Spectral Shifts of Semiconductor Clusters

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Abstract

The shifts of the electronic absorption spectra of GaAs and GaP semiconductor clusters are calculated using accurate pseudopotentials. In the absence of experimental data at present, these calculations provide estimates of expected spectral shifts in these clusters. In addition, these calculations show that Coulomb interaction between the electron and hole dominates over the confinement energy in small clusters, with the result that the electronic absorption spectra of small clusters exhibit redshift instead of blueshift as the cluster size is decreased.

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Semiconductor clusters exhibit electronic and optical properties quite different from those of molecules and solids [1,2]. For this reason, there have been several spectroscopic studies on these systems, designed to elucidate the evolution of their optical properties with cluster size [3–10]. The ultimate benefit gained from such studies is the detailed and microscopic insights into the size dependence of the cluster properties. Such a knowledge may enable us to engineer materials with applications in microelectronics and computer industry.

In support of these experimental efforts, we recently developed a band structure model for calculating the spectral shifts of semiconductor clusters as a function of cluster size [11,12]. The spectral shift refers to the shift of the leading edge of the electronic absorption spectrum of a semiconductor cluster as the cluster size is varied. Our calculated spectral shifts were in excellent agreement with experimental values for CdS clusters [11]. We also carried out similar calculations on GaAs and GaP clusters [11]. However, all those calculations employed local empirical pseudopotentials. Since non-local pseudopotentials are more accurate than the local pseudopotentials, we now performed calculations on GaAs and GaP clusters using non-local pseudopotentials. The results of these calculations are reported here.

Our electronic structure calculations utilize the empirical pseudopotential method (EPM) that has been previously used for the investigations of the optical properties of bulk semiconductor materials and clusters [11,12,13]. This method consists of solving the Schrödinger equation using an empirically determined pseudopotential for the valence electron,

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V_p,$$

(1)

$$V_p(r, E) = V_L(r) + \sum_{l=0}^{\infty} \Pi_l A_l(E) f_l(r) \Pi_l,$$

(2)

where the first term is the purely local part, the second term gives the non-local ($V_{NL}$) part, and $\Pi_l$ is the projection operator for angular momentum states $l$. The function $A_l(E)$ is the energy dependent well depth and $f_l(r)$ is conveniently taken to be the square well

$$f_l(r) = \begin{cases} 
1 & \text{r} < R_l \\
0 & \text{r} \geq R_l.
\end{cases}$$

(3)

The local part of the pseudopotential is given by
\[ V_L(r) = \sum_G \left[ V_S(G)S_S(G) + iV_A(G)S_A(G) \right] \exp(iG \cdot r), \tag{4} \]

where \( V_S \) and \( V_A \) are the symmetric and anti-symmetric form factors, respectively, determined by fitting them to the experimental optical data. Similarly, \( S_S \) and \( S_A \) are the symmetric and anti-symmetric structure factors, respectively, determined from the crystal structure \([13]\). The local EPM employs only \( V_L(r) \) in its Hamiltonian.

To apply EPM to the calculation of the semiconductor clusters we assume that these clusters have the crystal structure of the bulk semiconductor. This assumption is justified because we are considering relatively large clusters containing tens to hundreds of atoms. Indeed, these clusters are large enough that they are characterized by their size rather than by the number of atoms. Furthermore, the X-ray and TEM experiments on CdS, CdSe, and Si clusters have shown that the bulk lattice structure is preserved even when the cluster radii are as small as \( R = 7 \, \text{Å} \) \([4–9,15]\). The probable reason that even these small clusters assume bulk crystal structure is that the dangling bonds on the surfaces of these clusters are passivated by the organic ligands attached to them.

In bulk semiconductors the allowed wave vectors \( \mathbf{k} \) of the electronic states are continuous. On the other hand, only discrete \( \mathbf{k} \)-states are allowed in clusters. If we model the cluster as a rectangular box with dimensions \( L_1, L_2, \) and \( L_3 \), then a reasonable approximation is to use the bulk pseudopotential \( V_p(r) \) inside the cluster and terminate this potential at the surface by an infinite potential. The wave vectors of the lowest allowed states are then given by the quantization condition \( \sin(k_x L_1) \sin(k_y L_2) \sin(k_z L_3) = 0 \), whose solution is

\[ \mathbf{k} = \pi \left( \frac{n_x}{L_1}, \frac{n_y}{L_2}, \frac{n_z}{L_3} \right), \tag{5} \]

where \( n_x, n_y, \) and \( n_z \) are the quantum numbers of a particle in a box with infinite potentials at the boundaries. For the low energy excitations under consideration, the assumption of infinite potentials at the boundaries is a good approximation. The energy levels at these allowed \( \mathbf{k} \)-states constitute the band structure of a rectangular box.

Similarly, if we model the cluster as a spherical object of radius \( R \), the energy levels of the valence electrons will be quantized because of the spherical boundary. The wave vectors of the lowest allowed states are given by \( j_0(k_n R) = 0 \), whose solution is \( k_n = n\pi/R \) \([16]\).
Since \( k_n \) is along the radial direction, we project it onto each of the cartesian axes with equal magnitude to obtain cartesian components of \( k \). This procedure yields

\[
k = \frac{\pi}{\sqrt{3}R} (n_x, n_y, n_z).
\] (6)

The energy levels at these \( k \)-states constitute the \( l = 0 \) band structure of the clusters. Modification of this formalism to finite depth potentials at the boundaries is also possible. However, the choice of the well depth remains arbitrary and hence we do not employ such potentials here.

We calculated the band structures of GaAs and GaP clusters by diagonalizing \( 137 \times 137 \) Hamiltonian matrices constructed as outlined above, with \( k \) given by eq. (6). We employed the square well non-local potential Eq. 3 for GaAs, instead of the Gaussian well employed in Ref. [14]. In addition, the spin-orbit term in GaAs pseudopotential [14] is omitted and the remaining parameters adjusted to obtain good bulk band structure. These two modifications simplified the GaAs pseudopotential Hamiltonian without affecting its accuracy. The band structures of GaAs crystal obtained using local and non-local EPM are displayed in Fig. 1 along with some experimental data. The non-local EPM band structure is seen to agree better with experimental data than the local EPM band structure.

From the band structures of the clusters thus calculated we determined the energy differences between the highest occupied (HOMO) and the lowest unoccupied (LUMO) orbitals. These are the band gaps \( (E_g) \) of the clusters. We corrected these band gaps to take into account the electron-hole Coulomb attraction and correlation energies, to obtain [4,17]

\[
E_x = E_g - \frac{1.786e^2}{eR} - 0.248E_{Ry},
\] (7)

where \( E_x \) is the spectral shift (or exciton energy) of the cluster of radius \( R \), \( \epsilon \) is the bulk dielectric constant, and \( E_{Ry} \) is the effective Rydberg energy of the exciton.

The virtue of EPM is that it reproduces the bulk band structures and band gaps to better than 0.03 eV accuracy [11,12]. Specifically, our predicted indirect band gap of 0.43 eV for a 10 Å radius silicon cluster was found to be in good agreement with recent experimental value of 0.5 eV obtained by Louis Brus and co-workers [15]. Likewise, EPM yielded excellent results for CdS clusters in comparison with experiment [11,12]. Other methods are less...
accurate, especially for the calculations of the band gaps. For example, the calculations based on the density functional theory within the local density approximation (LDA) typically underestimates the band gaps by about 30-50% \cite{13}. Furthermore, the LDA calculations are computationally far more expensive compared to EPM. Consequently, EPM is suitable for the investigation of the electronic structures of semiconductor clusters. Full details of our computational methodology are given in Refs. \cite{11,12}.

The spectral shifts of GaAs and GaP clusters thus calculated are displayed in Figs. 2 and 3, respectively. Since GaP is an indirect gap semiconductor, we present spectral shifts of both the direct and indirect transitions. The results obtained from the use of both local and non-local EPM are shown in these figures. From these figures it is clear that over a large range of cluster sizes the local EPM is able to reproduce spectral shifts as accurately as non-local EPM. However, at small cluster sizes the non-local correction on the spectral shifts is significant. Furthermore, at large cluster sizes the absorption spectrum shifts to higher energies with decreasing cluster size. This blueshift is expected due to confinement of the electron-hole pair in the cluster. However, at small cluster sizes the absorption spectrum of GaAs clusters shifts to lower energies with decreasing cluster size; a trend opposite to that observed for large clusters. In the case of GaP, which is an indirect gap semiconductor, the lowest energy transition exhibits blueshift at both large and small cluster sizes. But this transition is not observable because it is forbidden. The origin of the absorption spectrum, corresponding to the observable direct transition, shifts to lower energies with decreasing cluster size at small cluster sizes. Both local and non-local pseudopotentials exhibit the same qualitative behavior.

We can explain the observed trends in the following way. At large cluster sizes the electron and hole are both confined in a spherical well. This quantum confinement increases the band gap with decreasing cluster size and it is the dominant effect in this size regime. In these large clusters, the negatively charged electron and the positively charged hole are spatially separated and hence the coulomb attraction between them is negligible. However, in small clusters the coulomb attraction energy between the electron-hole pair cannot be neglected. While the band gap still increases with decreasing cluster size, in small clusters this increase is sufficiently overcome by the coulomb energy that the spectra shift to lower
energies. Consequently, in this small cluster size regime the absorption spectra of clusters may exhibit redshift instead of the blueshift.

At present reliable experimental data on these systems are not present, partly because of considerable experimental difficulties that arise in trying to synthesize III-V semiconductor clusters with narrow size distribution. However, our calculations provide reasonable estimates of the expected spectral shifts of these clusters.

In summary, our band structure calculations of GaAs and GaP semiconductor clusters have shown that local empirical pseudopotentials are reasonably accurate compared to the non-local empirical pseudopotentials for the calculations of the spectral shifts of these clusters. The non-local corrections on the spectral shifts are most important in small cluster sizes. In addition, our calculations have shown that, while quantum confinement energy is the dominant factor affecting spectral shifts in large clusters, the Coulomb interaction between the electron and hole has significant effect in small clusters. The attractive Coulomb interaction is sufficiently strong in small clusters that it overcomes the confinement energy of the electron-hole pair and gives rise to redshift, instead of the blueshift, of the electronic absorption spectrum.

This is the sixth paper in this series on optical properties of semiconductor clusters. This research is supported by the New York University and the Donors of The Petroleum Research Fund (ACS-PRF Grant # 26488-G), administered by the American Chemical Society.
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FIGURES

FIG. 1. The band structure of zinc-blende GaAs crystal obtained using non-local (solid line) and local (dashed line) pseudopotentials. The experimental points are also plotted for comparison. The non-local pseudopotential calculations are seen to agree better with the experimental data than the local pseudopotential calculations.

FIG. 2. The calculated spectral shifts or exciton energies of zinc-blende GaAs clusters for low energy excitations. The open circles are obtained using local pseudopotentials and filled circles are obtained using non-local pseudopotentials.

FIG. 3. The calculated spectral shifts or exciton energies of zinc-blende GaP clusters for low energy a) direct and b) indirect excitations. The open circles are obtained using local pseudopotentials and filled circles are obtained using non-local pseudopotentials.