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Electronic structure

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u i,(r)e' ', respectively. Equation (9) is clearly diB'er-
ent Rom the pure sine form of Eq. (3). Note that the
boundary conditions at z = 0 and z = L can be satis-
fied either by the trigonometric functions appearing in
Eq. (9) or by the Bloch-periodic parts, if the latter have
nodal planes at the boundaries. The periodic function
u g. (r) can have such nodes if its orbital character is
p) d, etc., but not s. A constant phase factor is implicit in gb"&i".(r) in Eq. (7), as well as in u A..(r) in Eq. (9). It has to be determined by the boundary conditions. (iv) Using this complete TC basis set, a film eigenstate

(f) at I' can be expanded as

@g,r(r) =)).a-,f(k.*)&.

,

'k;(r)

Since.'",*
oc j and j = 0, 1, 2,..., jl, we have a total of
jI.+ 1 states, hence one of these states is unphysical. VA return to this point in Sec. IIIE.
One can now proceed and directly diagonalize the film Hamiltonian [with the potential in Fig. 2(a)] using the representation of Eq. (10). This will produce the exact film eigenvalues

f &(r) —y I, (r) v 2[u & (r) sin(k*z)

+u„„.(r) cos(k,*z)] (12)

TC b111k

where

(13)

Note that Eq. (14a) is derived for a special case where the film orientation e is in the z direction. More generally,
k,*

in Eqs. (12) and (13) should be replaced by

Our central observation here is that such a matrix rep-resentation of Eqs. (10) and (11)is essentially diagonal in the band index n and nave vector k,. This is evidenced by the fact (see below) that a single TC basis function can reproduce well the results of the direct diagonaliza-tion. The truncated crystal approximation to Eqs. (10) and (ll) thus consists of retaining in these expansions just the dominant terms. In its simplest form, we retain in these equations just a single basis function with f = (n, j), so

in Eq. (14) should start at k* = ko, not at I'. To avoid
confusion, we reserve the symbol j for ka ——0 (I)
and use j' for ko P 0. Equations (12)—(14) define the simplest TC

approximation. These expressions should be contrasted with the EMA Eqs. (3), (6), and (4), respectively.
To the extent that the TC approximation is sufBciently accurate (see below), it provides an exceedingly simple and useful result: it predicts a one-to-one mapping be-tiveen the flm energy eigenvalues and those of the pe riodic bulk e "&". at some special k points k*. This is

z

precisely the procedure followed empirically in the early TC

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piece Vi, »~s;, (r) inside the film and potential walls out, —
side it. In practice, we construct V"i (r) from a su-
perposition of atomic pseudopotentials. Equation (15)
is solved by imposing periodic boundary conditions on

the N-layer film straddled by N, „„ layers of vacuum.
This transforms the film problem into a Bloch-periodic band structure problem, solved here by expanding gf"' in plane waves. We checked that the results are indepen-dent of the number of vacuum layers to within 0.02 eV

for N,„„sd,where d is the interlayer spacing. The

solution of Eq. (15) is repeated for films with different
thickness L and different layer orientations, e(ppy) and
~(xxo) ~

Figure 4(a) depicts the xy-planar averaged potential V '

(z) for a 12 atomic layer Si(001) film embedded in 8 layers of vacuum. This potential was constructed from a superposition of empirical local Si atomic pseudopoten-tials fitted to the bulk band structure and the film's work

function [see the Appendix (Refs. 12—19)]. In the interior of the film the potential is quasiperiodic, having an aver-age value V [thick horizontal line in Fig. 4(a)]. Outside the film the potential approaches the vacuum level. The position of the valence-band maximum in bulk Si is in-dicated in this figure by the horizontal dashed line. It

0

(a) S

CC

)

G$

Q)
O
CL

CO

CD
G$

CD

O

-0.8

- 1.2

0

-Q4

Vav

I

'I ~ ~

R" AV'
- 15 -10

(b) GaAs(110)

EPM

--- LDA

10

-0.8

- 1.2
-20 -10 10

Distance z (a.u.)

FIG. 4. (a) The 2:y-planar averaged potential for a 12-
layer Si(001)film. The solid line gives the EPM result whereas the dotted line is the local part of the self-consistent LDA po-
tential. The origin of the potential is at the vacuum level and
the origin of the z axis is at a position half interlayer spacing outside the surface atom (the "truncated crystal boundary"). V is the z averaged potential at the interior of the film. This
is used to determine the position of the valence-band maxi-
mum (VBM) and the work function 4 (Ref. 15). (b) The zy-planar averaged EPM potential for a 14-layer GaAs(110) film. Solid dots indicate the positions of atomic planes.

qbulk(r) eik r

) jg (C)

eiK r

C

(16)

where C are reciprocal lattice vectors and R (G) are the variational expansion coefBcients.
The direct solution of the film problem [Eq. (15)]
avoids the approximations underlying the efFective-mass particle-in-a-box model in that (i) the solutions are valid at any k value (not just near a band edge), (ii) the bound-ary conditions imposed by the external potential can cou-ple to the quasiperiodic potential, and (iii) intervalley coupling is allowed. The direct solution also avoids the
truncated crystal approximation, i.e., use of a single TC
basis function. In what follows, we will compare the pre-
dictions of the simple EMA and TC approaches with the "exact" film solutions, thus assessing the utility of the
former methods.

B. Structure and symmetry of (001)
and (110) films

Equation (14) shows that the wave vectors k* enter-ing the TC representation depend on the film's geometry through its layer orientation e and thickness L.
Figure 5 illustrates the relation between the film's ge-ometries and the bulk crystal structure shown in a cubic

is determined by aligning V in the interior of the film with the same quantity calculated in bulk periodic Si (a procedure analogous to that used in determining hetero-junction band offsets '

). The work function 4 (4.9
eV) is then given by the distance of the VBM from the
vacuum level. Since the I i„-I'25 valence-band width of
Si is 12.6 eV, the total confining potential [Fig. 1(a)] is
12.6 + 4.9 = 17.5 eV. A similar plot of the averaged po-
tential for a 14 layer GaAs(110) film is shown in Fig. 4(b).
These "exact" film problems differ from ideal text-
book depictions [e.g., Td ([e.)Tj ET BT /Xi4 9.26 Tf 396I8 BT /X4BT /X

48)) 209

b) ($ 'I 0) Fll T / 2 =

d 11Q T&~p ~ip

) (pp]

) Film

pp1

Tpp1 2dpp]

The bulk tr }ation vectoor Tg
he primitive

stant a-
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z of

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e

f

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holds, thus finding the limits of the applicability of the
EMA.

Equations (17a) and (17b) illustrate an important
point on the nature of "quantum confinement ": In the
EMA one finds that the band gaps of 2D periodic sys-
tems scale as eg oc 1/I [Eq. (6)]. This, however, refiects the choice of a simplified, parabolic dispersion relation in Eq. (1b). If such a parabolic dispersion is inserted in Eqs. (17a) and (17b) instead of eb"&", we will find too that e oc 1/I, [Fig. 3(a)]. However, the more general Eqs. (17a) and (17b) show that such a scaling is not a general property of 2D periodic systems. If the disper-sion relation of the HVB and the I CB is like that shown

schematically in Fig. 3(b), the band gap will first increase with L, then, at smaller L values, it will turn around and decrease with L. We term such a behavior "deconfine-

ment. " Equations (17a) and (17b) thus provide guide-
lines on how to select a bulk material such that a film made &om it will exhibit deconfinement.

D. Comparison o1' truncated crystal
and direct calculat ions

We next examine the accuracy of the truncated crystal approach by comparing with the results of direct calcu-lations.

Ence'gy lee el8

The left hand side of Fig. 6(a) shows as horizontal lines
the

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For the film conduction-band states, the projection of
Eq. (18) selects turo

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nodal (N) planes at the boundaries, (N, N), whereas in the other case (n

= 4), it reaches extrema [E

= either
a peak or

a minimum] at the boundaries, (E,E) T. he
(E,E) and (N, N) combinations correspond to sine- and cosine-type envelopes, respectively. For odd-layer Alms, both (E,E) and (N, N) are, however, symmetry forbid-
den. Instead, we have an (E, N) and an (N, E) combi-
nation. These imply that, for even-layer films, the quan-
tized k,*

is given by (k,*)'"'"

=

& j, whereas for odd-layer
films, (k,*)

= (k,*)'"'"—&

. Hence, the energy pattern

e "s 4(k,*) changes &om even to odd.
This pattern change can be phrased in

a slightly dif-
ferent way: since the spurious states to be removed
(Sec. III E) are always at the energy minima, one can postulate

a band dependent A."*, opposite to what has
been done so far, with its minimum always tied to
the energy minimum, same as in the EMA. Using this
notion, the quantized states in Figs.

8 and

9 for

a 12-

layer (001) film correspond to j'

= 5, not 1, with
k*

= kf~l

—k'*

=

—(—).

A prime for

j and k* is used
here to indicate that they do not start from I'. For the N = ll odd-layer film shown in Fig. 6(b), the smallest

k,*

for the

n

=
3 and

4 bands is
—(ii) given by j'

= 5,
instead of the familar form
—(ii). This leads to the
same energy pattern change discussed above. Of course,
since this pattern change (= energy oscillation) depends
on the existence of

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A. Intraband matrix elements

The dipole matrix element between the states (n, i)
and (m, f) is given by

M[(n t) (~ f)l =(@-,'lpl@-, X)

= —i „*;rV' f rdr (27)

direct transition can be as strong as allowed direct tran-sitions. These points are illustrated in what follows.

O
E
O

10'—

103—

104 =

(a) Empty-Film Model

4 II

~ . 7,8

6
~ .

'.5
~

' 3

~ TO 9

~

'

-II

6? 8
3

. 5

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Evolution of the Transition Energies as a Function of Sizes

L = L macro L —L mesos L- nm

s(D) = E (PD) s(D) & s (PD) E(D) & s (PD)

The patterns in Fig. 17 are the consequence of pari-
ties of the

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v((Al) TABLE V. Comparison between the EPM and experi-mental (Ref. 16) energy levels for Si and GaAs (in eV).

V(q) = bi(q' —b&)/(bse ' —1) (A2)
with bg ——0.53706, 62 ——