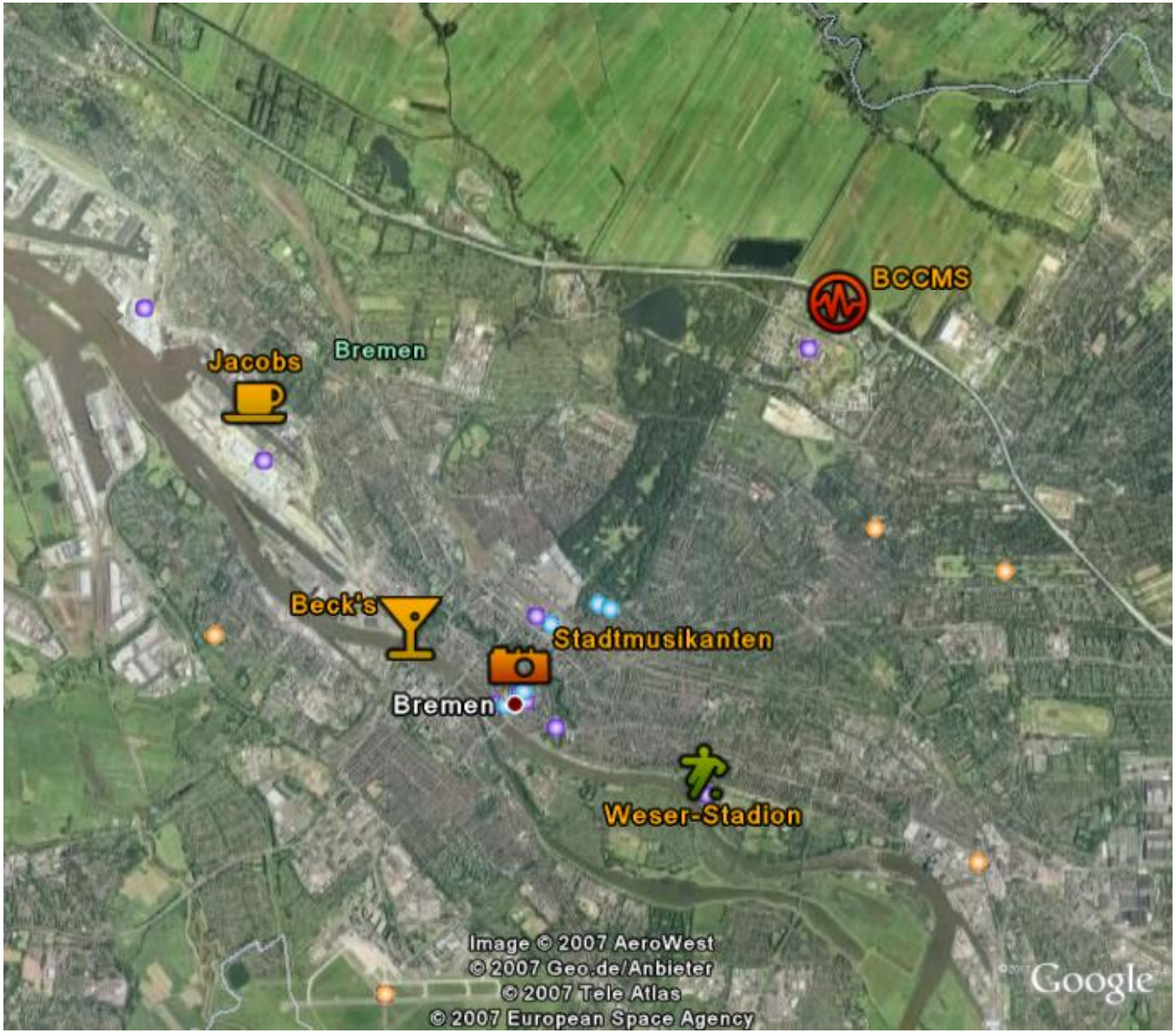
Light induced structural changes in Silicon nanostructures: From quantum dots to nanowires

Thomas Niehaus

Bremen Center for Computational Materials Science

Electron Dynamics in Complex Systems

NanoSeminar, Dresden, Spring 2009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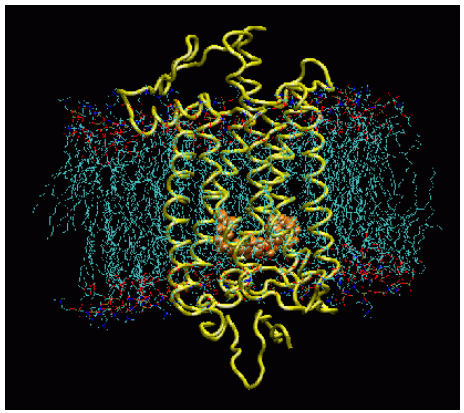
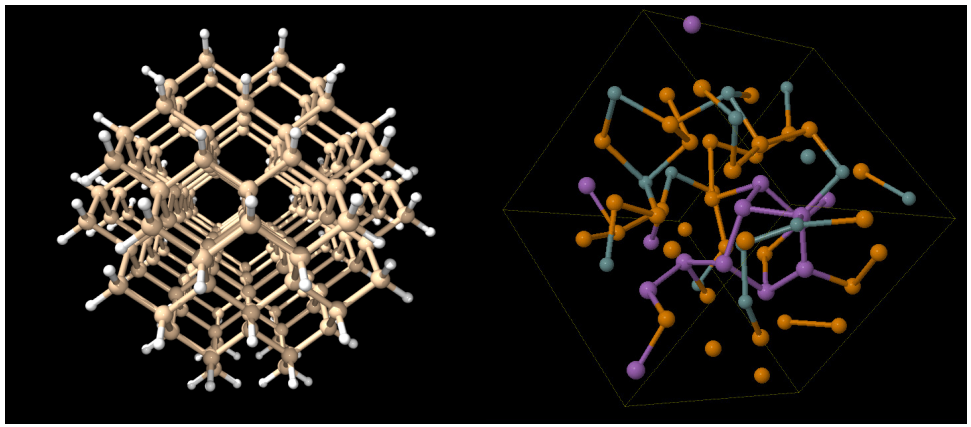
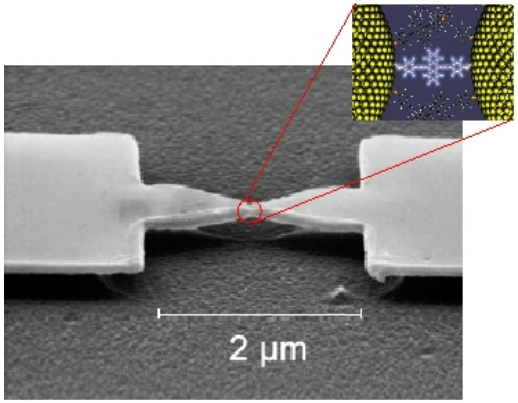
Electron Dynamics in Complex Systems



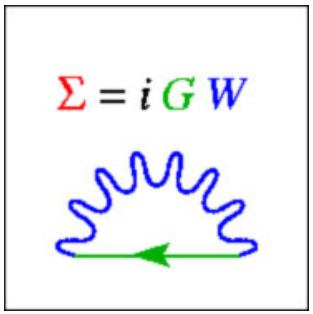
Dynamics of photoactive biosystems



Optical properties of nanostructures and amorphous systems



Molecular electronics

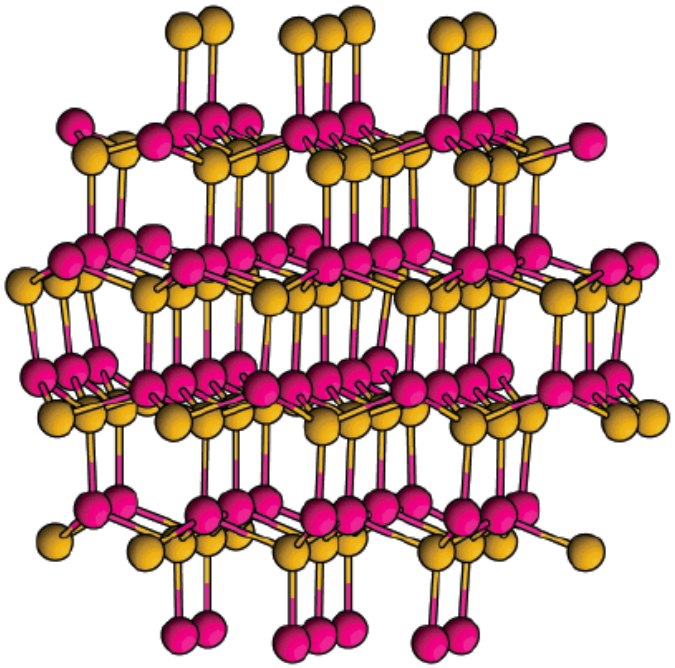


Method development

Outline

1. Motivation
2. Theoretical Methods
   - Time dependent DFT
   - Lightweight TDDFT $\Rightarrow$ TD-DFTB
3. Application to Silicon Nanostructures
   - Hydrogenated SiQD - Simple and boring?
   - Functionalization of Dots - Making them useful
   - Surface reconstruction - Energetics and Spectra
   - Curse and Blessing of Oxygen
   - Silicon nanowires - Confinement in radial and axial dimensions
4. Summary

What is a Quantum Dot?



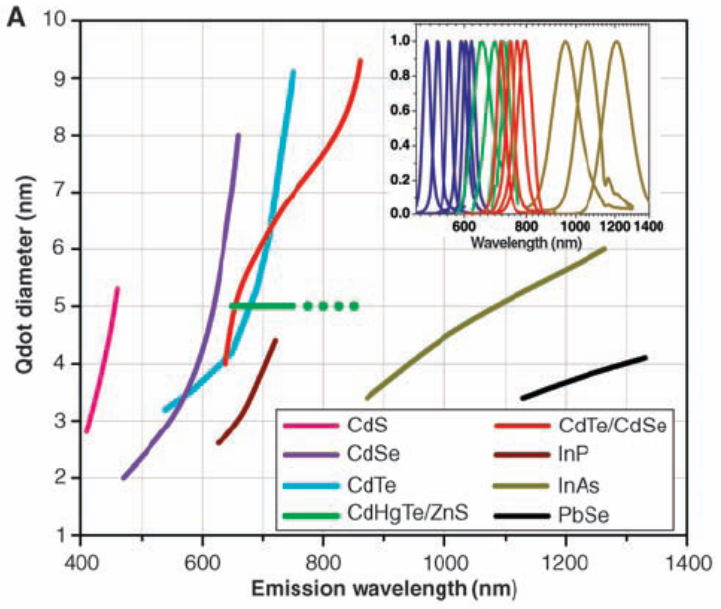
Characteristics

- An object that confines electrons in all three dimensions
- Made mostly from semiconductor material.
- Extension of nanometers
- Electronic level spacing comparable $k_B T$

Properties of Quantum Dots – Size dependent Emission

Fluorescence of Cadmium Selenide Quantum Dots

`www.chemie.uni-hamburg.de/pc/weller/`

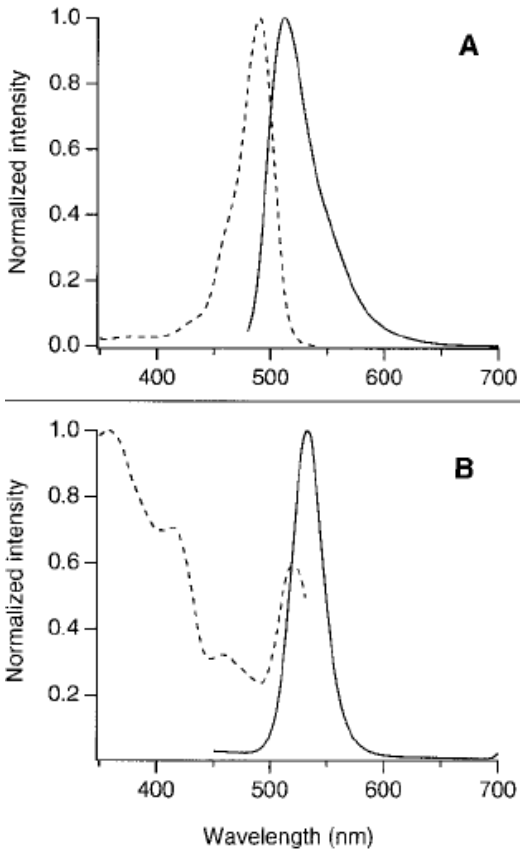


Range of Emission Wavelength

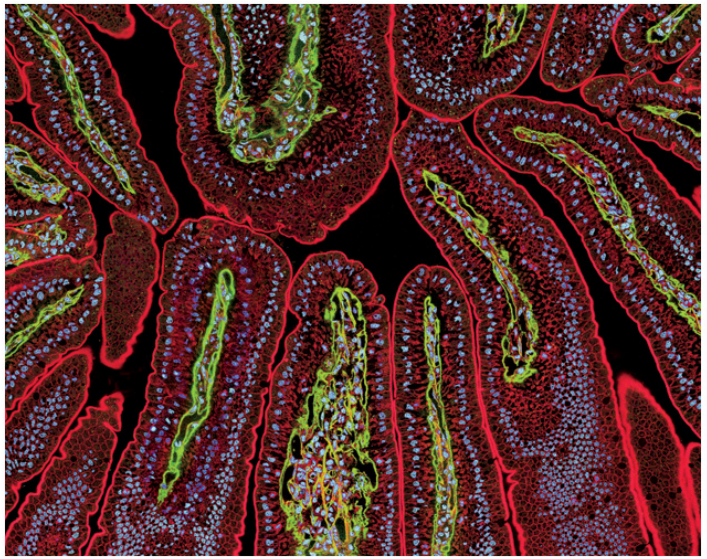
Michalet Science (2005)

Properties of Quantum Dots – Advantages over Dyes

Dye



Dot



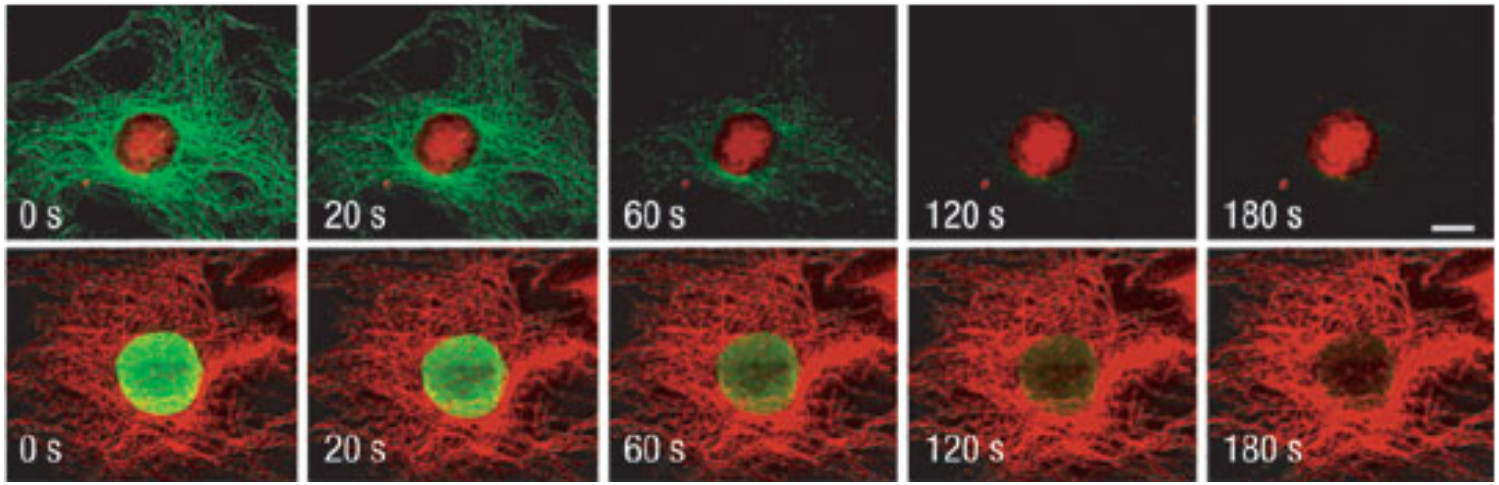
Mouse intestinal section

`http://probes.invitrogen.com`

Multi-color labelling possible

Properties of Quantum Dots – Advantages over Dyes

Medintz, Nature Materials (2005)

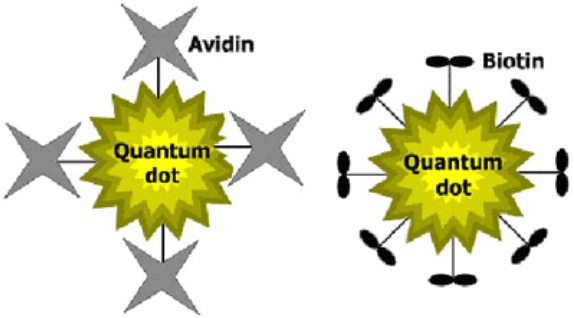


top: Nucleus labelled with Dot, microtubules with Dye

bottom: vice versa

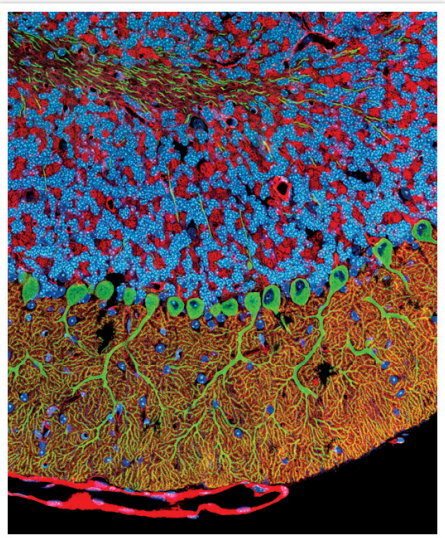
Quantum dots show only limited photobleaching

Quantum dots as markers in biology



Functionalization with antibodies or aptamers

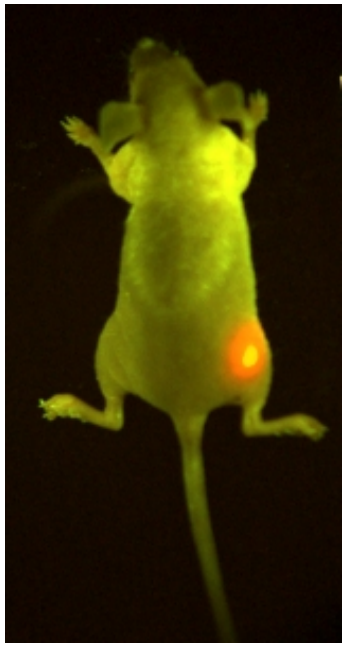
In vitro



Mouse cerebellum

`http://probes.invitrogen.com`

In vivo



Rat tumor

Gao, Science (2004)

Biocompatibility of Cadmium based Dots

NANO LETTERS

2004
Vol. 4, No. 1
11−18

Probing the Cytotoxicity of Semiconductor Quantum Dots

Austin M. Derfus, Warren C. W. Chan,† and Sangeeta N. Bhatia*

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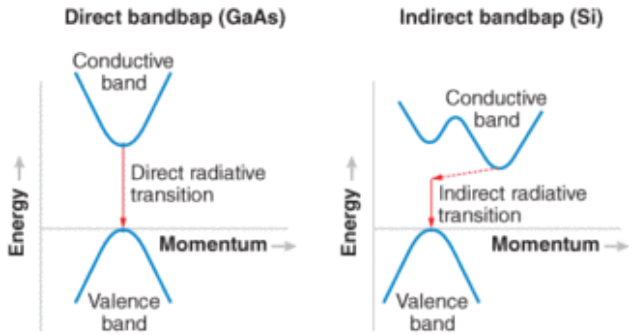
Received September 3, 2003; Revised Manuscript Received November 7, 2003

ABSTRACT

With their bright, photostable fluorescence, semiconductor quantum dots (QDs) show promise as alternatives to organic dyes for biological labeling. Questions about their potential cytotoxicity, however, remain unanswered. While cytotoxicity of bulk cadmium selenide (CdSe) is well documented, a number of groups have suggested that CdSe QDs are cytocompatible, at least with some immortalized cell lines. Using primary hepatocytes as a liver model, we found that CdSe-core QDs were indeed acutely toxic under certain conditions. Specifically, we found that the cytotoxicity of QDs was modulated by processing parameters during synthesis, exposure to ultraviolet light, and surface coatings. Our data further suggest that cytotoxicity correlates with the liberation of free Cd^{2+} ions due to deterioration of the CdSe lattice. When appropriately coated, CdSe-core QDs can be rendered nontoxic and used to track cell migration and reorganization in vitro. Our results provide information for design criteria for the use of QDs in vitro and especially in vivo, where deterioration over time may occur.

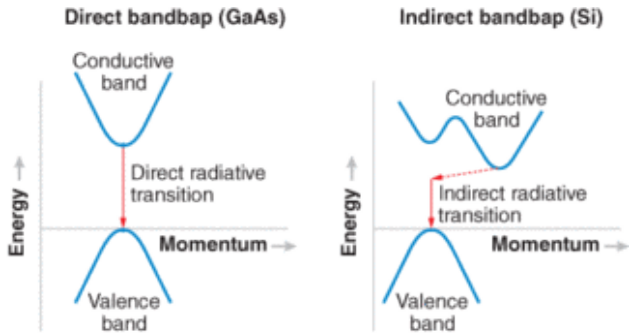
Silicon ???



Bulk Silicon

- phonon assisted emission
- fund. band gap of 1.13 eV

Silicon ???



Bulk Silicon

- phonon assisted emission
- fund. band gap of 1.13 eV

Emission from SiH nanoparticles under UV excitation, Belomin APL (2002)

Silicon Quantum Dots

- Dipole-allowed transition
- Bright emission in the visible

Outline

Time dependent Density Functional Theory

... describes the density evolution of a many electron system subject to a time dependent external potential

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r}, t)|^2$$

of an auxiliary noninteracting (KS) system

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r}, t) = \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}[\rho](\mathbf{r}, t)\right]\phi_i(\mathbf{r}, t)$$

with the local potential

$$v_{\mathrm{KS}}[\rho](\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\mathrm{xc}}[\rho](\mathbf{r}, t)$$

Typical approximations for v_{xc}

Adiabatic approximation

$$v_{xc}^{\text{adia}}[\rho](r,t) = v_{xc}^{\text{stat}}[n]\big|_{n=\rho(r,t)}$$

Property: local in time, no memory effects

Problems: charge transfer states, collective excitations

Typical approximations for v_{xc}

Adiabatic approximation

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Property: local in time, no memory effects
Problems: charge transfer states, collective excitations

Ground state functionals

$$\text{e.g. LDA:} \quad v_x = -c\rho^{\frac{1}{3}}$$

Property: local in space
Problems: $\lim_{r\to\infty} v_{KS} \neq -\frac{1}{r}$, wrong ionization treshold

Why is TDDFT useful?

Conventional DFT is only valid for the groundstate
Excited state properties are accessible within TDDFT

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r},t)$$

Perturbation theory

- Excitation energies
  $\Rightarrow$ UV-Vis spectra
- Forces
  $\Rightarrow$ Resonant Raman spectra
  $\Rightarrow$ Luminescence
- Dipolemoments, Polarizabilities

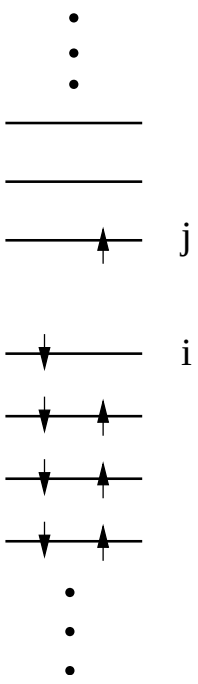
Numerical solution

- Interaction with strong laserfields
- Nonadiabatic effects
  $\Rightarrow$ Collisions
  $\Rightarrow$ Photochemical reactions
- Transport calculations

Why is TDDFT necessary?

Static many-body Hamiltonian H_{MB} provides spectrum directly

$$H_{\mathrm{MB}}(r_1 \dots r_N) \left|\psi_I\right\rangle = \omega_I \left|\psi_I\right\rangle$$



Static DFT Hamil. yields one-particle spectrum

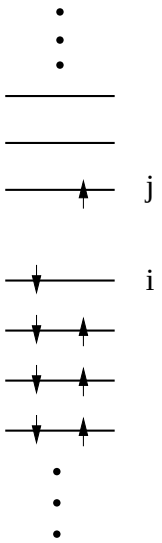
$$H_{\mathrm{DFT}}(r) \left|\phi_i\right\rangle = \epsilon_i \left|\phi_i\right\rangle$$

Zustand	ω_{KS}	Experiment
Ethylen $^1B_{1u}$	6.30	7.65
Propan $^1A'$	5.94	7.19
Butadiene ^1B_u	4.21	5.92

Observation: `Differences` $\omega_{KS} = \epsilon_j - \epsilon_i$ `underestimate optical excitation energies`

$\Rightarrow$ Use time-dependent density to obtain ω_I

Perturbation theory - linear response



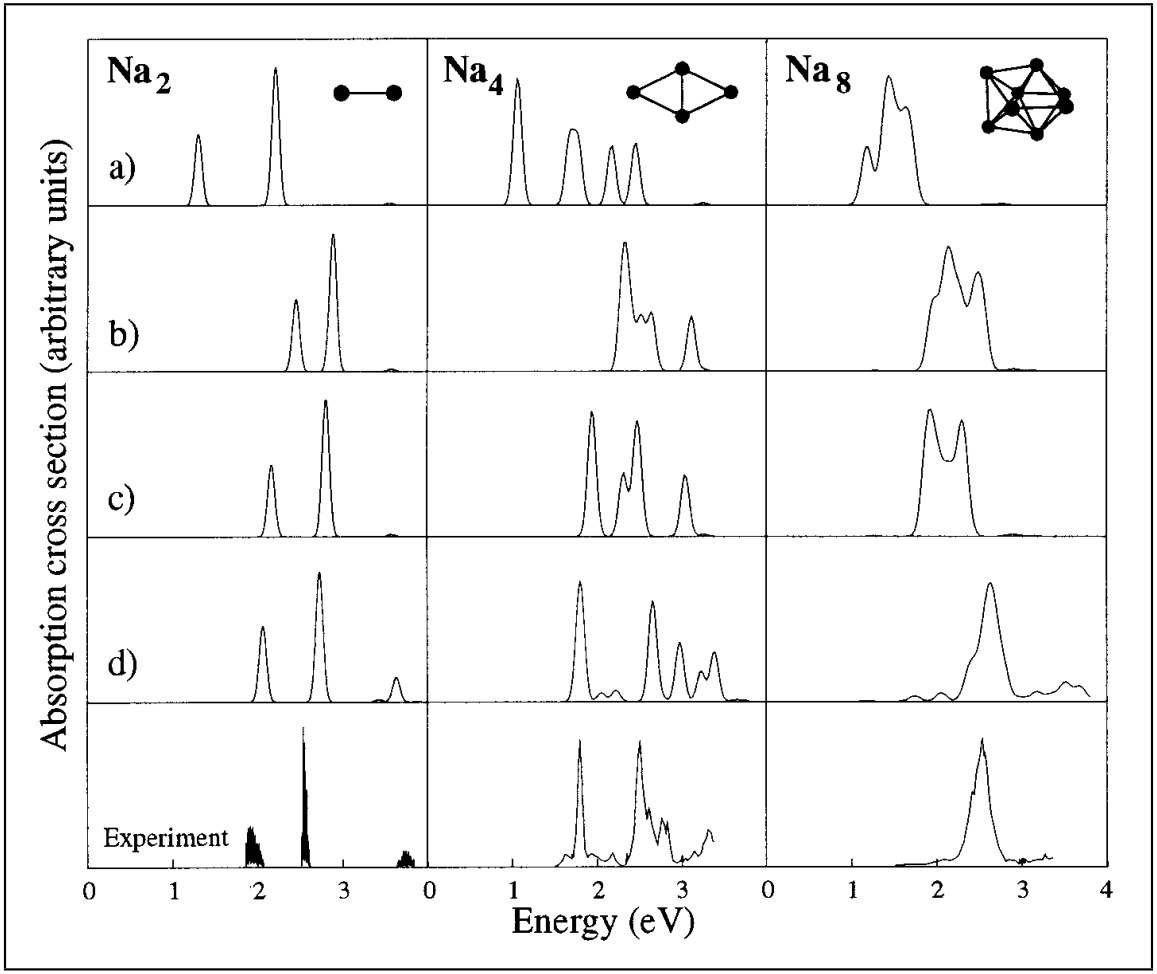
Equation to solve (Singlets):

$$\sum_{kl} \left[\omega_{ij}^2 \delta_{ik}\delta_{jl} + 2\sqrt{\omega_{ij}} K_{ij,kl} \sqrt{\omega_{kl}}\right] \; F_{kl}^{I} = \omega_I^2 \; F_{ij}^{I}$$

Couplingmatrix K leads to correction of single-particle picture

$$K_{ij,kl} = \iint' \psi_i(\mathbf{r})\psi_j(\mathbf{r}) \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) \; \psi_k(\mathbf{r}')\psi_l\,(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

Application to metal clusters



Vasiliev et al., PRL **82**, *1919 (1999)*

Outline

Density Functional based Tight Binding (DFTB)

Main approximations - Ground state

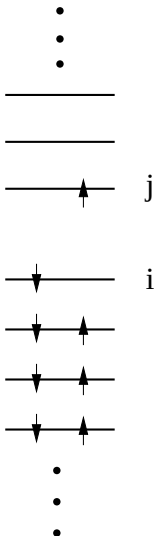
- Minimal AO basis: $\psi_i(\mathbf{r}) = \sum_\mu c_{\mu i}\phi_\mu(\mathbf{r} - \mathbf{R}_A)$
- Density divided into reference density (ρ_0) and fluctuation: $\rho = \rho_0 + \delta\rho$
- Total energy:

$$E_{\text{tot}} = \sum_i \sum_{\mu\nu} c_{\mu i} H^0_{\mu\nu}[\rho_0] c_{\nu i} + \sum_{AB} \gamma_{AB} \Delta q_A \Delta q_B + U_{\text{rep}}$$

- Two-center approximation, matrix elements calculated not fitted
- γ_{AB} represents e-e interaction (including xc)

Variational principle yields molecular orbitals and energies

DFTB approximation of TDDFT = TD-DFTB



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Get single particle energies $\{\epsilon_i\}$ from DFTB

Couplingmatrix K leads to correction of single-particle picture

DFT: $$K_{ij,kl} = 2 \iint \psi_i(\mathbf{r})\,\psi_j(\mathbf{r}) \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) \psi_k(\mathbf{r}')\,\psi_l\,(\mathbf{r}')\,d\mathbf{r}d\mathbf{r}'$$

DFTB: $$K_{ij,kl} = 2\sum_{AB} \quad q_A^{ij} \quad \gamma_{AB}(|\mathbf{R}_A - \mathbf{R}_B|, U_A, U_B) \quad q_B^{kl}$$

Niehaus, *PRB* **63** 085108 (2001)

TD-DFTB performance

Excitation energies (eV)

Molecule	State	Exp.	TD-DFTB		TDDFT[1]	
			ω_I	ω_{ij}	ω_I	ω_{ij}
Ethylen	$^3B_{1u}(\pi \rightarrow \pi^*)$	4.40	5.47	6.30	4.16	5.66
	$^1B_{1u}(\pi \rightarrow \pi^*)$	7.65	7.81	6.30	7.44	5.66
Propynal	$^3A''(n \rightarrow \pi^*)$	2.99	4.04	4.04	2.74	3.15
	$^1A''(n \rightarrow \pi^*)$	3.56	4.04	4.04	3.37	3.15

[1] BPW91//6-311+G**

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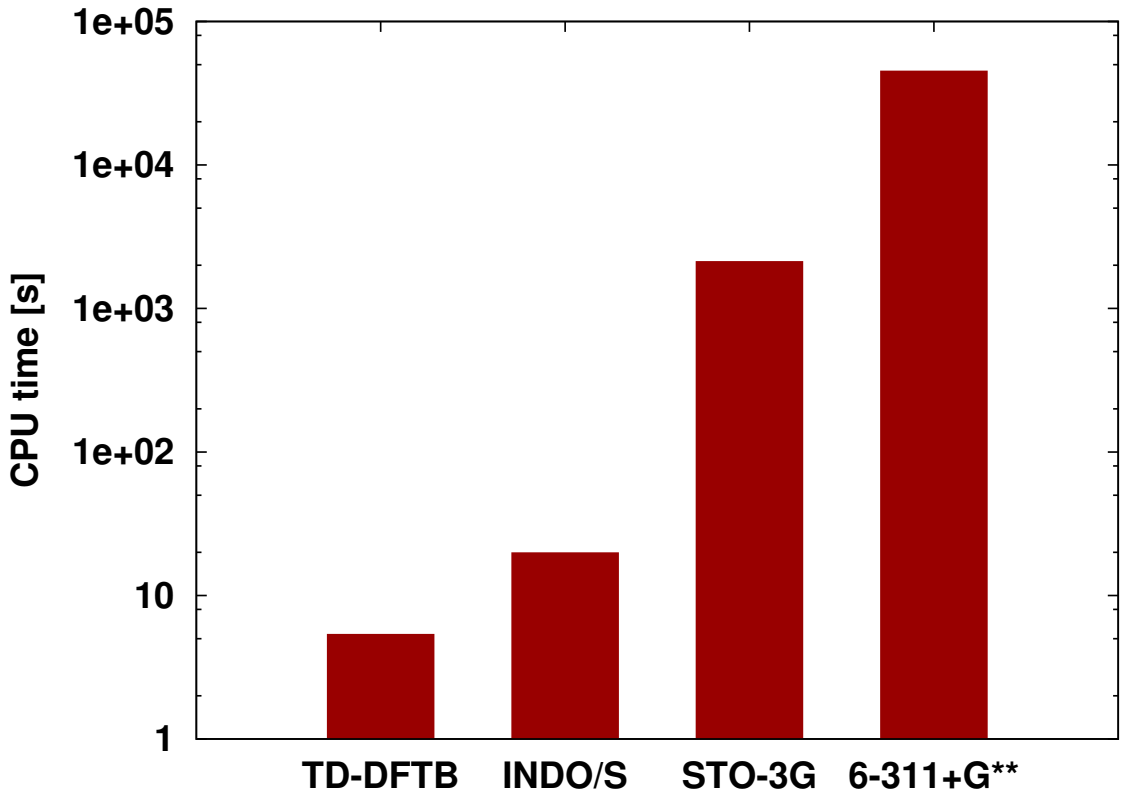
[1] BPW91//6-311+G**

Mean absolute error (eV)

	TD-DFTB	BPW91		INDO/S
		6-311+G**	STO-3G	
Sing. (16 Com.)	0.38	0.36	1.19	0.56
Trip. (13/11 Com.)	0.64	0.37	0.49	1.38

Numerical issues

Sum of CPU times (ground + excited state) for test set of 10 organic molecules ($<$ 10 atoms). TDDFT results are for the BPW91 functional.



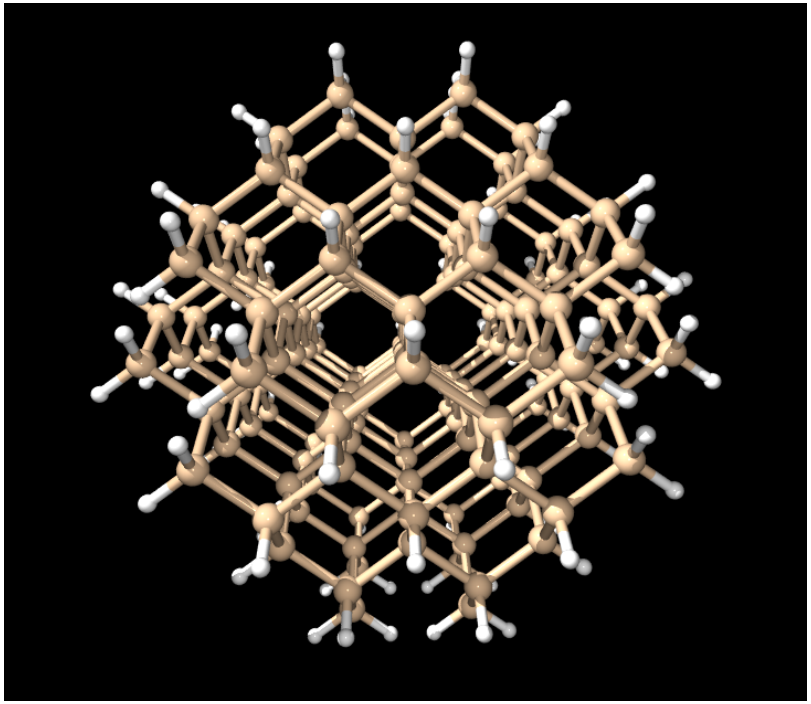
TD-DFTB performance

Characteristics

- No empirical parameters
- Accuracy better than TD-HF or CIS
- Scales N^3 with system size
- 10^3 to 10^4 times faster than TDDFT
- Analytical excited state gradients available

Outline

Generation of models



- Spherical fragments Si_{1-199} from bulk Si
- Passivation with Hydrogen and relaxation
- Si-Si bonds 2.33-2.38 Å
- T_d symmetry
- $d(Si_5) = 0.45$ nm to $d(Si_{199}) = 2.0$ nm

Validation of TD-DFTB

$S_1 - S_0$ energy [eV]

	DFTB	PBE	B3LYP	MR-MP2	exp
SiH_4	10.3	8.76	9.25		8.8
Si_5H_{12}	6.40	6.09	6.66	6.56	6.5
$Si_{29}H_{36}$	4.42	3.65	4.52	4.45	
$Si_{35}H_{36}$	4.37	3.56	4.42	4.33	

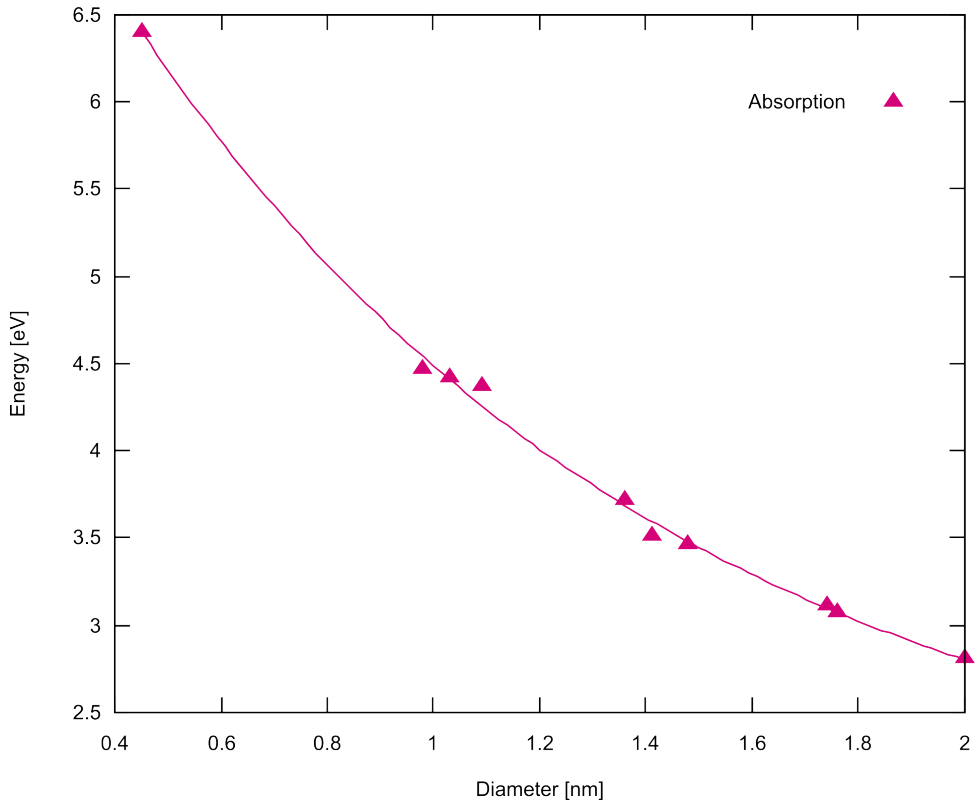
Validation of TD-DFTB

$S_1 - S_0$ energy [eV]

	DFTB	PBE	B3LYP	MR-MP2	exp
SiH_4	10.3	8.76	9.25		8.8
Si_5H_{12}	6.40	6.09	6.66	6.56	6.5
$Si_{29}H_{36}$	4.42	3.65	4.52	4.45	
$Si_{35}H_{36}$	4.37	3.56	4.42	4.33	

B3LYP functional of choice for SiQD
DFTB is fine for larger dots

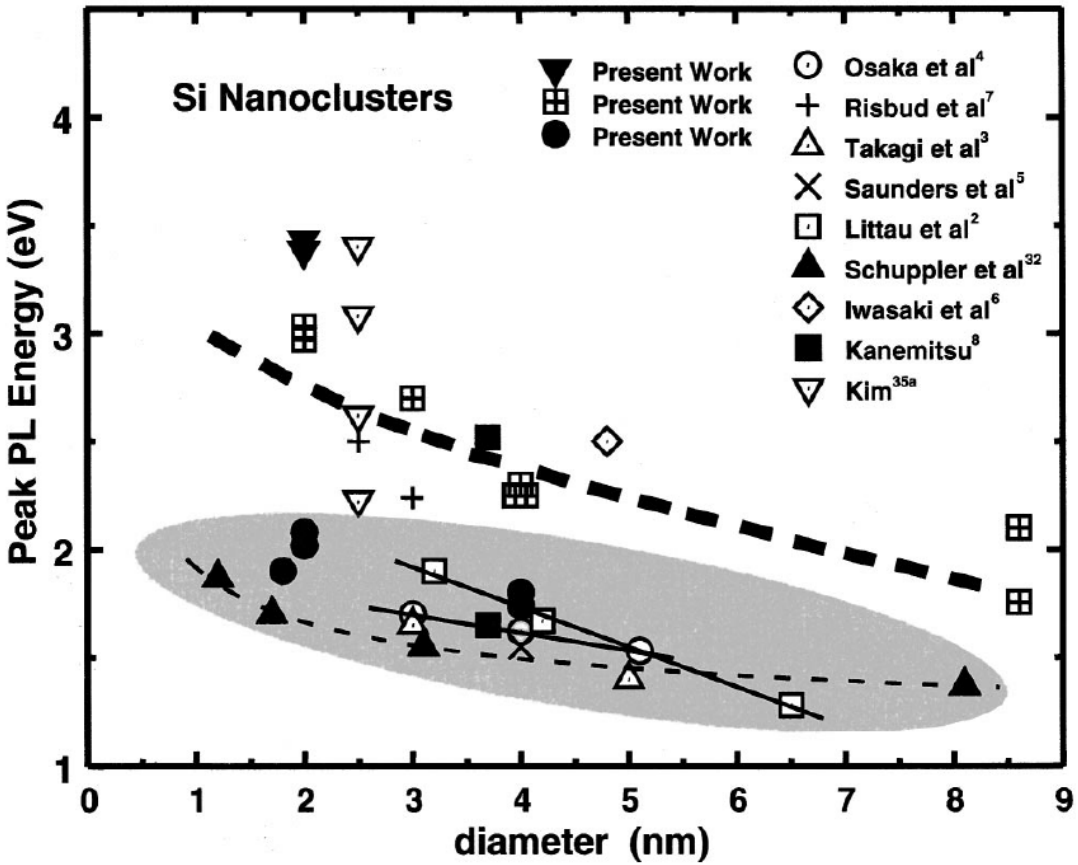
UV-Vis absorption energies of H-SiQD



Anticipated Particle-in-a-box behaviour

Wang, *JPC C* **111** 12588 (2007), *APL* **90** 123116 (2007)

Experimental reports on SiQD photoluminescence



Peak PL versus Si nanocrystal size

Wilcoxon et al. PRB **60** 2704 (1999)

Luminescence and excited state processes

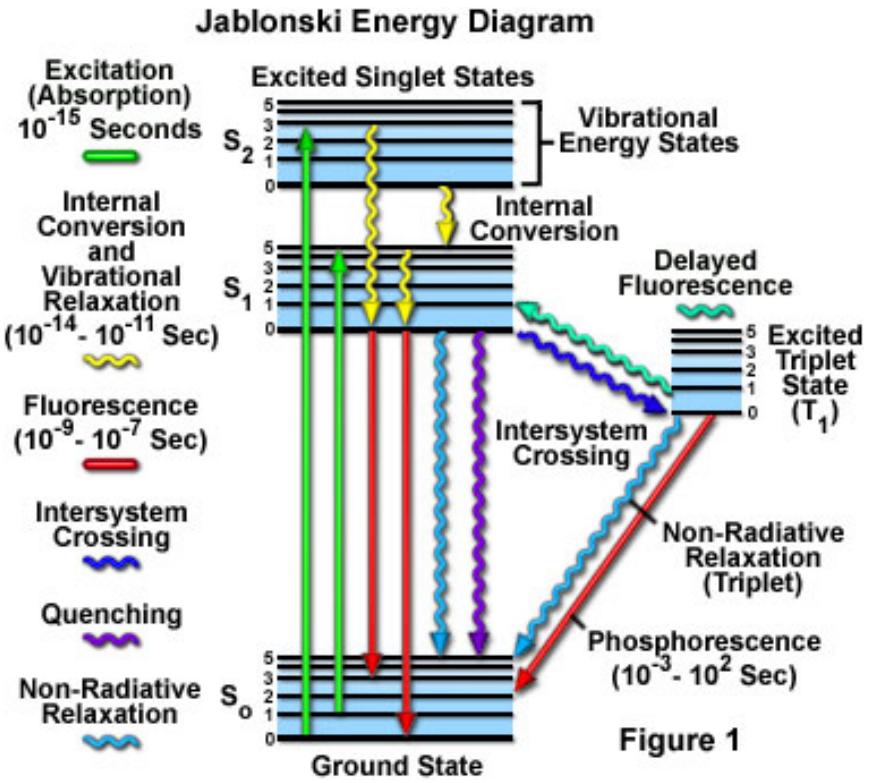


Figure 1

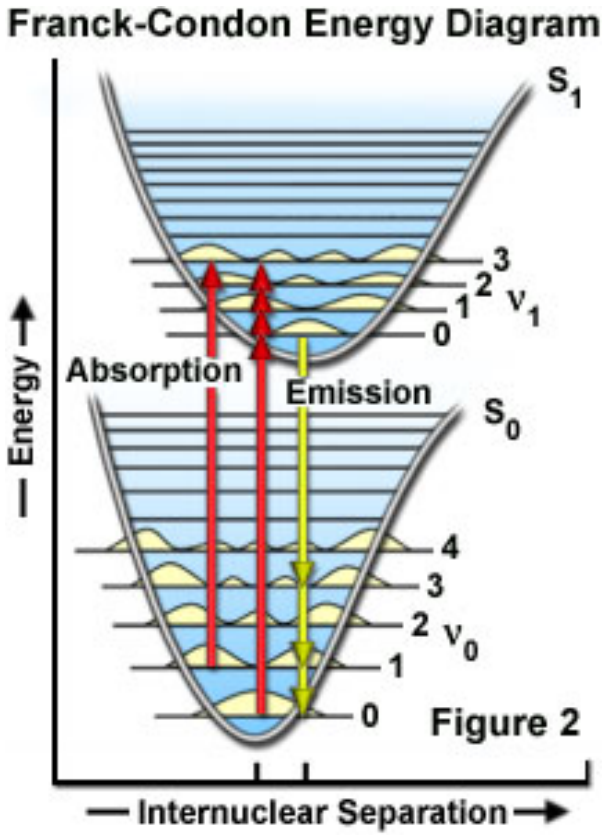
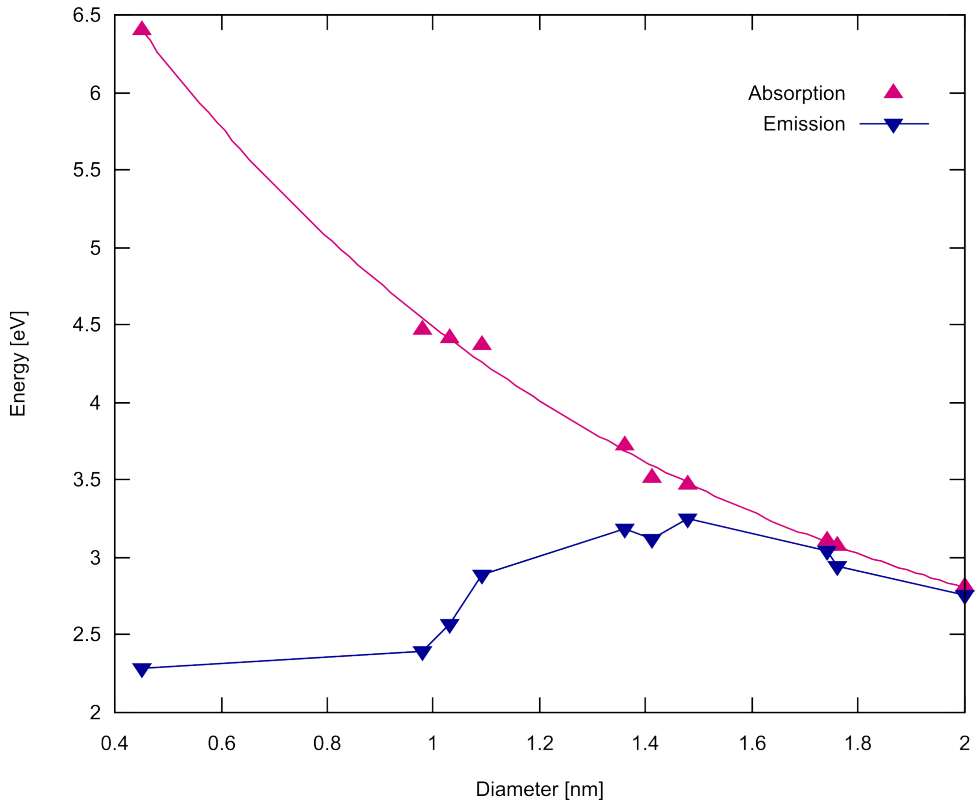


Figure 2

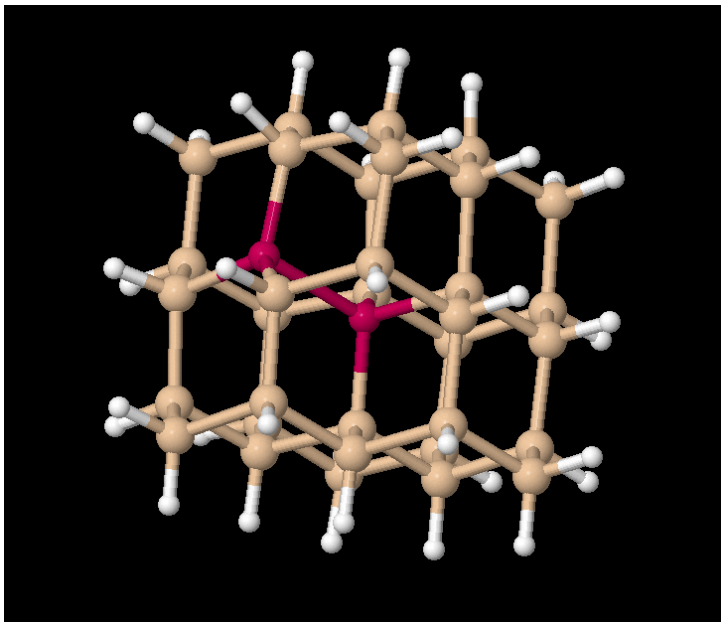
Luminescence properties of H-SiQD



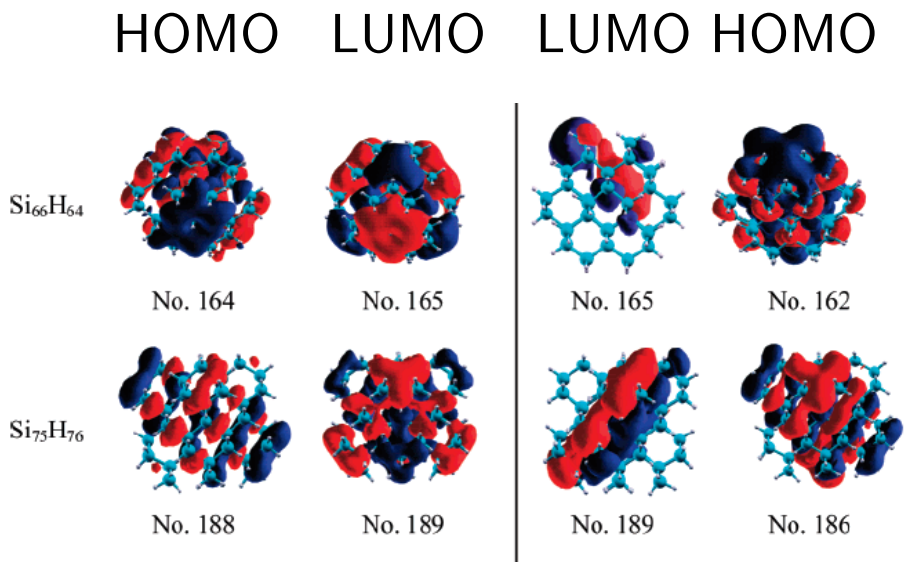
Huge Stokes shift for small particles

Wang, *JPC C* **111** 12588 (2007), *APL* **90** 123116 (2007)

Structure relaxation in the excited state



S_1 optimum of $Si_{35}H_{36}$

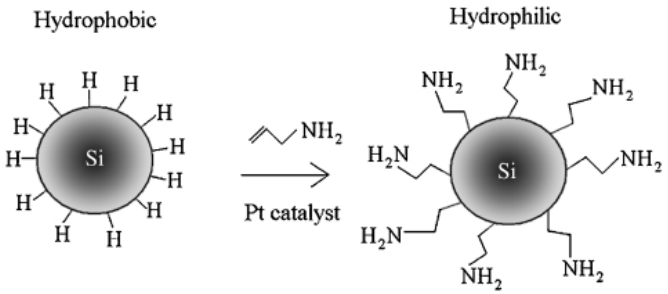


S_0 opt. S_1 opt.

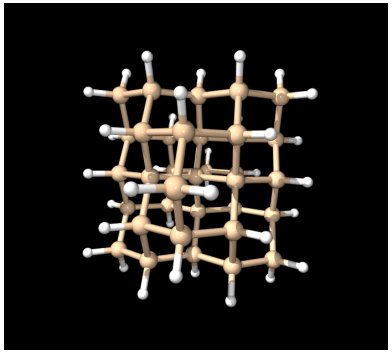
Formation of a self-trapped exciton

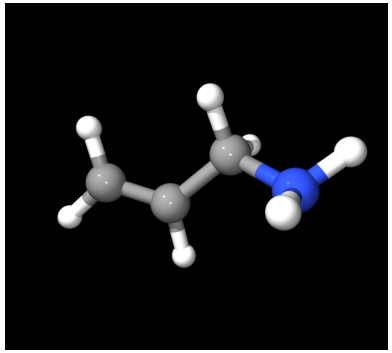
Outline

Functionalization of dots



Warner, *Angew. Chem.* (2005)



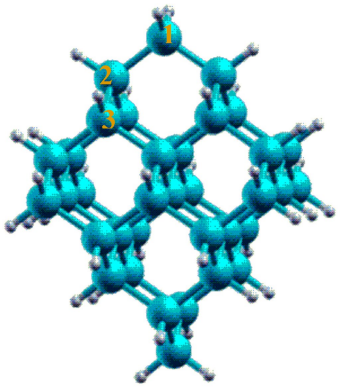


Functionalization with allylamine leads to

- Increased solubility
- Decreased aggregation
- Decreased oxidation

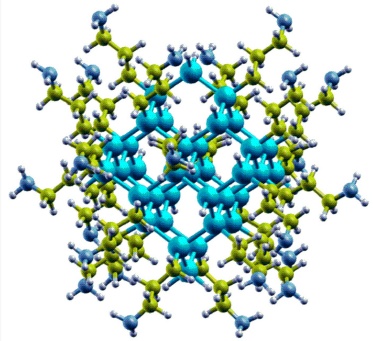
Does coating destroy the optical properties?

Generation of models



No preference in adsorption site

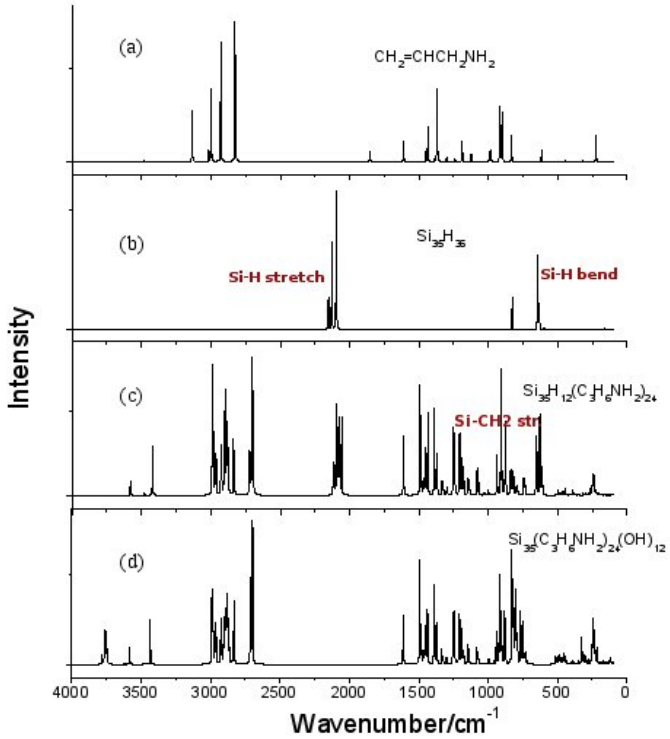
	Site	Binding energy [eV]
$Si_{35}H_{36}$	1	2.44
	2	2.43
	3	2.44
$Si_{59}H_{60}$	1	2.36
	2	2.44
	3	2.43



Complete coverage impossible

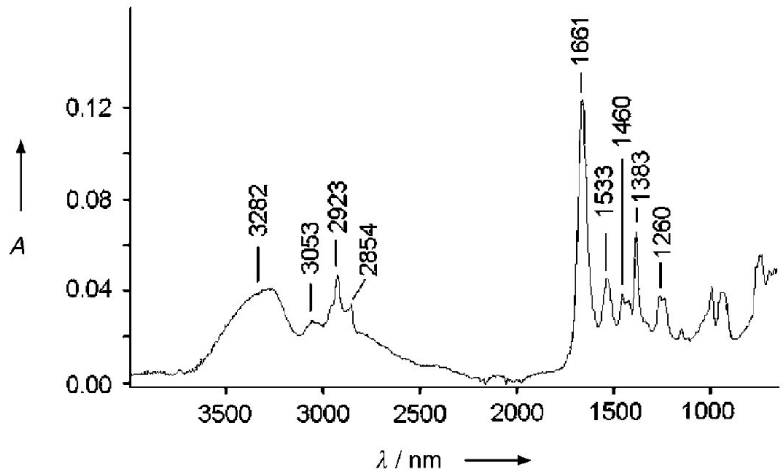
Wang, *JPC C* **111** 2394 (2007)

Simulated and experimental IR spectrum



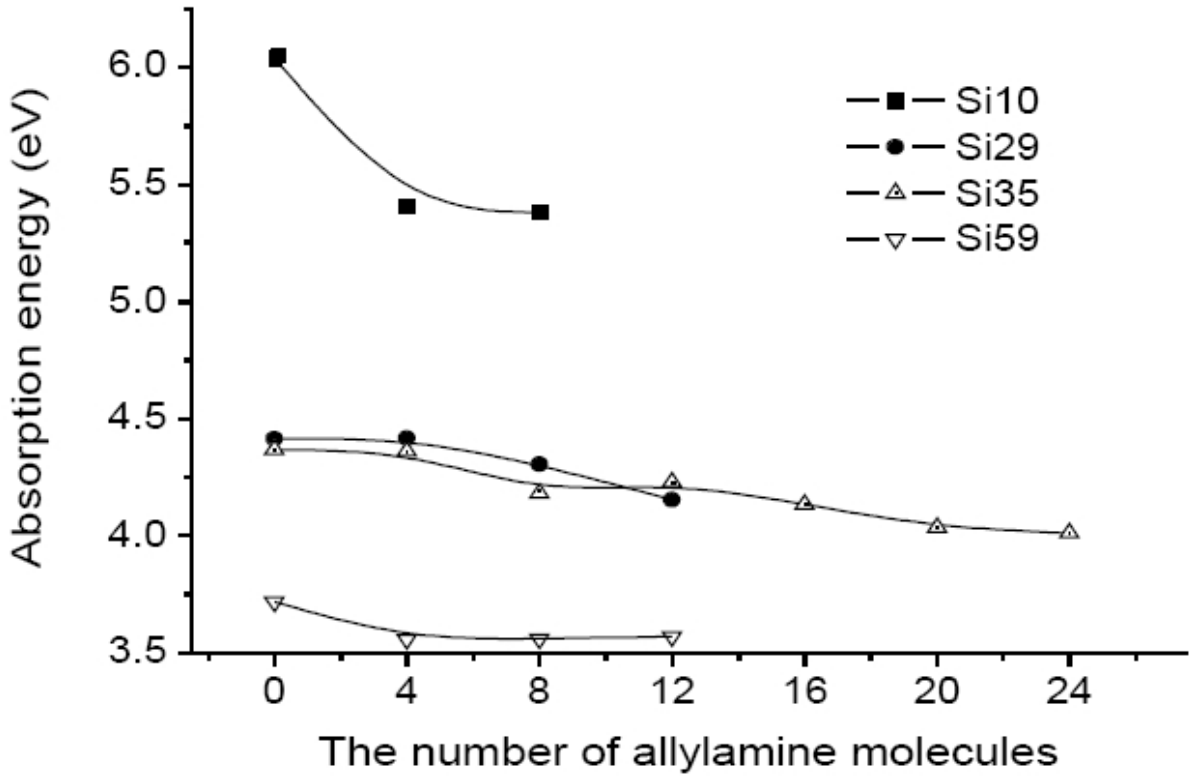
Wang, *JPC C* **111** 2394 (2007)

Partial oxidation?



Warner, *Angew. Chem.* (2005)

TD-DFTB absorption energies



Strong quantum size effect – Little dependence on passivation

Maximum absorption and emission peaks

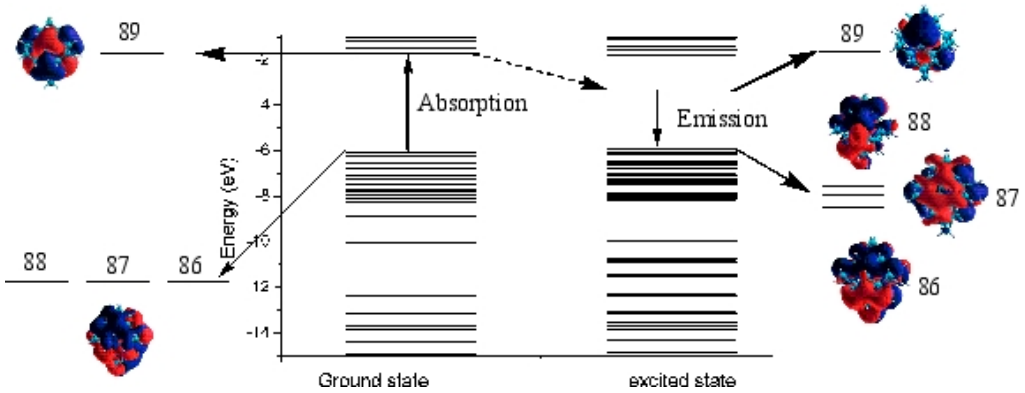
# Si	# allylamine	Absorption [nm]	Emission [nm]	Shift [nm]
10	0	205	421	216
29	0	281	405	124
35	0	284	429	145
	4	284	425	141
	8	297	462	165
59	0	334	390	56
Exp.		320	480	160

Results

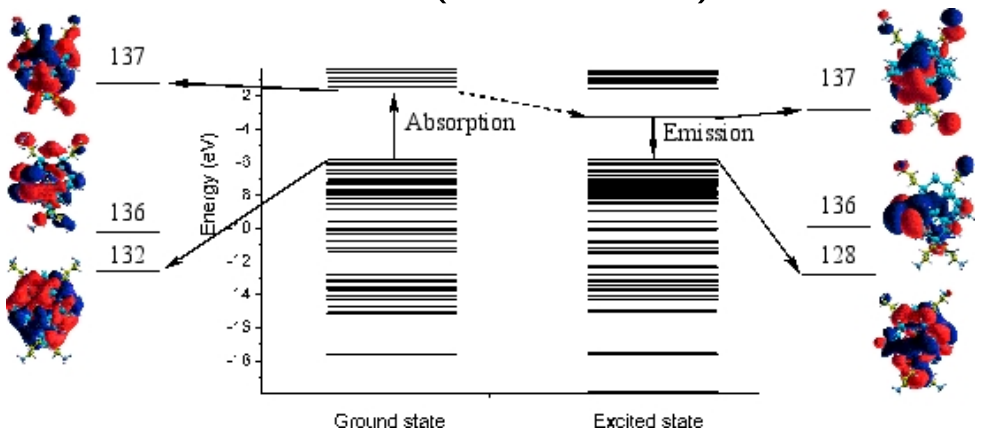
- Good agreement between exp. and theory for Si_{35}
- Red light emission requires larger dots as Si_{59}

Molecular orbital analysis

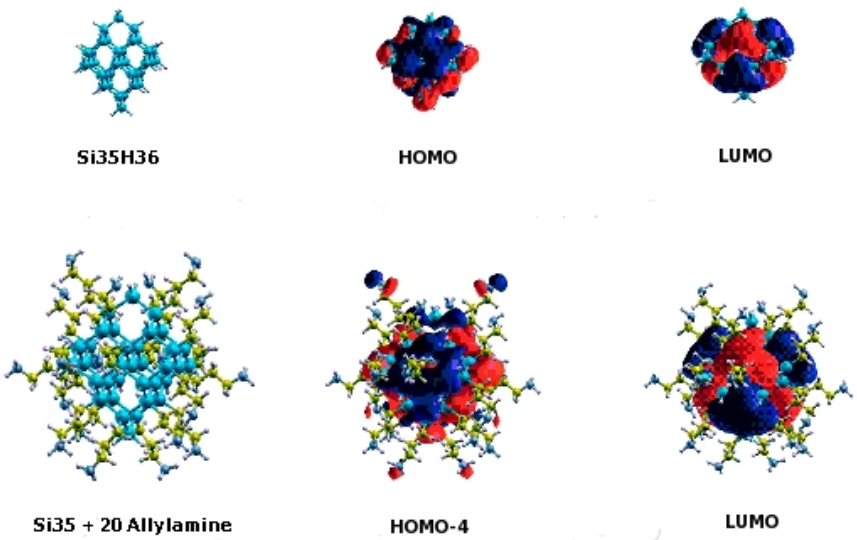
$Si_{35}H_{36}$



$Si_{35}H_{32}(C_3H_6NH_2)_4$



Conclusions on allylamine functionalization

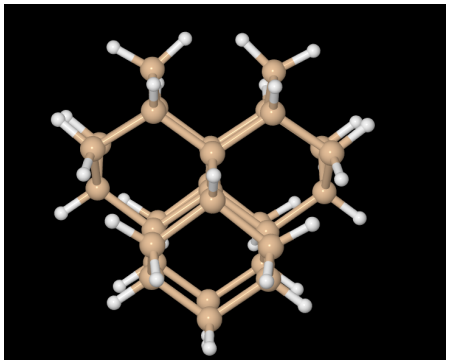


Allylamine is a promising candidate for protection and functionalization of Silicon quantum dots without perturbation of their favorable optical properties.

Wang, Zhang, Niehaus, Frauenheim *JPC C* **111** 2394 (2007)

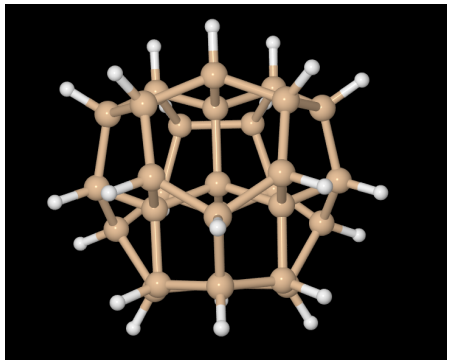
Outline

Reconstructed Silicon Quantum Dots



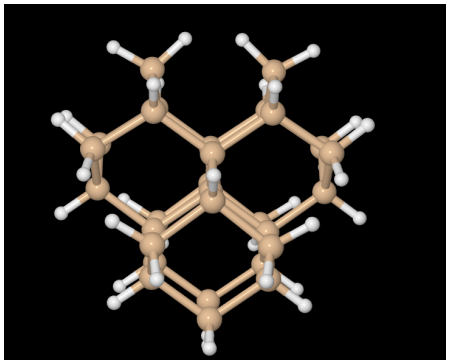
$Si_{29}H_{36}$

Dimer formation by H_2 abstraction



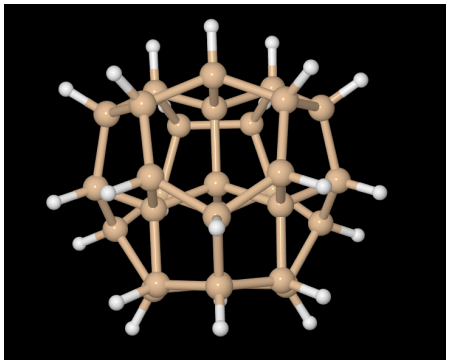
$Si_{29}H_{24}$

Reconstructed Silicon Quantum Dots

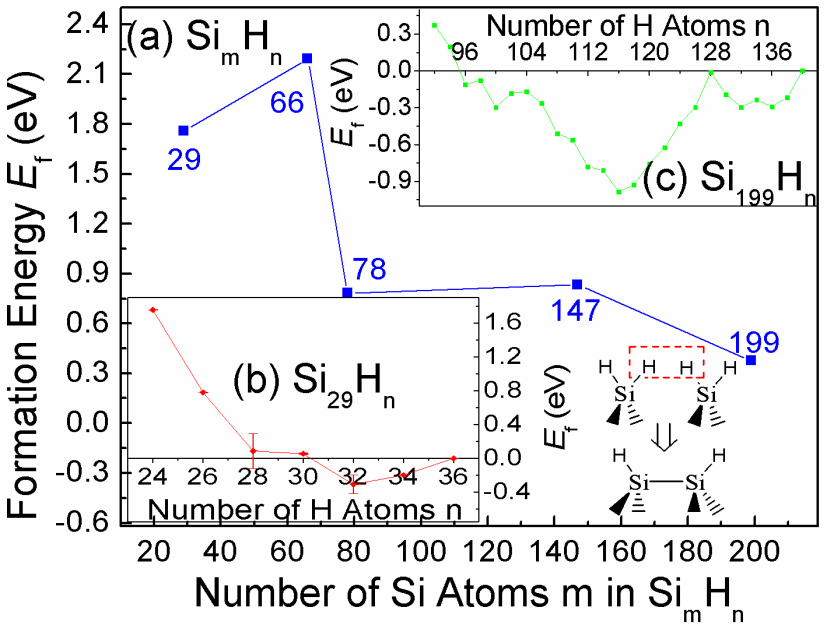


$Si_{29}H_{36}$

Dimer formation by H_2 abstraction



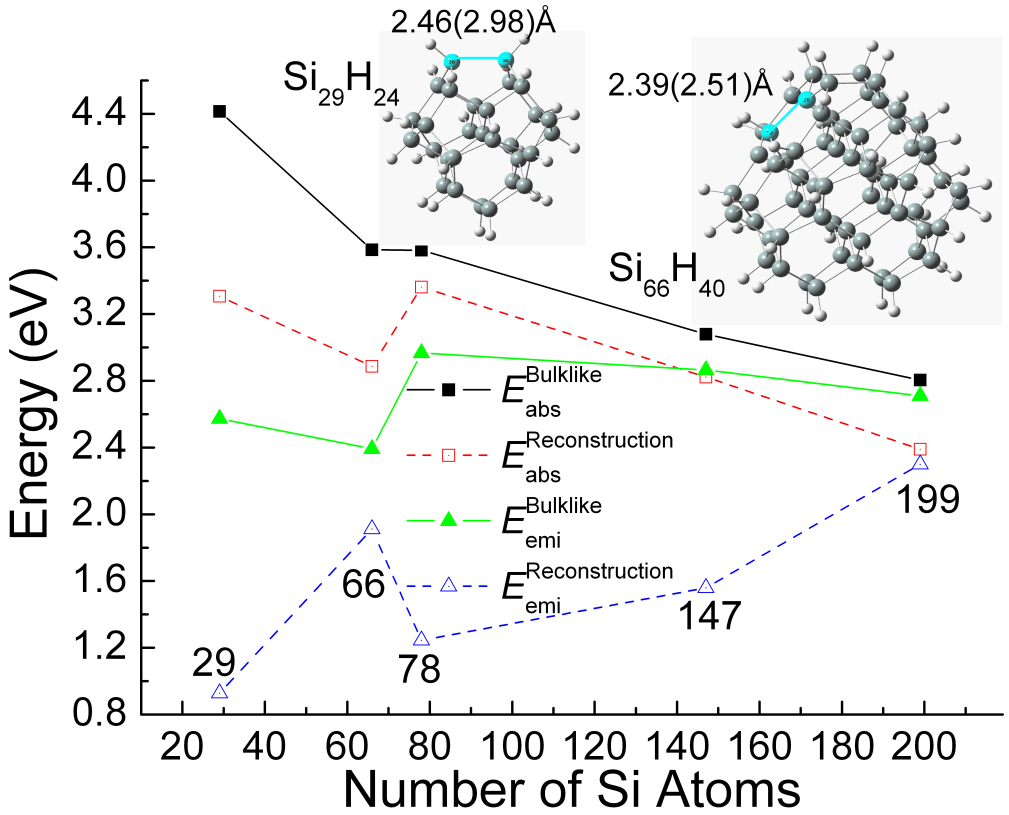
$Si_{29}H_{24}$



Formation energy:

$$E_f = E_{re} + (\Delta n/2) E_{H_2} - E_{bl}$$

Optical properties



"Inverse" quantum confinement effect

Wang, Zhang, Lee, Frauenheim, Niehaus *APL* **93** 243120 (2008)

Outline

Curse and Blessing of Oxygen – The Curse

VOLUME 82, NUMBER 1 PHYSICAL REVIEW LETTERS 4 JANUARY 1999

Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen

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(Received 25 September 1998)

Depending on the size, the photoluminescence (PL) of silicon quantum dots present in porous silicon can be tuned from the near infrared to the ultraviolet when the surface is passivated with Si-H bonds. After exposure to oxygen, the PL shifts to the red by as much as 1 eV. This shift and the changes in PL intensity and decay time, show that both quantum confinement and surface passivation determine the electronic states of silicon quantum dots. A theoretical model in which new electronic states appear in the band gap of the smaller quantum dots when a Si═O bond is formed, is in good agreement with experiments. This result clarifies the controversy regarding the PL mechanisms in porous silicon. [S0031-9007(98)08118-6]

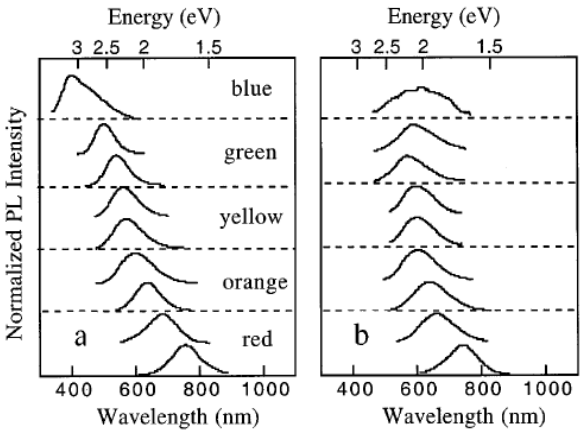
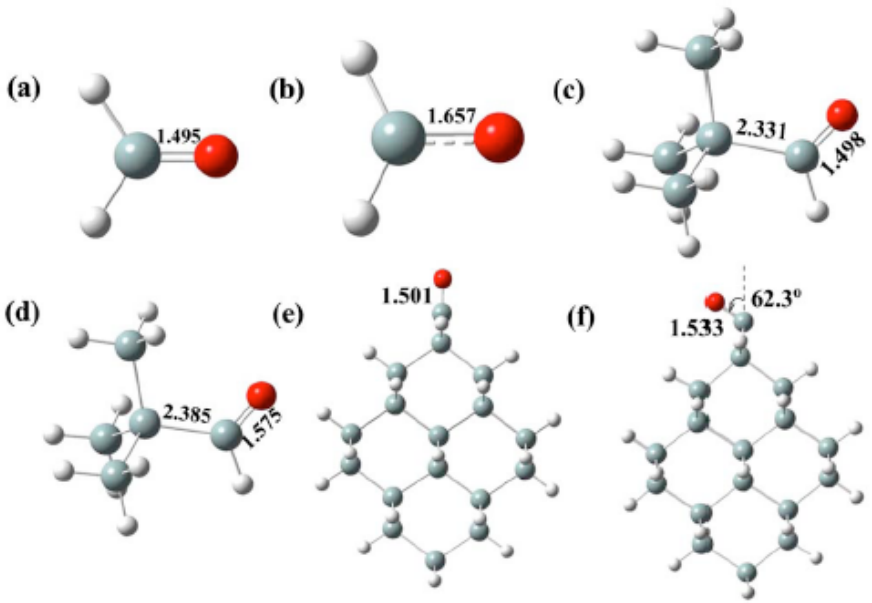


FIG. 1. Room temperature photoluminescence spectra from PSi samples with different porosities kept under Ar atmosphere (a) and after exposure to air (b).

Oxidation leads to

- Size-independent emission
- Weak luminescence

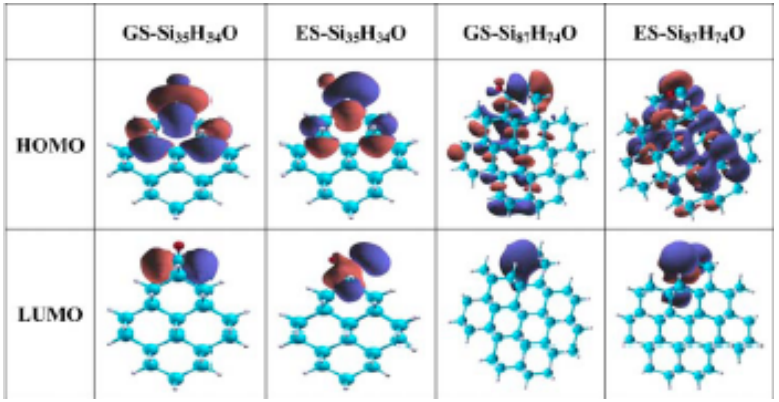
Curse and Blessing of Oxygen – The Blessing



SiQD with Si=O bond optimized in S_0 and S_1

Si_5H_{12} photodissociates

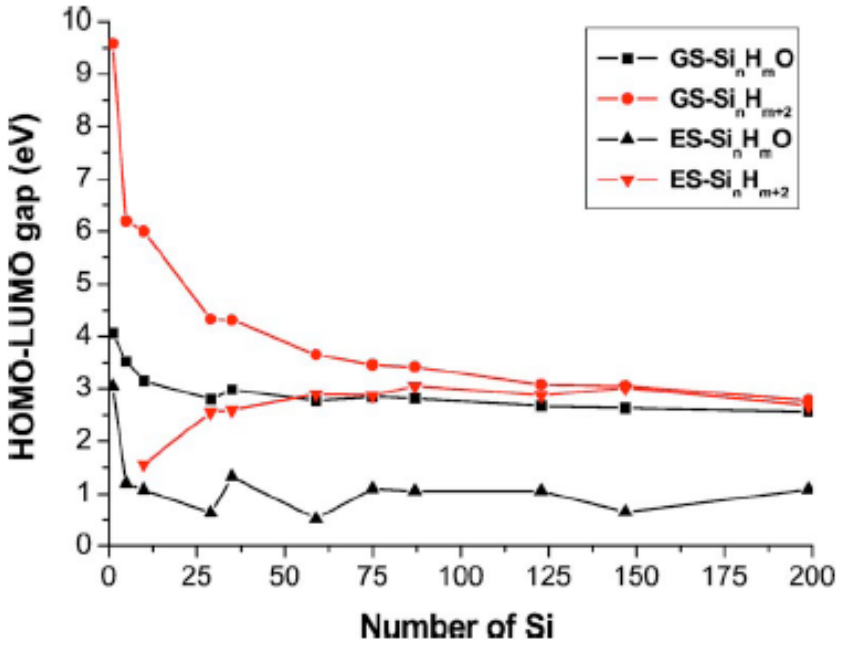
Li *APL* **91** 043106 (2007)



LUMO strongly localized around Oxygen

Oxygen stabilizes Silicon core

Curse and Blessing of Oxygen – The Blessing but . . .

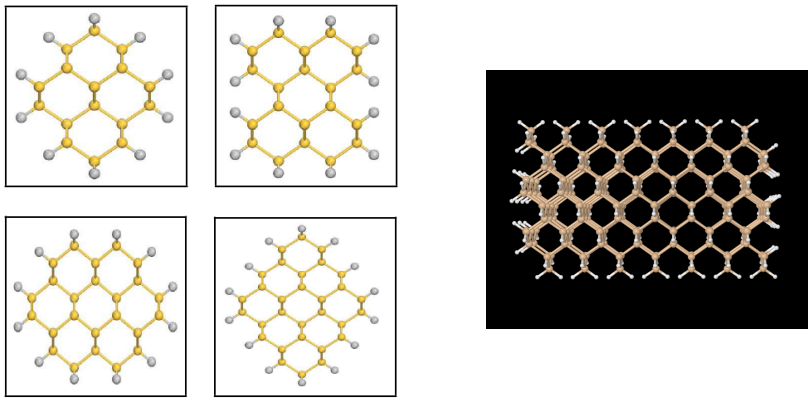


HOMO-LUMO gap of hydrogenated and oxidized SiQD

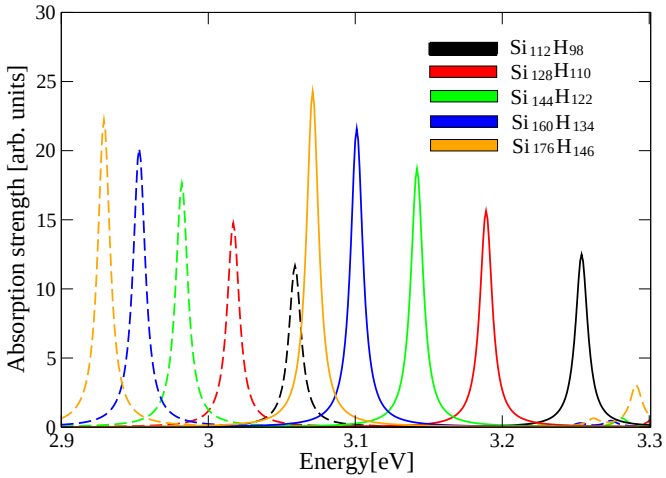
No size dependence, emission in the IR

Outline

Effects of confinement in radial and axial dimensions



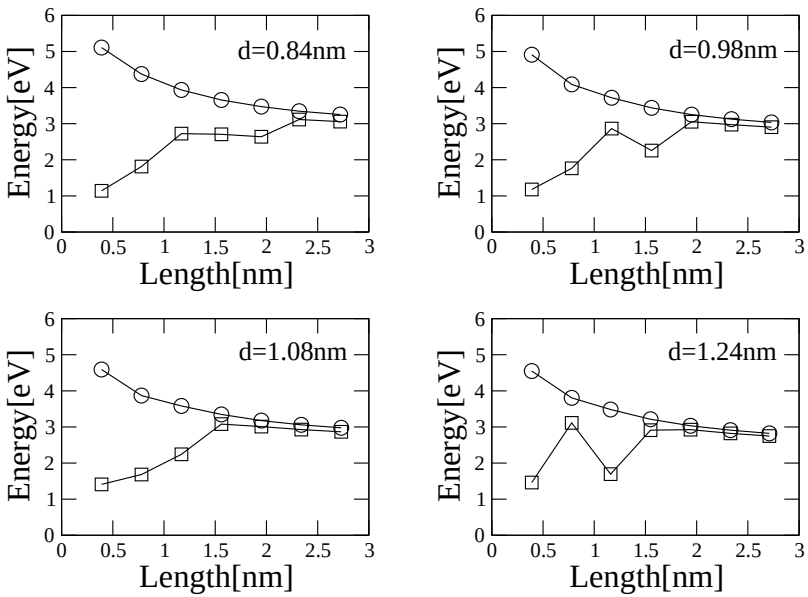
Finite models of SiNW with [110] growth direction



Absorption and emission spectra for SiNW with $d = 0.84$ nm

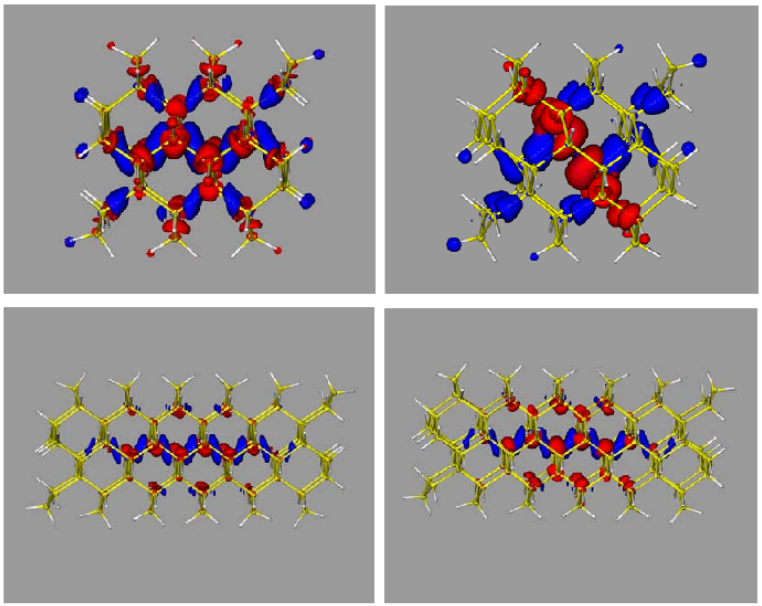
Excited state relaxation does not quench luminescence

Size dependence of exciton localization



HOMO and LUMO

d=0.84 nm and l=1.17 nm



d=0.84 nm and l=2.32 nm

Exciton delocalizes for rods with $l > 2$ nm

Wang, Zhang, Frauenheim, Niehaus *EPL* submitted

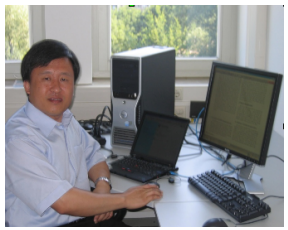
Summary

Main findings

- Excited state relaxation is crucial in Si nanostructures
- Self-trapped excitons form for nanostructures with dimension < 2 nm
- Weak size dependence of emission not necessarily due to oxidation
- Reconstruction has to be considered

Thanks ∞

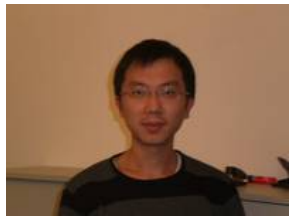
香港城市大學
City University of Hong Kong



Xian Wang, Quan-Song Li, Chensheng Lin and Ruiqin Zhang

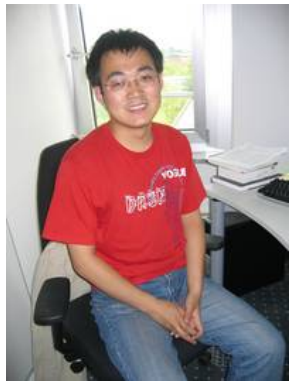
- The EDiCS group at BCCMS

Bernhard Grundkötter



ChiYung Yam

Setianto



Yong Wang