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Dielectric Constants of Silicon Quantum Dots

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Quantum mechanical pseudopotential calculations of the absorption spectra and static dielectric constant e, of Si quantum dots with —100—1300 atoms are presented. The predicted e, is found to be significantly reduced relative to the bulk value, but is considerably larger than the value deduced from currently available model calculations. A convenient parametrization of e, vs size R is provided. We

find that for quantum dots with R (20 A the electron-hole pair is confined by the physical dimension

of the dot, not by the Coulomb attraction.

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The static dielectric constant e„
2

e, = I + — e2(E)/EdE,

7T 0

is given by the integral of the absorption spectra e2(E),

e2(E) = —g 2 Mf;(E)B(E —Ef;),

fi fi

(2)

where A = 8n.2e2fi2/3m2, Ef; is the transition energy, and Mf, = I(fIpl i)l is the dipole transition matrix ele-ment between final state If) and initial state Ii), p is the momentum operator, and A is the volume. While cal-culated static dielectric constants of buIk semiconductors [1

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(a)

I I

) Bulk Si)

30—
20—

n10-

Exp.

eL

O 35- I
(0~3O-

25-
~ O—20-
0

15—
1O—

O

6$

K
0 25
20—

15

10-

(b)

JDOS

calculated using conventional k

.

p extrapolation meth-
ods [13] and a plane wave basis with an energy cutoff of 4.5 Ry. The results are shown in Fig. 2(a) where they are also compared with experiment [14]. While our re-sult compares well with similar previous calculations [15], they all lack the lower energy excitonic peak apparent in the experimental spectrum. This excitonic peak cannot be

described by our single particle theory. The "f-sum rule" [16](mfa/277 e2) fo Ee2(E) dE = N, where N is the total number of electrons inside volume A, is satisfied to within 0.1%. From Eq. (1)wefind Eb = 10.38forthebulk. This can be compared with the experimental result [17]of 11.4, the local density approximation result [2] 12.7, and the early value of Walter and Cohen [1] of 11.3. Our 10%
underestimation of the experimental value probably stems
from the neglect of exciton effects as well as from possi-ble imperfections in the pseudopotential. In what follows [Fig. 1(a)], we will thus scale our calculated (e, —1) using a factor of (11.4 —1) /(10.38 —1) = 1.109. The calcu-lated total density of states (DOS) of the bulk Si is shown in Fig. 3(a) along with the experimental x-ray photoemis-sion spectrum (XPS) [18]. The overall agreement is good. We conclude that we have a reasonable pseudopotential as far as the quantities of interest here [e2(E), e„DOS] are
concerned.

We next consider spherical Si quantum structures. We use interatomic distances taken from bulk since experimen-tal Si-Si interatomic distances in quantum dots are within 0.25% of the bulk value [19]. All surface dangling bonds
are saturated in our calculation by hydrogen atoms. The
surface Si-Si bond relaxations and H atom positions are

(a) I Bulk si I
1.5—

)Q)

tr)

Ql 0,5— (5
0
V)
Q)

~(gl200—

CO

Q soo-

a 400
O
(5 0
O
0

O
~ 150-
C
o

'(

XPS

(b) I a11315H4601

Surf
LDO

(c) I ai87 H76 I

surfa
0

LDOS

- 20 -15 -10

E (eV~

FIG. 3. Total and surface local density of states of Si systems
with different sizes. The XPS data in (a) is from Ref. [18]. The vertical arrows denote band edge positions (see Ref. [12]). The zero of energy is the vacuum potential level.

e.(E) = dE17(E1, E~)

X 6 [E —(E~ —Ei)]

modeled after experimental data and ab initio calculations of H-covered (100),(110),and (111)Si surfaces [12]. We believe that the error on the dielectric constant due to a pos-sible difference between the current surface model and the

real quantum dot should be small unless there are massive atomic reconstructions on the surface, about which there is currently no experimental information. The total potential

V(r) = Lfo~ ll 10/7/ (lr —R„,~ I) is given by a superposi-tion of local atomic pseudopotentials of Si and H. The hydrogen pseudopotential UH (r) is fitted [12]to the mea-sured spectra of the above mentioned three H-covered Si
surfaces. In the calculation, the quantum dots are placed
in periodic unit cells with the closest distance between two
neighboring quantum dots as 9 A. The plane wave ba-
sis set energy cutoff is 4.5 Ry„corresponding to 10 ba-sis functions for the largest system considered here. Such huge basis sets cannot be handled by conventional elec-tronic structure methods that seek all eigenstates. We use instead a newly developed generalized moments method, which is summarized in the following.
The calculation of the optical spectrum

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gen(J) (111

areTj ET BT /Xi1 7.85 Tf 52.25 53490Td (UH)en in

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VOLUME 73, NUMBER 7 PHYSICAL REVIEW LETTERS 15 AUGUsT 1994 v,„,(r) by u,'„,(r), which generates (after being screened