



The Abdus Salam  
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*WINTER COLLEGE ON OPTICS ON OPTICS AND PHOTONICS  
IN NANOSCIENCE AND NANOTECHNOLOGY*

( 7 - 18 February 2005)

*"Electrons and Excitons in Semiconductor  
Nanostructures*

presented by:

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Mumbai  
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**These are preliminary lecture notes, intended only for distribution to participants.**

# **Electrons And Excitons in Semiconductor Nanostructures**

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**Till 31 October 2004 at:**

**Centre for Advanced Technology, Indore**

**PROBLEM:**

**NANOSTRUCTURES ARE MESOSCOPIC:**

*i.e.*, MUCH LARGER THAN SMALL MOLECULES

MUCH TOO SMALL TO BE TREATED AS INFINITE SOLID;

$K_x, K_y, K_z$  NOT A GOOD QUANTUM NUMBER ( DIMENSIONALITY IMPORTANT)

LARGE FRACTION OF ATOMS AT THE SURFACE (RECONSTRUCTION)

**SOLUTION TWO APPROACHES**

**BOTTOM UP *i.e.* MOLECULAR METHODS AT LARGER SIZES**

**TOP DOWN *i.e.* SOLID STATE METHODS *i.e.* BULK SOLID**

**WITH QUANTUM CONFINEMENT EFFECTS**

**THIS IS ELABORATED IN THESE LECTURES**

***GOOD APPROXIMATION IF STRUCTURE IS STABILIZED TO BULK LIKE***

**..... MOSTLY TRUE FOR SEMICONDUCTORS**

**BUT SOME OTHER QUANTUM CONFINED SYSTEMS TOO**

$$\Delta x \Delta p \geq \hbar / 2$$

$$KE = \langle p^2 / 2m \rangle$$

$$\geq \langle p^2 / 2m \rangle - \langle p \rangle^2 / 2m$$

$$\geq (\Delta p)^2 / 2m$$

$$\geq \hbar^2 / (8m(\Delta x)^2)$$

**Discreteness  $\Delta E \gtrsim kT$  has thermodynamic implications,  
also influences electromagnetic response and relaxation pathways  
SPECTROSCOPY IS IMPORTANT**



# Evolution of solutions (Top down)

Effective mass approximation (EMA)

-single band

-multiband

EMPIRICAL TIGHT BINDING  
METHOD

Pseudo-potential Method

**COMPLICATION: SHAPES**

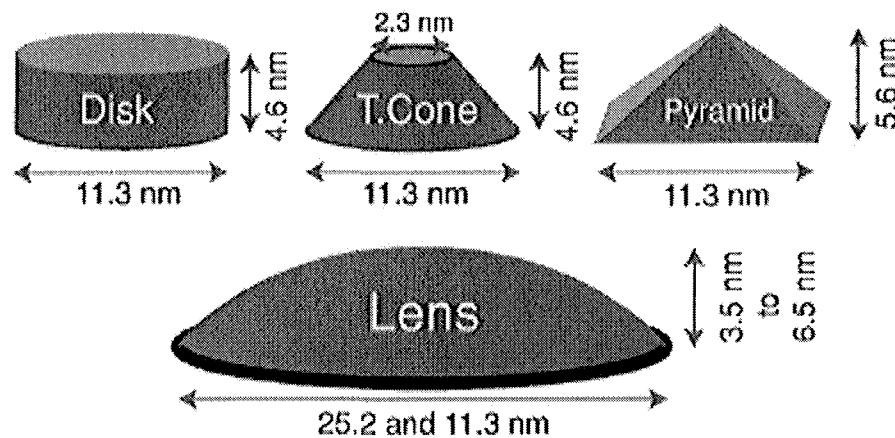
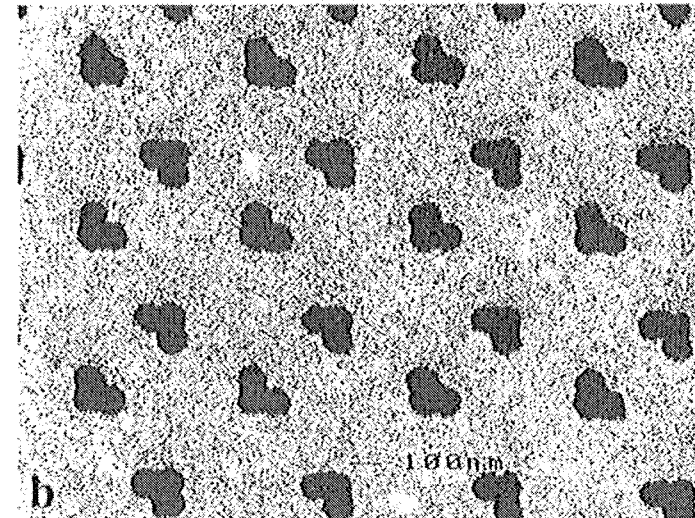


FIG. 1. Shapes and sizes of InAs/GaAs dots considered. Disk, truncated cone (T.Cone), pyramid, and lens.

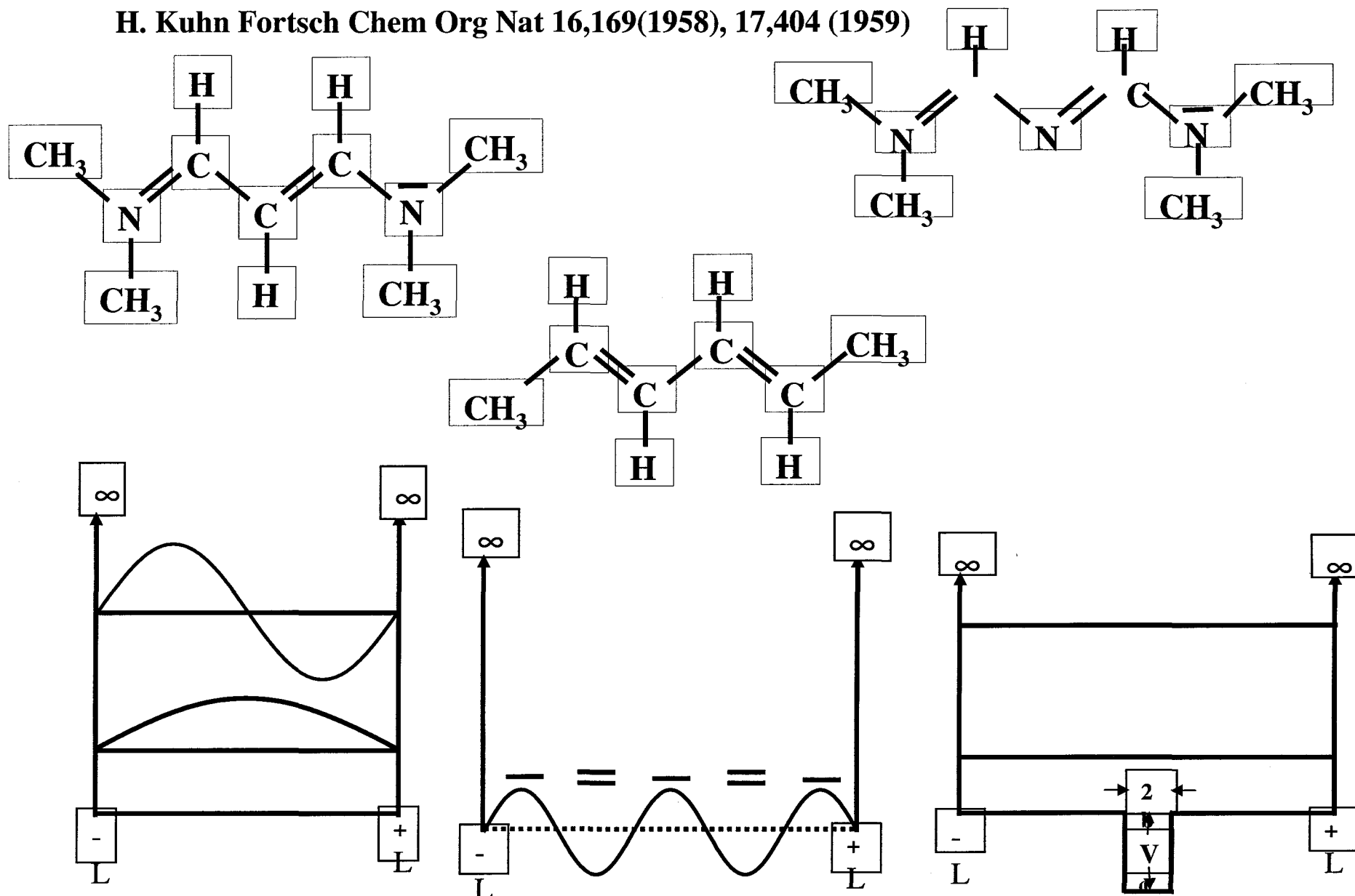


Gabriel Bester and Alex Zunger  
PHYSICAL REVIEW B 71, 045318 (2005)

B.Lamprecht *etal*  
Appl Phys.B68,419(1999)

# QUANTUM CONFINEMENT IN $\pi$ ELECTRON SYSTEMS

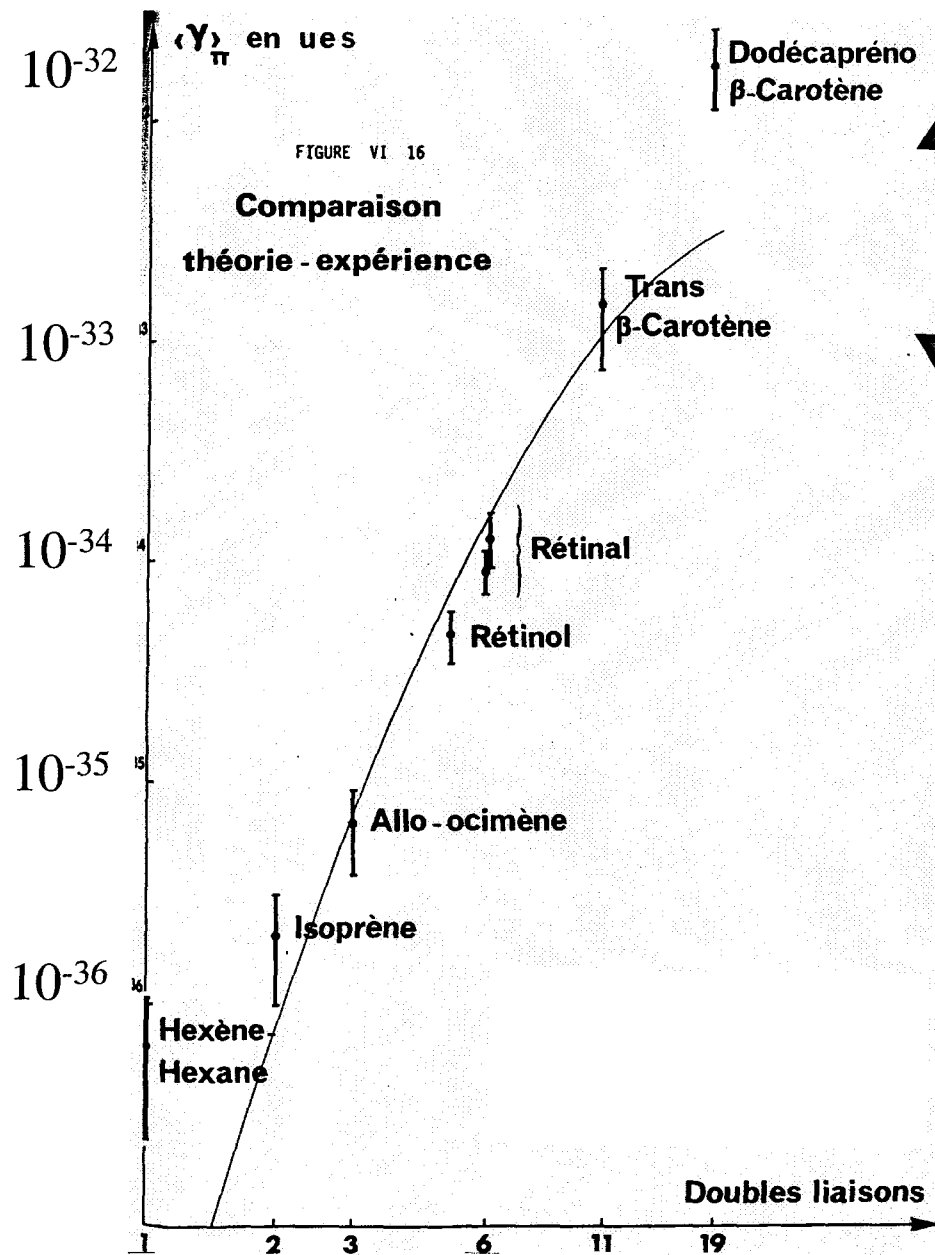
H. Kuhn Fortsch Chem Org Nat 16,169(1958), 17,404 (1959)



NONLINEAR SUSCEPTIBILITIES(Rustagi,Ducuing,Mehendale(1974,79))

$$\alpha = \frac{4L^4}{a_0} \sum_{n=1}^N \left\{ \frac{-2}{3\pi^2 n^2} + \frac{10}{3\pi^4 n^4} \right\}$$

$$\begin{aligned} \gamma &= \frac{128 L^{10}}{a_0^3 e^2} \sum_{n=1}^N \left\{ \frac{-2}{9\pi^6 n^6} + \frac{140}{3\pi^8 n^8} - \frac{440}{\pi^{10} n^{10}} \right\} \\ &\cong \frac{256 L^5 d^5}{45 a_0^3 e^2 \pi^6} \end{aligned}$$



**RESONANT ENHANCEMENT**

J.-P.Hermann These(1974)

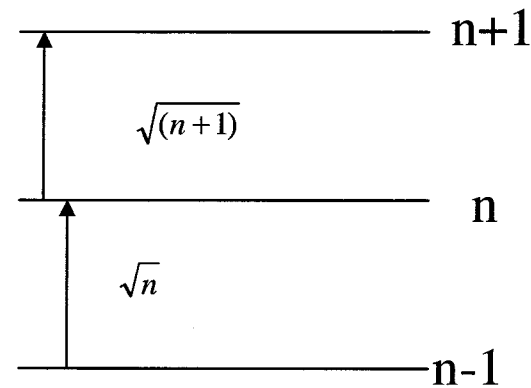
$$H_0 = p^2 / 2m + \frac{1}{2} m \omega_0^2 x^2$$

$$H = p^2 / 2m + \frac{1}{2} m \omega_0^2 x^2 - \frac{eEx}{m \omega_0^2}$$

$$H = p^2 / 2m + \frac{1}{2} m \omega_0^2 \left( x - \frac{eE}{m \omega_0^2} \right)^2 - \left( \frac{eE}{m \omega_0^2} \right)^2$$

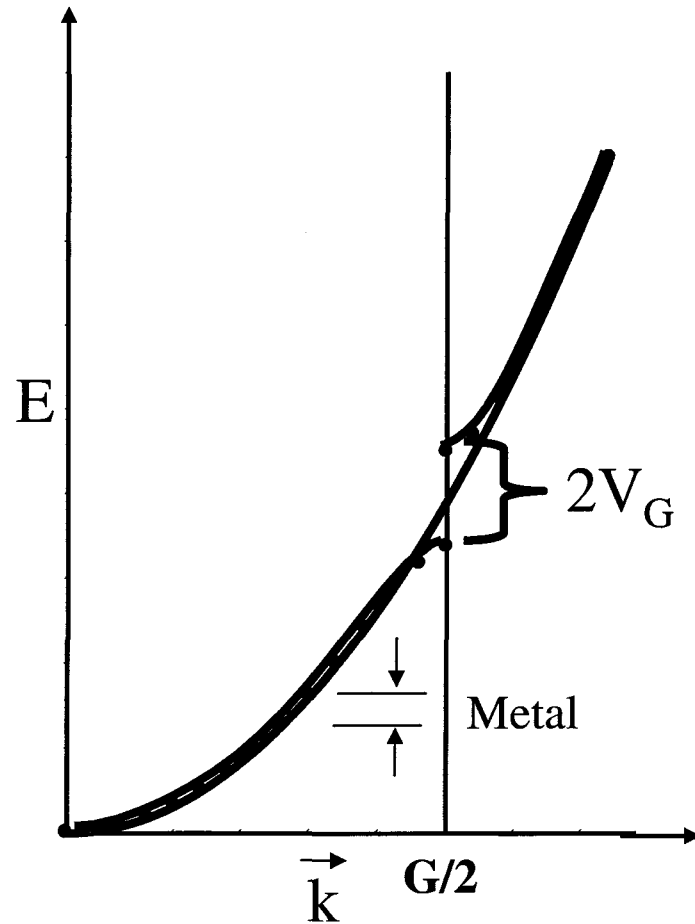
$$\alpha = \frac{e^2}{m \omega_0^2}$$

$$\beta = \gamma = 0$$



**One dimensional metal**

$$\lambda_{\max} \sim L$$



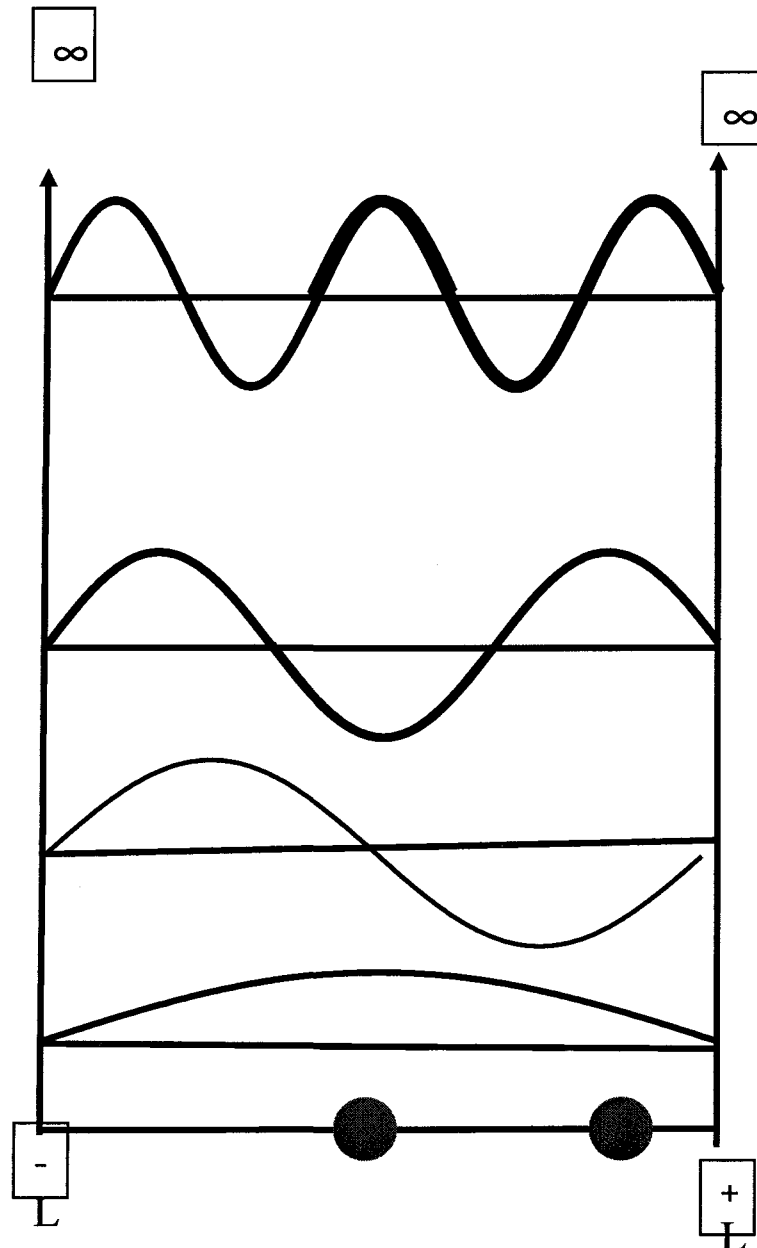
**One dimensional semiconductor**

$$\lambda_{\max} \sim \lambda_{gap} + A/L^2$$

**Localized perturbation in the middle  
lowers energy of alternate levels**

$$\lambda_{\max} \sim AL \pm B/L$$

**ENVELOPE APPROXIMATION GOOD**



$$E_n^{(1)} = \langle n | H' | n \rangle$$

....depends on  $|\psi|^2$   
at impurity position

**IN QUANTUM CONFINED SYSTEMS  
EFFECT OF SUBSTITUTION  
DEPENDS ON POSITION OF THE  
IMPURITY**

***For linear conjugated chains:***

***Rustagi and Ducuing Opt Comm 10,258(1974)***

***Nonlinearity increases rapidly with chain length***

***And with “anharmonicity”***

***which can be increased by chemical substitution***

***Mehendale and Rustagi Opt Comm 28,359(1979)***

***In NONLINEAR OPTICAL PROPERTIES OF POLYMERS  
(MRS, 1988)***

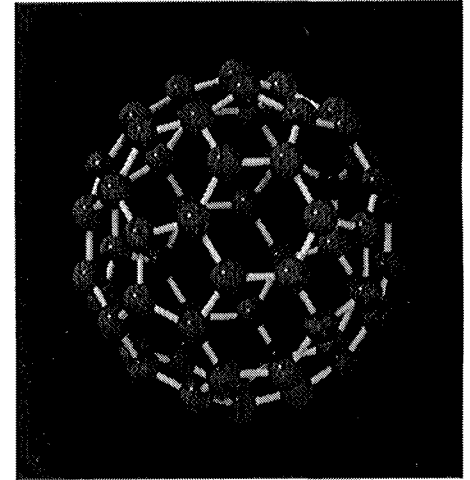
***S.H. Stevenson et al (DUPONT)***

***.... as predicted by Rustagi, significant enhancement of third-order nonlinear polarizability in a linear conjugated system can be achieved by simple structural modifications which act mainly to increase the anharmonicity of its representative effective oscillator.***

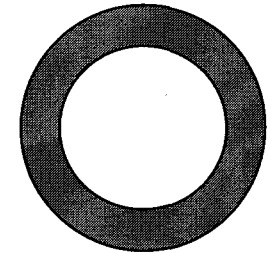


*For fullerenes: depolarization field reduces the effective field substantially*

*Implying much smaller nonlinearity than for linear molecules*



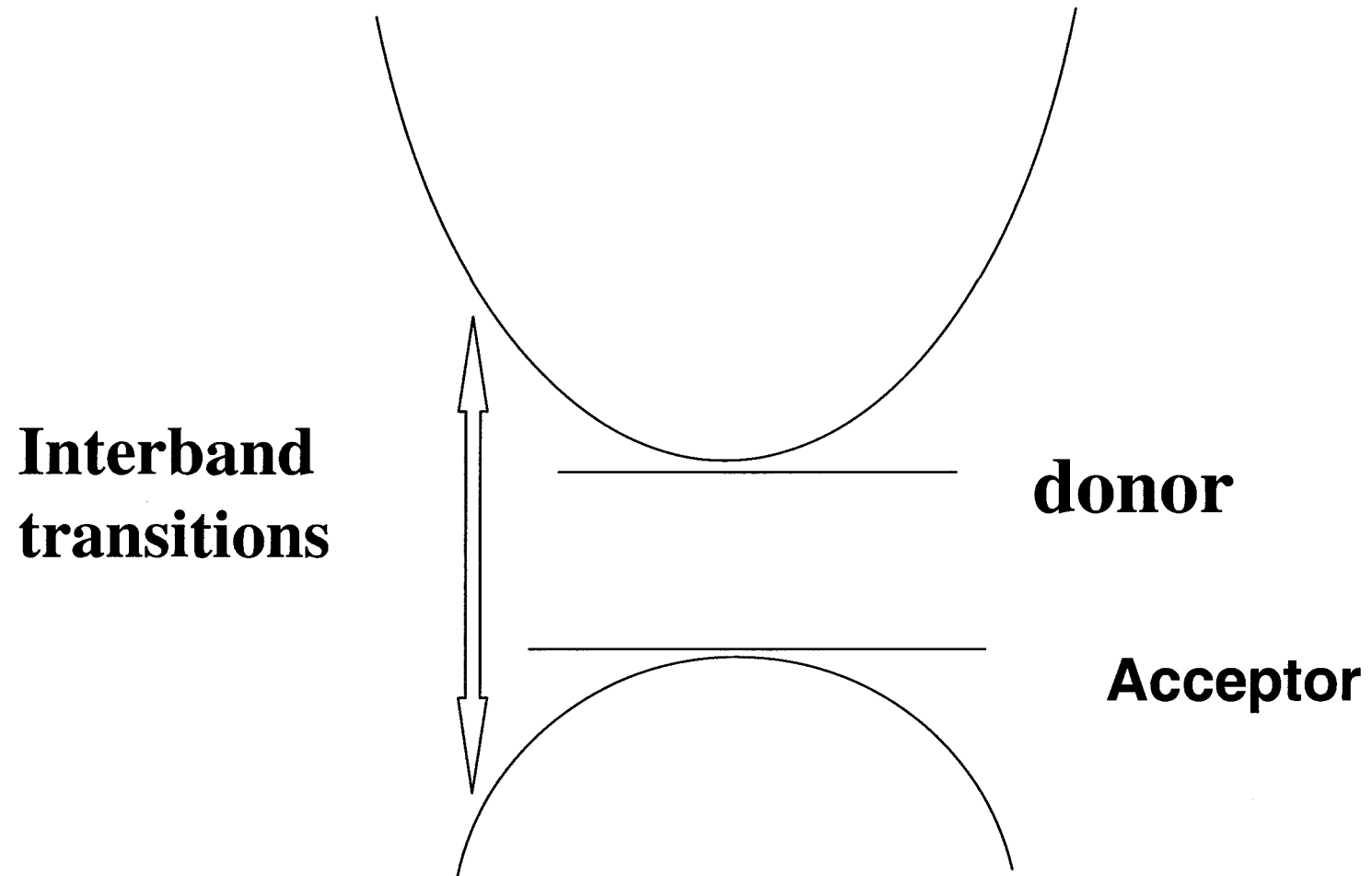
**ICOSAHEDRAL PSEUDOPOTENTIAL**



Nair  
1992

*Dimensionality matters a lot for nonlinear response!*

# Intrinsic Bulk Semiconductor



## EFFECTIVE MASS OR ENVELOPE FUNCTION METHOD

$$H = KE + V_{periodic} + V_{imp}$$

$$\Psi(r) = \psi(r)u_c(r)$$

$$(p^2 / 2m_{ij}^* + V_{imp})\psi(\vec{r}) = \epsilon\psi(\vec{r})$$

$m_{ij}^*$  effective mass

$$\hbar^2 / m_{ij}^* = \partial^2 E / \partial k_i \partial k_j$$

**Main Assumption** :  $V_{imp}$  varies slowly over lattice constant

**GENERALIZED TO DEGENERATE VALENCE BANDS**

*Kohn and Luttinger (1955)  
for shallow impurities*

**R J Elliot (1956) for excitons**

## Quantum confined systems

$$V_{imp} \longrightarrow V_{confinement}$$

$$V_{confinement} = V(z)$$

**Quantum Well**

$$V_{confinement} = V(x, y)$$

**Quantum Wire**

$$V_{confinement} = V(x, y, z)$$

**Quantum Dot/BOX**

$$\Psi(r) = \psi(r)u_c(r)$$

$$(p^2 / 2m_{ij}^* + V_{confinement})\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

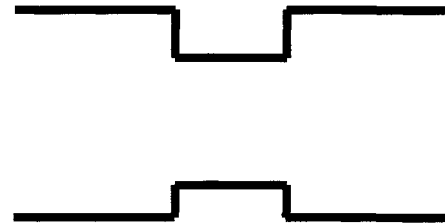
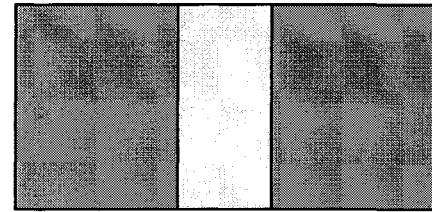
## Quantum Wells

Assume: confinement potential slowly varying

$u_c, u_v$  same in the two materials

SOLVE ENVELOPE FUNCTION EQUATIONS

MATCH AT THE BOUNDARY  $z = \pm L$



### PROBLEMS:

1. Barrier height? Quite often inferred indirectly from optical spectroscopy using rather simple theories, so still changing

2.  $m_{barrier}^* \neq m_{well}^*$

$$p_z^2 / 2m^* \rightarrow p_z (1/m^*(z)) p_z$$

e.g., M. Altarelli in *Interfaces, Quantum wells, and superlattices*, eds Leavens and Taylor, Plenum (1988)

Refs: G. Bastard "Wave mechanics applied to semiconductor heterostructures, Les Edision de Phys (1988)

C. Weisbuch and B. Vinter Quantum Semiconductor structures, Academic (1991)

## Spherical Quantum Dot

$$\psi_{nlm}(r, \theta, \phi) = \frac{2^{1/2}}{R^{3/2}} \frac{1}{j_{l+1}(\zeta_{nl})} j_l\left(\zeta_{nl} \frac{r}{R}\right) Y_{lm}(\theta, \phi),$$

$$E_0 = \frac{\hbar^2}{2m^* R^2} \zeta_{nl}^2$$

$\zeta_{nl}$  zeros of the spherical Bessel function.

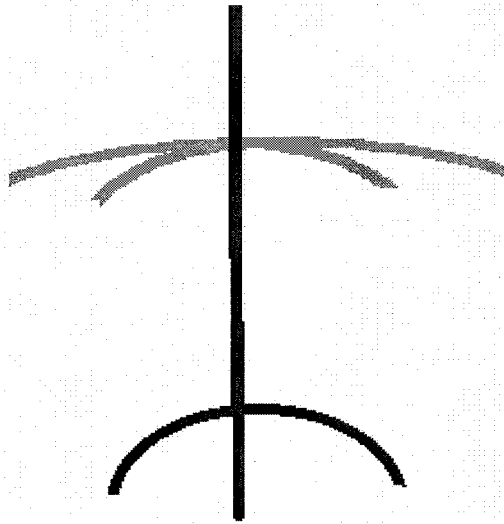
## Cylindrical Quantum Dot

$$\Psi_{\nu, n, s} = \frac{\sqrt{2}}{\sqrt{z_0}} \sin\left(\frac{\nu\pi}{z_0}(z + z_0/2)\right) \psi_{ns}(\rho, \phi), \quad \nu = 1, 2, 3, \dots$$

$$\psi_{ns}(\rho, \phi) = \frac{2}{\rho_0} \frac{1}{\sqrt{\pi} J_{n+1}(\alpha_{ns})} J_n\left(\alpha_{ns} \frac{\rho}{\rho_0}\right) \zeta_n(\phi)$$

$$n = 1, 2, \dots, \quad s = 1, 2, \dots,$$

## MULTI BAND EFFECTIVE MASS CALCULATION



$\Gamma_8$

$$u_{-3/2} = |X - iY\rangle \downarrow / \sqrt{2}$$

$$u_{3/2} = -|X + iY\rangle \uparrow / \sqrt{2}$$

$$u_{1/2} = -|X + iY\rangle \downarrow / \sqrt{6} + \sqrt{2/3}|Z\rangle \uparrow$$

$$u_{1/2} = |X - iY\rangle \uparrow / \sqrt{6} + \sqrt{2/3}|Z\rangle \downarrow$$

$\Gamma_7$

$$E(k) = (\hbar^2 / 2m)(\gamma_1 k^2 \pm [4\gamma_2^2 k^4 + 12(\gamma_3^2 - \gamma_2^2)(k_x^2 k_y^2 + k_y^2 k_z^2 + k_x^2 k_z^2)]^{1/2})$$

J.M.Luttinger Phys Rev 102,1030(1956)

$$H = (\hbar^2 / 2m) \begin{pmatrix} P_{3/2} & -S & R & 0 \\ -S^* & P_{1/2} & 0 & R \\ R^* & 0 & P_{-1/2} & S \\ 0 & R^* & S^* & P_{-3/2} \end{pmatrix}$$

$$P_{3/2} = P_{-3/2} = \gamma_1 k^2 + \gamma_2 (k_x^2 + k_y^2 - 2k_z^2)$$

$$P_{1/2} = P_{-1/2} = \gamma_1 k^2 - \gamma_2 (k_x^2 + k_y^2 - 2k_z^2)$$

$$R = -(\sqrt{3}/2)(\gamma_2 + \gamma_3)(k_x - ik_y)^2 + \sqrt{3}/2(\gamma_3 - \gamma_2)(k_x + ik_y)^2$$

$$S = 2/\sqrt{3}\gamma_3 k_z (k_x - ik_y)$$

$\gamma_i$  Luttinger parameters

$$\vec{k} = -i\vec{\nabla}$$

To get envelope equation

J.M.Luttinger Phys Rev 102,1030(1956)



***For semiconductor quantum dots grown by soft chemical methods confinement potential is relatively large and can be assumed to be infinite.***

***In semiconductors confined by a larger gap semiconductor the band offset is generally small  $\sim 0.1$  to  $1\text{eV}$  Resulting finite well problem is generally more difficult to solve***

**Also boundary conditions uncertain, but perturbative treatment possible for small variations in shape.**

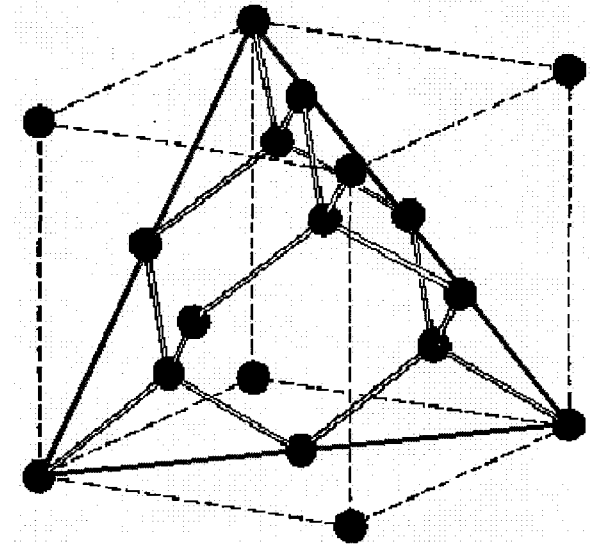
**Empirical Tight Binding method**  
**P.E. Lippens and M. Lannoo,  $sp^3$ \***  
**Phys. Rev. B 39, 10 935 (1989)**

**S. Sapra, N. Shanthi, and D.D. Sarma,**  
**Phys. Rev. B 66, 205202 (2002)**

**S. Sapra, and D.D. Sarma,**  
**Phys. Rev. B 69, 125304 (2004)**

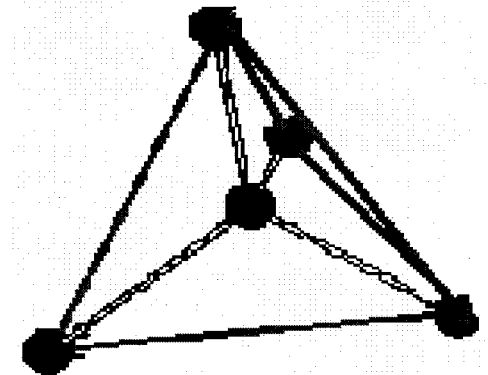
**for II-VI COMPOUND QUANTUM DOTS  $sp^3d^5$**

**“Direct diagonalization methods are practical only for cluster sizes containing less than ;1500 atoms. For larger clusters, we use the Lanczos iterative method”**



		ZnS	ZnSe	ZnTe	CdS	CdSe	CdTe
$a(\text{Å})$		5.41	5.67	6.10	5.82	6.05	6.48
$N_s$	$N$	$d(\text{Å})$					
12	1285	36.49	38.24	41.14	39.25	40.80	43.70

**EFFECTIVE BOND ORBITAL MODEL(Y.C. CHANG)**



**REDUCED NUMBER OF ORBITALS CAN MANAGE LARGER PARTICLES**  
**ALSO FEWER PARAMETERS, BUT NOT FROM BASIC THEORIES**

## VALENCE BAND MODEL

Y.-C. Chang PRB 37,8215(1988)

6 orbitals =  $x \uparrow, x \downarrow, y \uparrow, y \downarrow, z \uparrow, z \downarrow,$

$$\langle R\alpha | H | R'\alpha' \rangle = E_p \delta_{R,R'} \delta_{\alpha\alpha'} +$$

$$\sum_{\tau} \delta_{R-R',\tau} \{ E_{xy} \tau_{\alpha} \tau_{\alpha'} (1 - \delta_{\alpha\alpha'}) + [E_{xx} \tau_{\alpha}^2 + E_{zz} (1 - \tau_{\alpha}^2)] \delta_{\alpha\alpha'} \}$$

$|R,\alpha\rangle$  orbital at  $R$  and  $\alpha = x, y, z$   $\tau$  nearest neighbor displacement vectors  
 $E_p$  site energy,  $E_{xx}, E_{xy}, E_{zz}$  interaction energies

## Conduction Valence Band Model

$$\langle \mathbf{R}_s | H | \mathbf{R}'_s \rangle = E_s \delta_{\mathbf{R},\mathbf{R}'} + \sum_{\tau} E_{ss} \delta_{\mathbf{R}-\mathbf{R}',\tau}$$

$$\langle \mathbf{R}_s | H | \mathbf{R}'_{\alpha} \rangle = \sum_{\tau} E_{sx} \tau_{\alpha} \delta_{\mathbf{R}-\mathbf{R}',\tau}$$

Nair, Ramaniah, Rustagi PRB 45,5969(1992)

**To include spin orbit coupling**

**Form combinations transforming like  $j=3/2$ , or  $j=1/2$  states**

**Shift  $j=3/2$  like states above  $j=1/2$  like states**

**The new matrix elements are related to the old ones by  $C(\alpha, \sigma; J, M)$  Clebsch-Gordon coefficients**

$$\begin{aligned} \langle \mathbf{R}, JM | H | \mathbf{R}', J'M' \rangle = & \sum_{\alpha, \alpha', \sigma} C^*(\alpha \sigma; JM) \\ & \times C(\alpha' \sigma; J'M') \\ & \times \langle \mathbf{R} \alpha | H | \mathbf{R}' \alpha' \rangle \end{aligned}$$

**USE SYMMETRY TO REDUCE MATRIX SIZE**

**FORM LINEAR COMBINATIONS THAT TRANSFORM LIKE  
IRREDUCIBLE REPRESENTATIONS OF TETRAHEDRAL GROUP**

$$\sum_{n,i,v} C_n^{iv} u_v^{\Gamma_i} (R_n)$$



**$n$  th component of  $\Gamma_i$  irreducible representation**

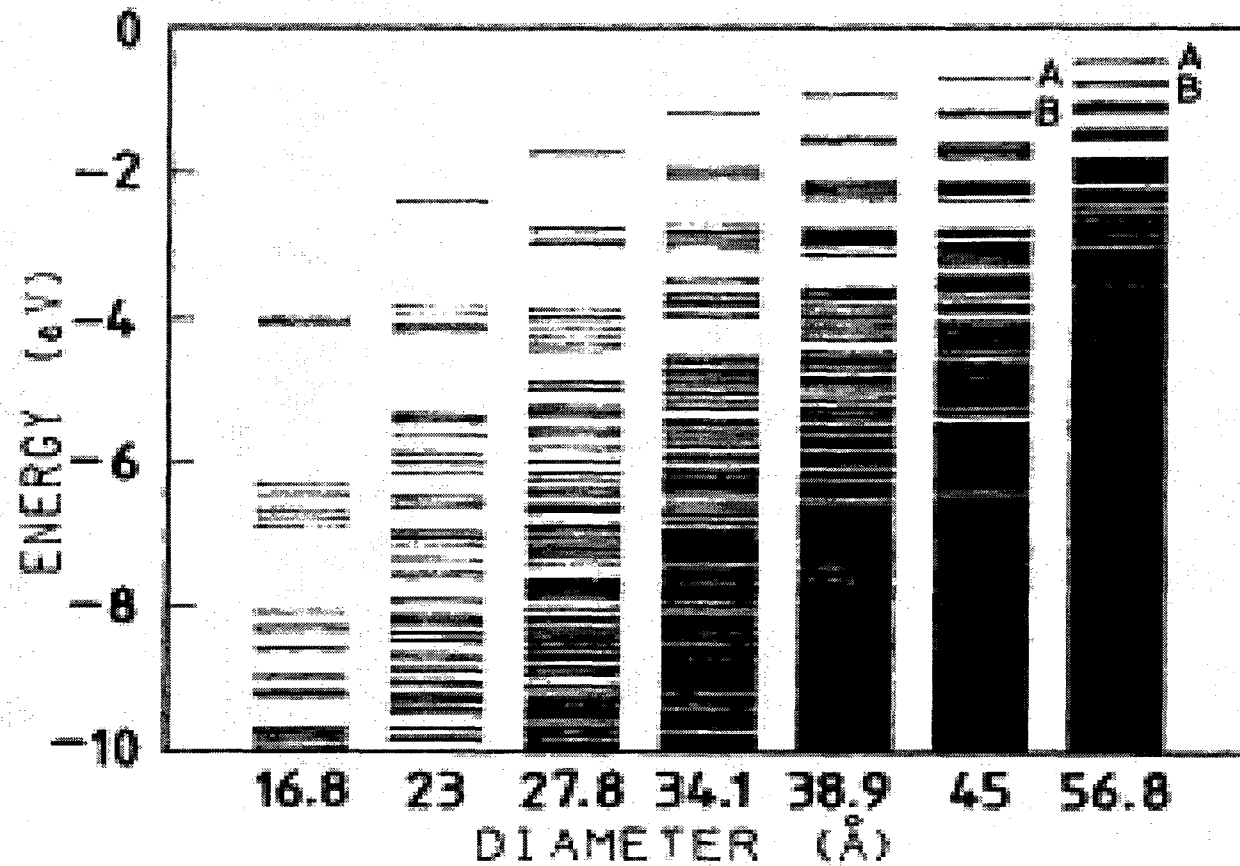
## FITTING PARAMETERS NEAR ZONE CENTER

$$\begin{aligned}
 H_{\alpha\alpha'}(\mathbf{k}) = & [(E_p + 8E_{xx} + 4E_{zz}) - (E_{xx} + E_{zz})k^2 a^2 / 2 \\
 & + (E_{zz} - E_{xx})k_\alpha^2 a^2 / 2] \delta_{\alpha\alpha'} \\
 & + (-E_{xy} k_\alpha k_{\alpha'} a^2) (1 - \delta_{\alpha\alpha'}) .
 \end{aligned}$$

TABLE II. Tight-binding parameters for VBM and CVBM, which reproduce band structure close to the  $\Gamma$  point accurately.  $\mathcal{E}_0 = \hbar^2 / 2m_0 a^2$ .

VBM	CVBM
$E_p = E_c - 12\gamma_1 \mathcal{E}_0$	$E_{xx} = (\gamma_1 - 2\gamma_2) \mathcal{E}_0 + X_{\text{LH-SO}} / 16$
$E_{xx} = (\gamma_1 + 4\gamma_2) \mathcal{E}_0$	$E_{zz} = (\gamma_1 - 2\gamma_2) \mathcal{E}_0 - X_{\text{LH-SO}} / 16$
$E_{zz} = (\gamma_1 - 8\gamma_2) \mathcal{E}_0$	$E_{xx}^2 = E_g / 8 [(\gamma_1 + \gamma_2) \mathcal{E}_0 - (3E_{xx} + E_{zz}) / 4]$
$E_{xy} = 6\gamma_3 \mathcal{E}_0$	$E_{xy} = 6\gamma_3 \mathcal{E}_0 + 16E_{xx}^2 / E_g$
	$E_s = E_c + 12\hbar^2 / 2m_c - 64E_{xx}^2 [2/E_g + 1/(E_g + \Delta)]$
	$E_{ss} = -\hbar^2 / 2m_c + [2/E_g + 1/(E_g + \Delta)] 16E_{xx}^2 / 3$
	$E_p = E_c - (8E_{xx} + 4E_{zz})$

Nair, Ramaniah, Rustagi PRB 45, 5969 (1992)



**FIG. 2.** The energy levels of GaAs crystallites calculated using the VBM with parameters obtained by fitting the  $\Gamma$ -point masses. The results for seven different crystallite sizes ranging from 16.8 to 56.8 Å diameter are shown. The zero of the energy scale is at the bulk valence-band edge.

Nair,Ramaniah,Rustagi PRB 45,5969(1992)

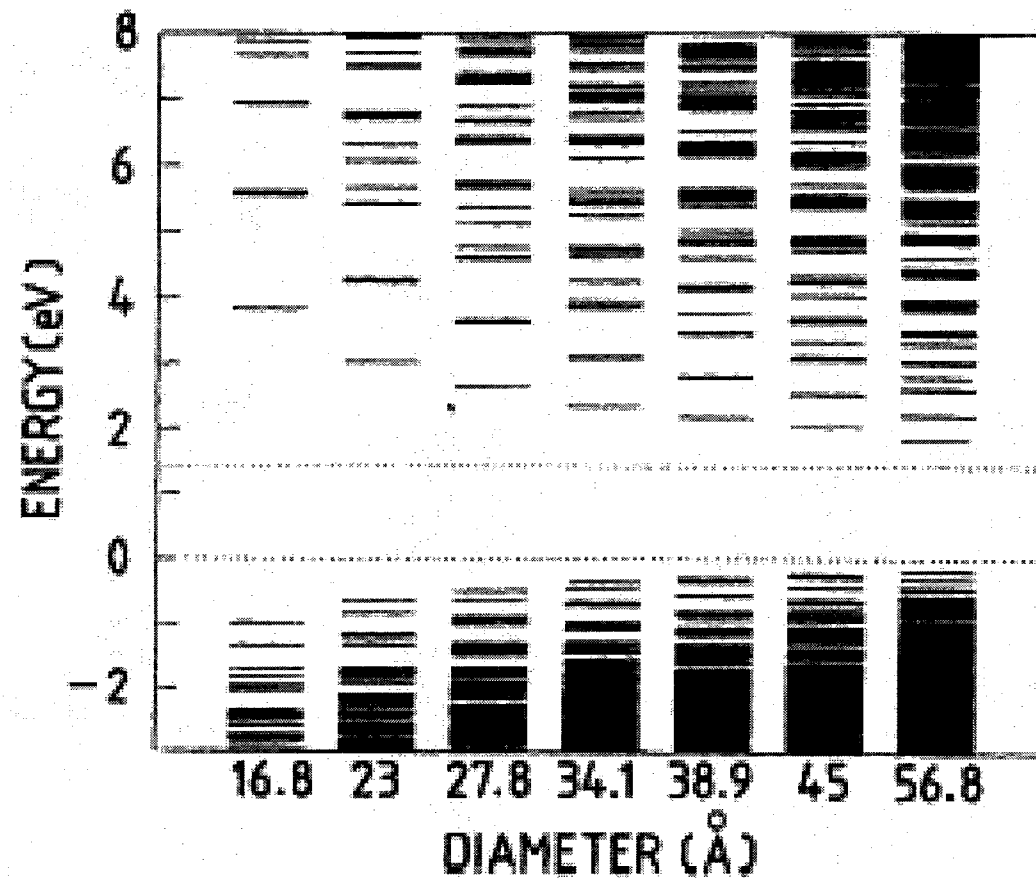


FIG. 4. The electron- and hole-energy levels of GaAs crystal-lites given by CVBM. The positions of the bulk valence- and conduction-band edges are indicated by dotted lines.



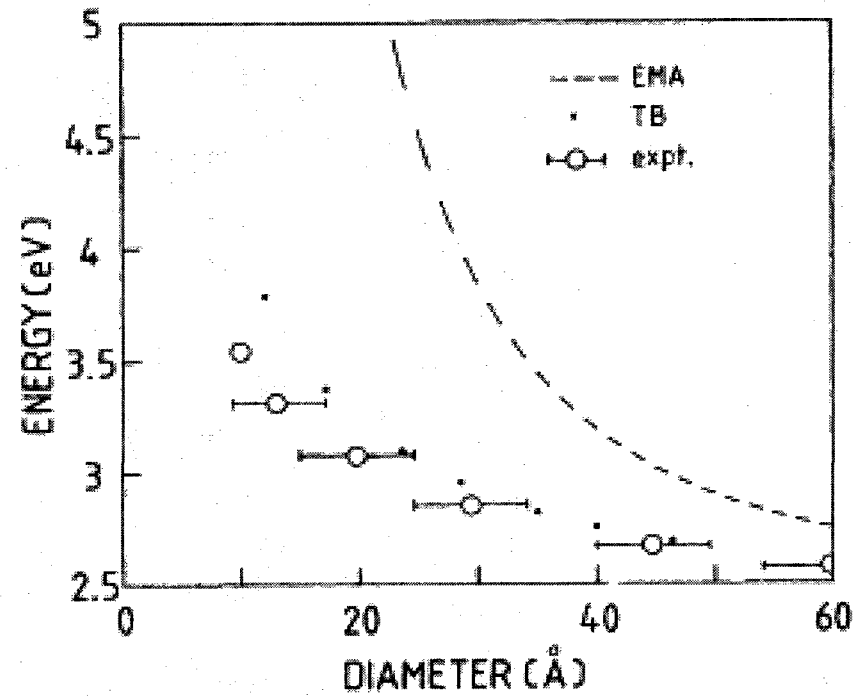


FIG. 9. The size dependence of the exciton position in CdS crystallites. The dots represent the result of a tight-binding calculation using CVBM. The dashed line is given by an effective-mass calculation using a three-band model for the valence band and a single-band model for the conduction band. The open circles represent experimental data (Ref. 7).

**TABLE I.** The confinement energies (in eV) for a few top-most valence-band levels in CdS quantum dots. The symmetry of each level is also indicated.

<b>Diameter (Å)</b>	<b>One-band EMA</b>	<b>Multiband EMA</b>	<b>Tight-binding (EBOM)</b>
<b>70</b>	<b>0.038</b>	<b>0.076 (<math>\Gamma_8^+</math>)</b>	<b>0.07 (<math>\Gamma_8^+</math>)</b>
		<b>0.106 (<math>\Gamma_6^+</math>)</b>	
		<b>0.091 (<math>\Gamma_8^-</math>)</b>	
		<b>0.139 (<math>\Gamma_7^-</math>)</b>	
<b>38</b>	<b>0.130</b>	<b>0.236 (<math>\Gamma_8^+</math>)</b>	<b>0.19 (<math>\Gamma_8^+</math>)</b>
		<b>0.266 (<math>\Gamma_6^+</math>)</b>	<b>0.22 (<math>\Gamma_6^+</math>)</b>
		<b>0.299 (<math>\Gamma_8^-</math>)</b>	<b>0.20 (<math>\Gamma_8^-</math>)</b>
		<b>0.347 (<math>\Gamma_7^-</math>)</b>	<b>0.25 (<math>\Gamma_7^-</math>)</b>
<b>24</b>	<b>0.326</b>	<b>0.576 (<math>\Gamma_8^+</math>)</b>	<b>0.43 (<math>\Gamma_8^+</math>)</b>
		<b>0.606 (<math>\Gamma_6^+</math>)</b>	<b>0.46 (<math>\Gamma_6^+</math>)</b>
		<b>0.743 (<math>\Gamma_8^-</math>)</b>	<b>0.41 (<math>\Gamma_8^-</math>)</b>
		<b>0.791 (<math>\Gamma_7^-</math>)</b>	<b>0.46 (<math>\Gamma_7^-</math>)</b>

Refs: Colvin et al PRL 66,2786(1991), Nair et al PRL 68,893(1992)

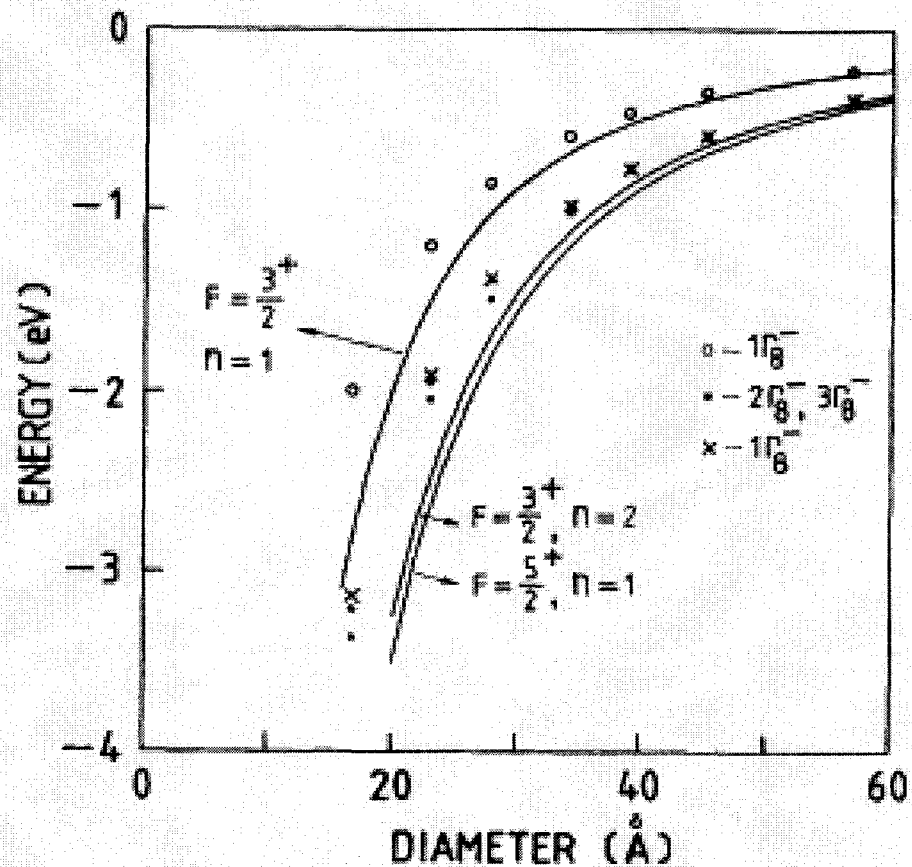


FIG. 3. The size dependence of a few topmost valence-band levels (circles, crosses, and dots) in GaAs crystallites obtained using VBM. The solid lines represent the corresponding results given by a multiband effective mass calculation. The notation  $n\Gamma_v^\pm$  stands for the  $n$ th level of  $\Gamma_v^\pm$  symmetry.

Nair,Ramaniah,Rustagi PRB 45,5969(1992)

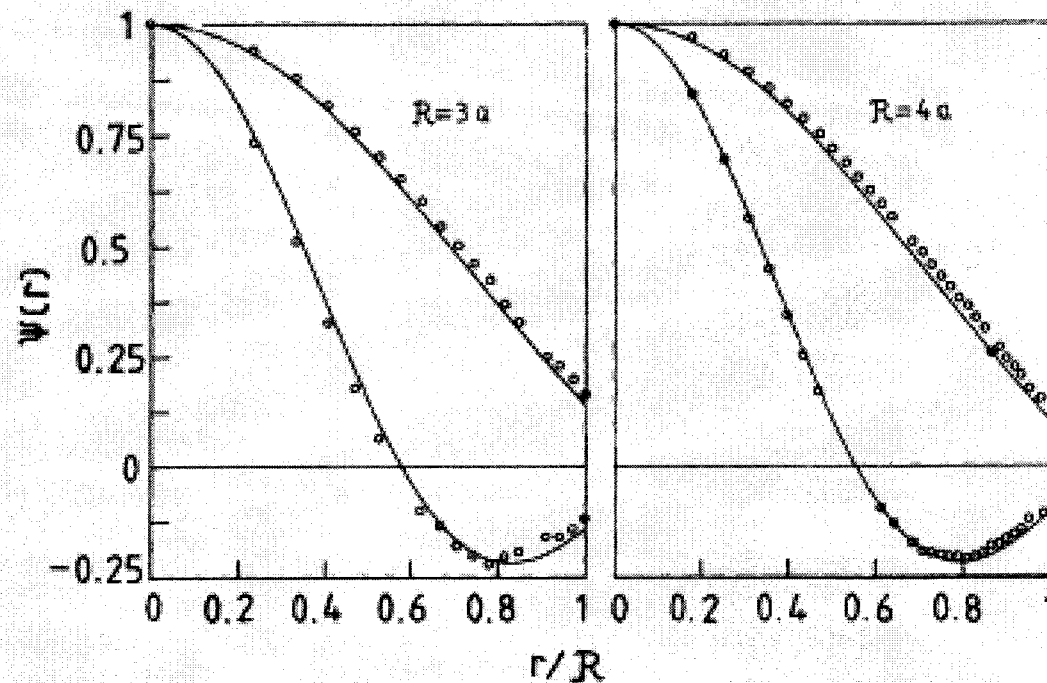


FIG. 6. The lowest two  $l=0$  EMA envelope functions for the conduction band obtained using a single parabolic band model with a confining potential of 10 eV (solid line) compared with the corresponding wave function given by CVBM for GaAs crystallites (open circles). The results for two crystallite sizes are shown.

Nair,Ramaniah,Rustagi PRB 45,5969(1992)

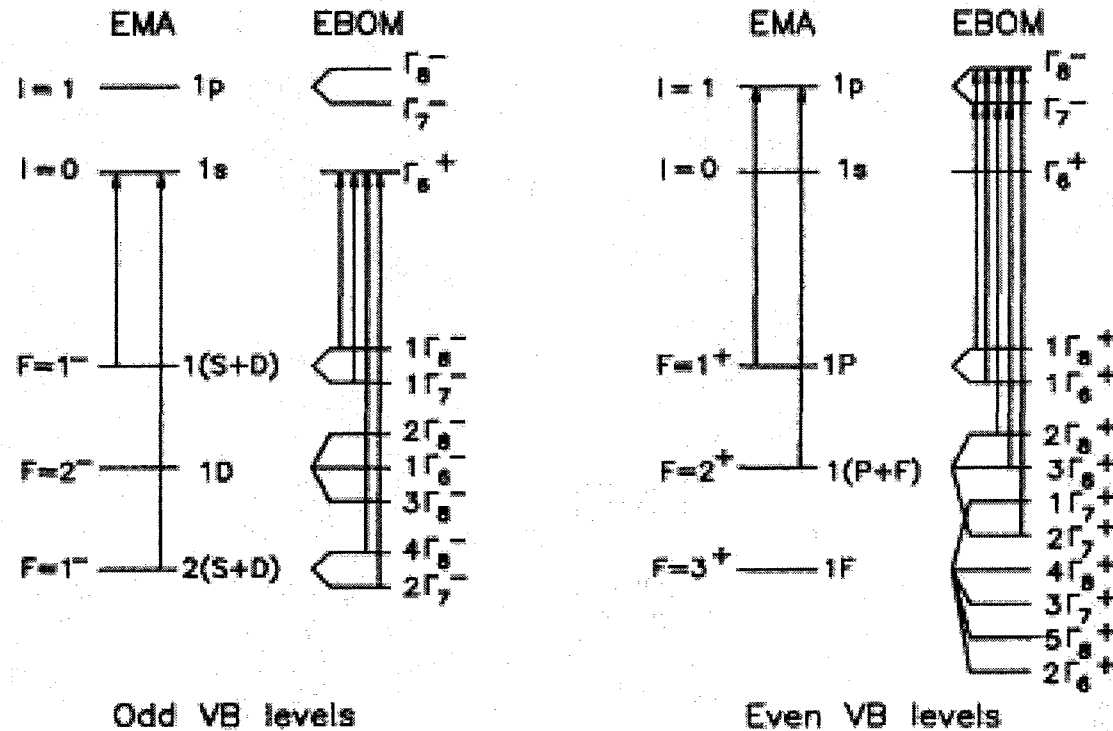


FIG. 1. Correspondence between the qualitative level structure of the near-band-edge energy levels obtained using the EBOM and the EMA, for CdS QD's. In the EMA, a three-band model for the valence band (VB) and a single-band model for the conduction band (CB) have been used. The interband transitions, allowed according to the EMA selection rules, are also indicated.

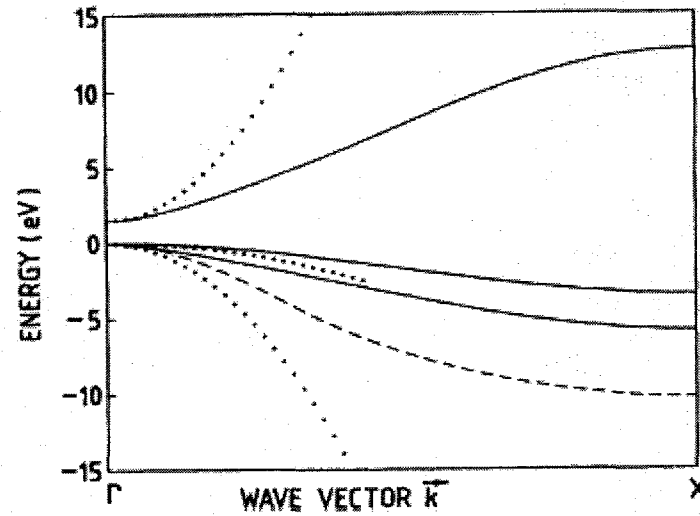


FIG. 1. The calculated band structure of the valence and conduction bands for GaAs along the  $\Gamma$ -X direction using an effective bond-orbital model with parameters obtained by fitting the bulk  $\Gamma$ -point masses. The dashed lines are obtained in a valence-band model (VBM), while the solid lines are given by the CVBM which includes a conduction-band orbital also; both give identical dispersions for the heavy-hole band. The parabolic dispersions given by the band-edge masses are also shown (dotted lines).

Nair,Ramaniah,Rustagi PRB 45,5969(1992)

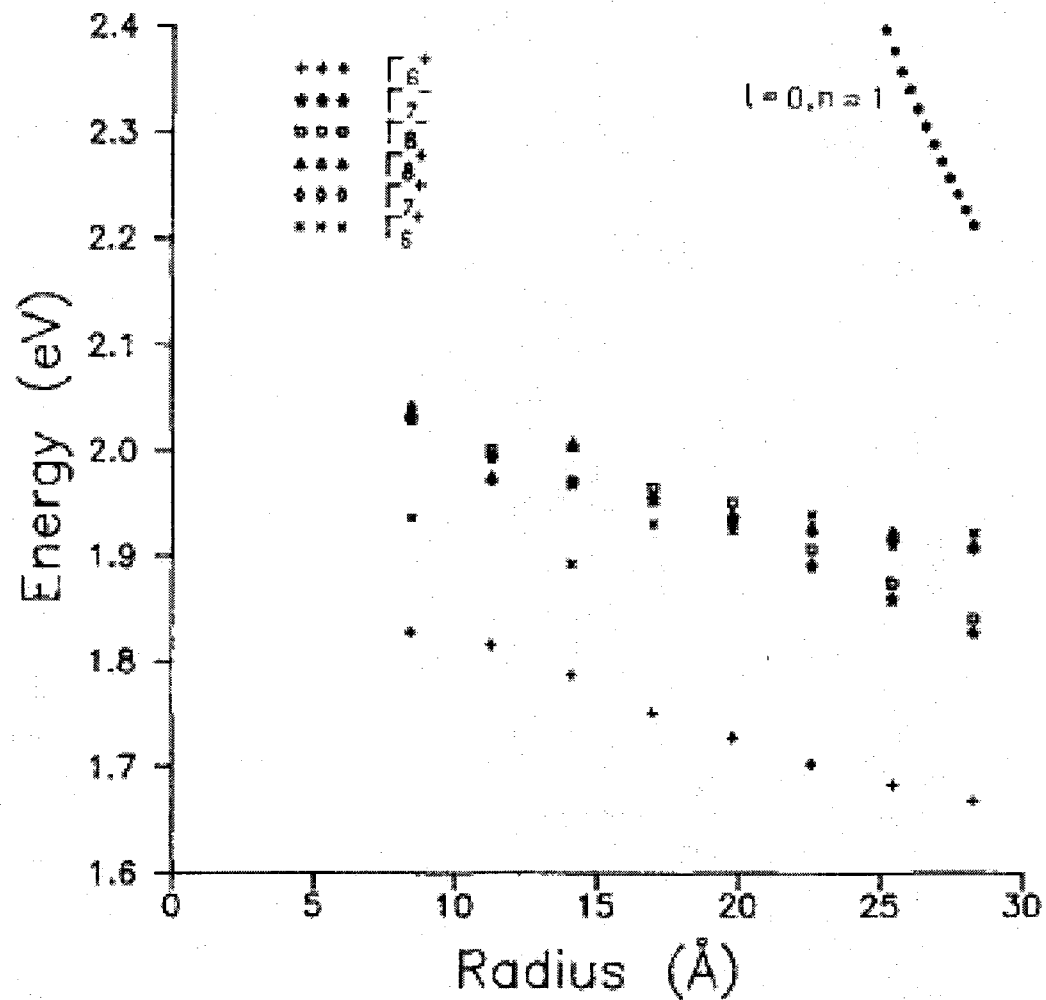


Fig. 2. The size dependence of the first six CB levels (pluses, stars, squares, triangles, diamonds, and crosses) in GaAs QDs, calculated within the effective-bond-orbital-model. The  $l = 0, n = 1$  level predicted by a single band effective mass approximation is also shown.

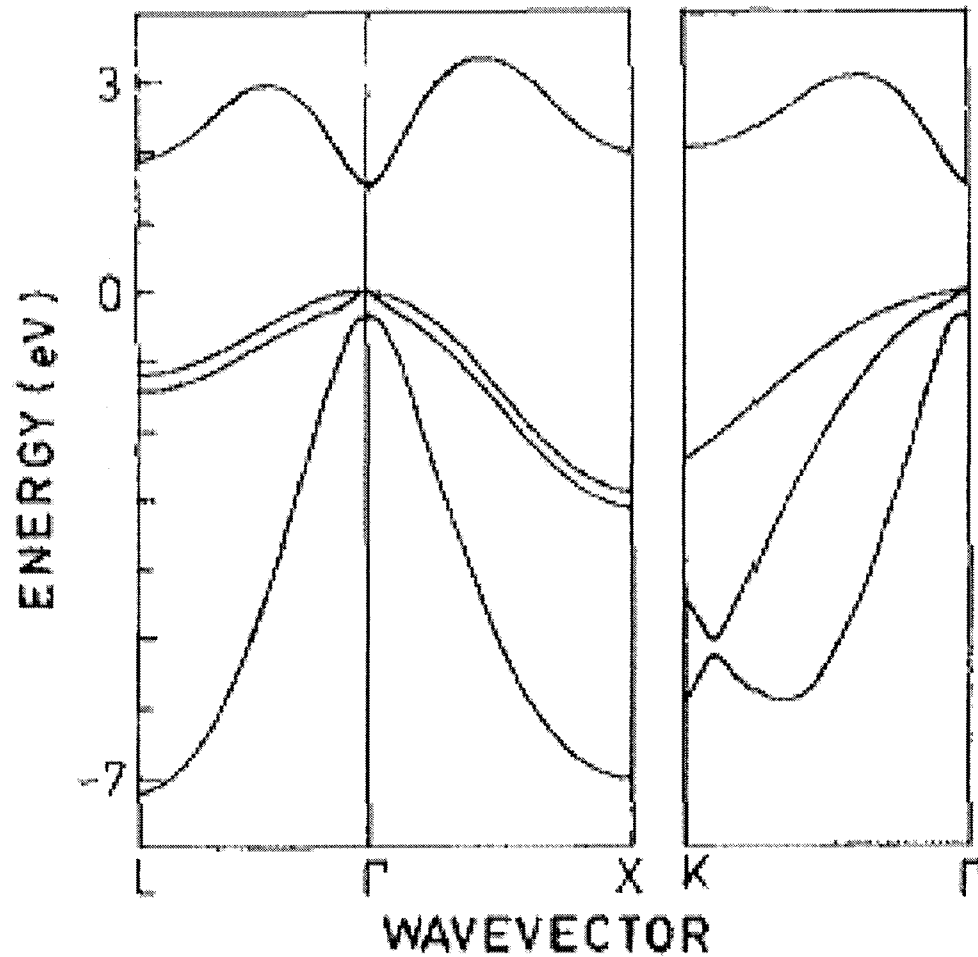


Fig. 1. The bulk band structure of cubic GaAs obtained using the effective-bond-orbital-model.



## SELECTION RULES

band index,

$$\Psi = \sum_b \int d\vec{k} A^b(\vec{k}) e^{i\vec{k}\cdot\vec{r}} u_{b\vec{k}}(\vec{r})$$

$$[\mathcal{E}(-i\vec{\nabla}) + U(\vec{r})]F_n(\vec{r}) = \varepsilon_n F_n(\vec{r})$$

$$F_n(\vec{r}) = \int e^{i\vec{k}\cdot\vec{r}} A_n(\vec{k}) d\vec{k}$$

$$F_{nlm}(\vec{r}) = \frac{\sqrt{2}}{R^{3/2}} \frac{1}{j_{l+1}(\zeta_{nl})} j_l\left(\zeta_{nl} \frac{r}{R}\right) Y_{lm}(\theta, \phi)$$

$$\langle vnlm | \vec{p} | cn'l'm' \rangle =$$

$$\sum_{kk'} \sum_{\vec{R}_i} A_{nlm}^* (\vec{k}) A_{n'l'm'} (\vec{k}') e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_i}$$

$$\int_{\text{cell}} u_{v\vec{k}}^* (\vec{r}) (\hbar \vec{k}' + \vec{p}) u_{c\vec{k}'} (\vec{r}) e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} d\vec{r}$$

**FOR INFINITE SOLIDS**

$$\sum_{\vec{R}_i} e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}_i} = \delta_{\vec{k}, \vec{k}'}$$

**FOR QD CORRECTIONS ~ a/R**

$$\langle vnlm | \vec{p} | cn'l'm' \rangle \approx \vec{p}_{cv}(0) \delta_{nlm, n'l'm'}$$

$$IF \quad \vec{p}_{cv}(0) = 0$$

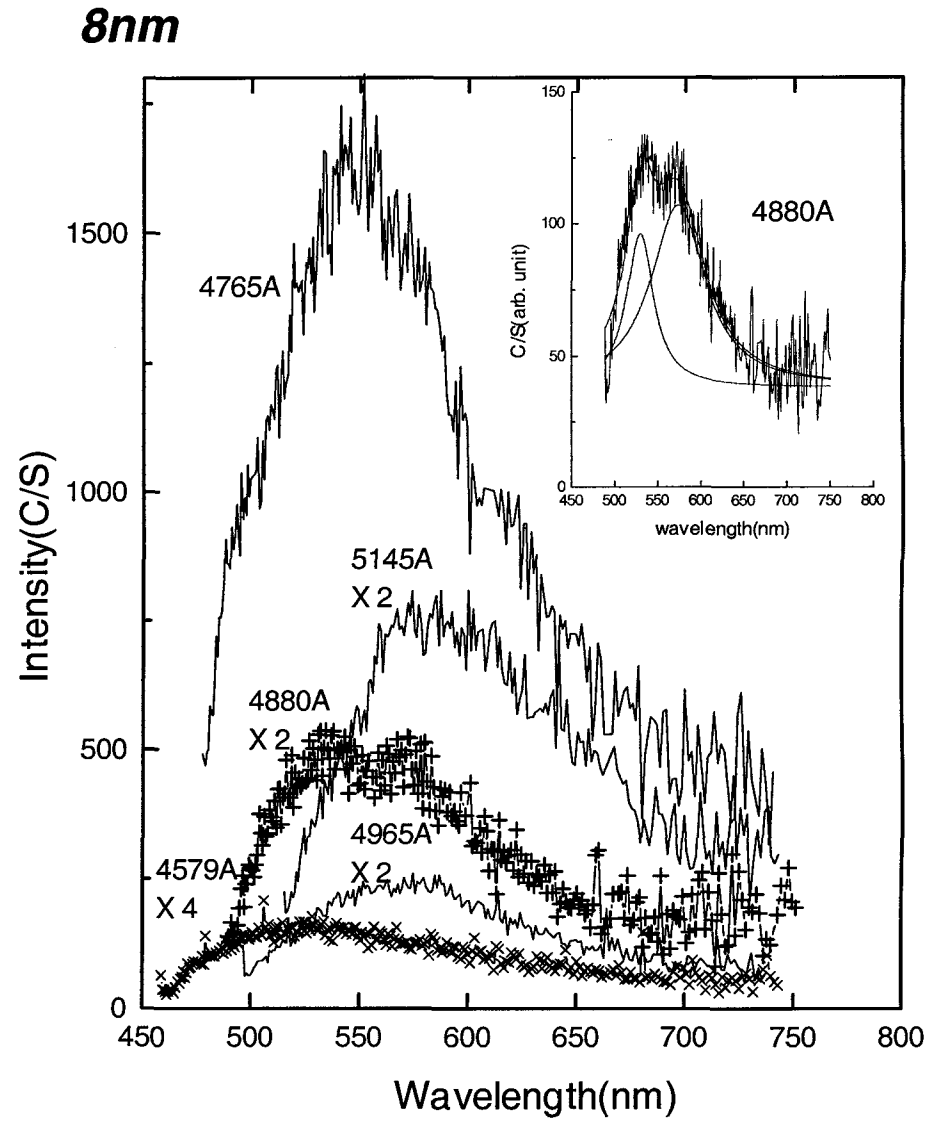
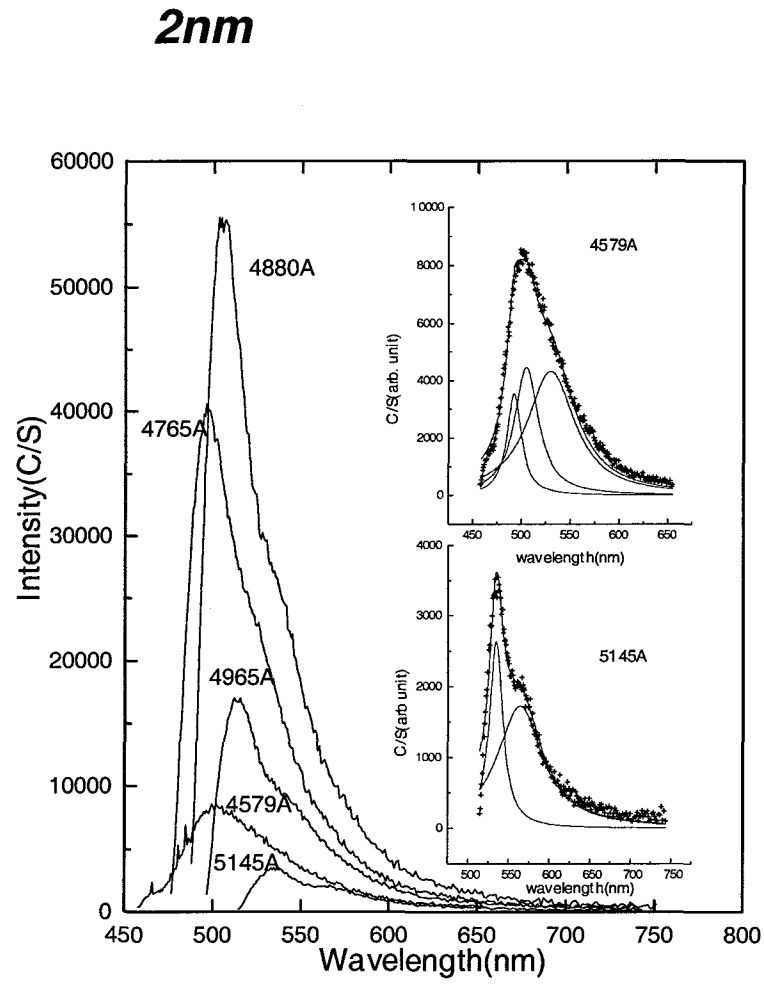
$$\langle vnlm | \vec{p} | cn'l'm' \rangle = M_{cv}^{\mu\nu} \int F_{nlm}(\vec{r}) \vec{p} F_{n'l'm'}(\vec{r}) d\vec{r}$$

$$M_{cv}^{\mu\nu} = \frac{1}{\hbar} \left. \frac{\partial \vec{p}_{cv}^{\mu}(\vec{k})}{\partial \vec{k}^{\nu}} \right|_{k=0}$$

$\sim 1/R$

**Transition Rate  $\sim 1/R^2$**

Alka Ingale, Kavita Borgohain, Shailaja Mahamuni and K.C. Rustagi(unpublished)



Alka Ingale, Kavita Borgohain, Shailaja Mahamuni and K.C. Rustagi(unpublished)

## ***structural changes also change energy levels!***

PHYSICAL REVIEW B 71, 045318 (2005)

### **Cylindrically shaped zinc-blende semiconductor quantum dots do not have cylindrical symmetry: Atomistic symmetry, atomic relaxation, and piezoelectric effects**

Gabriel Bester and Alex Zunger

*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*

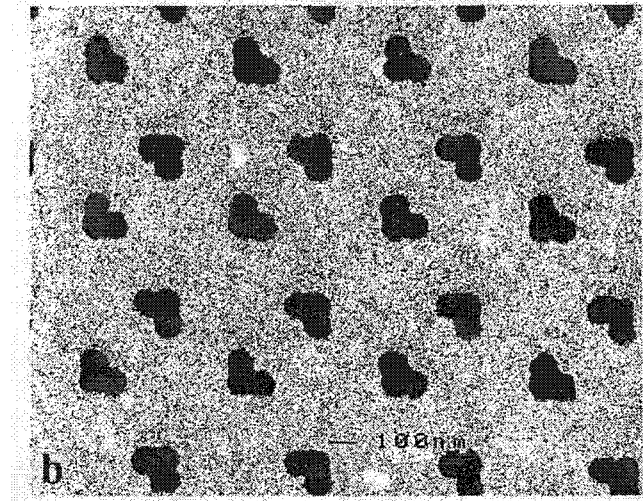
(Received 1 April 2004; published 14 January 2005)

Self-assembled quantum dots are often modeled by continuum models (effective mass or  $\mathbf{k}\cdot\mathbf{p}$ ) that assume the symmetry of the dot to be that of its overall geometric shape. Lens-shaped or conical dots are thus assumed to have continuous cylindrical symmetry  $C_{\infty v}$ , whereas pyramidal dots are assumed to have  $C_{4v}$  symmetry. However, considering that the III-V dots are made of atoms arranged on the (relaxed) positions of a zinc-blende lattice, one would expect the highest possible symmetry in these structures to be  $C_{2v}$ . In this symmetry group all states are singly degenerate and there are no *a priori* reason to expect, e.g., the electron  $P$  states (usually the second and third electron levels of dominant orbital  $P$  character) to be degenerate. Continuum models, however, predict these states to be energetically degenerate unless an irregular shape is postulated. We show that, in fact, the true (atomistic) symmetry of the dots is revealed when the effects of (i) interfacial symmetry, (ii) atomistic strain, and (iii) piezoelectricity are taken into account. We quantify the contributions of each of these effects separately by calculating the splitting of electron  $P$  levels for different dot shapes at different levels of theory. We find that for an ideal square-based pyramidal InAs/GaAs dot the interfacial symmetry of the unrelaxed dot splits the  $P$  level by 3.9 meV, atomistic relaxation adds a splitting of 18.3 meV (zero if continuum elasticity is used to calculate strain) and piezoelectricity reduces the splitting by  $-8.4$  meV, for a total splitting of 13.8 meV. We further show that the atomistic effects (i) and (ii) favor an orientation of the electron wave functions along the  $[1\bar{1}0]$  direction while effect (iii) favors the  $[110]$  direction. Whereas effects (i) + (ii) prevail for a pyramidal dot, for a lens shaped dot, effect (iii) is dominant. We show that the 8-band  $\mathbf{k}\cdot\mathbf{p}$  method, applied to pyramidal InAs/GaAs dots describes incorrectly the splitting and order of  $P$  levels ( $-9$  meV instead of 14 meV splitting) and yields the orientation  $[110]$  instead of  $[1\bar{1}0]$ .

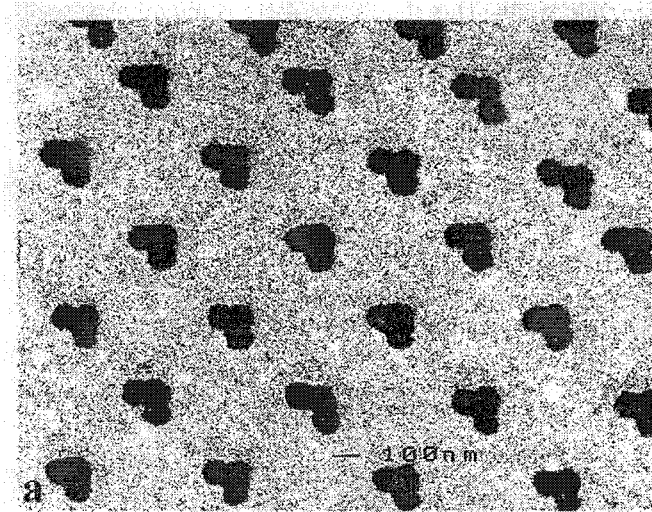
## ENVELOPE FUNCTIONS FOR OTHER SHAPES

**B.Lamprecht *etal***

**Appl Phys.B68,419(1999)**



**SHG(>>) ~ 40SHG(<>)**



## METAL NANOPARTICLES

Third harmonic generation in metals was measured by Burns and Bloembergen in 1969

Theory? Free particle nonlinearity negligible

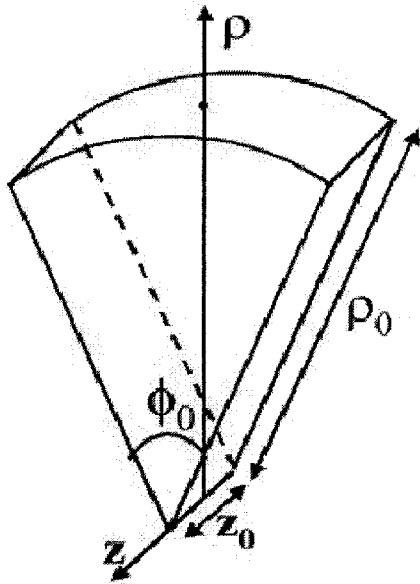
Surface? Collisions? Higher order multipoles?

*In nano particles:*  $\chi^{(3)}_{\text{eff}} = \chi^{(3)}_{\text{metal}} f^2 |f|^2$

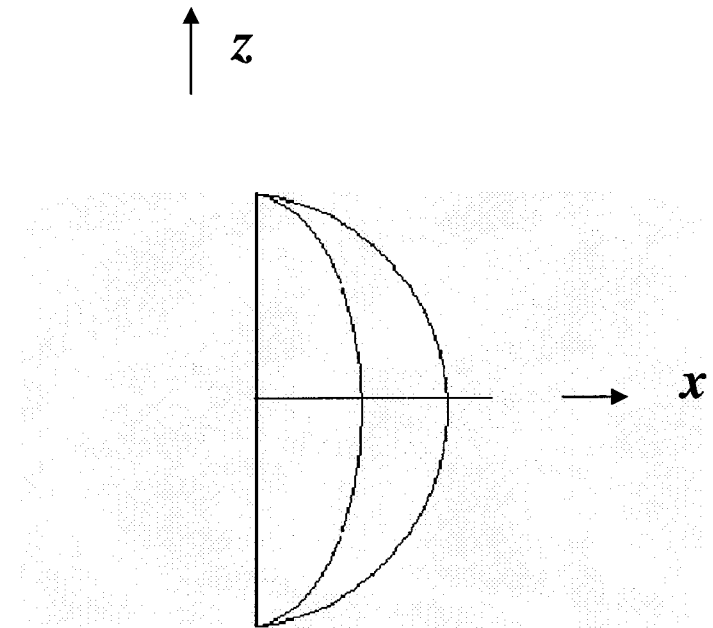
$$\chi^{(3)}_{\text{metal}} = ???$$

***Size quantization main cause of nonlinearity***

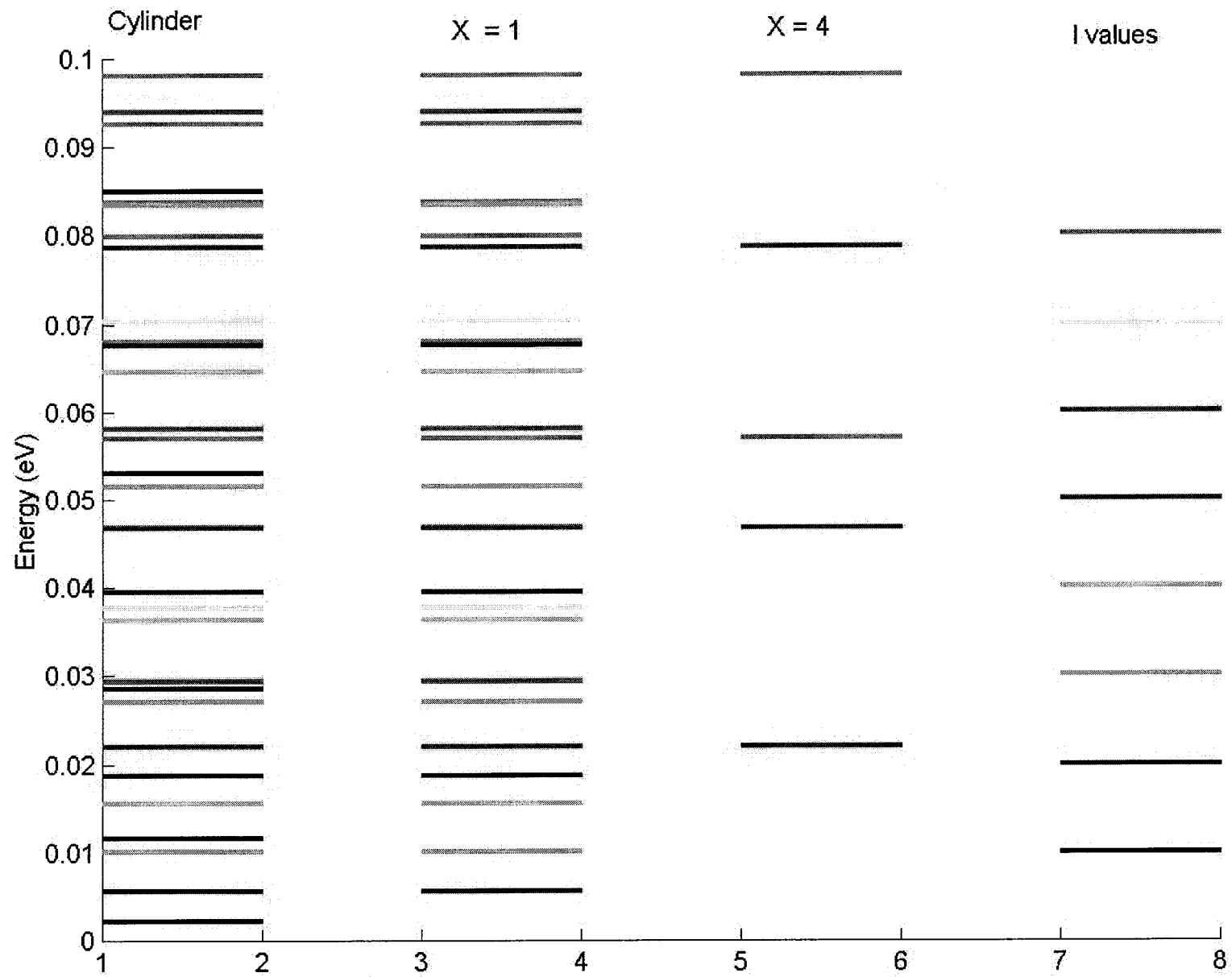


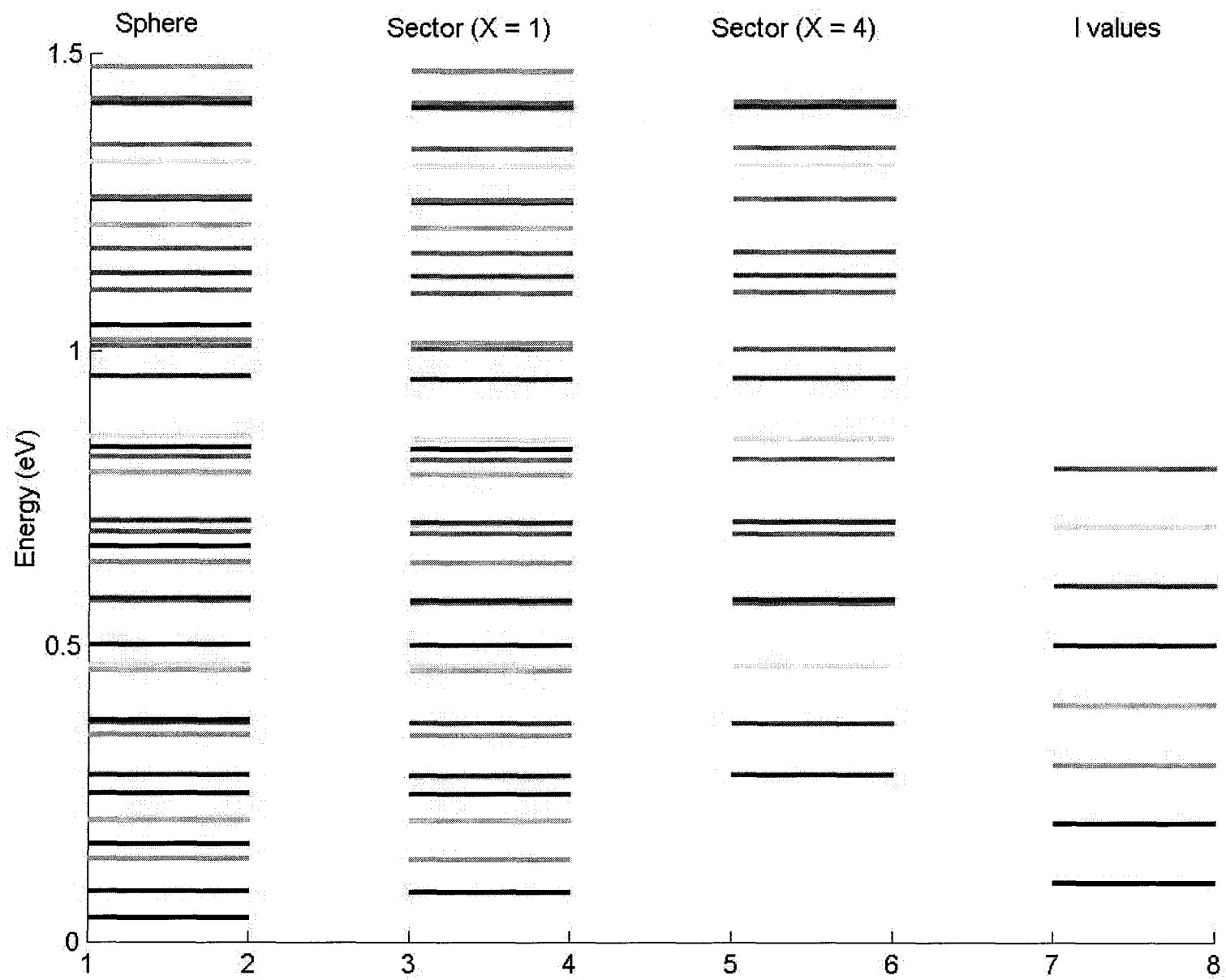


Easy solutions for apex  
angle= $\pi/\text{integer}(X)$



$X=1$  means hemisphere





## Spherical Quantum Dot

$$\psi_{nlm}(r, \theta, \phi) = \frac{2^{1/2}}{R^{3/2}} \frac{1}{j_{l+1}(\zeta_{nl})} j_l\left(\zeta_{nl} \frac{r}{R}\right) Y_{lm}(\theta, \phi),$$

$$E_0 = \frac{\hbar^2}{2m^* R^2} \zeta_{nl}^2$$

$\zeta_{nl}$  zeros of the spherical Bessel function.

## Hemispherical Quantum Dot:

Out of these solutions, select those which vanish at  $z=0$  plane

Lowest state  $l=1$

For same volume :

hemispherical QD has larger confinement energy

## Effect of electron-electron interaction

## Dielectric Confinement

Screening -- depolarization field,  
sensitive to shape  
plasmon resonance -Correlated motion :  
beyond single particle picture

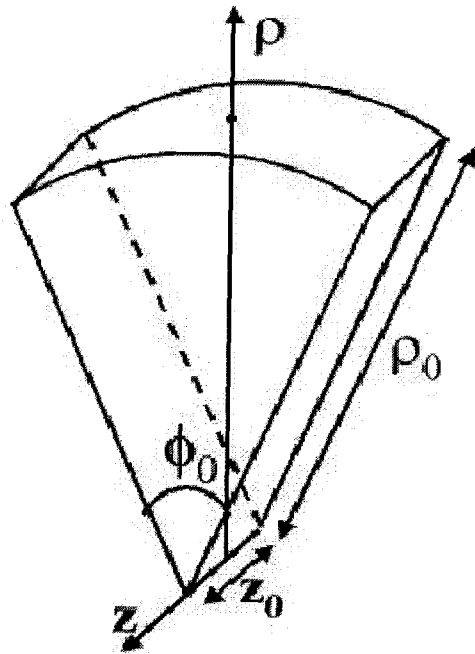
### Generalized Kohn Theorem

Interacting electrons in Harmonic oscillator potential absorb only at  $\omega_0$

Screened  $\gamma =$  single particle  $\gamma$  . local field factor

$$f_x(\omega) = \frac{1}{1 + L_x(\epsilon_{xx} - 1)}$$
$$L_x = \frac{abc}{3} \int_0^\infty \frac{dq}{(a^2 + q^2)^{3/2} (b^2 + q^2)^{1/2} (c^2 + q^2)^{1/2}}$$

For long molecules:  $L_x \rightarrow 0$



$$\phi_0 = \frac{\pi}{X},$$

X integer

$$\Psi_{\nu, n, s} = \frac{1}{\sqrt{z_0}} \sin \left( \frac{\nu\pi}{z_0} (z + z_0 / 2) \right) \psi_{ns}(\rho, \phi),$$

$$\nu = 1, 2, 3, \dots,$$

$$\psi_{ns}(\rho, \phi) = \frac{2}{\rho_0} \sqrt{\frac{X}{\pi}} \frac{1}{J_{Xn+1}(\alpha_{ns})} J_{Xn} \left( \alpha_{ns} \frac{\rho}{\rho_0} \right) \zeta_n(\phi),$$

$\alpha_{ns}$  zeros of the Bessel function.

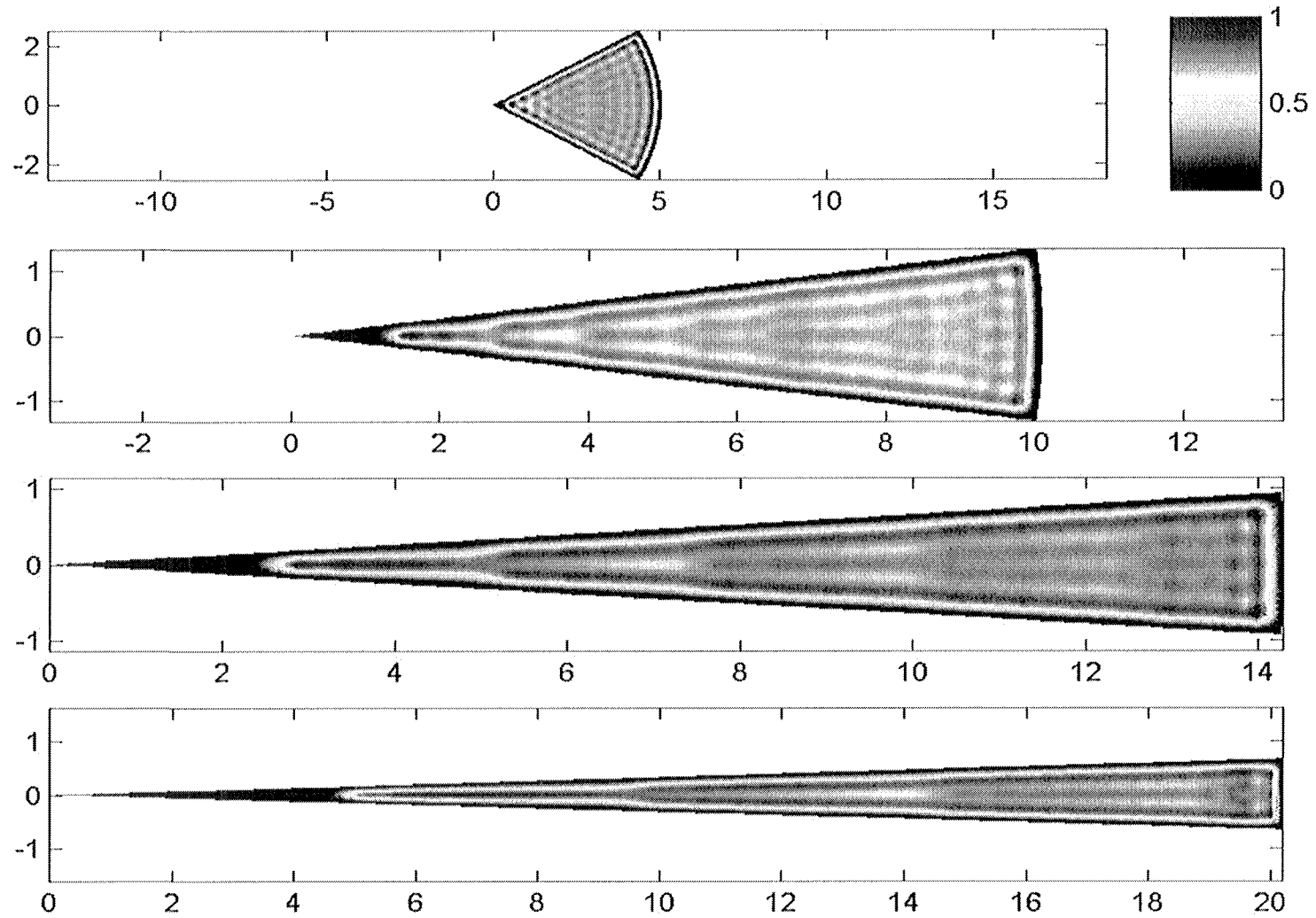
$$n = 1, 2, 3, \dots,$$

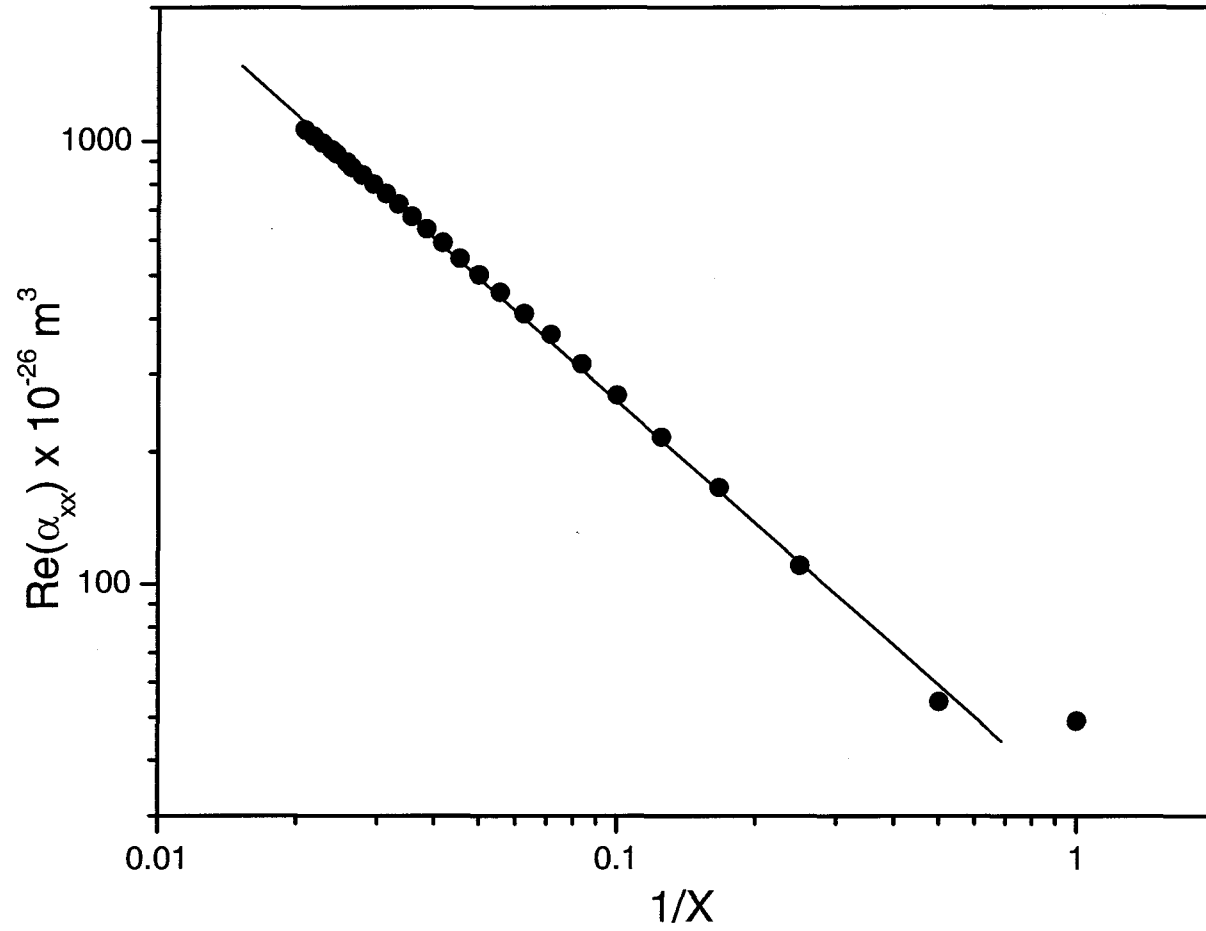
$$s = 1, 2, \dots,$$

$$E_{\nu ns} = \alpha_{ns}^2 E_0 + \nu^2 E_z, \quad E_z = \frac{\hbar^2 \pi^2}{2mz_0^2}, \quad E_0 = \frac{\hbar^2}{2m\rho_0^2}$$

# Electronic density

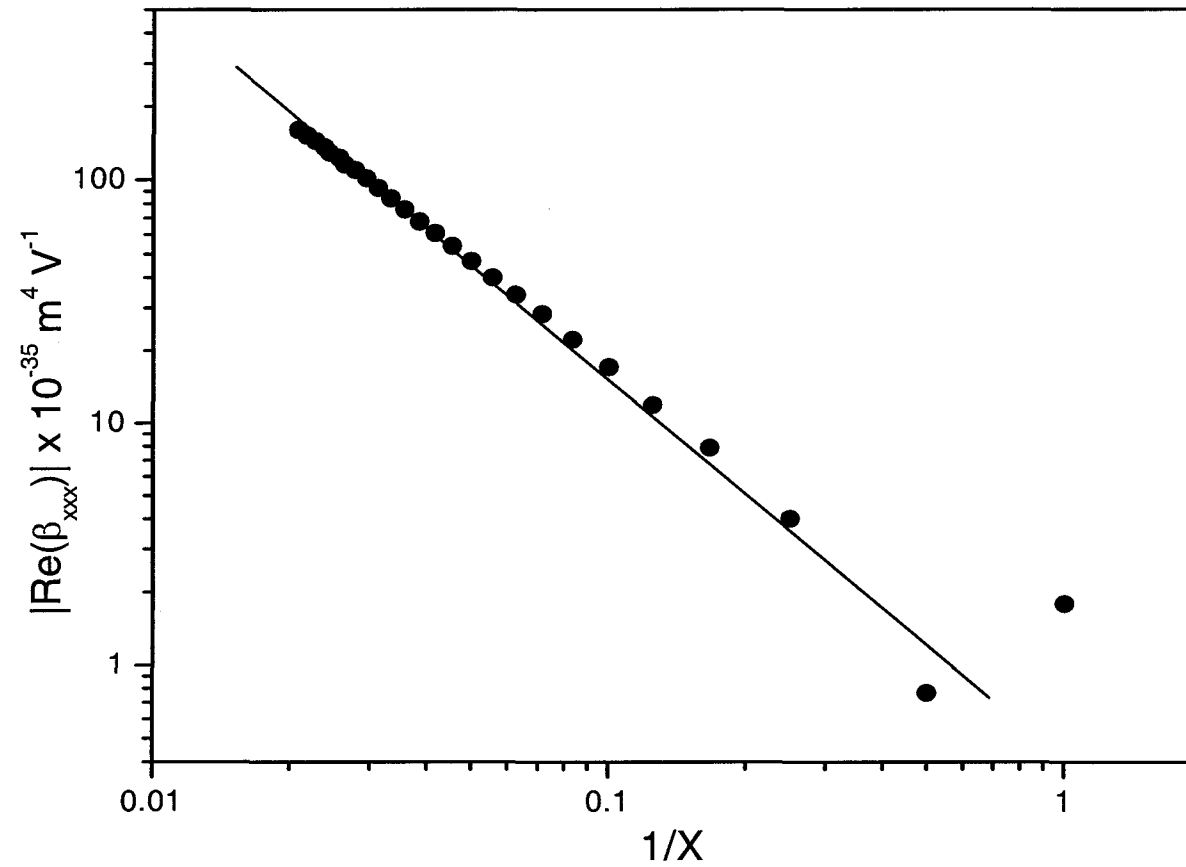
Jayabalan etal PRB (2003)



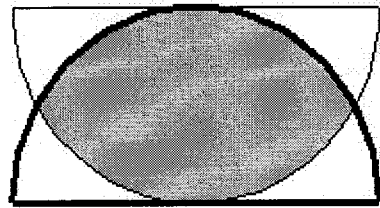


**Jayabalan etal PRB (2003)**

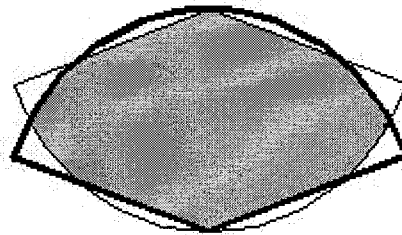




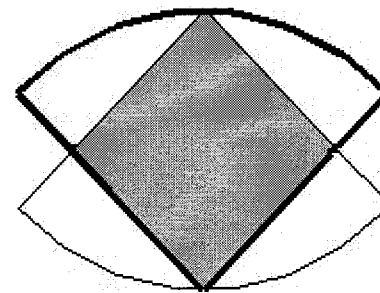
**Jayabalan etal PR B (2003)**



(a)



(b)



(c)

**Jayabalan etal PR B(2003)**

## EXCITONS

Exciton wave function has the form:

$$\Psi(r_1, r_2) = \psi(r_1, r_2) u_c(r_1) u_v(r_2)$$

Envelope function varies slowly and obeys wave equation:

$$\left[ -\frac{\hbar^2 \nabla_1^2}{2m_1} - \frac{\hbar^2 \nabla_2^2}{2m_2} - \frac{e^2}{4\pi\epsilon_0\epsilon r_{12}} + V_0 \right] \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2) ,$$

With boundary condition:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = 0 \text{ for } r_1 \text{ or } r_2 \geq R .$$

**LIMITING CASES(Efros & Efros(1982))**

**Strong confinement Confinement energy < coulomb energy**

**Weak confinement: Confinement energy < coulomb energy**

**Exciton with quantized center of mass motion**

$$E = E_g + E_{ex} + \frac{\hbar^2 \pi^2}{2MR^2}$$

$$\psi \sim \frac{\sin(\pi r_{c.m.} / R)}{r_{c.m.} / R} e^{-r_{12}/a_0},$$

***Not compatible with boundary conditions***

Strong confinement

Confinement energy  $\gg$  coulomb energy

electron and hole motion quantized

Coulomb interaction treated perturbatively

(Efros & Efros(1982))

$$E = E_g + E_{ex} + \frac{\hbar^2 \pi^2}{2\mu R^2} - 1.786 \frac{e^2}{\epsilon R} - 0.248 \frac{\mu e^4}{2\epsilon^2 \hbar^2}$$

Nair et al PRB(1987)

Nair et al PRB(1987)

Variational calculation with trial wave function:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} N \left[ \frac{\sin(\pi r_1/R)}{r_1/R} \right]^{\alpha_1} \left[ \frac{\sin(\pi r_2/R)}{r_2/R} \right]^{\alpha_2} \exp(-\beta r_{12}/R) & \text{for } r_1, r_2 \leq R \\ 0 & \text{outside,} \end{cases}$$

Centre of mass quantization?

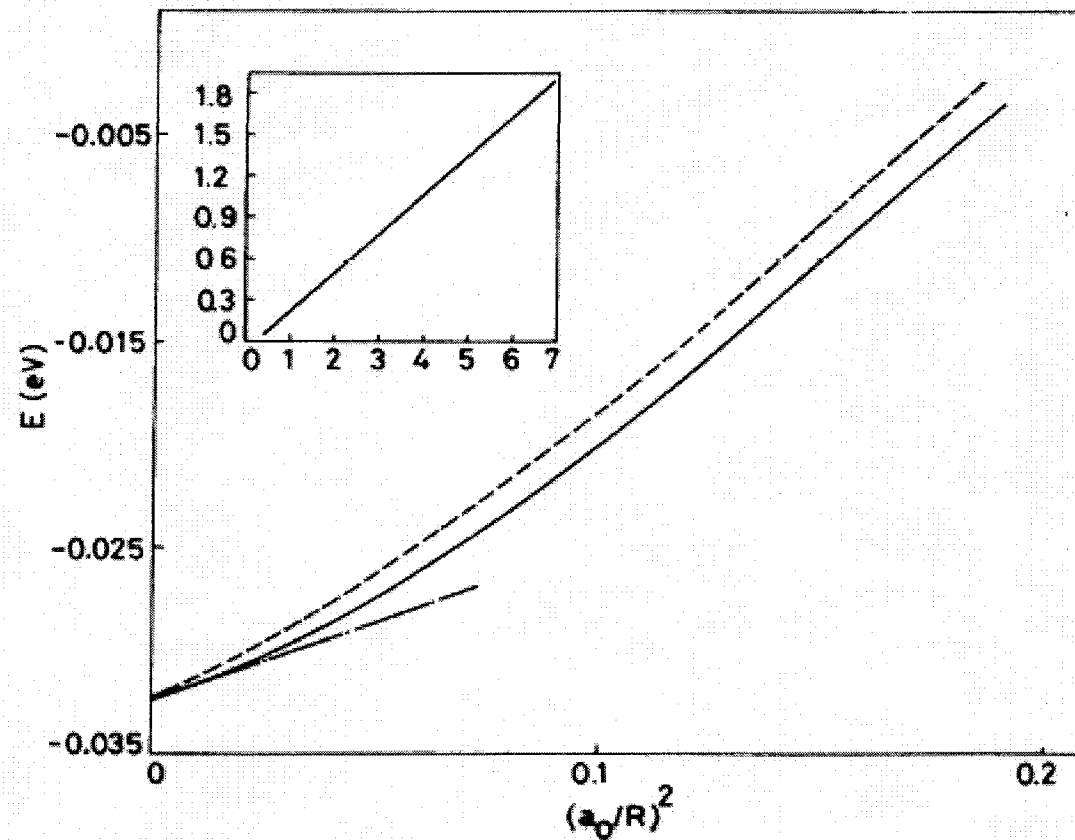
$$E = E_g + E_{ex} + \frac{\hbar^2 \pi^2}{2M(R+d)^2}$$

See Also Kayanuma SSC (1986), PRB (1988)

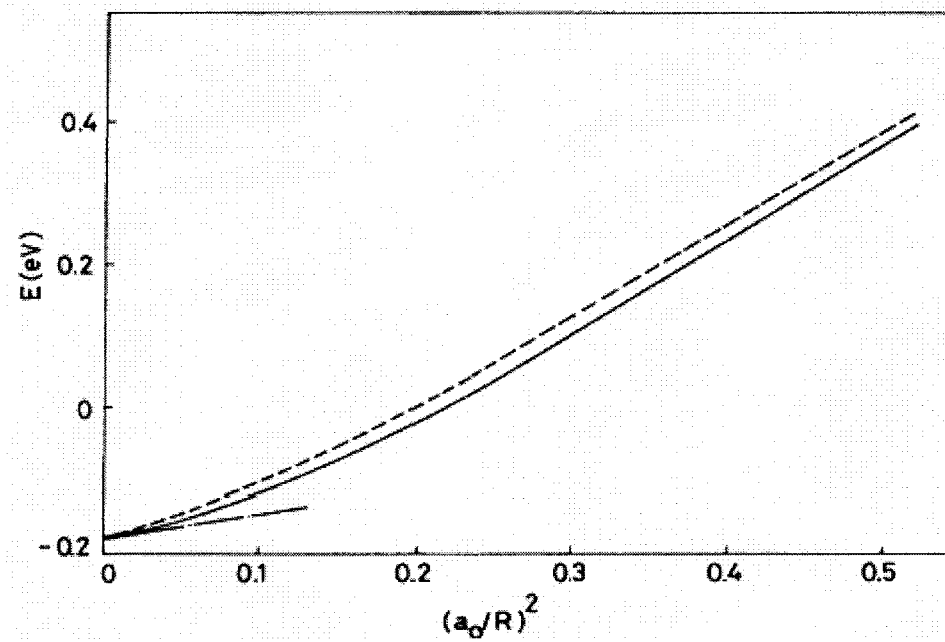
Nair et al PRB(1987) CdS:

----- one parameter calc.

\_\_\_\_\_ 3 parameters calc



Nair et al PRB(1987) CuCl





## Biexcitons in Quantum dots and nonlinear response

*Nair and Takagahara PRB 55,5153(1997)*

$$\phi_0(\mathbf{r}_e, \mathbf{r}_h) = \sum_{l=0}^{l_{\max}} \sum_{m=0}^{m_{\max}} \sum_{n=0}^{n_{\max}} c_{lmn} W_m(r_e) W_n(r_h) r_{eh}^l \times \exp(-r_{eh}/a_{ex})$$

$$W_m(r) = \prod_{k=1}^m \left[ r^2 - \left[ \frac{k}{m} R \right]^2 \right]$$

$$H_{xx} = -\frac{\hbar^2}{2m_e} (\nabla_{e_1}^2 + \nabla_{e_2}^2) - \frac{\hbar^2}{2m_h} (\nabla_{h_1}^2 + \nabla_{h_2}^2) - \frac{e^2}{\epsilon |\mathbf{r}_{e_1} - \mathbf{r}_{h_1}|} - \frac{e^2}{\epsilon |\mathbf{r}_{e_1} - \mathbf{r}_{h_2}|} - \frac{e^2}{\epsilon |\mathbf{r}_{e_2} - \mathbf{r}_{h_1}|} - \frac{e^2}{\epsilon |\mathbf{r}_{e_2} - \mathbf{r}_{h_2}|} + \frac{e^2}{\epsilon |\mathbf{r}_{e_1} - \mathbf{r}_{e_2}|} + \frac{e^2}{\epsilon |\mathbf{r}_{h_1} - \mathbf{r}_{h_2}|} \quad (7)$$

**Nair and Takagahara PRB 55,5153(1997)**

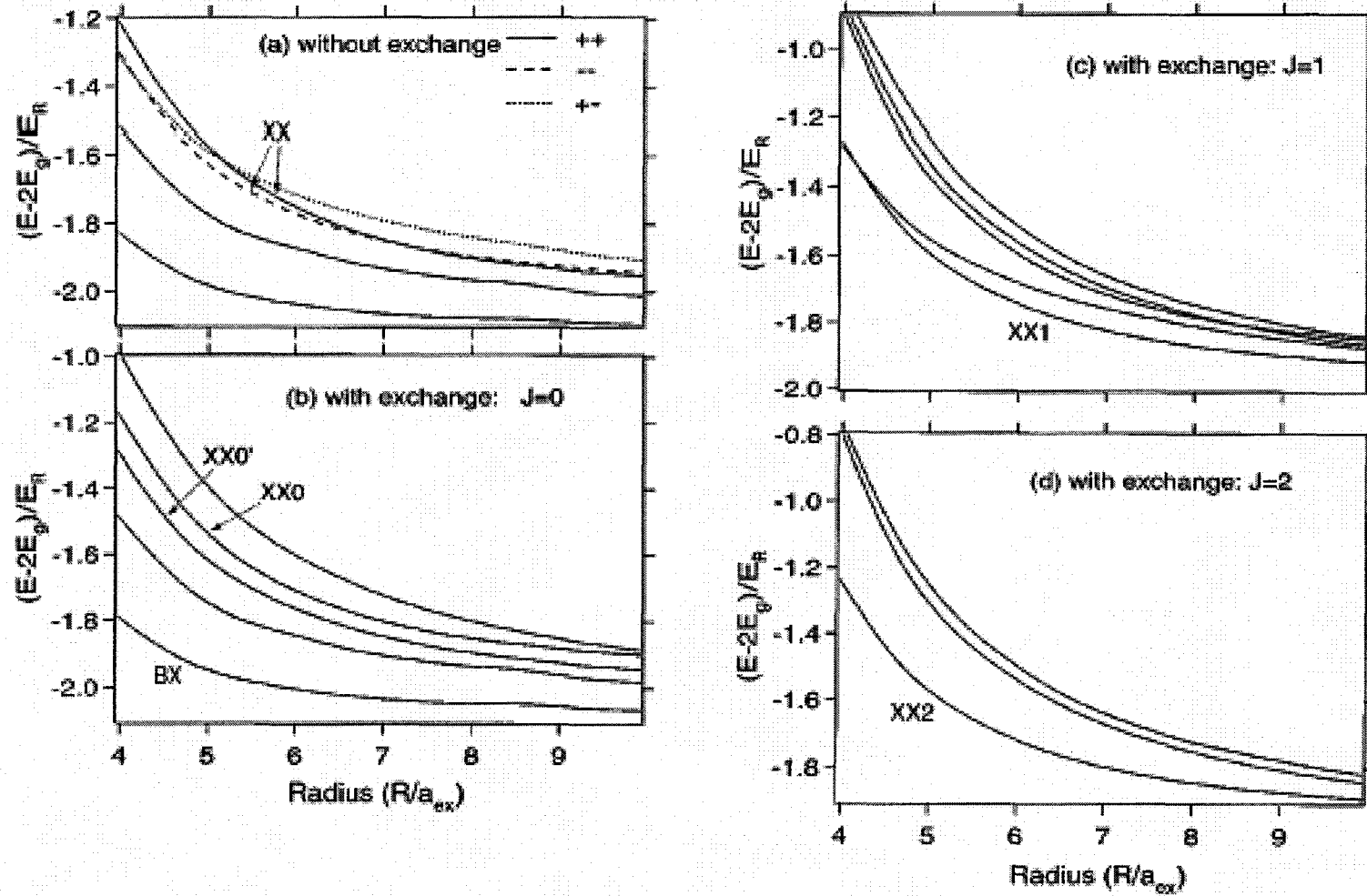


FIG. 2. Calculated energies of the biexciton states (a) without and (b–d) with the electron-hole exchange interaction included. *BX*, *XX0* (*XX0'*), *XX1*, and *XX2*, respectively, denote the biexciton ground state and the weakly correlated exciton-pair states with  $J=0, 1$ , and  $2$ . Notations are the same as in Fig. 1.

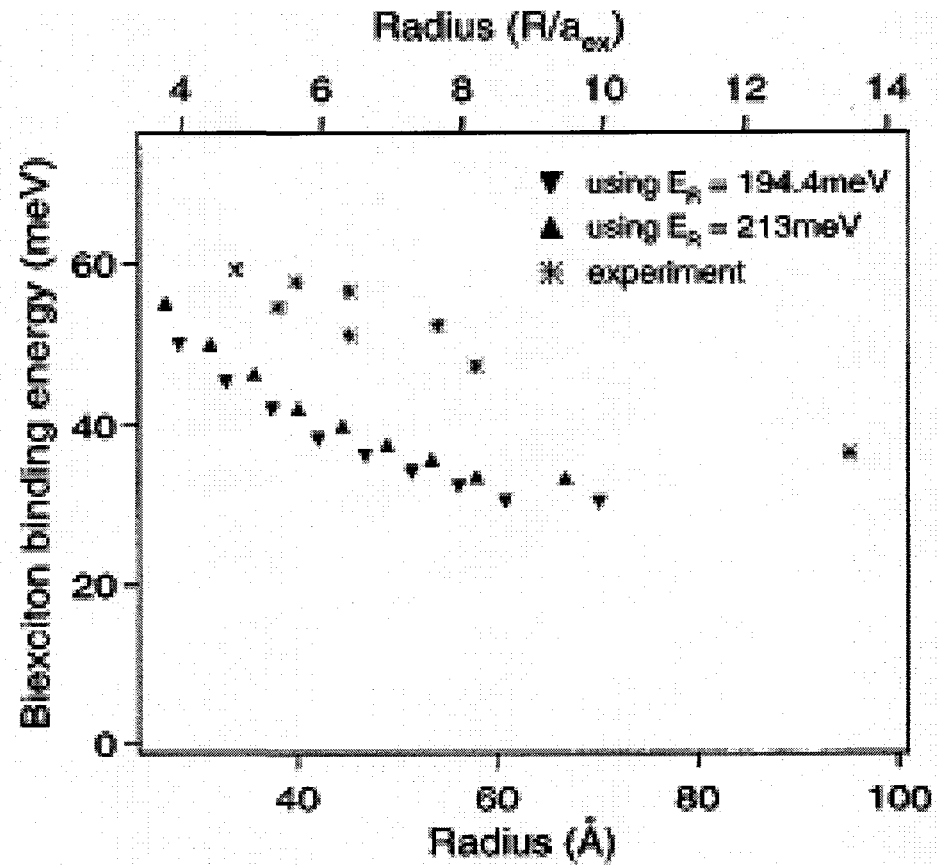
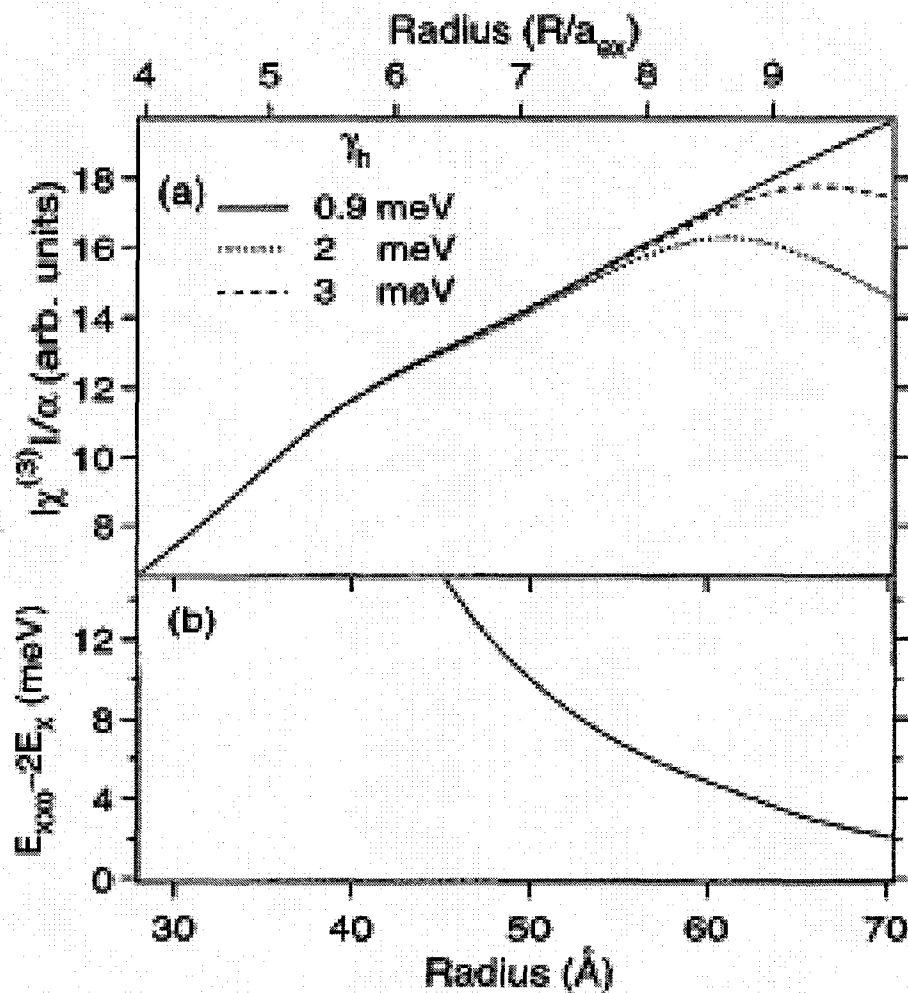


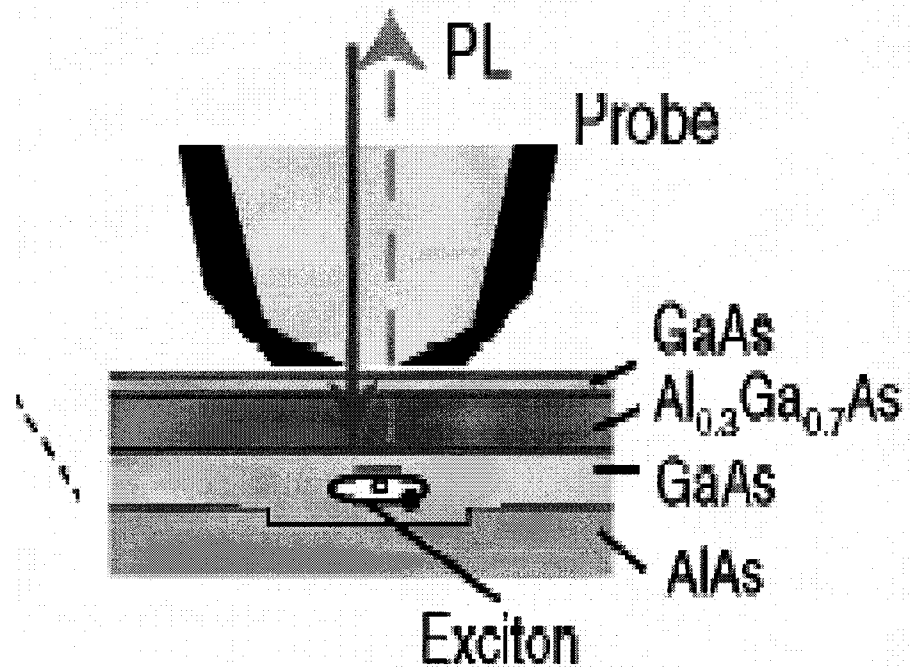
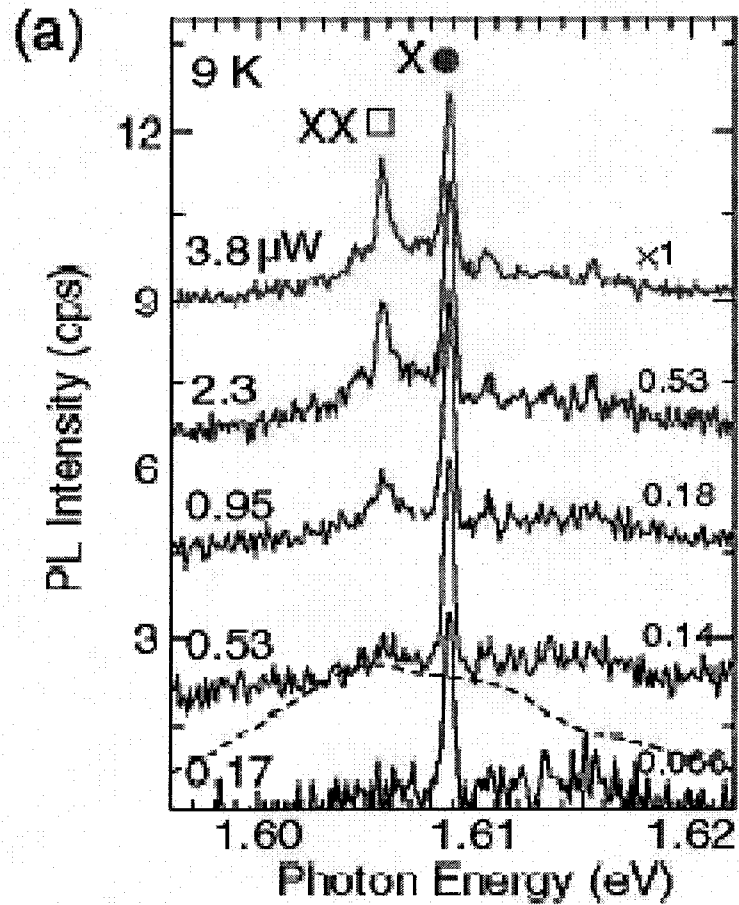
FIG. 3. The calculated size dependence of the biexciton binding energy in CuCl quantum dots. Two sets of results corresponding to the exciton Rydberg  $E_R = 194.4$  meV and 213 meV are shown. The experimental results of Ref. 40 are also shown.



**(a) Calculated size dependence of the peak value of  $(c(3) / a)$  near the exciton resonance in CuCl QD's. All the curves are scaled to the same value at  $R=28 \text{ \AA}$ . The hump seen at  $R \sim 40 \text{ \AA}$  arises from the assumed size dependence of  $\gamma_h$  and has no special physical significance. (b) The size dependence of the energy difference between the weakly correlated exciton-pair state ( $E_{xx0}$ ) and twice the exciton ground state energy ( $E_x$ ).**

Experimental details from

K Matsuda et al PRL 91 (2004)



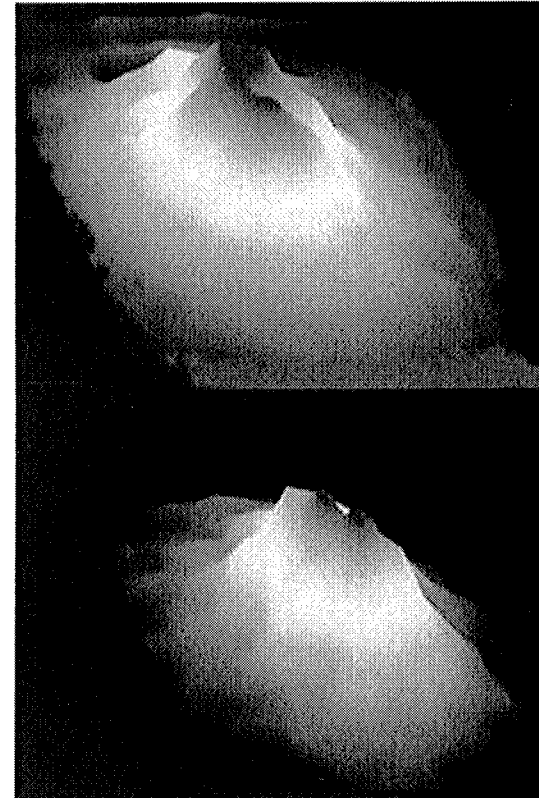
## Near-field Optical Mapping of Exciton Wave Functions in a GaAs Quantum dot

K. Matsuda, T. Saiki, S. Nomura, M. Mihara, Y. Aoyagi, S. Nair, and T. Takagahara

Phys. Rev. Lett. **91**, 177401

(issue of 24 October 2003)

**Trapped and tracked.** The first images of the motion of an exciton--a particle essential to modern electronics--and a biexciton show that the lighter exciton (top) roams farther.

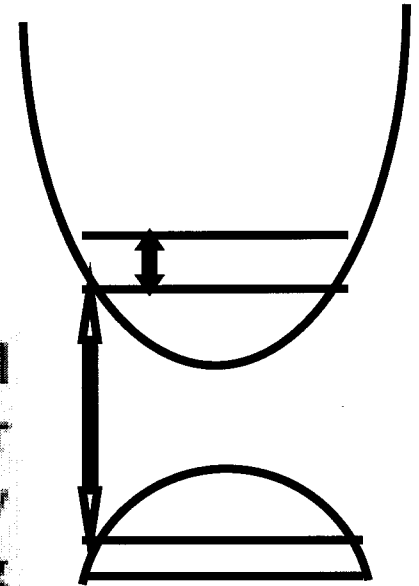


<http://www.physicscentral.com/pictures/pictures-03-10.html>

## *Does quantum confinement enhance nonlinearities?*

*Inter sub band transitions ~ R*

To conclude, we have shown that three-dimensional quantum confinement can alter radically the nonlinear optical properties of semiconductors in the transparency region. The results of this study may have far-reaching consequences for practical devices such as ultrafast optical switches.



$$\chi^{(3)} = \frac{2N\hbar(e/m)^4}{3V\epsilon_0(\hbar\omega)^4} \sum_{abcd} \rho_{ab} \rho_{bc} \rho_{cd} \rho_{da} \left[ \frac{1}{(\Omega_{av} - \omega)(\Omega_{bv} - 2\omega)(\Omega_{cv} - \omega)} + \right.$$

*5 similar terms*

*Cotter et al PRL 68,1201(1992)*

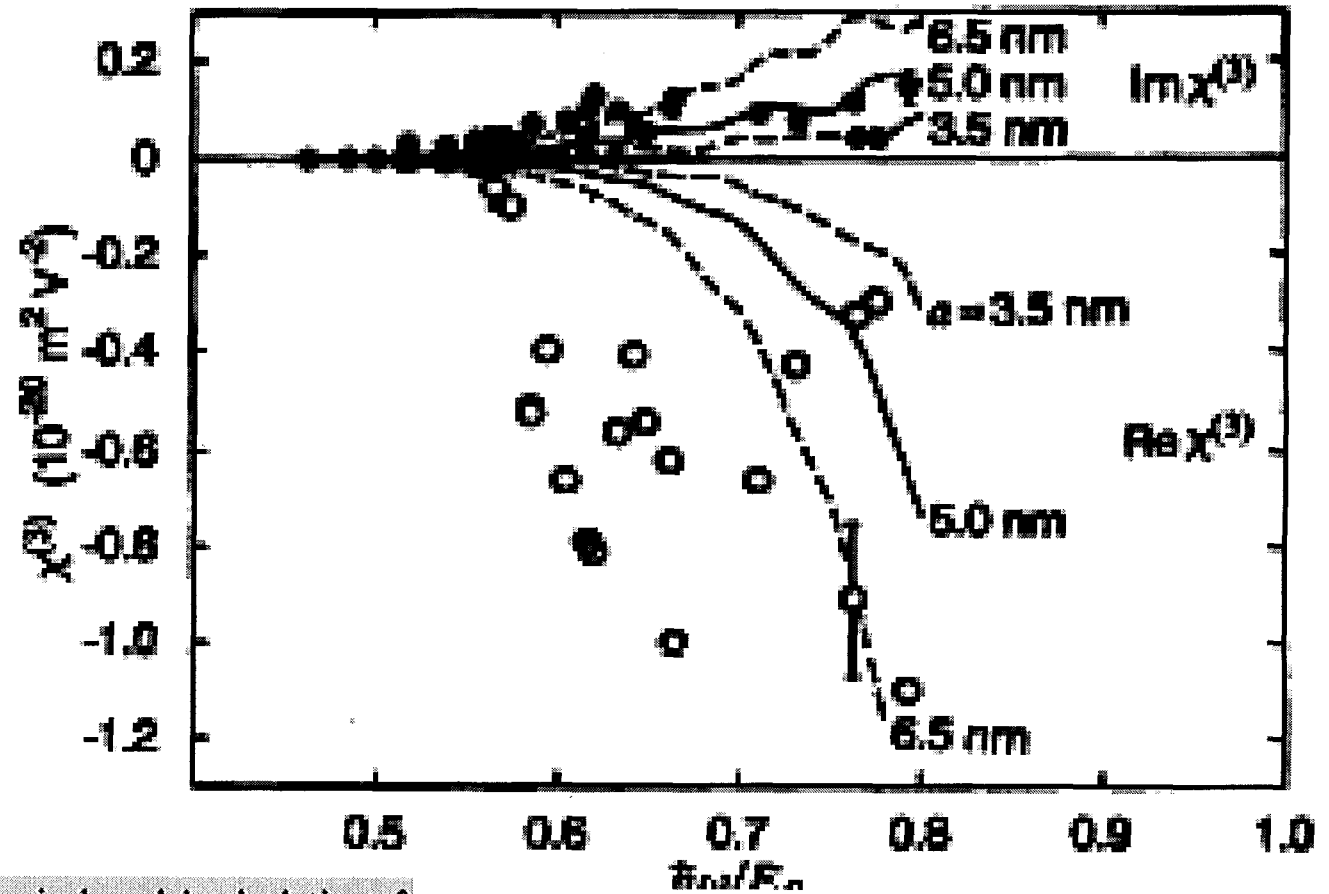


FIG. 1. The solid curves show a typical model calculation of  $\chi^{(3)}$  for a sphere of radius  $a=5$  nm with  $m_c=0.15m$ ,  $m_v=0.8m$ ,  $\hbar\omega=1.17$  eV ( $1.06\ \mu\text{m}$ ),  $\Delta E=35$  meV,  $|f|^4=0.2$ , and  $\varepsilon=0.01$ . The dashed curves are for the same semiconductor parameters and number density, but different radii  $a$ . The curves are plotted vs the normalized photon energy  $\hbar\omega/E_0$ , taking  $E_0$  as a variable parameter. The distinctive features of these curves are found to be typical of quantum-confined particles (and are robust to changes in parameters), but quite different from those of bulk semiconductors [2]. Values of  $\text{Im}\chi^{(3)}$  (solid circles) and  $\text{Re}\chi^{(3)}$  (open circles) measured at  $1.06\text{-}\mu\text{m}$  wavelength for 24 semiconductor-doped glass samples are shown.

*Cotter et al PRL 68,1201(1992)*



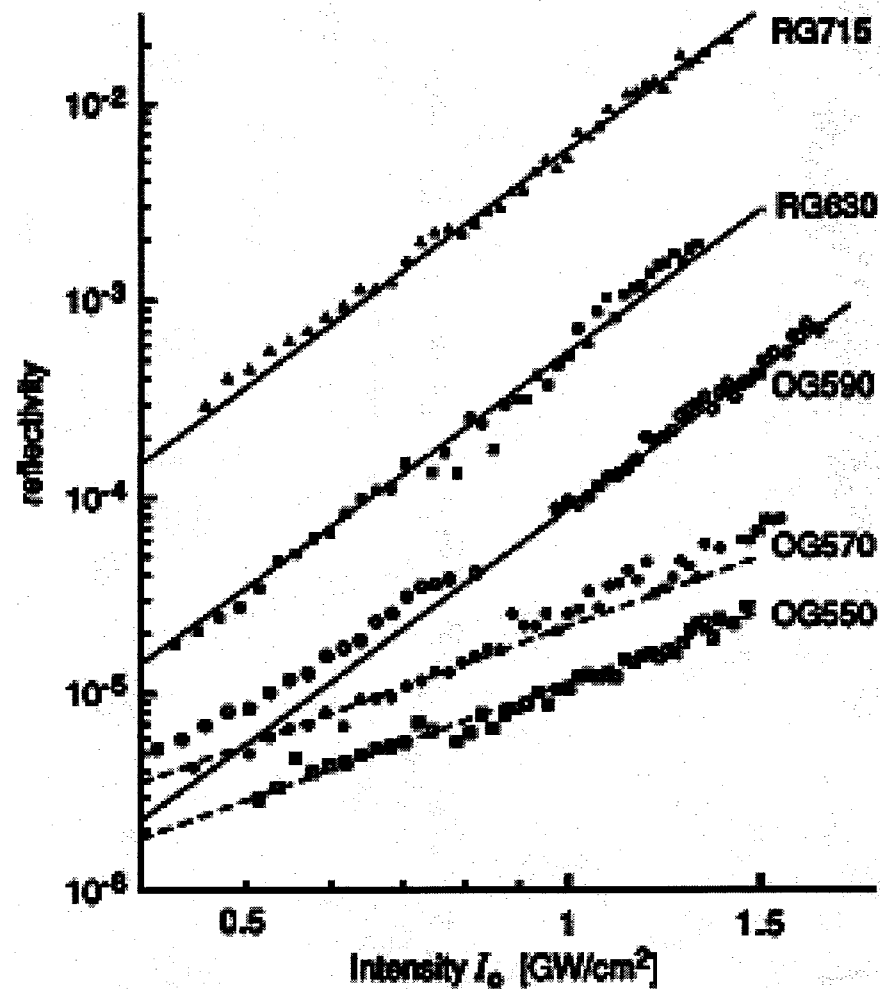


Fig. 2. Reflectivity versus intensity for some SDG's. Data are taken with  $f$ ,  $b$ , and  $p$  in temporal coincidence and with parallel polarizations. Sample thickness, 3 mm. Solid lines,  $R \propto I_0^4$ ; dotted lines,  $R \propto I_0^2$ . The intensity at the interference maxima of  $f$  and  $b$  is  $\approx 3.5 \times I_0$ .

Cotter et al( 1992): Semiconductor doped glasses have large third order non-linearity of electronic origin(75ps pulses)

*Quantum confinement enhances nonlinearity!*

Pavia group: fifth order nonlinearity at relatively low intensities (35 ps pulses)

Bindra

Repeated DFWM and z-scan with 20ps pulses

Nonlinearity apparently fifth order at low intensity  
third order at higher intensities!

**So THE PROBLEM IS REAL!**

Resolution:

Nonlinearity is indeed fifth order, but at higher intensities there is saturation of DFWM signal due to nonlinear absorption

Probe beam intensity is much reduced because of Two Photon absorption and linear absorption by the generated ***e,h's***

Similarly , z -scan signal at higher intensities saturates

Bindra et al PRB (1999), Opt Comm (2000)

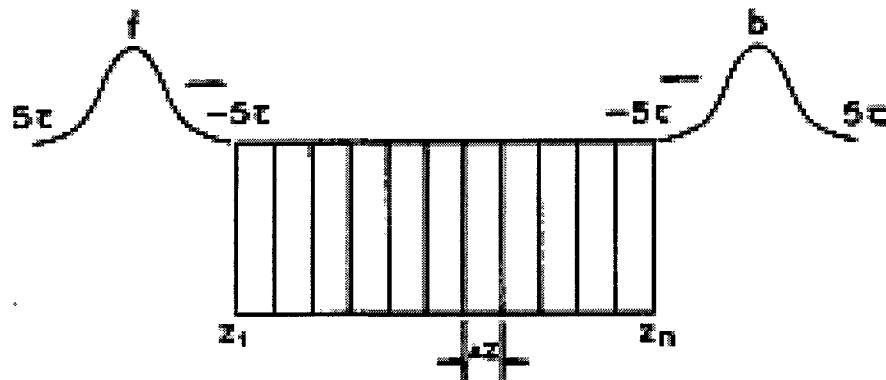


FIG. 7. Sample length is divided into equal segments of thickness  $\Delta z$ . The forward and backward pump beams for  $t = 0$  at time  $t = -5\tau$  are incident on face  $z_1$  and  $z_n$  of the sample, respectively.

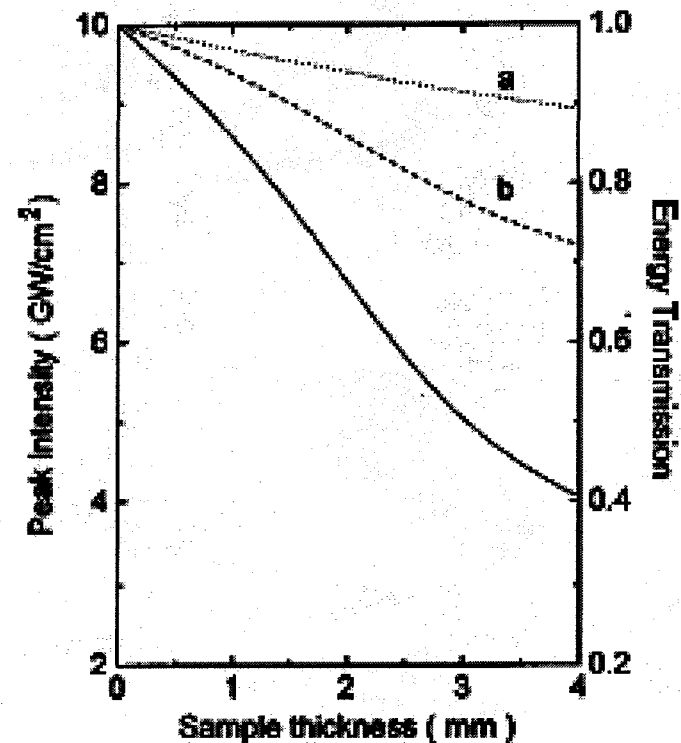


FIG. 3. Energy transmission for forward pump beam (a) when only forward pump beam is present, (b) in the presence of all interacting beams. The solid line shows the reduction of *peak intensity* of forward pump beam in the presence of all beams.

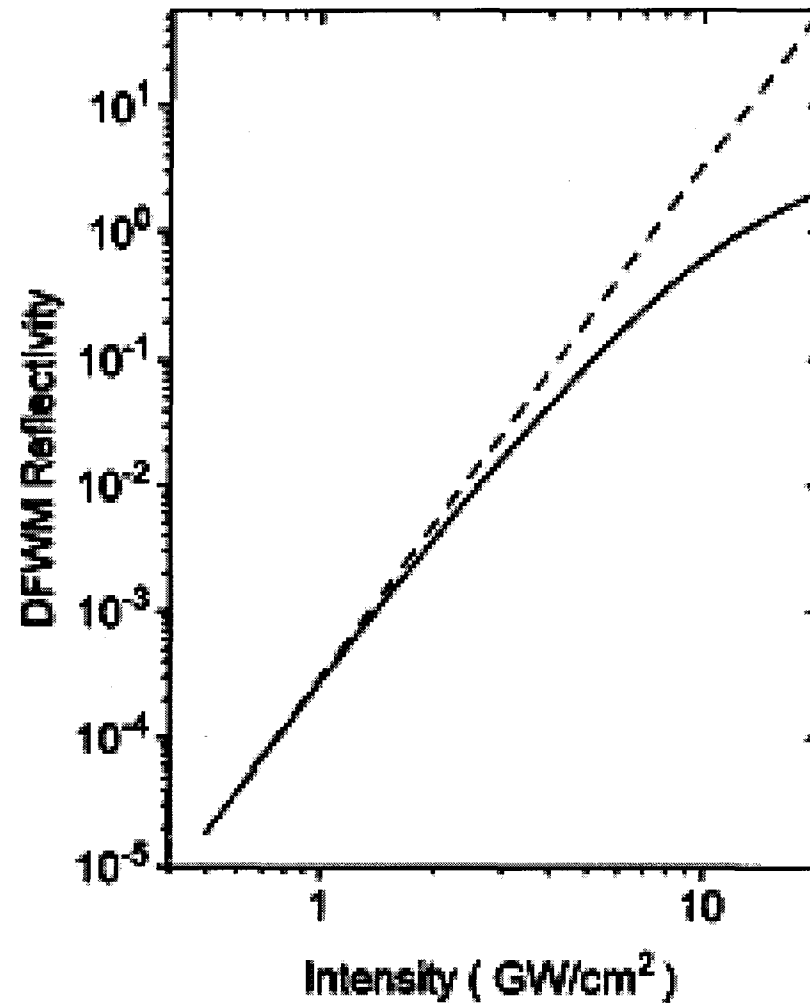
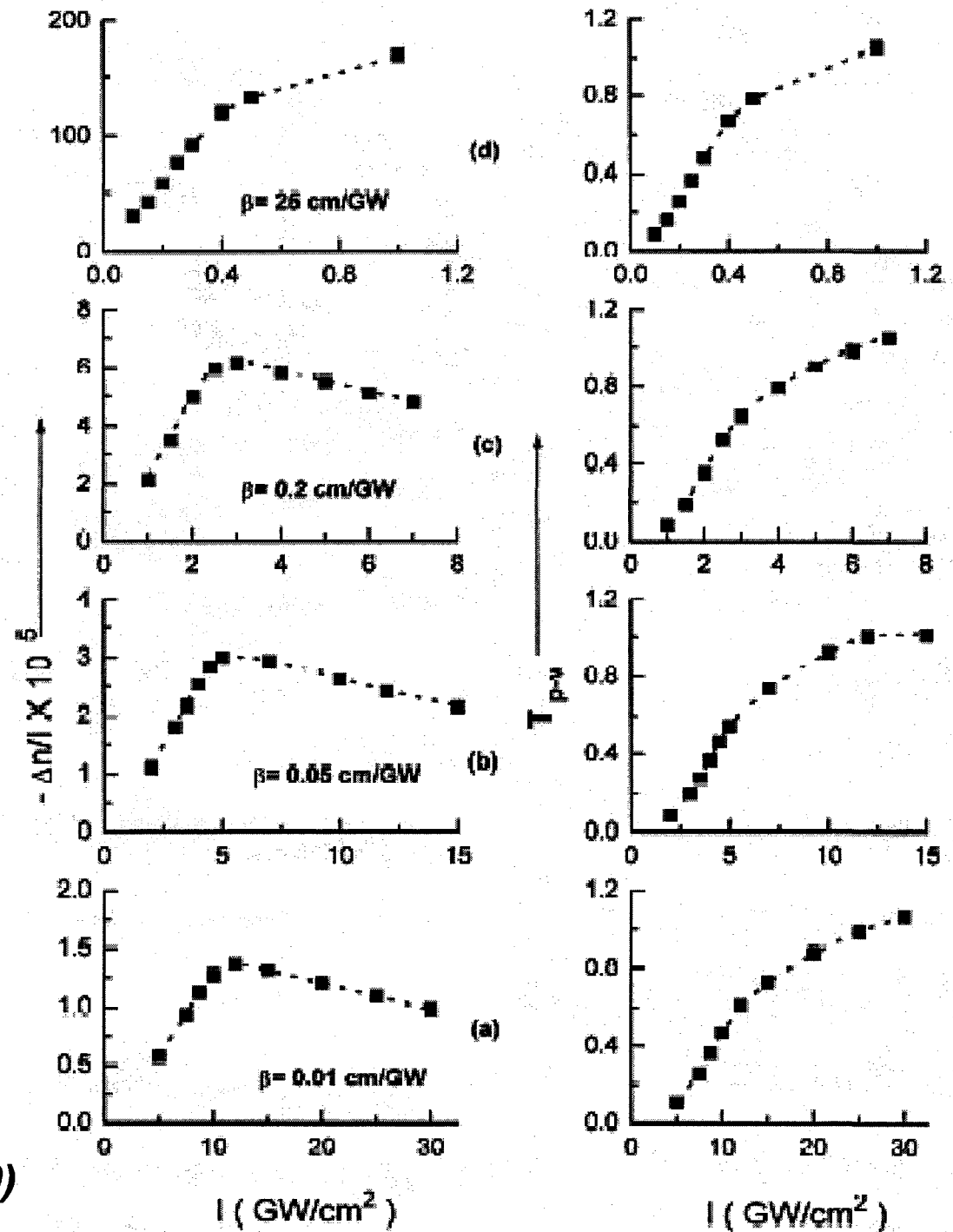


FIG. 4. Phase conjugate reflectivity versus pump intensity estimated with depletion of all interacting beams by nonlinear absorption for filter RG850. Dashes show the  $I^4$  dependence.

***Bindra et al PRB (1999)***

Intensity dependence  
 $\Delta n/I$  and  $T_{p-v}$



*Bindra et al Opt Comm (2000)*

6ps  
→

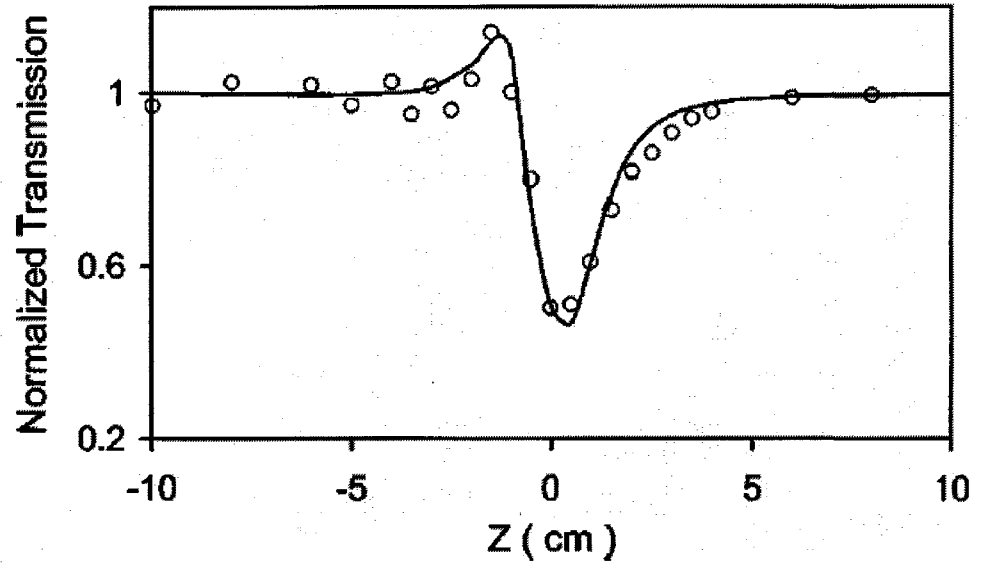


FIG. 1. Closed-aperture z-scan for the sample RG850 with 6 ps pulses.

100 fs

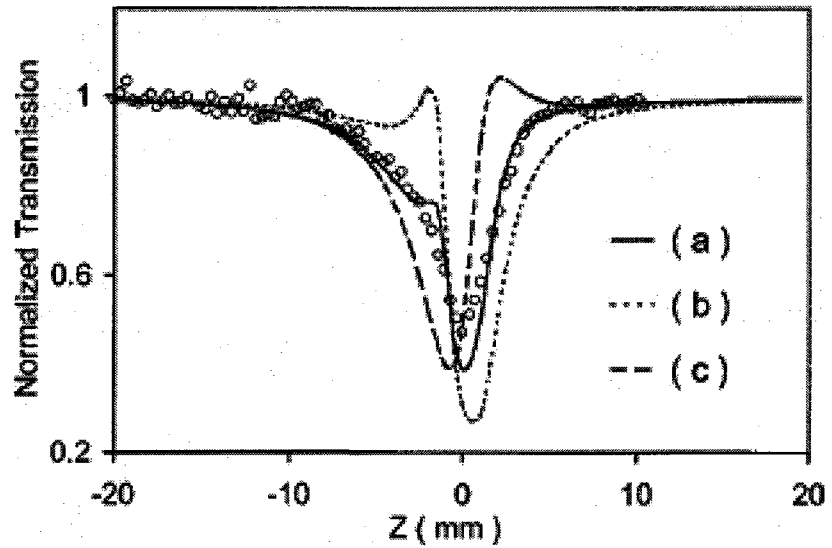


FIG. 3. Closed-aperture z scan for the sample RG850. Circles are the experimental data points. Solid line is the fit obtained with TPA coefficient  $=6 \times 10^{-13} \text{ mW}^{-1}$ , free carrier cross section  $=-1.5 \times 10^{-22} \text{ cm}^3$  and  $n_2 = 14 \times 10^{-20} \text{ m}^2\text{W}^{-1}$ . Curve (b) is obtained by neglecting the effect of  $n_2$ . Curve (c) is obtained by neglecting the effect of fifth-order nonlinearity.

$n_2$   
**TPA generated e-h pairs**  
**Generated carrier absorption**

**Bindra and Kar APL79,3761(2001)**

## Intrinsic Optical Bistability

$$E_s = 3E_h / (\epsilon_s / \epsilon_h + 2)$$

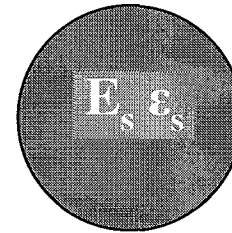
$$\epsilon_s / \epsilon_h = \epsilon_0 + \gamma |E_s|^2$$

Rustagi( 1997)

$$\gamma = |\gamma| e^{i\theta}$$

$$\text{Re}((\epsilon_0 + 2)e^{-i\theta}) < 0$$

$$3|\epsilon_0 + 2|^2 / 4 < (\text{Re}(\epsilon_0 + 2)e^{-i\theta})^2 < |\epsilon_0 + 2|^2$$



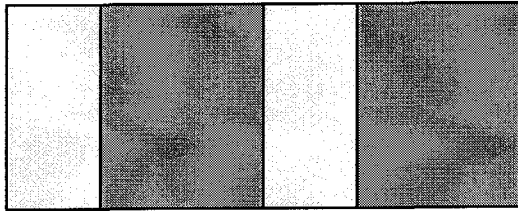
$E_h \epsilon_h$

Leung(PRA 1984)

Selfconsistent solutions  
give optical bistability

Assumed real  $\gamma$





$$\alpha d + (1 - \alpha)d$$

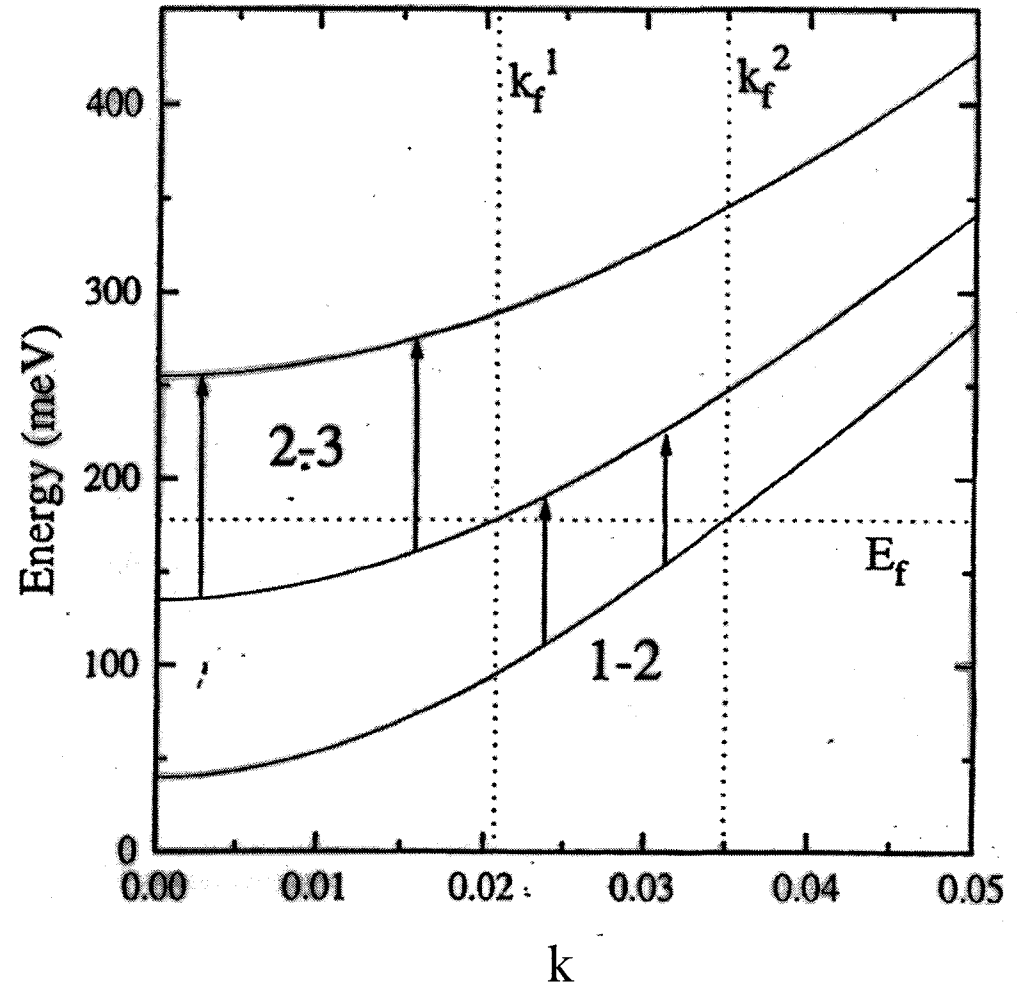
$$(\epsilon_W)_{zz} \quad (\epsilon_B)_{zz}$$

$$E_{1k} = E_1 + \frac{\hbar^2 k^2}{2m^*}$$

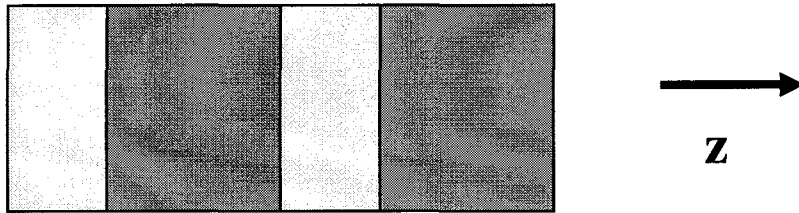
$$E_{2k} = E_2 + \frac{\hbar^2 k^2}{2m^*}$$

$$E_{1k} - E_{2k} = E_1 - E_2$$

Warburton et al PRL(1998)



effective medium theory : intersub-band resonances



$$\alpha d + (1 - \alpha)d$$

$$(\epsilon_W)_{zz} \quad (\epsilon_B)_{zz}$$

$$1/\langle \epsilon \rangle = \alpha / \epsilon_W + (1 - \alpha) / \epsilon_B$$

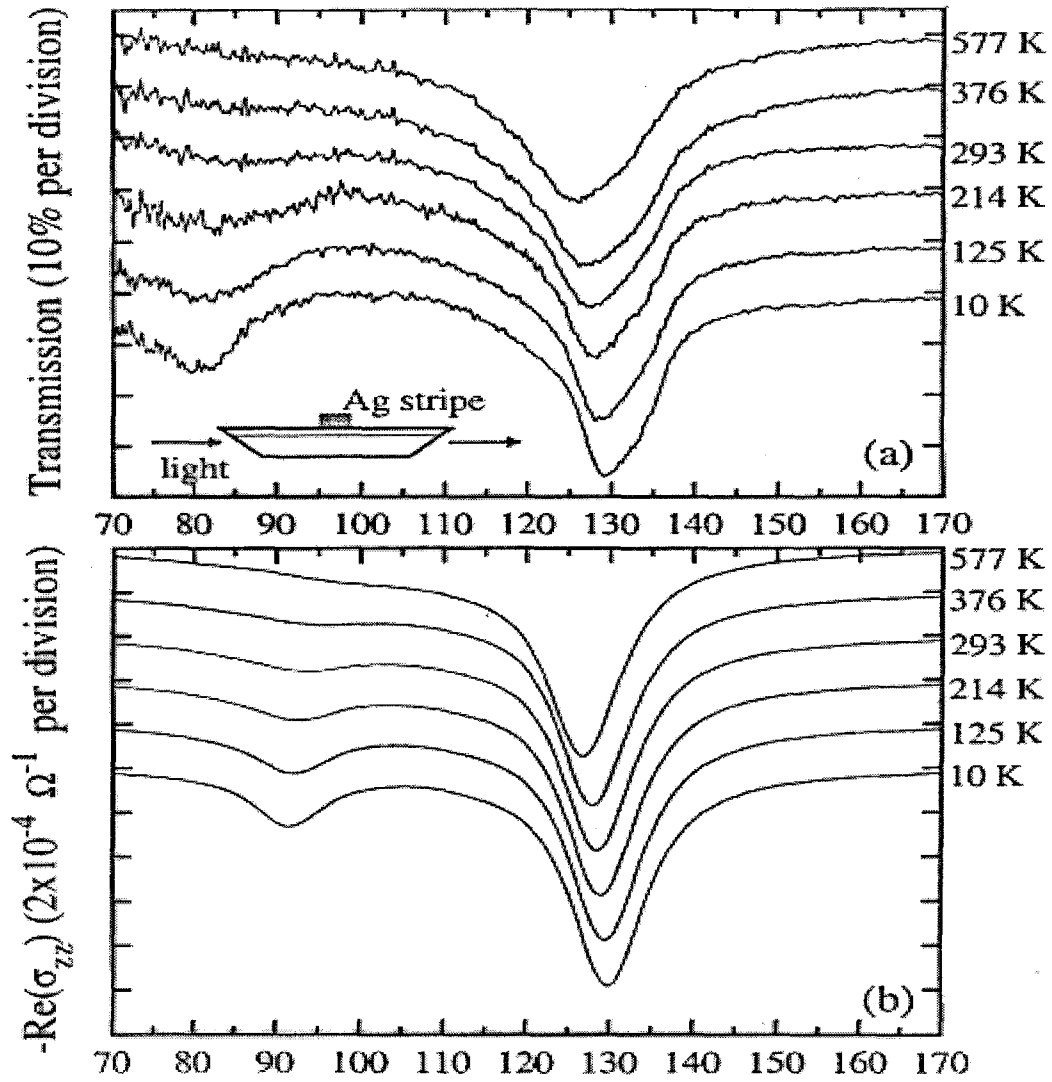
$$\epsilon_W = \epsilon_{W \text{ bulk}} + \epsilon_{W \text{ inter-sub-band?}}$$

$$E_W = \epsilon_B \langle E \rangle / \{ \epsilon_B \alpha + \epsilon_W (1 - \alpha) \},$$

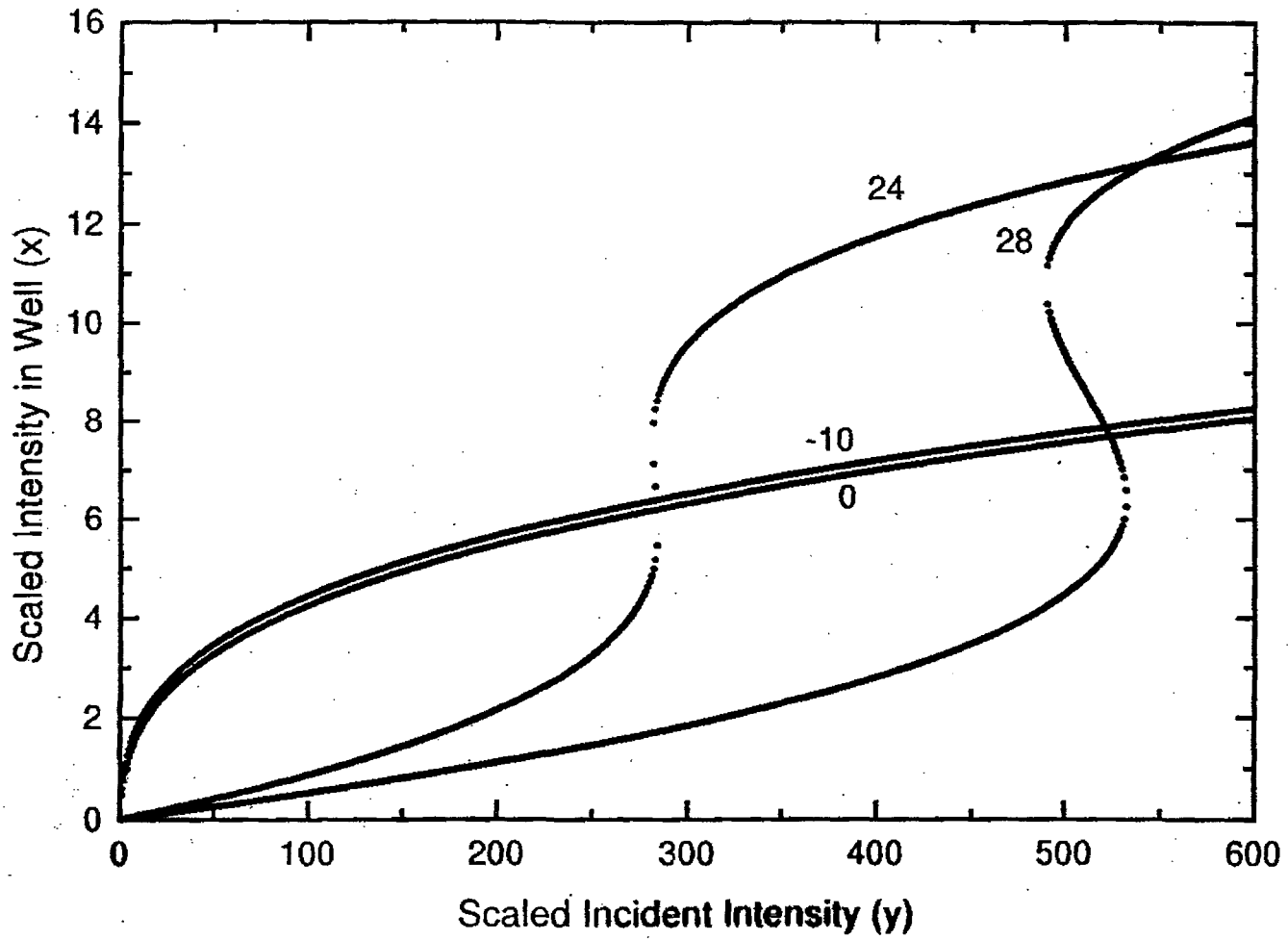
$$E_B = \epsilon_W \langle E \rangle / \{ \epsilon_B \alpha + \epsilon_W (1 - \alpha) \}$$

$$\langle E \rangle = \alpha E_W + (1 - \alpha) E_B$$

**inter-sub-band plasmon :  $1/\langle \epsilon \rangle \rightarrow 0$**



**S Mukhopadhyay+KCR(1999)**



**S Mukhopadhyay+KCR(1999)**

## **SUMMARY**

***EMPIRICAL PSEUDOPOTENTIAL AND TIGHT BINDING CALCULATIONS  
BECOMING RELIABLE FOR SPHERICAL QUANTUM DOT SPECTRA  
SELECTION RULES LESS STRICT FOR SMALL QUANTUM DOTS***

***NEAR FIELD METHODS EXCITING FOR SINGLE QD SPECTROSCOPY***

***SHAPE DEPENDENCE OF QUANTUM CONFINEMENT AND  
DEPOLARIZATION FIELDS IMPORTANT***

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***References:***

**H. Kuhn Fortsch Chem Org Nat 16,169(1958), 17,404 (1959)**

**Semiconductor Quantum Dots - Physics, Spectroscopy and Applications**

**Y.Masumoto and T.Takagahara (eds) *Springer (2002)***

One important advantage of the TB theory is that it can treat even non-spherical shapes quite easily, whereas it would be practically impossible to solve the corresponding envelope-function equations.

**Nair,Ramaniah,Rustagi PRB 45,5969(1992)**