diamondoids are negative values, which slightly reduce the kubo energy shifts. The surface energy shifts of two isomers of tetramantane exhibit a bit of a difference due to different atomic numbers at the surface. Lu et al[18] employed a high level ab initio molecular orbital theory to calculate the concerned diamondoids. Their calculated HOMO–LUMO gap shifts are in excellent agreement with our results, indicating that the influence of the H-terminal of diamondoids on gap shifts might be weak.

The results of the nanosilicon with spherical shapes are also listed in Table 1. Here we also take the bond length data of bulk silicon as that of inside of the silicon clusters and take the bond length of silicon nanocage with the adamantine structure as the bond length of the outside bonds of silicon clusters. The optimized bond length of inside and outside of the silicon clusters is 2.330 and 2.319 Å, respectively. Table 1 shows that the surface energy shifts of the nanosilicon are so small that it could be neglected. Thus, their energy gap shifts rest with kubo energy shifts. The exceptionally good agreement between the experimental and the calculated values for the nanosilicon further demonstrate the predictive power of our method.

In the case of polar semiconductors, besides the covalent component, the contribution from heteropolar gap C has to be considered. The heteropolar C part is defined as[7,11]

$$C = 14.4b(Z_A - nZ_B)e^{-k_s r_0}/r_0 \qquad \text{(eV)} \qquad (5)$$

$$f_i = C^2/E_g^2 \qquad (6)$$

where f_i is ionicity of chemical bond, Z_A is the number of valence electrons of A ion, k_s is Thomas–Fermi screening wavenumber of valence electron, $r_0 = d/2$, $b = \beta \cdot N_c^2$, the constant β can be determined via the long-wave dielectric constant $\varepsilon(\infty)$ of the crystal, and N_c is the average coordination number. In nanosystems, Mason[20] successfully employed the average surface atom coordination number to study electronic structure of nanocrystal. The average surface atom coordination number is equal to the total bond number at the surface divided by the number of the surface atoms in the nanocrystal.

The CdS, CdSe, ZnS, InP, InAs, and GaAs crystals are the typical binary semiconductors, whose clusters have been extensively studied experimentally, and reliable values on their energy gap shifts are available.[6,21–27] Here we carried out the systematic calculations of these clusters with spherical shape using this proposed method. The optimized lattice constants of the CdS, CdSe, ZnS, InP, InAs, and GaAs crystals are 5.916, (4.333, 7.134), 5.413, 5.934, 6.115, and 5.653 Å, respectively. And the obtained the anion and cation bond lengths of surface bonds of these clusters are 2.519, 2.630, 2.280, 2.538, 2.60, and 2.380 Å, respectively. Figure 1a–f gives the energy gap shifts calculated for zinc blend CdS, ZnS, InP, InAs, GaAs and wurtzite CdSe clusters, respectively, along with the experimental data and the results from other models. Since we show the change in energy gaps as a function of the size with respect to that of the bulk, the zero of the energy axis corresponds to the bulk values. The experimental results are in good agreement with our calculated values. EMA is found to indeed overestimate the bandgaps in every case. Figure 1c also shows that the values calculated from the ETBM model underestimate the experimental energy shifts of the ZnS clusters. In particular, we may find that the curve of energy shifts with decreasing cluster size shows a zigzag shape, which is dramatically different from traditional results of smooth curves. The results reveal that the energies do not always shift to blue with decreasing cluster size. For example, for CdS clusters of 9.8–12 Å in diameter, it shifts to blue first and then to red. In less-ionicity III–V clusters, this effect is weaker than in II–VI clusters. As will be shown later in the text, the zigzag feature of the energy shift curve arises mainly from the surface effect of clusters.

To understand the effect of cluster shape on the energy shifts, we study the CdS clusters with cubic shapes. The results are presented in Figure 1a. In this case, D is taken as the edge length of cubic clusters. From Figure 1, it is seen that the physical shape has significant effect on the energy gap shifts. We may also tune the properties of clusters by controlling their shapes.

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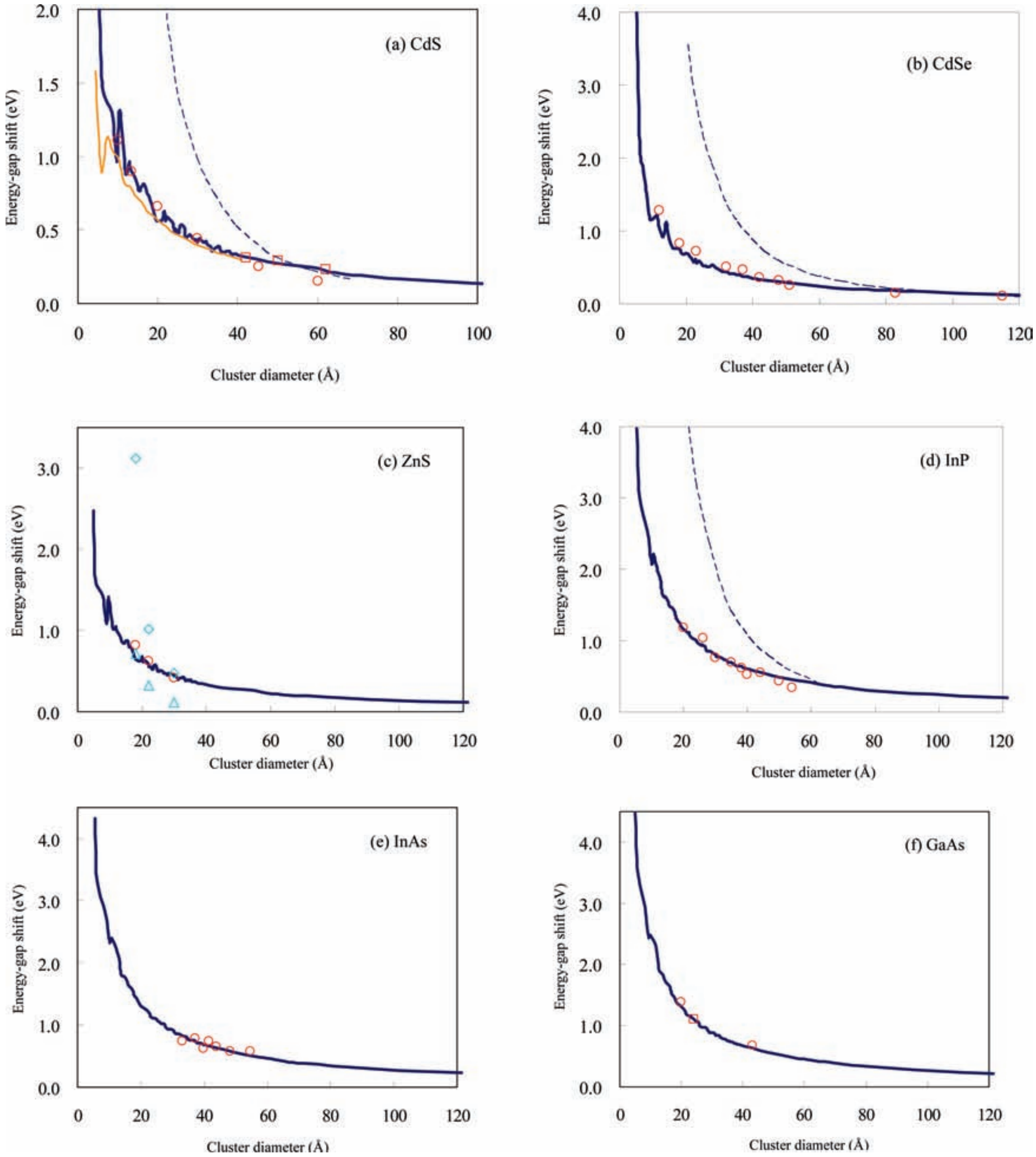

Figure 1. Experimental and calculated energy gap shifts of zinc blend (a) CdS, (c) ZnS, (d) InP, (e) InAs, (f) GaAs and (b) wurtzite CdSe clusters. The blue and yellow solid lines are from our calculations of the spherical and cubic clusters, respectively. The curves obtained from EMA are shown by the dashed line. The open circles and squares are the experimental data [a, refs 6 and 21 (open circles and squares); b, ref 22 (open circles); c, ref 23 (open circles); d, ref 24 (open circles); e, ref 25 (open circles); and f, refs 26 and 27,(open squares and circles)]. For ZnS (c), calculated results based on EMA and ETBM (open diamonds and triangles) from ref 23.

Titanium oxide (TiO_2) is a well-known photocatalysis material. Since the energy gap shift may affect its catalytic properties, the investigation on its quantum size effect is of intense interest. Serpone's study examined the absorption and the photoluminescence of anatase TiO_2 nanoclusters with mean sizes 2.1,13.3, and 26.7 nm. No significant blue shifts of the absorption threshold in UV−vis spectra were observed.[28] Recently, the subnanometer TiO_2 clusters were prepared using the DPA G4 template. The quantum size effects were observed in the clusters, and the energy gap exhibited a blue shift with decreasing particle size and was dependent on the crystal form of the material.[29] Here, using our proposed method the energy gap shifts of sphercial rutile and anatase clusters with decreasing cluster size are calculated and presented in Figure 2a and b, respectively. Both rutile and anatase clusters give good agreement with Satoh's experimental results.[29] Also, Figure 2 shows that the energy gap shifts curve of the rutile clusters differs from that of the anatase TiO_2 clusters, which implies the significant effect of the crystal structure on the energy shifts.

Figure 2b shows that the energy gap shifts of the anatase TiO_2 clusters ΔE are about 0 eV for the $D = 0.86, 1.02, 1.20,$

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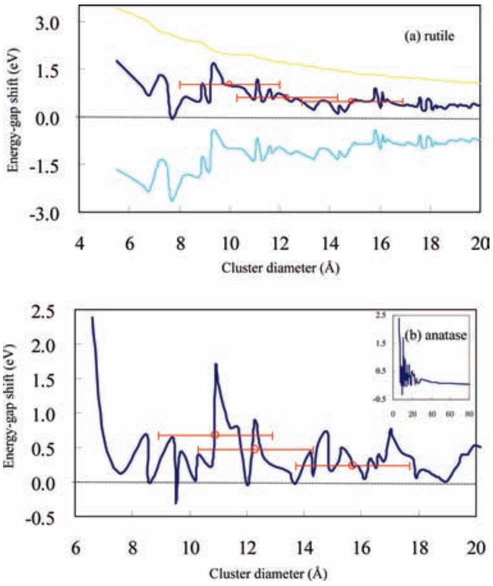

Figure 2. Dependence of energy shifts of TiO_2 on cluster size. Solid lines are from our calculations of spherical clusters. Open circles represent experimental data from ref 25. (a) Rutile TiO_2 clusters: the blue, yellow, and green lines represent ΔE, ΔE^{kubo}, and $\Delta E^{\text{surface}}$, respectively. (b) Anatase TiO_2 clusters: the blue line represents ΔE. Inset shows the trend of ΔE.

1.37, 1.61, 1.89, 1.90, and 2.3 nm clusters. It can also be seen from the figure's inset that ΔE approaches zero on the energy axis when $D > 6$ nm. These rusults may explain why no blue shifts in UV−vis spectra were observed in Serpone's work.[28] In addition, the energy gap of some anatase TiO_2 clusters can be smaller than that of the bulk phase. For example, in the 0.95 nm anatase TiO_2 clusters, there is a considerable red shift, $\Delta E = -0.31$ eV, which leads to the reduction of its energy gap down to, 2.89 eV, the visible light range. It is well-known that one severe disadvantage of the anatase TiO_2 semiconductor is that its photoactivity is limited to the UV region. There is great interest in extending the energy gap of TiO_2 into the visible range. Although the doping ion into TiO_2 is an effective approach, doped materials suffer from thermal instability.[30] Here, our calculations for the spectra of anatase TiO_2 clusters suggest a possible method extending the energy gap of TiO_2 into the visible range via size control of the cluster.

It is important to understand the variations of the kubo and surface energy shifts separately, since the calculated energy gap shift is obtained from the difference between the kubo and surface energy shifts. The variations of ΔE^{kubo} and $\Delta E^{\text{surface}}$ as a function of size for the rutile TiO_2 clusters are shown in Figure 2. From Figure 2, it can be seen that with increasing the size of the clusters, ΔE^{kubo} smoothly approaches the bulk values. But the curve of $\Delta E^{\text{surface}}$ shows a intense zigzag shape, which is significantly similar to that of ΔE. This indicates that the shape of the energy gap shift curve is dominated by that of the $\Delta E^{\text{surface}}$.

The standard deviations in the sizes of TiO_2 clusters prepared using the DPA G4 template are about 0.2 nm.[29] In order to compare the calculation results with the experimental data, we may take the average of the calculation values considering the size distribution. The calculated average

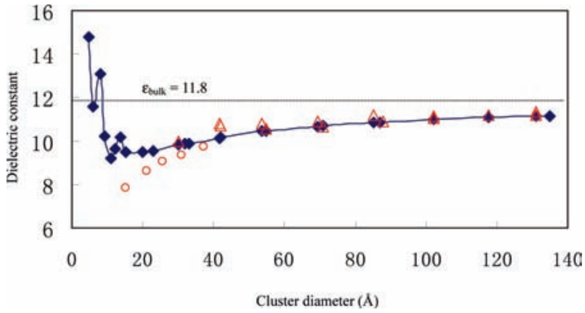

Figure 3. Experimental and calculated dielectric constants of Si clusters. The blue solid line is from our calculations of the spherical clusters. The open triangles are the experimental data from ref 33 (the open triangles in Figure 1 in ref 33). The calculated results based on quantum mechanical pseudopotential calculations (open circles) from ref 31.

energy gap shifts, 0.83, 0.55, and 0.42 eV, are very close to the corresponding experimental ones,[29] 1.0 , 0.6, and 0.47 eV for 1.0 ± 0.2, 1.23 ± 0.2, and 1.49 ± 0.2 nm rutile TiO_2 clusters, respectively. The calculated average energy gap shifts, 0.53, 0.52, and 0.32 eV, are also close to the corresponding experimental ones,[29] 0.68, 0.47, and 0.24 eV for 1.09 ± 0.2, 1.23 ± 0.2, and 1.57 ± 0.2 nm anatase TiO_2 clusters, respectively.

In addition, our calculations reveal that, from IV−IV, III−V, and II−VI clusters to TiO_2 clusters, $\Delta E^{\text{surface}}$ becomes more negative with their increasing ionicity, leading to the complexity of spectra of oxides clusters with strong ionic feature, such as TiO_2 clusters.

There have been numerous experimental and theoretical reports on the size dependence of dielectric constants for various semiconductor nanostructures. There is not yet a coherent understanding of dielectric screening in semiconductor nanostructures. Wang[31] thought that the reduction is due to quantum confinement effects. Delerue[32] thought that the decrease of dielectric constant was not attributed to the breaking of polarizable bonds at the surface and is not due to the opening of the band gap induced by the confinement. Here, the dielectric constant of the crystal can be calculated from the Kramers−Kronig relation of dielectric function at the long wave limit, which is written as

$$\varepsilon(\infty) = 1 + [(4\pi N_e e^2/m)D^u/(E_g)^2](1 - E_g/4E_F + (E_g)^2/48(E_F)^2) \qquad (7)$$

where E_F is Fermi energy, and D^u is periodic dependent constants tabulated in ref 8. We can use ${E_g}^{\text{kubo}}$, ${E_g}^{\text{surface}}$, and ${E_g}^{\text{bulk}}$ to calculate the Kubo, $\varepsilon(\infty)^{\text{kubo}}$, the surface bond of the nanocrystal, $\varepsilon(\infty)^{\text{surface}}$, and the bulk phase, $\varepsilon(\infty)^{\text{bulk}}$, dielectric constants, respectively. The dielectric constant shift of the nanocluster can be calculated as

$$\Delta\varepsilon(\infty) = (\varepsilon(\infty)^{\text{kubo}} - \varepsilon(\infty)^{\text{bulk}}) + F^{\text{surface}}(\varepsilon(\infty)^{\text{surface}} - \varepsilon(\infty)^{\text{bulk}}) \qquad (8)$$

Our calculations of silicon clusters indicate that the size dependence of dielectric constant roots in both the kubo

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and the surface effects. They play opposing roles. The kubo effect reduces the dielectric constants of Si clusters, but the surface effect increases the dielectric constants of Si clusters. The calculated results are plotted in Figure 3, which are in good agreement with the recent experimental values.[33] In particular, we predict that the dielectric constants of some of small Si clusters can be even larger than that of bulk Si, which is consistent with the results of polarization measurements.[34]

For simplicity, we have just studied the nonterminal clusters. Some other factors affecting band gap have not been considered in our present model. Besides quantum confinement effects, the terminal element or capping molecule of nanoclusters would also play an important role in the band gap engineering.[35−37]

Conclusion

In summary, we carried out a systematic investigation of quantum size effects in IV−IV, III−V, and II−VI and TiO_2 clusters using the chemical bond theory instead of the exciton confinement theory. The calculated energy gap shifts of these clusters with spherical shape are in excellent agreement with experiment over a wide range of cluster sizes. We find that the atoms at the surface of the clusters play an important role in determining the energy gap shifts. Results indicate that the shape of the energy gap shift curve is dominated by that of the surface energy shift curve. The energy gap shifts are sensitive to the physical shape of the clusters. Our calculations based on chemical bond theory, which incorporates quantum mechanical effects into properties of chemical bonds through algebraic relations rather than through variational solutions of the wave equation, are much simpler than that of other methods based on the exciton confinement mechanism. The method can be readily applied to calculate the energy gap shifts and the dielectric constants for clusters of all sizes. Finally, we predict the significant red shift of band energies in TiO_2 clusters, which suggests a new method extending the energy gap of TiO_2 into the visible range via size control of the clusters. Such effects would open a novel approach of tuning the optical and catalytic properties of the clusters. We predict that the dielectric constants of some of the small Si clusters can be even larger than that of bulk Si. These effects cannot be explained, even qualitatively, using previous theories.

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