Exciton Spectra of Semiconductor Clusters

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The band gaps and exciton energies of CdS and GaP clusters are calculated for the first time using pseudopotentials. The calculated exciton energies of CdS over a wide range of cluster sizes are in excellent agreement with experiment. Furthermore, the exciton states of clusters with zinc-blende and hexagonal lattices are similar in large clusters, but differ dramatically in small clusters. Finally, the spectra of small GaP clusters shift to red, instead of to the blue, with decreasing cluster size. These effects provide novel ways of tuning the optical properties of clusters.

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Theoretical and experimental investigation of clusters is a rapidly growing area of research activity today. The main focus of these efforts is to understand the effect of dimensionality and size on the quantum-mechanical properties of many-particle systems [1-3]. The metal [2], semiconductor [3], and van der Waals (insulator) clusters [1] have all played a prominent role in this regard. These efforts have yielded some understanding of metal and van der Waals clusters. In sharp contrast, much less is known about the semiconductor clusters, and that is the subject of this Letter.

Recently, it was discovered [3] that the semiconductor clusters of approximately 7-25 Å in radius can be synthesized in colloidal suspensions by controlled liquid-phase precipitation reactions. Very sophisticated experiments are currently underway to understand the absorption and luminescence spectra of these clusters as a function of their size [4]. Simple effective-mass models (EMM) have been employed to qualitatively explain the observed blueshift of the absorption spectrum. However, this model gives quantitatively accurate results only for very large clusters [4]. Hence, there is a need for microscopic calculations geared towards mapping out the energy-level structure of these clusters and explain the salient features of their absorption spectra. Such studies are very important because the low-dimensional semiconductor materials are expected to exhibit anomalously high nonlinear optical polarizabilities, because of which these clusters may be useful as ultrafast optical switching devices.

Our interest in this study is in intermediate to large clusters for which structural and optical data are available experimentally. These clusters have zinc-blende crystal structure and spherical shapes, but the electronic excited states display quantum confinement effects (QCE). Since total-energy calculations are not feasible, we investigate the excited states using pseudopotentials. Among the available pseudopotential techniques, the empirical pseudopotential method (EPM) has proved to be an elegant and simple means of obtaining the band structures of semiconductor crystals with reasonable accuracy [5,6]. Our objective here is to use the same pseudopotentials to explain the cluster properties also.

The energy levels of the valence electrons in either the cluster or the crystal are determined by the Schrödinger equation

$$H\psi_{n,\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n,\mathbf{k}}(\mathbf{r})\,. \tag{1}$$

In the pseudopotential method the exact crystal potential is replaced by the pseudopotential $V_p(\mathbf{r})$ to obtain the Hamiltonian

$$H = -(\hbar^2/2m)\nabla^2 + V_p(\mathbf{r})\,. \tag{2}$$

Since $V_p(\mathbf{r})$ has the contributions from all the atoms in the crystal, it is given by

$$V_p(\mathbf{r}) = \sum_{\mathbf{R},j} v_j(\mathbf{r}-\mathbf{R}-\mathbf{d}_j)\,, \tag{3}$$

where v_j is the atomic pseudopotential of the jth basis atom at a lattice site, $\mathbf{R}$ is the direct lattice vector, and $\mathbf{d}_j$ is the position vector of the jth basis atom relative to $\mathbf{R}$. The atomic potentials v_j may now be expanded in plane waves of the reciprocal-lattice vectors $\mathbf{G}$. For zinc-blende crystals, this procedure yields [6]

$$V_p(\mathbf{r}) = \sum_{\mathbf{G}} [V_S(G)S_S(\mathbf{G}) + iV_A(G)S_A(\mathbf{G})] \times \exp(i\mathbf{G}\cdot\mathbf{r})\,, \tag{4}$$

where the form factors V_S and V_A are given by

$$\begin{aligned} V_S(G) &= \tfrac{1}{2}[v_1(G)+v_2(G)], \\ V_A(G) &= \tfrac{1}{2}[v_1(G)-v_2(G)]\,, \end{aligned} \tag{5}$$

and the structure factors are given by $S_S(\mathbf{G}) = \cos(\mathbf{G}\cdot\mathbf{t}_1)$, $S_A(\mathbf{G}) = \sin(\mathbf{G}\cdot\mathbf{t}_1)$, with $\mathbf{t}_1 = (1,1,1)a_0/8$, a_0 being the lattice constant. In EPM, the form factors are the adjustable parameters to be determined by fitting them to the experimental optical data.

Once $V_p(\mathbf{r})$ is determined, the energy levels of the valence electron as a function of $\mathbf{k}$ are calculated by repeated diagonalization of the Hamiltonian matrix $H(\mathbf{k})$, which is constructed in the plane-wave $\exp[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}]$ basis. Figure 1(a) gives such a band structure for zinc-blende CdS crystal obtained using EPM, 137 basis functions, $a_0 = 5.818$ Å, and the form factors given in Ref. [6]. The calculated band gap of 2.44 eV is in good agreement with the experimental value of 2.5 eV. The corresponding calculations employing the local-density approximation (LDA) underestimate the band gap by $\approx 30\%$, because LDA does not describe the conduction bands at the same level of accuracy as the valence bands [7].

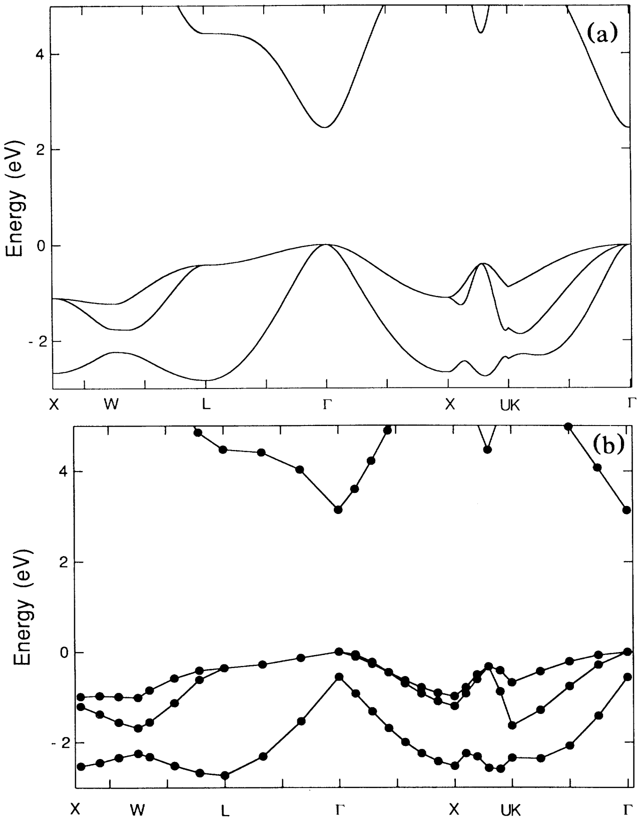

FIG. 1. (a) A portion of the zinc-blende CdS crystal band structure near the top of the valence band. (b) The band structure of a 15-Å radius CdS cluster.

Suppose now that the physical dimensions of the crystal are reduced from all sides to give a cubic cluster of side length $L=2R$, where R is the radius of the cluster. The energy levels no longer form a continuum now; instead we obtain quantized energy levels with wave vectors

$$\mathbf{k}=(\pi/2R)[n_x,n_y,n_z]\,, \tag{6}$$

where n_x, n_y, and n_z are the quantum numbers of a particle in a box. On the other hand, if we model the cluster as a sphere of radius R, the wave vectors of the lowest allowed states are given by $j_0(k_nR)=0$, whose solution is $\mathbf{k}_n=n\pi/R$. Since $\mathbf{k}_n$ is along the radial direction, we project it onto each of the Cartesian axes with equal magnitude to obtain Cartesian components of $\mathbf{k}$. This procedure yields

$$\mathbf{k}=(\pi/\sqrt{3}R)[n_x,n_y,n_z]\,. \tag{7}$$

The discrete energy levels thus calculated for these allowed quantum states are shown in Fig. 1(b) for an $R=15$ Å cluster. We also found that the corresponding band structure for the $R=15$ Å cluster, modeled as a cube of side length $L=30$ Å, is very similar to that given in Fig. 1(b). These calculations employed 137 $\mathbf{G}$ vectors to converge the energies to about 0.01 eV. For both cubic and spherical cluster models, the top of the valence and the bottom of the conduction bands lie at the smallest $\mathbf{k}$ given by $(n_x,n_y,n_z)=1$. For the lowest-energy transition being studied here, only the energy gap at this $\mathbf{k}$ is of interest.

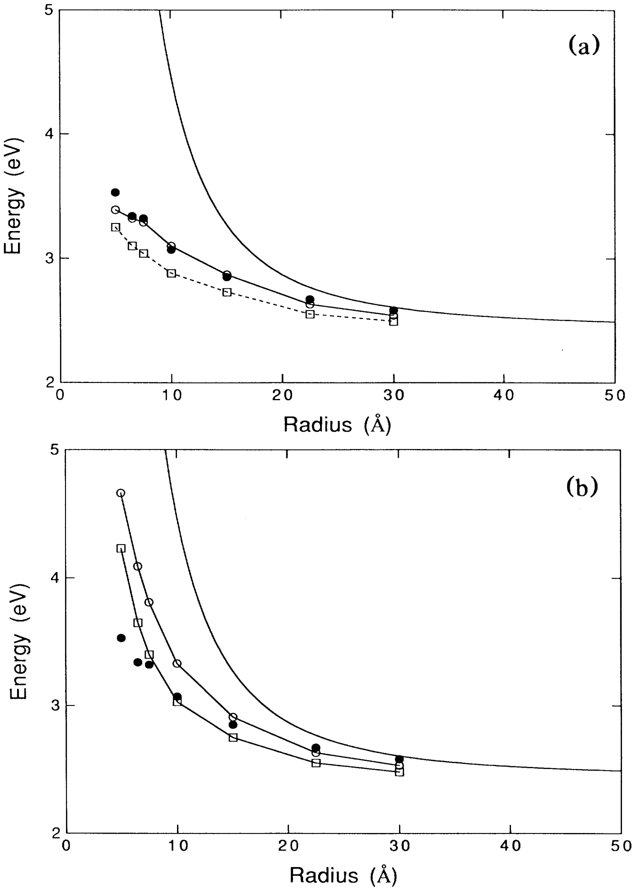

FIG. 2. Experimental and calculated exciton energies of CdS clusters. The solid circles are the experimental data [4] and the solid line is the result due to Brus's effective-mass model with $m_e=0.19$, $m_h=0.80$, $\epsilon=5.5$, and $E_g=2.5$ eV [3,8]. (a) The open circles and squares are from our calculations of the zinc-blende CdS clusters with spherical and cubic shapes, respectively. (b) Same as (a), except that the open circles and squares are calculated for the hexagonal CdS clusters.

From the band structures presented above we calculated the band gaps (E_g) as a function of the cluster size. We diagonalized a 283×283 matrix for each cluster, to converge E_g to better than 0.01-eV accuracy. To the band gap we added the electron-hole Coulomb and correlation energies to obtain the exciton energies E_x (in atomic units) [3,8]:

$$E_x=E_g-1.786e^2/\epsilon R-0.248E_{\mathrm{Ry}}\,. \tag{8}$$

In Eq. (8), ϵ is the dielectric constant of CdS and $E_{\mathrm{Ry}}=\mu e^4/2\epsilon^2\hbar^2$ is the effective Rydberg energy of the exciton, μ being its reduced mass [8]. The exciton energies thus calculated are plotted in Fig. 2(a), along with the results from Brus's EMM [3,8] and the experimental data of Wang and Herron [4]. The lattice constants of $R=10.0$, 7.5, and 6.5 Å clusters are reduced from their bulk values by 1.4%, 3.0%, and 3.9%, respectively. We estimated these values from the shift of the (111) x-ray-diffraction peak of the clusters [4]. If we use the bulk lattice constant for these clusters, then the exciton energies would be higher by 0.16, 0.30, and 0.41 eV, respectively. The $R=5$ Å cluster has a pyramidal shape, but the details of its structure are unknown [4]. Consequently, the exciton energies for this cluster are obtained by extrapolation. Using the experimental lattice constants and radii we estimate that the $R=5.0$, 6.5, 7.5, 10.0, 15.0, 22.5, and 30.0 Å clusters have 13, 26, 39, 89, 287, 969, and 2297 CdS molecules, respectively. From Fig. 2(a) and these estimates what we observe is that over a range of cluster sizes, the experimental results are in exceptionally good agreement with our theoretical predictions, especially for clusters with spherical shape.

Another aspect of QCE is the effect of crystal structure on the exciton energies. To investigate this we repeated the above calculations for clusters with hexagonal symmetry. These results are displayed in Fig. 2(b). What we find is that our theoretical results are in agreement with experiments for large clusters, but not for small clusters. This result differs quite dramatically from that for zinc-blende CdS for which both large and small clusters give uniformly good agreement with experiment. This indicates that small CdS clusters are probably zinc-blende type, rather than hexagonal. This prediction is in accord with the experimental data [4]. In addition, our calculations reveal that the crystal structure has a significant effect on the band gaps and exciton energies of small clusters, but not in large clusters. These results clearly indicate that the exciton energies in small clusters are sensitive to the crystal structure. Currently, there are no experimental data on hexagonal CdS clusters with which to compare our theoretical results. This is the first study to address the effect of crystal structure on QCE and future experiments on hexagonal CdS clusters will be helpful.

The clusters of interest here, except for the $R=5$ Å cluster, are experimentally determined to have spherical shapes [4]. Nonetheless, we considered cubic clusters in order to understand the effect of physical shape on the exciton energies. From the results presented in Fig. 2 we conclude that the shape has a significant effect on the exciton energies even in large clusters. For zinc-blende CdS clusters, for which experimental data are available, the spherical shape gives better agreement with experiment for all cluster sizes, confirming that these crystallites are approximately spherical. Since we know that the kinetic energy of a particle in a box is smaller than that in a sphere of radius $R=L/2$, the cluster exciton energies are underestimated in the cubic clusters, as seen in Fig. 2(a). The spherical shape increases the kinetic energy just enough to bring the theoretical results into agreement with experiment. The exciton energies of rectangular and ellipsoidal clusters will be in between these two curves, depending on their precise geometry. The sensitivity to shape observed here is indicative that the exciton wave functions in these clusters have not converged to the bulk limit, even though these clusters have bulk crystal structure.

We also found that when a_0 is reduced by 0.1 Å the exciton energies of $R=5.0$, 30.0, and ∞ Å zinc-blende clusters are decreased by 0.17, 0.24, and 0.27 eV, respectively. Similar results are obtained for hexagonal clusters also. These results indicate that the exciton energies of small clusters are less sensitive to the lattice constant than those of large clusters. This is a consequence of the decreasing curvature of the valence and conduction bands as one moves away from the band edges.

Finally, we investigated the direct transition in GaP clusters using EPM. These results, presented in Fig. 3, reveal that the exciton energies increase first and then decrease, with decreasing cluster size. We observed a similar trend in GaAs clusters also. This anomalous redshift effect awaits experimental verification, but it cannot be explained using EMM. However, our calculations quantitatively reproduced the lone experimental exciton energy of the $R=12$ Å GaAs cluster, thus further enhancing confidence in our method.

The effect of size on exciton energies has been previously investigated [3,9,10]. However, this is the first time that a satisfactory agreement between theory and experiment is obtained over a large range of cluster sizes. This success is due to the microscopic nature of our calculations. Previous studies have employed either EMM or an empirical tight-binding Hamiltonian (TBH) [3,9,10]. EMM is accurate only near $\mathbf{k}=0$ and hence it considerably overestimates the kineic energies in small clusters. On the other hand, TBH describes the occupied molecular orbitals more accurately than the unoccupied orbitals [10]. Furthermore, even with the simplest basis sets TBH

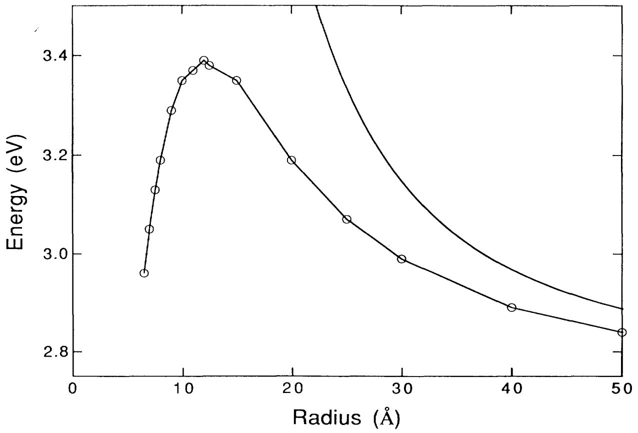

FIG. 3. Exciton energies of spherical GaP clusters calculated using EPM (circles) and the effective-mass model (solid line).

calculations are computationally very demanding, requiring diagonalization of $\approx 10^4 \times 10^4$ matrices [10]. On the other hand, our calculations are much simpler to carry out. We have also gone beyond the investigation of size effect, and examined the effect of other factors, such as lattice structure and lattice relaxation, on the exciton energies. The dominant surface effect in small clusters is the lattice relaxation. We accounted for this effect in our calculations by using the experimentally determined lattice constants.

In summary, we carried out a systematic investigation of quantum confinement effects in clusters using pseudopotentials. Our study provides a global understanding of the changes taking place in the electronic structure of clusters as the cluster dimensions, crystal structure, physical shape, and the lattice constant are varied. The calculated exciton energies of CdS clusters are in excellent agreement with experiment over a wide range of cluster sizes. These calculations also revealed that the exciton energies of zinc-blende and hexagonal clusters are nearly the same for large clusters, but significantly different for small clusters. Hence, the optical spectra of small clusters are sensitive to the crystal structure and the available optical data are consistent with the zinc-blende lattice structure. The exciton energies are also sensitive to the physical shape and the lattice constant of the clusters. The spherical shape gave best agreement with experiment, indicative that even small clusters are approximately spherical. Small contraction of the lattice constant also has an important effect on the exciton energies in small clusters. Finally, we predict anomalous redshift of the exciton energies in small GaP and GaAs clusters. These effects cannot be explained, even qualitatively, using the effective-mass approximation.

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