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Electron-electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state

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We model, in an elementary way, the excited electronic states of semiconductor crystallites sufficiently small (~ 50 Å diam) that the electronic properties differ from those of bulk materials. In this limit the excited states and ionization processes assume a molecular-like character. However, diffraction of bonding electrons by the periodic lattice potential remains of paramount importance in the crystallite electronic structure. Schrödinger's equation is solved at the same level of approximation as used in the analysis of bulk crystalline electron-hole states (Wannier excitons). Kinetic energy is treated by the effective mass approximation, and the potential energy is due to high frequency dielectric solvation by atomic core electrons. An approximate formula is given for the lowest excited electronic state energy. This expression is dependent upon bulk electronic properties, and contains no adjustable parameters. The optical f number for absorption and emission is also considered. The same model is applied to the problem of two conduction band electrons in a small crystallite, in order to understand how the redox potential of excess electrons depends upon crystallite size.

I. INTRODUCTION

The band gap of a semiconductor is, by definition, the energy necessary to create an electron (e^{-}) and hole (h^{+}) , at rest with respect to the lattice and far enough apart so that their Coulomb attraction is negligible. If one carrier approaches the other, they may form a bound state (Wannier exciton) approximately described by a hydrogenic Hamiltonian

$$\widehat{H} = -\frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{\epsilon |r_e - r_h|}$$
(1)

at an energy slightly below the band gap.^{1.2} Here m_h (m_e) is the effective mass of the hole (electron) and ϵ is the semiconductor dielectric constant. The effective masses of the two charges are often only a small fraction of an electron mass. Small masses naturally imply that localization energies for the hole and electron are large. The dielectric constant in inorganic semiconductors is typically in the range 5–12, implying that the Coulomb attraction is almost entirely screened. This combination of small masses and weak attraction causes the exciton wave function to extend over a large region. For example, the lowest 1S exciton of CdS has a diameter of $\simeq 60$ Å in the center of mass coordinate system.

In terms of a hydrogen atom analogy, the band gap is the ionization limit of the hydrogenic electron-hole bound states. Photon absorption at higher energies creates "free" electrons and holes with excess kinetic energies inside the semiconductor.

In this paper we consider crystallites sufficiently small that this bulk energy level scheme is not valid. We suggest that the size of the 1S exciton provides a natural, intrinsic measure of linear dimension at which crystallite size effects will create a qualitatively different situation. As the crystallite approaches this size, the electron and hole interactions with the crystallite surfaces will dominate the dynamics. In this "molecular" limit, the energy level scheme will depend upon the size and shape of the crystallite as well as upon the nature of the material. There will be a series of excited, discrete bound states approaching an ionization limit corresponding to a positively charged crystallite and a free electron in vacuum. The crystal is essentially not large enough for the intrinsic band gap to form, i.e., to sustain noninteracting, Bloch-type plane wave electron and hole eigenstates at the band edges.

We describe now elementary model calculations which attempt to identify the principal electronic phenomena which should occur in these crystallites. We use experimental data from bulk crystalline materials to predict the major changes occurring as crystallite diameter decreases to 40–50 Å. Our calculation is similar to a perturbation calculation without adjustable parameters. We neglect possible complications of the problem, such as size dependent structural lattice rearrangements, which may be important in some specific cases. Our model treats the fate of "bulk" states in the limit of small size, and we do not consider possible surface states. We work at the same level of approximation as involved in the analysis of the bulk bound excited states via the Wannier Hamiltonian [Eq. (1)].

In an earlier paper labeled I, we considered the problem of the ionization limit itself as a function of crystallite size.³ We modeled the elementary quantum mechanics of a crystallite containing one mobile charge. That paper discusses the major assumptions of the model: (a) the use of the effective mass in the kinetic energy, and (b) the use of an interaction potential based upon high frequency dielectric solvation.

This work is motivated by recent experimental interest in the transformation between molecular and bulk properties in small aggregates. Small semiconductor crystallites approaching the sizes considered here are used as catalysts and photosensitizers.⁴⁻⁷ In the case of CdS crystallites, moderate changes in electronic absorption and resonance Raman excitation spectra have been reported and interpreted in terms of the quantum size effects we model here.⁸

Related phenomena, generally of smaller magnitude,

have been observed and understood since 1974 in thin semiconductor layers made by molecular beam epitaxy techniques.⁹ We treat kinetic energy via the same effective mass approximation used in layer exciton theory.¹⁰ We treat electrostatic effects exactly, as there are large dielectric discontinuities in our problem. In the layer exciton theory, an effective dielectric constant approximation is used as the discontinuities are smaller.

II. THE POTENTIAL ENERGY

The fact that the Coulomb interaction is screened in Eq. (1) has interesting consequences in small crystallites. Significant screening necessarily implies a significant dielectric solvation energy. We model small crystallites where the electron and hole kinetic energies are several tenths of an electron volt. At these frequencies ($\sim 5 \times 10^{13}$ Hz), dielectric solvation principally results from polarization of atomic core electrons. We assume that this polarization, in response to a mobile charge, will not saturate, in contrast to, e.g., the *static* orientational polarization of water molecules near ionic solutes. It appears physically valid to construct a potential energy for Schrödinger's equation from a consideration of the classical electrostatics involved. The potential will involve polarization charge at the crystallite surfaces.

A sphere of radius R and dielectric coefficient ϵ_2 is surrounded by a medium of coefficient ϵ_1 . Two charges of magnitude e exist at positions \overline{S}_1 and \overline{S}_2 inside the sphere. Following the procedure employed in I, the work $V(\overline{S}_1, \overline{S}_2)$ classically necessary to assemble this charge distribution is

$$V(\overline{S}_{1},\overline{S}_{2}) = \mp \frac{e^{2}}{\epsilon_{2}|\overline{S}_{1} - \overline{S}_{2}|} + P(\overline{S}_{1}) + P(\overline{S}_{2}) \mp P_{\mathcal{M}}(\overline{S}_{1},\overline{S}_{2}).$$
(2)

As in I,P is defined

$$P(\overline{S}) = \sum_{n=0}^{\infty} \alpha_n \left[\frac{S}{R}\right]^{2n} \frac{e^2}{2R},$$
(3)

where

$$\alpha_n = (\epsilon - 1)(n+1)/[\epsilon_2(\epsilon n + n + 1)]$$
 and $\epsilon = \epsilon_2/\epsilon_1$.
(4)

 P_{M} is

$$P_{\mathcal{M}}(\overline{S}_1, \overline{S}_2) = \sum_{n=0}^{\infty} \alpha_n \, \frac{e^2 S_1^n S_2^n}{R^{2n+1}} \, P_n(\cos \theta), \tag{5}$$

where θ is the angle between \overline{S}_1 and \overline{S}_2 , and P_n is a Legendre polynomial. If the two charges have opposite signs, the - sign holds; the + sign holds if the charges have equal signs.

Note that in the limit of a localized state in a large sphere, i.e., $R > S_1$ and S_2 , we have $V \rightarrow e^2/\epsilon_2 |\overline{S}_1 - \overline{S}_2|$. This is the screened Wannier result of Eq. (1). As described in I, we have dropped *R*-independent terms from *V* that mathematically represent the infinite polarization energies that classically exist near point charges. If $\epsilon_2 > \epsilon_1$ then $P(\overline{S})$ is a positive term increasing in magnitude as *R* decreases. It represents loss of dielectric solvation energy as the volume of high dielectric constant ϵ_2 material becomes small. $P(\overline{S})$ describes a relatively weak radial \overline{F} electric field pulling the charge to S = 0, the point of highest dielectric stabilization. $P_{\mathcal{M}}(\overline{S_1, S_2})$ is a mutual polarization term that can be thought of as the interaction of one charge with the surface polarization charge created by the other charge. $P_{\mathcal{M}}$ depends upon the absolute position of $\overline{S_1}$ and $\overline{S_2}$ as well as the relative separation $|\overline{S_1} - \overline{S_2}|$.

If we limit ourselves to S wave functions for e^- and h^+ , simplifications occur in the three polarization energy terms. The Hamiltonian matrix elements of all P_M terms for $n \ge 1$ will be zero. The n = 0 term of P_M is $(\epsilon - 1)e^2/\epsilon_2 R$ and is independent of the S wave function. If the two charges have opposite signs as appropriate for an electron and hole, then this n = 0 term will cancel the two n = 0 terms of $P(\overline{S_1})$ and $P(\overline{S_2})$. The potential energy Eq. (2) reduces to

$$V_{0}(\overline{S}_{1},\overline{S}_{2}) = \frac{-e^{2}}{\epsilon_{2}|\overline{S}_{1}-\overline{S}_{2}|} + \sum_{n=1}^{\infty} \alpha_{n} \frac{(S_{1}^{2n}+S_{2}^{2n})}{R^{2n+1}} \frac{e^{2}}{2},$$
(6)

where the subscript "0" indicates that the sphere has a net charge of zero. V_0 is the potential energy appropriate in modelling crystallite excited electronic states. If the two charges have the same sign, then the appropriate potential V_2 is

$$V_{2} = + \frac{e^{2}}{\epsilon_{2}|\overline{S}_{1} - \overline{S}_{2}|} + \frac{2(\epsilon - 1)e^{2}}{\epsilon_{2}R} + \sum_{n=1}^{\infty} \alpha_{n} \frac{(S_{1}^{2n} + S_{2}^{2n})}{R^{2n+1}} \frac{e^{2}}{2}.$$
 (7)

This is the potential for a small crystallite with two electrons in the conduction band, or two holes in the valence band.

III. THE LOWEST EXCITED STATE

Schrödinger's equation for the crystallite excited states, within the confines of our elementary model, can be written

$$\begin{bmatrix} -\frac{\hbar^2}{2m_e} \nabla_e^2 + \frac{-\hbar^2}{2m_h} \nabla_h^2 + V_0(\overline{S}_e, \overline{S}_h) \end{bmatrix} \Phi(\overline{S}_e, \overline{S}_h)$$
$$= E\Phi(\overline{S}_e, \overline{S}_h). \tag{8}$$

For the moment we take V_0 to be infinite outside the sphere. The equation (8) Hamiltonian becomes the bulk Wannier Hamiltonian [Eq. (1)] in the limit of large R. The energy Ecalculated from Eq. (8) is relative to the bulk gap, as are the Wannier energies in Eq. (1). This formulation is appropriate to direct gap materials, in which the valence and conduction band minima are above each other in K space.

At large R, the wave function Φ will be intermediate between the hydrogenic form, and a form influenced by carrier confinement within the sphere. E will be on the order magnitude of the bulk Wannier binding energy, typically 10^{-2} eV.

At smaller values of R, Φ will become dominated by carrier confinement, and E will increase. We seek an approximate solution to Φ in this limited size range. A natural basis is given by the S wave functions for a particle in a sphere:

$$\Psi_n(r) = \frac{C_n}{r} \sin(n\pi r/R)$$
(9)

with

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mR^2},\tag{10}$$

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where *m* is the appropriate effective mass.

We shall find that the simple uncorrelated solution

$$\boldsymbol{\Phi}_{0} = \boldsymbol{\Psi}_{1}(\overline{\boldsymbol{S}}_{e})\boldsymbol{\Psi}_{1}(\overline{\boldsymbol{S}}_{k}) \tag{11}$$

is a fair approximation for some materials in this range of R. In order to explore the relative magnitude of various terms in Eq. (8), and to attempt to understand systematic trends, we first explore Φ_0 solutions. We then consider more complex solutions as necessary.

With the wave function Φ_0 the energy of the lowest excited state becomes

$$E = \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon_2 R} + \frac{e^2}{R} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R} \right)^{2n},$$
(12)

where the bar in the third term means average over a Ψ_1 function. This third term is a function of both ϵ_2 and ϵ_1 . Recall that *E* is a shift with respect to the bulk band gap.

The first term is the quantum energy of localization, increasing as R^{-2} for both electron and hole. In a formal sense, the second term is the Coulomb attraction, and the third term is the solvation energy loss. Both terms increase as R^{-1} . The solvation energy term has an interesting classical origin. The time average charge distribution corresponding to Φ_0 is zero throughout the crystal; there is no static \overline{F} either inside or outside. However, the instantaneous stored energy density in a dielectric is proportional to $-\overline{P}\cdot\overline{F}$; i.e., varies as F^2 . As the charges move, the time average value of F^2 is not zero.

In Table II we have calculated the magnitude of these three terms for (arbitrarily chosen) 60 Å diameter spheres of ZnO, CdS, GaAs, and InSb in vacuum. As seen in Table I, these materials exemplify the range of physical constants observed from large gap materials (ZnO) to small gap materials (InSb). ϵ_2 increases and m_e decreases typically as the gap decreases.

In Table II the positive polarization term is smaller than the negative Coulomb term. (In a solvent with $\epsilon_1 > 1$, the polarization term would be smaller yet.) The net negative electrostatic contribution is smaller than the positive localization kinetic energy for these materials. The kinetic energies of localization are significant and increase rapidly, as the band gap and m_e decrease, going across the table for R = 30Å.

The wave function Φ_0 is valid for cases where the kinetic energy is much larger than the electrostatic energy. At R = 30 Å this is a good approximation for small band gap materials, and a poor one for the larger gap materials ZnO

TABLE II. Energy terms in eV from Eq. (12) for R = 30 Å spheres of the indicated materials. In InSb, the effective mass approximation for kinetic energy fails, and we indicate an approximate lower limit for the kinetic energy.

	ZnO	CdS	GaAs	InSb
Kinetic	0.27	0.27	<u>~0.65</u>	> 1
Coulomb	- 0.24	- 0.15	- 0.08	- 0.06
Polarization	0.06	0.05	0.03	0.02
Total Shift	0.09	0.17	$\simeq 0.60$	>1

and CdS. As the kinetic and electrostatic energies scale differently with R, in each material the approximation is valid for sufficiently small R.

In order to correctly describe the larger diameter sizes of each material, it is necessary to use a more general wave function. Physically, the Coulomb term will introduce correlation into the wave function, in that the electron and hole will attempt to reside near each other in order to maximize the Coulomb attraction. Also, the polarization term "pushes" both e^- and h^+ towards the sphere center, which is the point of maximum dielectric stabilization. These effects occur at the cost of increased kinetic energy of localization.

We perform a simple variational calculation incorporating radial but not angular correlation between electron and hole. Consider the function

$$\boldsymbol{\Phi}_{1} = \boldsymbol{\Psi}_{1}(\overline{\boldsymbol{S}}_{e})\boldsymbol{\Psi}_{1}(\overline{\boldsymbol{S}}_{h}) + \boldsymbol{\beta}_{e}\boldsymbol{\Psi}_{2}(\overline{\boldsymbol{S}}_{e})\boldsymbol{\Psi}_{1}(\overline{\boldsymbol{S}}_{h}) + \boldsymbol{\beta}_{h}\boldsymbol{\Psi}_{1}(\overline{\boldsymbol{S}}_{e})\boldsymbol{\Psi}_{2}(\overline{\boldsymbol{S}}_{h}),$$
(13)

where Ψ_2 is the 2S particle in a sphere wave function. Φ_1 has two adjustable parameters β_e and β_h . Adding 2S character allows the electron or hole to move either inward or outward depending upon the sign of β_e or β_h . We obtain $\beta_e \beta_h$ and E by minimization of E (after normalization) in Eq. (8) with the polarization term removed from V_0 . The polarization energy is subsequently obtained by first order perturbation theory.

Numerical results for CdS crystallites as a function of R appear in Table III. The small positive values of β_e and β_h at larger R indicate that both electron and hole move slightly towards the sphere center to increase their overlap. The hole moves more as it is less costly in kinetic energy (the hole has the heavier mass). At 80–100 Å the electrostatic and kinetic energies nearly cancel. For smaller diameters the kinetic en-

TABLE III. Energy terms in eV from Eq. (12) using the variational wave function Eq. (13). The best fit parameters β_e and β_h are indicated for each CdS crystallite diameter.

TABLE I. Electronic parameters for the indicated crystalline direct gap semiconductors, ϵ is the dielectric coefficient at optical frequencies. The effective masses are in units of the free electron mass. E_g is the band gap.

	<i>E_g</i> (0 K) (eV)	m *	m [*] _h	E
InSb	0.24	0.015	0.39	15.6
GaAs	1.52	0.07	0.68	10.9
CdS	2.58	0.19	0.8	5.7
ZnO	3.44	0.24	0.45	3.7

Diameter (Å)					
Parameter	100	80	60	50	40
β _e	0.1	0.1	0.1	0	0
β _h	0.3	0.2	0.2	0.2	0.1
Kinetic	0.10	0.15	0.27	0.38	0.59
Coulomb	- 0.10	- 0.13	- 0.17	- 0.19	- 0.23
Polarization	0.02	0.03	0.04	0.05	0.07
Total shift	0.02	0.05	0.14	0.24	0.43

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FIG. 1. Energy of the lowest excited electronic state as a function of crystallite diameter, as calculated via wave function (13). Short horizontal solid lines are the bulk band gap energies of the indicated materials. Dot-dashed line for InSb incorporates surface carrier charge density as described in the test.

ergy dominates, and the lowest excited state shifts blue of the bulk band gap.

Excited state energies as a function of R for ZnO, CdS, GaAs, and InSb appear in Fig. 1. The two larger gap materials have moderate Coulomb terms and relatively (compared with GaAs and InSb) large effective masses. This combination keeps the excited state energy near the bulk bandgap for diameters larger than ~ 60 Å. The small gap materials GaAs and InSb must reach remarkably large crystallite sizes, however, before the excited state approaches the bulk bandgap. This occurs because m_e is extremely small, and the Coulomb attraction is strongly shielded.

At small R our model will fail in a number of ways. The effective mass approximation is no longer valid when the electron (i.e., lighter particle) kinetic energy becomes substantial. Inspection of band structure calculations^{11,12} for these materials indicates that beyond ~0.5 eV, the kinetic energy increases with K substantially less steep than $K^2/2m^*$. In Fig. 2 we have indicated these regions with a dashed curve. One could incorporate a more complex (anisotropic if necessary) representation of E(K).

At high kinetic energy there is a second potential error in that the basis functions [Eq. (9)] go to zero at the crystallite surface. We demonstrated in Sec. C of I that, for smaller diameter crystallites in materials with small effective masses, the calculated surface carrier charge density is substantial if one assumes the Ben Daniel and Duke¹³ boundary condition at a finite potential energy step. The present calculation overestimates the kinetic energy if the surface charge density is important. This should occur principally in smaller gap materials.

In InSb the electron effective mass is extremely small. The Coulomb interaction is almost entirely screened, and the equation (12) energy E is essentially electron localization energy. In this case the Ben Daniel and Duke boundary con-



FIG. 2. Calculated size dependence of the indicated redox processes.

dition gives a size dependent localization energy indicated by the dot-dashed curve in Fig. 1. We suggest this curve be taken as a semiquantitative estimate. The validity of the Ben Daniel and Duke boundary condition in this physical situation needs to be more carefully investigated. It may be necessary to go beyond the effective mass approximation. These ambiguities should be less important in the larger gap materials.

IV. OSCILLATOR STRENGTHS AND THE ABSORPTION SPECTRUM

In bulk materials, if one assumes that the valence to conduction band optical matrix element is independent of K, then the oscillator strength density is uniform throughout K space. The absorption coefficient is proportional to the density of states in K space and increases rapidly with energy above the band gap. Almost all of the oscillator strength exists above the gap in transitions creating free electrons and holes.

The absorption strength of the bound electron-hole exciton can be considered to derive from a Fourier transform of the exciton wave function into a distribution of plane wave K states, for both electron and hole.¹⁴ In heuristic terms, the more compact the exciton wave function, the higher the values of necessary $|\overline{K}|$ and the greater the exciton oscillator strength. The oscillator strength scales as the volume of K space necessary to form the exciton.

Even though the exciton oscillator strength is small relative to the above gap region, it can be large in comparison to free molecules. For example, the 1*S* exciton in CdS, when weakly bound at a lattice defect, has a radiative lifetime of $\simeq 1$ ns.¹⁵ Henry and Nassau have theoretically considered the oscillator strengths of arbitrary (nonhydrogenic) electron-hole bound wave functions $\phi(\bar{r}_e, \bar{r}_h)$ in bulk CdS.¹⁵ Following the earlier work of Rashba and Gurgenishvili,¹⁶ they derived an expression for the *f* number in terms of f_{ex} , the intrinsic hydrogenic 1S *f* number for crystalline bulk CdS:

$$f = f_{\rm ex} \frac{\left| \int \phi(\bar{x}, \bar{x}) dx \right|^2}{|\boldsymbol{\Phi}_{\rm ex}(0)|^2 \boldsymbol{\Omega}_M} \frac{\omega_{\rm ex}}{\omega}.$$
 (14)

Here Φ_{ex} is the hydrogenic 1S wave function and Ω_M is the volume of one CdS diatomic unit. $f_{ex} = 0.00256$ from the work of Thomas and Hopfield.¹⁷ ω_{ex}/ω is the ratio of emission frequencies of bulk CdS to the small crystallite.

This expression is applicable to the lowest excited state of small crystallites, for those sizes where the effective mass approximation and the K independence of the transition dipole remain valid. As a general property, the integral in Eq. (14) is unity if both the electron and hole are in the same spatial wave function. As we have seen, this physically happens in small crystallites when carrier confinement dominates the electrostatic terms. Equation (14) predicts that fhas only a weak size dependence through ω .

This result physically represents a cancellation of two different effects. The absolute interband f number density in K space is proportional to the number of CdS molecules, and thus to the crystallite volume. At any size this f number is distributed over all the excited electron-hole quantum states. The fraction taken by the lowest bound state varies strongly with size. If the crystallite diameter is halved, then the diameter of the lowest wave function is halved and the absolute values of $|\overline{K}|$ needed to synthesize the bound wave function is doubled in both electron and hole space. If $|\overline{K}|$ doubles, then the volume \overline{K} space devoted to the lowest exciton increases by a factor of 8. This cancels the factor of 2 smaller crystallite.

The net result is that *relative* intensity shifts into the lowest bound state as crystallite size decreases. The exciton becomes more prominent in the absorption spectrum. In those regions where the electron and hole wavelengths are smaller than the crystallite dimension, the spectrum remains relatively unchanged. The absolute f number calculated from Eq. (14) is $f\simeq 0.3$ if we take $\omega = \omega_{ex}$. This is the same order of magnitude as the f number of 1S hydrogenic excitons ($d\simeq 60$ Å) bound at lattice defects in bulk CdS.

V. COMPARISON WITH EXPERIMENT

In the related problem of an exciton trapped in a thin semiconductor layer, extensive spectroscopic work has been performed with small band gap materials. In this situation, the wave function is compressed in one dimension, yet remains extended in the other two. Quantitive agreement is generally obtained with simple models based upon the effective mass approximation.¹⁰

However, almost no experimental work has been reported on well characterized crystallites of the sizes we consider here. We report a $\simeq 0.25$ eV shift in the absorption edge of *in situ* colloid CdS crystallites (zinc-blend structure) of

average diameter $\simeq 45$ Å.⁸ This shift is in approximate agreement with Fig. 1. More recently larger shifts have been observed in colloidal crystallites of smaller diameters; these experiments will be described in a forthcoming publication. Shifts in the lowest excited state can also be observed via the resonance Raman excitation spectra of LO crystallite phonons.⁸

VI. ELECTRON AFFINITIES AND REDOX POTENTIALS

Consider the following charge transfer or "ionization" processes involving crystalline CdS:

$$[\operatorname{CdS}]_{n}^{=} \to e^{-} + [\operatorname{CdS}]_{n}^{-}, \qquad (15)$$

$$[\mathrm{CdS}]_{n}^{-} \rightarrow e^{-} + [\mathrm{CdS}]_{n}, \qquad (16)$$

$$[\operatorname{CdS}]_{n}^{*} \rightarrow e^{-} + [\operatorname{CdS}]_{n}^{+}, \qquad (17)$$

$$[\operatorname{CdS}]_{n}^{+} \to h^{+} + [\operatorname{CdS}]_{n}, \qquad (18)$$

$$[\operatorname{CdS}]_{n}^{*} \to h^{+} + [\operatorname{CdS}]_{n}^{-}.$$
⁽¹⁹⁾

Here $[CdS]_n$ represents a crystallite of n CdS diatomic units, * represents the lowest excited state (effective band gap state), and + or - represents an excess hole or electron. In large crystals when individual h^+ and e^- are in thermal equilibrium with the lattice, one has the simple situation that the energies of e^- and h^+ are those of the conduction and valence band edge, respectively. In addition, the binding energies of Wannier excitons are negligible, and interelectron repulsion is negligible as the e^- are far apart. In this limit the energy required for the first three processes is the same—it is simply ΔE between the conduction band edge and the $e^$ reference state in vacuum (conventionally called the electron affinity E.A.). In a similar fashion, the energy for the last two processes is the same— $E_g + E.A.$, the difference from the valence band edge.

In small crystallites, all five processes require differing amounts of energy. This occurs because (a) there is a size dependent interaction for two e^- , or for a h^+ and e^- , confined inside a crystallite, and (b) there are size dependent energies of localization and polarization for a single h^+ or e^- . The size dependence of $[CdS]_n^+$ and $[CdS]_n^-$ was considered in I. Section III considers $[CdS]_n^*$. We now consider $[CdS_n]^-$.

A. Two conduction band electrons

Using the electrostatic potential V_2 Schrödinger's equation becomes

$$\left[\frac{-\tilde{n}^2}{2m_e}(\nabla_1^2+\nabla_2^2)+V_2\right]\boldsymbol{\Phi}(\overline{S}_1,\overline{S}_2)=E\boldsymbol{\Phi}(\overline{S}_1,\overline{S}_2),\quad(20)$$

whereas before

$$V_{2} = \frac{e^{2}}{\epsilon_{2}|S_{1} - S_{2}|} + \frac{2(\epsilon - 1)e^{2}}{\epsilon_{2}R} + \sum_{n=1}^{\infty} \frac{\alpha_{n}(S_{1}^{2n} + S_{2}^{2n})e^{2}}{2R^{2n+1}}.$$
 (21)

The Coulomb term is now repulsive, and the two electrons will try to minimize their overlap. There are two polarization terms. The second one, the smaller of the two, is identical to the polarization term in V_0 . The first term is independent of the wave function, and is the classical "charging" energy of a

TABLE IV. Energy terms in eV for the two e^- problem [Eqs. (20) and (21)]. β is the best fit parameter in Eq. (22) for CdS crystallites of the indicated diameter.

Dian	neter(Å)				
Parameter	120	100	80	60	40
β	- 0.1	- 0.1	- 0.1	0	0
Kinetic	0.11	0.16	0.24	0.42	0.61
Coulomb	0.07	0.08	0.11	0.15	0.18
Charging	0.20	0.24	0.30	0.40	0.59
Polarization	0.03	0.03	0.04	0.05	0.06
Total shift	0.41	0.51	0.69	1.02	1.45

dielectric sphere.

There is an interesting comparison between $[CdS]_n^{-1}$ and $[CdS]_n^{-1}$ for the charging term $2(\epsilon - 1)e^2/\epsilon_2$ above. In I, we have seen that the equivalent term for $[CdS]_n^{-1}$ is onefourth (*not one-half*) this term in $[CdS]_n^{-1}$. This occurs, heuristically, because the stored polarization energy scales as F^2 , so that a doubling of average field leads to a factor of 4 increase in polarization energy.

We take correlated wave function

$$\Psi(\overline{S}_1, \overline{S}_2) = \Psi_1(\overline{S}_1)\Psi_1(\overline{S}_2) + \beta \left[\Psi_2(\overline{S}_1)\Psi_1(\overline{S}_2) + \Psi_1(\overline{S}_1)\Psi_2(\overline{S}_2)\right],$$
(22)

which is symmetric in space coordinates. The two spins must couple into a singlet state, so that the overal wave function will be antisymmetric, and will satisfy the Pauli Principle for indistinguishable electrons. As a numerical example we consider CdS crystallites in water. Table IV shows an energy breakdown of the variational solution for Eq. (20). As before the reference energy is (twice) the conduction band edge in the bulk crystal. The dominant term for diameters greater than 40 Å is the classical charging term. Large shifts are predicted, in comparison with $[CdS]_n^-$ and $[CdS]_n^*$. Note also that all terms here are positive, i.e., act to destabilize the small charged sphere case with respect to the large sphere case. The principal limitation of this calculation is the possibility of carrier charge density on the crystallite surface. This effect will lower the kinetic energy contribution. The small negative values of β in Table III indicate the two electrons have moved nearer the surface in order to minimize their overlap.

The formulation described here could be alternatively used to describe two holes in the conduction band.

B. Redox potentials

In order to demonstrate the different size dependencies of reactions (15)-(19), we have performed numerical calculations for CdS crystallites in water. We subtract the calculated shifts for the initial and final states of each process. The results are plotted in Fig. 2.

Reactions (15) and (16) are cathodically shifted, as a function of decreasing diameter, from the valence band. Reaction (15) has the larger shift due to the large charging term in Eq. (21). Reaction (18) shows almost no shift, as the e^- is

stabilized in the excited state by attraction to the hole. Note that Henglein¹⁸ has argued, from the point of view of surface capacitance, that negative charge buildup on small crystallites will give a large shift in electron redox potential.

The conduction band reaction (18) shows an anodic shift, as discussed in I, due to the localization energy of the hole in the crystallite. The excited state conduction band process [reaction (19)] shows a cathodic shift as the attraction for the e^- is greater than the localization energy.

VII. DISCUSSION AND SUMMARY

Our elementary calculations model an intermediate size regime for small crystallites. The excited states and ionization potentials are a strong function of size; bulk properties have not been reached even though the crystallite contains thousands of individual "molecular" units. Nevertheless, the bulk band structure, through the effective masses, is of critical importance in determining the deviation from bulk properties. The model implies that size dependent standing wave diffraction of valence electrons, occurring as an electron moves through the interior and senses the periodic lattice potential and the crystallite boundaries, is the dominant physical effect for these materials.

These materials have strong chemical bonds between individual molecular units, in contrast to dielectric crystals of organics or rare gas atoms, for example. Strong bonding implies large widths for the valence and conduction bands, and a strong tendency to delocalize electrons involved in the bonding, as embodied numerically in the small effective masses. In an Ar crystal, by way of contrast, excited electronic states would localize on individual Ar atoms (Frenkel excitons). The lattice would distort around the excited state, tending to trap the excited state, and leading to a slow "hopping" rate for the excitation.

In the excited state problem, electrostatic effects are less important. The \overline{F} field originates on one charge and terminates on the other within the crystallite. The field mainly resides inside the crystallite, with the result that the Coulomb attraction is shielded by ϵ_2 with small polarization terms. In the two e^- problem (Sec. VI), the field originates on the two e^- and terminates at infinity on two positive charges. The field is strong outside the crystallite, and size dependent polarization terms are more significant.

The model predicts that small gap materials must reach a large crystallite size before optical absorption occurs at the bulk band gap. Large gap materials achieve the bulk band gap at intermediate sizes (~ 60 Å diam) through an approximate cancellation of quantum localization and electrostatic effects. At the smaller diameters where the simple result [Eq. (12)] predicts large blue shifts, it will be necessary to go beyond the effective mass approximation and to consider charge density at the crystallite surface in order to obtain accurate results.

It is interesting to note that metallic crystallites appear to behave like bulk metals in the same size range we consider here.^{19,20} Kreibig concluded that normal metallic properties are present in a silver cluster of 400 atoms (22 Å diam).¹⁹ He suggested that clusters would have to be substantially smaller to show quantum effects.

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