THE QUANTUM MECHANICS
OF LARGER SEMICONDUCTOR
CLUSTERS ("QUANTUM DOTS")

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INTRODUCTION

How can one understand the excited electronic states of a nanometer sized semiconductor crystallite, given that the crystallite structure is simply that of an excised fragment of the bulk lattice?

This question is motivated by recent experiments on chemically synthesized "quantum crystallites," sometimes called "quantum dots," in which it is observed that the optical spectra are quite sensitive to size. For example, bulk crystalline CdSe is a semiconductor with an optical band gap at 690 nm, and continuous optical absorption at shorter wavelengths. However, 35–40 Å diameter CdSe crystallites containing some 1500 atoms exhibit a series of discrete excited states with a lowest excited state at 530 nm (1-3). With increasing size, these states shift red and merge to form the optical absorption of the bulk crystal. Electron microscopy and Bragg X-ray scattering measurements show that these crystallites have the same structure and unit cell as the bulk semiconductor. Such changes have now been observed in the spectra of many different semiconductors.

This phenomenon is a "quantum size effect" related to the development of the band structure with increasing crystallite size (4). Smaller crystallites behave like large molecules (e.g. polycyclic aromatic hydrocarbons) in their spectroscopic and photophysical properties. They are true "clusters" that do not exhibit bulk semiconductor electronic properties. In this review

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we chart, as much as is presently known, the evolution from electrons in
discrete molecular orbitals in smaller crystallites, to electrons and holes in
continuous bands in the bulk crystal.

In the first section we discuss the development of band structure in
polymeric systems having strong chemical bonding. These ideas have heu-
ristic application to three dimensional semiconductor crystallites. In the
second section we treat the molecular orbital theory for the lowest several
excited states of three dimensional semiconductor crystallites. In the sub-
sequent section we improve upon this simple model by including electron-
hole correlation. We then describe synthesis, structural characterization,
and electronic spectroscopy of authentic nanoclusters. The first through
third sections consider general questions of theory and modeling, and
the fourth section focuses on a major area of experimental work—the
spectroscopy of CdSe crystallites.

BAND STRUCTURE IN POLYMERS OF VARYING LENGTH

Strong and localized chemical bonding characterize crystalline semicon-
ductors such as silicon and gallium arsenide. "Tight binding" or Huckel-
type molecular orbital theories that neglect explicit electron-electron cor-
relation provide an accurate picture of electronic structure in the bulk
crystals (5), and also provide a natural model for size evolution of bulk
properties (6). Semiconductors contain two electronic bands of interest: a
filled valence band and an empty conduction band. The following model
shows in general how individual bands develop discrete molecular orbitals
for short polymerization lengths.

The Huckel description of a conjugated, linear polyene contains the
essential physics of the electronic quantum size effect. The pi molecular
orbitals (MOs) are modeled by a chain of \( N \) one-electron, one-orbital
atoms separated by a distance \( a \). (A single atom on the chain corresponds
to one unit cell in a semiconductor.) The orbital energy \( e \) is \( \langle \phi_n | H | \phi_n \rangle \)
and the resonance integral beta is \( \langle \phi_n | H | \phi_{n+1} \rangle \), where \( H \) is the electronic
Hamiltonian and \( \phi_n \) is the orbital on the \( n \)th atom. Neglecting orbital
overlap, the one-electron eigenvalues for this system are given by

\[
E(m, N) = e + 2\beta \cos \left( \frac{m\pi}{N+1} \right)
\]

\[
m = 1, 2, \ldots, N
\]

\[
= e + 2\beta \cos (k_m a) \quad \text{where} \quad k_m = \frac{m\pi}{(N+1)a}.
\]
As $N$ approaches infinity, $k$ becomes a continuous variable running from 0 to $\pi/a$ (the Brillouin zone), and $E(k)$ becomes continuous over the range $e+2\beta$ to $e-2\beta$, as shown in Figure 1.

Figure 1 also shows the discrete eigenvalues for finite chains of 11 and 13 atoms. These discrete eigenvalues fall on the same dispersion curve as the infinite chain; a finite chain simply selects out those MOs of the infinite chain that have nodes at the ends of the chain. The lowest MO has no additional nodes within the chain. As $N$ increases the lowest level becomes more stable, asymptotically approaching the lower band edge energy $e+2\beta$. However, since this MO has nodes on the chain ends, its energy is shifted higher than the band edge: This is in essence the “quantum size effect.” Higher MOs have an increasing number of internal nodes. States near $e$ have a node on every other atom and are essentially nonbonding.

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**Figure 1** Polyene chain band structure (adapted from Ref. 6). Discrete eigenvalues for $N = 13$ and $N = 11$ chains are also shown. ($e = \phi$)
MOs. All these states are discrete, standing electron waves formed because the electron coherently senses both ends of the chain.

For $k_m a \ll 1$, Eq. 2 expands to give

$$E(k_m) = (e + 2\beta) + \frac{2\beta k_m^2 a^2}{2} = E_0 + \left(\frac{\pi^2}{2L^2}\right)2\beta a^2 m^2$$

where

$$L = (N+1)a.$$  

The energy spectrum of a particle of mass $m^*$ in an (infinitely high) potential well of dimension $L$ is

$$E_p(n) = \pi^2 \frac{\hbar^2 n^2}{2L^2 m^*}.$$  

Comparison of Eqs. 3 and 4 indicates that the MO eigenspectrum of the $N$ atom chain, over a limited range of energy near the lower band edge, is the same as that of a particle of mass $m^* = \hbar^2/(2\beta a^2)$ in a potential well of length $L$.

This analogy is simple yet still instructive. The limited $ka \ll 1$ corresponds to the electron wavelength being much larger than the internuclear separation $a$. The line of atoms is essentially continuous, and the internal potential felt by the electron is a constant. The effective mass approximation fails when the wavefunction develops more nodes in higher states; now the electron samples the potential frequently enough to sense modulation at the atomic scale. (Also note that, since beta is a measure of the strength of the covalent bonds in the chain, the effective mass is a measure of bond energy in a specific band. In real materials $m^*$ is often a small fraction of the real electron mass.)

**MOLECULAR ORBITALS FOR $sp^3$ HYBRIDIZED CRYSTALLITES**

These ideas have been extended to three dimensional semiconductor crystallites, in a model originally outlined by Slater & Koster (7) and Coulson and coworkers (8) for four-electron $sp^3$-hybridized atoms (Figure 2). In this model the basis orbitals are not atomic orbitals as above, but bond orbitals between nearest neighbor atoms: a set of bonding orbitals sigma and a set of antibonding orbitals sigma star. As for the polyene, discussed above, each of these localized bond orbital sets forms MOs extending over the three dimensional crystallite as it grows. The highest energy orbital in the sigma (i.e. valence) band is the crystallite HOMO, and the lowest
energy orbital in the sigma star (i.e. conduction) band is the crystallite LUMO. In the limit of the bulk crystalline solid, the HOMO-LUMO spacing becomes the band gap, and the bands become separately continuous in energy.

In a II–VI or III–V zinc blende crystal such as GaAs, each Ga atom is surrounded tetrahedrally by four As atoms, and vice versa. With a minimal atomic basis of three $P$ and one $S$ atomic orbital (AO) on each cation and each anion, there will be four occupied electronic bands (analogous to sigma above) and four unoccupied electronic bands (9). The bands have the Bloch form

$$e^{iK \cdot r} \chi_n(\vec{r})$$

where $\chi_n$ is a symmetrized combination of bond orbitals within one unit cell. The bands have a complex structure as a function of $K$ inside the Brillouin zone and cannot be characterized by one scalar effective mass valid over the entire zone. However, for crystallites of diameter $D$, the HOMO and LUMO are principally formed from regions of $|K| \leq \pi/D$ around the top of the highest occupied band and the bottom of lowest
unoccupied band, respectively (10). If $D$ is much larger than a unit cell dimension, then the region of the Brillouin zone involved is relatively small, and effective mass approximations can be used.

The conduction band is nondegenerate (ignoring spin) and shows an isotropic $E(K)$ near the bottom at $K = 0$, and therefore the effective mass $m_e$ is a scalar. For a crystallite in the shape of a sphere, the discrete (particle-in-a-box) lowest few unoccupied MOs are characterized by radial $N$ and angular $L$ quantum numbers (11), in partial analogy with the hydrogen atom. For example, calculated MOs for a 45 Å diameter ZnSe crystallite appear in Figure 3 (12). The lowest state is $N = 1$ and $L = 0$ and is designated a “1s” state. Note that the allowed quantum numbers, and energetic ordering of states, are different from those of hydrogen because the radial ordering potential is a square well and not Coulombic.

Discrete occupied MOs near the top of the valence band have a far more complex structure. Three of the four occupied valence bands of the bulk crystal are degenerate at $K = 0$, due to the underlying three-fold degeneracy of $p$ AOs. Away from $K = 0$ these bands split and can be described by a $6 \times 6$ tensor “hole” Hamiltonian (13) that, in a spherical harmonic

![Molecular Orbital Diagram](Molecular_Orbital_Diagram.jpg)

*Figure 3* Molecular orbital energy levels for a 45 Å diameter ZnSe crystallite (from Ref. 12). The lowest two allowed transitions are indicated.
basis, can be written

\[ \hat{H}_h = \hat{H}_s + \hat{H}_d. \]

\( \hat{H}_s \) is a diagonal matrix containing \( s \)-like hole momentum operators and the spin-orbit energy. \( \hat{H}_d \) contains \( d \)-like operators and is nondiagonal. If \( \hat{H}_d \) is ignored, there are two series of occupied discrete MOs offset by a spin-orbit energy \( \Delta \), as shown in Figure 3 (12). (In materials containing heavier elements, delta can be a significant fraction of an eV.) A single isotropic hole mass describes the size dependence of these levels. Spin, \( L \), \( N \), and total angular momentum \( J(=L+S) \) are individually good quantum numbers. The HOMO-LUMO transition corresponds to the \( 1s \) (electron)-\( 1s \) (hole) excited state. In this review, we always designate the electron state first.

If the complete hole Hamiltonian is included, then only \( J \) remains a good quantum number. A recently reported calculation (14) including major parts of \( \hat{H}_d \) shows a slight splitting of initially degenerate levels containing different \( J_s \), mixing of \( S \) and \( D \) wavefunctions, and mixing of different values of \( N \). Two independent scalar "masses" are required to describe all hole levels. The highest "\( s \)" hole state (the crystallite HOMO) behaves as a \( J = 3/2 \) particle in (cubic) zinc blende crystallites. Quantitative calculations for uniaxial materials such as wurzite have not been reported.

Mixing induced by \( H_d \) has consequences for optical selection rules. With no mixing, where \( N \) and \( L \) are good quantum numbers, allowed transitions exhibit \( \Delta N = 0 \) and \( \Delta L = 0 \). The lowest transitions are \( 1s-1s \) and \( 1p-1p \), each split by the spin-orbit coupling. These transitions conserve the number of nodes in the wavefunctions and are equivalent to \( K = 0 \) transitions in the bulk crystal. When the full hole Hamiltonian is used, only \( J \) is a good quantum number, and some forbidden transitions acquire oscillator strength. In ZnSe, for example, the low lying \( 1s-2s \) transition becomes about one third as strong as the \( 1s-1s \) (14).

This pattern of MOs applies to spherical crystallites. The shape of the crystallite obviously affects angular momentum degeneracies. In the limit of platelet shape, for example, the valence band MO pattern is different and has a distinctive pattern similar to that of an infinite semiconductor sheet (a "single quantum well" in solid state physics).

The use of the effective mass model for MO energies is an approximation that is correct only asymptotically in the limit of large crystallites. This occurs because typically the bands are parabolic only for small regions of the Brillouin zone near the band extrema. The approximation overestimates the shift, and can be improved by considering the finite potential step at the crystallite surface (15, 16). Alternately, in PbS an improved effective-mass-like model appropriate for hyperbolic bands has been developed (17). Quite recently, a version of the electronic "tight binding"
method has been applied to ZnO and CdS, with the result that the 1s electron shift is only about half that estimated by the effective mass model for intermediate sizes (18). The independence of this important result on surface bonding and model approximations needs to be examined; the effective mass model is known to be a quite adequate approximation for zinc blende materials in superlattice physics.

**ELECTRON-HOLE CORRELATION**

The preceding section describes an independent particle MO model for crystallite excited states, and therefore electron and hole motion are uncorrelated. In bulk crystals, a simple physical idea accurately describes electron-hole interaction for distances greater than a unit cell (ca. 5 Å): The electron and hole attract each other via (shielded) Coulomb forces. This suggests a model Hamiltonian for the lowest 1s–1s excited state (19):

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\varepsilon|\vec{r}_e - \vec{r}_h|}.$$  

Equation 6 describes internally correlated, bound “excitons” in bulk crystals and in superlattices quite well. In crystallites, the Coulomb term induces electron-hole correlation and is relatively more important at large diameters, because the kinetic energies vary as $(1/R^2)$ and the Coulomb term as $(1/R)$ (19), where $R$ is the crystallite radius. The Coulomb term mixes higher lying states into the 1s–1s state. In the limit of small $R$, mixing is minor due to large state splittings in zero order, and the wavefunction approaches 1s–1s. This is the molecular limit.

Only in the limit of large $R$ does an internally correlated, hydrogenic electron-hole “exciton” form. The electronic polarizability becomes quite high as the eigenspectrum becomes dense. In the limit of continuous band structure near the band edges, such large crystallites could conduct electricity in an excited state with an electron and hole present in the presence of an electric field.

In the small crystallite, 1s–1s limit, the energy is (19, 20)

$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon_o R}.$$  

Here the Coulomb energy is simply evaluated in first order perturbation theory. If the kinetic energies are a few tenths of an eV, then the optical dielectric coefficient is used. We have neglected in Eq. 7 a smaller term due to the dielectric discontinuity at the crystallite surface. This surface polarization term has the effect of making the Coulomb energy modestly
less shielded. The predicted 1s–1s energies for several semiconductors appears in Figure 4. Note that the approach to the bulk band gap is quite slow in GaAs and InSb where the electron effective masses are very small, since the Ga–As and In–Sb bonds are strong.

Coulombic correlation can become significant at intermediate sizes. If \( m_e \ll m_h \), then for some range of \( R \) the Coulomb energy will be intermediate between the electron and hole kinetic energies. In an adiabatic approximation, the hole will be attracted to the time average electron density toward the crystallite center (21a,b). The hole wavefunctions are approximately those of a three dimensional harmonic oscillator, and the \( \Delta N = 0 \) selection rule is no longer obeyed. In real crystallites, however, this simple model is likely to be complicated by the previously mentioned tensor valence band Hamiltonian, and a non-negligible hole mass.

If \( m_e \sim m_h \) then the correlation is principally angular, and not radial as in the previous paragraph. With correlation present, the total orbital momentum of the electron/hole pair remains a good quantum number, even though individual angular momenta mix. The \( 1p-1p \) state has \( L = 0, 1, \) and 2 components. Calculation (M. G. Bawendi, unpublished result)

![Figure 4](image-url)  
*Figure 4* Lowest allowed electronic transition energy versus size (from Ref. 19).
shows that the Coulomb term mixes the $L = 0$ component (which, in fact, carries all the absorptive oscillator strength of $1p - 1p$) into $1s - 1s$. This mixing is stronger than $S$ type radial mixing. The hole tends to be on the same side of the crystallite as the electron.

In CdS the hole mass is about four times larger than the electron mass. A simple variational calculation shows that the Coulomb term by itself causes the $1s - 1s$ state to have approximately 1% admixture of both $1p - 1p$ and $1s - 2s$ (M. G. Bawendi, unpublished result), for a 50 Å diameter crystallite. In order to calculate absorption oscillator strengths and energies accurately, however, the hole tensor Hamiltonian should be included.

In a bulk semiconductor, the diameter of the Coulombic “exciton” is (by definition) twice the Bohr radius $a_0$. This diameter is about 60 Å in CdS. In crystallites, the HOMO-LUMO state transforms from $1s - 1s$ like, to exciton like, at $R = 2-3$ $a_0$. Calculations on large, internally correlated crystallites have been done directly via the quantum Monte Carlo method (24) or via the variational method using a single particle basis or the Hylleraas-type wavefunction (19, 25-27). [The transformation has also been studied in rectangular shaped crystallites (28).] At this diameter, the lowest excited state occurs quite close to the band gap energy; however, the spectrum remains discrete. An accurate calculation, including all important phenomena, of the discrete yet dense excited state spectrum expected at this size would be quite complex. Both electromagnetic (i.e. polariton) and quantum size effects are equally significant at this size (29, 30).

Large crystallites with significant electron-hole correlation are fascinating. For example, the summed oscillator strength for all valence to conduction band discrete transitions will scale as the number of unit cells. The “$1s - 1s$” oscillator strength per crystallite, however, is predicted to be independent of size (excluding a wavelength factor) as long as the wavefunction shows no correlation (19). As correlation develops, the oscillator strength per crystallite increases, and the purely radiative lifetime decreases from about a nanosecond to a few picoseconds (“giant oscillator strength” effect) (26, 31–33). The electron-hole correlation in such large crystallites is due to a weak, long range shielded Coulomb attraction, and therefore this large correlated state should be especially sensitive to thermal (i.e. vibration), inhomogeneous, and/or electromagnetic dephasing in real crystallites (34).

Electron-hole correlation is also important if the crystallite contains two holes and two electrons (“biexciton”), such as would result from sequential photon absorption. The Pauli principle allows the electron $1s$ orbital to be doubly occupied; the hole $J = 3/2$ orbital could in principle contain four holes. Neglecting the Coulomb interaction and Franck-Condon
effects, this state occurs at twice the $1s-1s$ energy. If the Coulomb interaction is included, then in most cases it appears that the sequential photon transition creating the biexciton is redshifted from the initial transition to $1s-1s$ (35, 36). These calculations neglect possible complications caused by hole MO degeneracy. Also, if the effective mass approximation overestimates MO energies, then the mixing due to the Coulomb term will be even greater than calculated.

The splitting between $1s-1s$ and biexciton transitions is predicted to become larger if the medium outside the crystallite has a low dielectric constant (36). This occurs because the Coulomb interaction is enhanced by fringing electric fields (i.e. surface polarization) (37). As correlation develops, this sequential transition also develops giant oscillator strength, similar to the initial transition.

The presence of close-lying exciton and biexciton transitions with predicted giant oscillator strengths suggests that large third order nonlinear optical effects will occur. In all theories, the linewidths of these transitions are critical and uncertain parameters. The resonant nonlinear coefficients are predicted to be quite large if the linewidths are small (31, 33, 36). The question of a large nonresonant, nonlinear coefficient, at energies below the $1s-1s$ transition, remains unclear at this time (38, 39).

EXPERIMENTAL ELECTRONIC SPECTRA

A 40 Å diameter crystallite of CdSe has some 1500 atoms, about one third of which are on the surface and interact with adsorbed species. Structural and compositional characterization is absolutely critical in understanding the spectra of such real crystallites. Characterization of large clusters requires the development of new physical and synthesis methodology. It would be a tremendous achievement to make a macroscopic sample of crystallites of this size, identical at the atomic scale. Molecular beam technology is central to the study of smaller, mass selected clusters, and is undergoing vigorous development at present. It has not yet been shown, however, that clusters of this large size can be made, characterized, and/or accumulated in useful amounts by using beam technology.

Various forms of “arrested precipitation” are used to make crystallites, either at high temperature in hosts such as silicate glasses or NaCl, or at room temperature in solution. In the solid hosts, the optical spectra often show relatively sharp spectral features; this suggests that high quality crystallites have been made (40–49). Size can be varied through different annealing procedures, but it is difficult physically to characterize and/or purposefully modify the crystallites. Synthesis in solution creates a metastable colloid that can be modified by adsorption of dissolved species (50).
Yet in situ characterization of structure and/or surface species is difficult, and a broader distribution of sizes is often present. GaAs crystallites made by molecular beam epitaxy on amorphous silica have been reported (51). Gas aggregation methods have also been used to make crystallites in the quantum size effect regime (52).

We synthesize crystallites that have organic moieties bound to the surface. A key synthesis step occurs in an inverse micelle, in which, for example, CdSe crystallites reside with surfactant molecules adsorbed on their otherwise reactive surfaces. As outlined in Figure 5, an organometallic reagent containing the Se-phenyl moiety displaces the surfactant and reacts with the Cd rich surface. When phenyl groups are chemically bonded to the crystallite, it becomes hydrophobic. This surface derivatization prevents fusion of crystallites, and enables recovery of macroscopic amounts of pure, size-selected, “capped” quantum crystallites as a free-flowing powder (1). Quantum crystallite powders stabilized with an inorganic polymer adsorbed on the surface have also been reported (53). In a few cases, capped, layered particles, formed from two different semiconductors, have been grown in inverse micelle media (54). Such capped crystallites dissolve in organic liquids and can then be further modified and/or physically characterized. Certain yeasts are also known to grow CdS particles of approximately 20 Å capped with short peptides, also isolatable in pure form (55).

Capped CdSe crystallites in the 20 to 50 Å range have been characterized by powder X-ray scattering, transmission electron microscopy, elemental analysis, ⁷⁷Se NMR (56), IR, resonance Raman, fluorescence, and absorption hole-burning spectroscopy. The internal crystallite structure is better understood than the surface structure. Figure 6 shows powder X-ray patterns and theoretical fits, calculated numerically from the Debye equa-

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Figure 5 Schematic diagram of synthetic process that “caps” a CdSe crystallite with phenyl groups (Ref. 1).
Figure 6  Bragg powder X-ray scattering spectra of CdSe crystallites (from Ref. 57).

tion for two different ca. 35 Å CdSe syntheses (57). One reaction yields essentially wurtzite single crystallites, whereas the other yields particles that switch between wurtzite and zinc blende, apparently randomly, as growth occurs. Modeling shows that powder patterns measure average long range structure, and are relatively insensitive to deviations from the average. Such deviations can be either random (thermal motion and/or defects) or systematic (position dependent strain and/or surface reconstruction). NMR and EXAFS measurements, however, do provide partial information about surface bonding and structure (P. R. Reynders and M. Marcus, unpublished results).
Spectroscopic measurements are limited by the fact that real samples have a distribution of sizes and shapes, and most probably a distribution of surface compositions and structures for a given size and shape. These effects create inhomogeneous spectroscopic broadening and complex averaging in photophysics. For example, a CdSe crystallite distribution, of 40 Å average diameter and standard deviation 10%, has a 1500 cm$^{-1}$ inhomogeneous absorption width, as calculated from Eq. 7. There is a partial analogy here with low temperature protein spectroscopy, in which numerous conformational isomers are "frozen in" and create inhomogeneous broadening.

The upper panel of Figure 7 shows the 10 K absorption spectrum of

![Figure 7](image.png)

*Figure 7* Hole-burning spectra of capped CdSe crystallites at low temperature (from Ref. (59a,b)). *Upper panel:* optical absorption. *Lower panel:* change in optical density observed 10 nsec after pumping with an intense, spectrally narrow laser.
capped CdSe clusters in polystyrene. The broad feature at 530 nm is assigned as the 1s–1s excited state. Transient photophysical hole burning experiments show that this width is largely inhomogeneous (59a,b). A photoexcited crystallite luminesces on a nanosecond to microsecond time scale, and during this period a narrow hole can be observed in the remaining ground state absorption. This sample shows a 940 cm⁻¹ inhomogeneous width, and a 1s–1s homogeneous lineshape exhibiting weak Franck-Condon coupling to an optical vibration. In this 205 cm⁻¹ normal mode, Cd ions and Se ions vibrate out of phase with each other along the crystallite radius. This coupling of the excited state to this specific optical vibration is also seen in CdSe resonance Raman (RR) spectra (60). [Optic vibration RR experiments on larger ZnTe crystallites have been recently reported (52).]

If the excited state potential for this mode is modeled as a displaced harmonic oscillator, then the normalized displacement is about four times smaller in the crystallite than in the bulk (60). That is, the excited state Franck-Condon coupling is far weaker in the quantum crystallite than in the bulk. This result is unambiguously demonstrated in a series of capped CdS cluster powders, in which a smooth variation with size occurs (61). It was earlier predicted, from analysis of Frohlich vibronic coupling, that the coupling to optic vibrations should decrease in small particles as electron hole overlap increases (62).

The homogeneous 1s–1s lifetime in small CdS crystallites, derived from the RR fit, is 50 fs (61). CdSe crystallite 1s–1s optic vibronic transitions also show a homogeneous width (59a,b) on the order of 100 cm⁻¹; this may be “lifetime” broadening and/or coupling to low frequency motions in the excited state. Bulk hydrogenic excitons, with no surface present, typically show far sharper optic vibronic spectra.

Luminescence excitation experiments can also reveal the homogeneous absorption spectra of size selected crystallites. The 25 K absorption spectra of the wurtzite crystallites whose X-ray scattering spectra are displayed in Figure 5 appear in the top of Figure 8. Also shown is the luminescence spectrum observed for excitation in the ultraviolet, where homogeneous widths are large and all crystallites are excited equally. The width of this structureless luminescence spectrum is almost entirely inhomogeneous (63). The excitation spectrum of a narrow band of luminescence at 530 nm is shown in the lower panel. This spectrum shows more structure than the absorption spectrum. It preferentially records the luminescence of a few of the smaller crystallites whose spectra are shifted to higher energy. The 1s–1s peak observed is actually the (1, 0) optic vibronic transition; the (2, 0) is visible as a shoulder.

At least three additional electronic states can be resolved in the excitation
Figure 8  Steady state fluorescence excitation spectrum of CdSe crystallites at low temperature in an organic glass (Ref. 63). *Upper panel:* optical absorption and fluorescence spectra. *Lower panel:* excitation spectrum of 1 nm wide band of luminescence centered at 530 nm.

Spectrum. The bump at ca. 500 nm may be the 1s–1p transition, and the weak feature at 460 nm may be the 1s–2s transition. The stronger and broader feature at 440 nm, also seen directly in absorption, is probably the higher spin orbit component of 1s–1s. The broad continuum in the ultraviolet corresponds to higher excited states including 1p–1p.

In general, quantum crystallite luminescence is quite sensitive to surface composition and structure. Figure 9 schematically illustrates the types of processes that may occur. The figure compares the discrete MOs of nanometer crystallites with the standard band diagram of a bulk semiconductor. The CdSe luminescence observed in Figure 8 appears to be the 1s–1s state in fluorescence, although a complete understanding of vibrational and electronic reorganization between absorption and fluorescence has not yet been worked out. In this state, the electron and hole are inside the crystallite; recall that the 1s wavefunction has a node on the surface (in the limit of an infinite barrier).
Even before quantum size effects were recognized, it was discovered that a single atom of a strongly electropositive metal on the surface of an aqueous colloidal CdS particle quenches crystallite luminescence (64, 65). This atom appears to act as a localized surface state, trapping the 1s electron. Adsorbed organic species that have redox potentials inside the cluster “band gap” also act as surface traps, and charge transfer to these species from crystallites has been observed via transient optical absorption and RR spectroscopies (66). A novel quantum theory of the reverse process, electron transfer from an excited adsorbed molecule into a semiconductor particle, has recently been proposed and compared with experiment (67a,b).

In some cases, a low energy, broad luminescence is observed that is thought to occur from electrons and/or holes individually trapped in uncharacterized, naturally present surface states (50). The lifetime and temperature dependence of this luminescence are characteristic of separately localized carriers strongly coupled to lattice phonons (68). At room temperature the recombination is principally nonradiative.

In the case of CdS colloids, adsorption of organic amines from solution can shift crystallite luminescence to higher energy, and increase the quan-
turn yield (69). It appears that amine complexation to the surface eliminates surface states that otherwise would trap the electron. In a similar fashion, an apparent monolayer of Cd(OH)$_2$ on CdS (70), or ZnS on CdSe (54) can convert surface trapped luminescence into apparent $1s-1s$ luminescence.

These examples illustrate a remarkable and potentially useful property of quantum crystallites: The excited state photophysics can be tailored, via surface modification, while the optical absorption can be left largely unchanged. At the same time, the optical absorption can be independently varied via the size and shape of the crystallite. In order to take full advantage of these ideas, advances in the methods of synthesis, surface modification, and characterization are necessary.

SUMMARY

We have reviewed the electronic quantum size effect in nanometer-scale fragments of inorganic tetrahedral semiconductors. The effect is a consequence of strong chemical bonding. We have described the nodal patterns and energies of discrete, size dependent crystallite molecular orbitals. Molecular orbital effects, along with Coulombic attraction between the electron and hole, can be incorporated into an effective mass Hamiltonian. The resulting discrete eigenspectrum of crystallite excited states shows a rich structure. Electron-hole correlation, and a continuous band structure, develop gradually with increasing size. Large crystallites, of diameter several times the bulk exciton Bohr radius, are predicted to have giant oscillator strengths and large resonant optical nonlinearities.

The calculated discrete electronic spectra may need modification to incorporate ultrafast excited state internal conversion processes. Quantitative calculations will require improvement beyond the effective mass approximation. The atomic nature and structure of intrinsic surface states, and the general question of possible surface electronic bands and reconstruction, remain largely unexplored. The dephasing of physically large, yet correlated electron-hole bound states needs to be addressed. Experiments on CdSe crystallites clearly demonstrate the reality of the electronic quantum size effect. Detailed interpretations are partially hindered by averaging over inhomogeneous distributions of size, shape, and surface composition.

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