Electronic states
in
ideal free standing films

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Abstract

Exact and general results on the electronic states in ideal free standing films bounded between $\tau_3 a_3$ and $(\tau_3 + N_3) a_3$ - here $a_3$ is the only primitive vector out of the film plane, $\tau_3$ is the bottom boundary and $N_3$ is a positive integer indicating the thickness of the film - are presented. In many interesting cases, such as in FCC (001) films and in FCC(110) films, the energies of most electronic states in the film can be analytically obtained from the corresponding energy band structure of the bulk: For each energy band of the bulk and each two-dimensional wavevector $\hat{k}$ in the film plane, there are $N_3 - 1$ electronic states in the film whose energy is dependent on the film thickness $N_3$ but not on the film boundary $\tau_3$ and maps the energy band of the bulk exactly and one electronic state whose energy is dependent on $\tau_3$ but not on $N_3$ and is above or at the highest energy in that energy band with that $\hat{k}$. This approach can be further extended to obtain exact and general results on electronic states in quantum wires and quantum dots.

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Bloch theorem has been playing a central role in our current understanding on the electronic structures of crystals in modern solid state physics. However, any real crystal always has a finite size and does not have the translational invariance on which Bloch theorem is based. A clear understanding of the properties of electronic states in real crystals of finite size has both theoretical and practical significant importance. Nevertheless, the lack of translational invariance has been a major obstacle in obtaining exact and general results on the electronic states in crystals of finite size. Thus most previous theoretical investigations on the electronic structure of finite crystals were based on approximate and/or numerical approaches and were usually on a specific material and/or based on a specific model. Recently the author obtained exact results on the electronic states in ideal general one dimensional crystals bounded at $\tau$ and $\tau + L$ - where $\tau$ is a real number and $L$ is a length equal to a positive integer times of the potential period $a$ - by using a differential equation theory approach. One of the major results of [2] is that the electronic states in one dimensional crystals of finite length can be classified as $L$- dependent or $\tau$-dependent - the energy of the electronic state is dependent on either the length of the crystal $L$ or the crystal boundary $\tau$. It also shows that the obstacle due to the lack of translational invariance in one dimensional finite crystals in fact can be circumvented. The basis of [2] is a clear understanding of the zeros of solutions of ordinary differential equations with periodic coefficients obtained by mathematicians. Now we extend our investigations into the three dimensional cases. In this work, we treat the simplest case - the electronic states in ideal free standing films. The most significant difference between the problem treated in this work and [2] is, the corresponding Schrödinger equation for the electronic states in films is a partial differential equation and thus the problem is now a more difficult one. Furthermore, for the zeros of solutions of three dimensional partial differential equation with periodic coefficients, much less was understood. Nevertheless, based on the results of a new eigenvalue problem - an extension of a mathematical theorem in [4] - we demonstrate that in many interesting cases exact and general results on how the eigenvalues of electronic states in ideal free standing films depend on the thickness can be analytically obtained, many eigenvalues can be directly obtained from the energy band structure of the bulk. Again, the major obstacle due to the lack of translational invariance can be circumvented.
We will mainly be interested in films with face-center cubic (FCC) lattices, including diamond structure and zinc-blend structure.

The Schrödinger equation for three dimensional crystals can be written as

\[- \nabla^2 y(x) + [v(x) - \lambda]y(x) = 0, \tag{1}\]

where

\[v(x + a_1) = v(x), \quad v(x + a_2) = v(x), \quad v(x + a_3) = v(x).\]

\(a_1, a_2\) and \(a_3\) are three primitive vectors of the crystal. The corresponding primitive vectors in \(k\) space are denoted as \(b_1, b_2\) and \(b_3\) and \(a_i \cdot b_j = \delta_{i,j}\). The position vector \(x\) can be written as \(x = x_1a_1 + x_2a_2 + x_3a_3\) and the \(k\) vector as \(k = k_1b_1 + k_2b_2 + k_3b_3\).

The eigenfunctions of (1) satisfying the condition

\[\hat{\phi}(\hat{k}, x + a_i; \tau_3) = \hat{\phi}(\hat{k}, x; \tau_3) exp(i k_i) \quad - \pi < k_i \leq \pi \quad i = 1, 2, 3 \tag{2}\]

are three dimensional Bloch functions. In this work the three dimensional Bloch functions and the energy bands are denoted as \(\phi_n(k, x)\) and \(\lambda_n(k)\): \(\lambda_0(k) \leq \lambda_1(k) \leq \lambda_2(k) \leq \ldots\).

The energy band structure in the Cartesian system is denoted as \(\lambda_n(k_x, k_y, k_z)\).

For the electronic states in ideal free standing films we assume that the atomic positions in the film are the same as in the bulk, the potential \(v(x)\) inside the film is the same as in (1) and all the electronic states are confined in the film. We choose primitive vectors \(a_1\) and \(a_2\) in the film plane and use \(\hat{k}\) to express the two dimensional wavevector: \(\hat{k} = k_1\hat{b}_1 + k_2\hat{b}_2\). \(\hat{b}_1\) and \(\hat{b}_2\) are in the film plane and \(a_i \cdot \hat{b}_j = \delta_{i,j}\).

Suppose \(A\) is a parallelogram which has \(a_i\) forming the sides which meet at a corner and has the bottom defined by \(\tau_3a_3\). The function set \(\hat{\phi}(\hat{k}, x; \tau_3)\) is defined by the condition

\[\hat{\phi}(\hat{k}, x + a_i; \tau_3) = \hat{\phi}(\hat{k}, x; \tau_3) exp(i k_i) \quad - \pi < k_i \leq \pi \quad i = 1, 2\]

\[\hat{\phi}(\hat{k}, x; \tau_3) = 0 \quad if \ x \in \partial A_3 \tag{3}\]

here \(\partial A_i\) means two opposite faces of \(\partial A\) determined by the beginning and the end of \(a_i\).

The eigenvalues and eigenfunctions of (1) with the condition (3) are denoted by \(\hat{\lambda}_n(\hat{k}; \tau_3)\) and \(\hat{\phi}_n(\hat{k}, x; \tau_3)\), where \(\hat{k}\) is the two dimensional wavevector and \(n = 0, 1, \ldots\).
For the eigenvalues of two different eigenvalue problems defined by (2) and (3), we have the following theorem (See the Appendix):

\[ \hat{\lambda}_n(\hat{k}, \tau_3) \geq \lambda_n(k), \quad \text{for} \quad (k - \hat{k}) \cdot a_i = 0, \quad i = 1, 2. \tag{4} \]

Eq. (4) is more or less like the Theorem 3.1.2 in [4] in the one dimensional case, but not as strong as the latter: No upper limit of \( \hat{\lambda}_n(\hat{k}, \tau_3) \) is given except \( \hat{\lambda}_n(\hat{k}, \tau_3) \leq \hat{\lambda}_{n+1}(\hat{k}, \tau_3) \).

Note in Eqs. (3) and (4), \( k \) is a three dimensional wavevector and \( \hat{k} \) is a two dimensional wavevector. In Eq. (4) \( k \) and \( \hat{k} \) have the same two dimensional wavevector in the film plane. For each energy band \( n \) and each \( \hat{k} \), there is one \( \hat{\phi}_n(\hat{k}, x; \tau_3) \). Eq. (4) is true for any \( \tau_3 \), thus it indicates that in general a Bloch function \( \phi_n(k, x) \) does not have a "zero surface" \( \tau_3(x_1, x_2) \), except when it happens to be one of \( \hat{\phi}_n(\hat{k}, x; \tau_3) \).

For the electronic states in a film with \( N_3 \) layers in the \( a_3 \) direction, we look for the eigenvalues \( \hat{\Lambda} \) and eigenfunctions \( \hat{\psi}(\hat{k}, x) \) of the following two equations:

\[ -\nabla^2 \hat{\psi}(\hat{k}, x) + [v(x) - \hat{\Lambda}] \hat{\psi}(\hat{k}, x) = 0, \quad \text{if} \quad \tau_3 < x_3 < \tau_3 + N_3 \tag{5} \]

and

\[ \hat{\psi}(\hat{k}, x) = 0, \quad \text{if} \quad x_3 \leq \tau_3 \text{ or } x_3 \geq \tau_3 + N_3 \tag{6} \]

where \( x_3 = \tau_3 \) indicating the bottom of the film and \( N_3 \) is a positive integer indicating the film thickness. These electronic states \( \hat{\psi}(\hat{k}, x) \) are two dimensional Bloch waves in the film plane with additional index(es) indicating the confinement in the third direction.

One type of non-trivial solutions of (5) and (6) can be obtained from (3) by assigning

\[ \hat{\psi}_n(\hat{k}, x; \tau_3) = c_{N_3} \hat{\phi}_n(\hat{k}, x; \tau_3), \quad \text{if} \quad \tau_3 < x_3 < \tau_3 + N_3 \]

\[ = 0, \quad \text{if} \quad x_3 \leq \tau_3 \text{ or } x_3 \geq \tau_3 + N_3 \tag{7} \]

where \( c_{N_3} \) is a normalization constant. The corresponding eigenvalue \( \hat{\Lambda}_n(\hat{k}; \tau_3) = \hat{\lambda}_n(\hat{k}; \tau_3) \) is dependent on \( \tau_3 \) but not on \( N_3 \). A consequence of (4) is that for each energy band index \( n \) and each two dimensional wavevector \( \hat{k} \), there is one such solution (7) of Eqs. (5) and (6). We will further discuss this types of solutions later. Now we try to find out other solutions of (5) and (6).
The problem is simpler if the band structure of the crystal has the following symmetry

\[ \lambda_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3) = \lambda_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 - k_3 \mathbf{b}_3). \]  

If this is the case, we note that

\[ f_{n,k_1,k_2,k_3}(x; \tau_3) = c_{n,k_1,k_2,k_3} \phi_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3, x) + c_{n,k_1,k_2,-k_3} \phi_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 - k_3 \mathbf{b}_3, x), \]

where \( c_{n,k_1,k_2,k_3} \) and \( c_{n,k_1,k_2,-k_3} \) are constant coefficients and are not zero, is a non-trivial solution of (5) due to (8). Non-trivial solutions of (5) and (6) can be obtained by assuming

\[
\hat{\psi}_{n,j_3}(\hat{\mathbf{k}}, x; \tau_3) = f_{n,k_1,k_2,k_3}(x; \tau_3) \quad \text{if} \quad \tau_3 < x < \tau_3 + N_3
\]

\[
= 0, \quad \text{if} \quad x_3 \leq \tau_3 \text{ or } x_3 \geq \tau_3 + N_3
\]

where \( \hat{\mathbf{k}} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 \), or \( \hat{k}_1 = k_1 \) and \( \hat{k}_2 = k_2 \), and

\[ \kappa_3 = j_3 \pi/N_3, \quad j_3 = 1, 2, 3, \ldots, N_3 - 1. \]

Here \( j_3 \) can be considered as a sub-band index. Because from (10) we have \( e^{i\kappa_3 N_3} - e^{-i\kappa_3 N_3} = 0 \), then we can always choose \( c_{n,k_1,k_2,\kappa_3} \) and \( c_{n,k_1,k_2,-\kappa_3} \) which are not zero to make

\[ f_{n,k_1,k_2,\kappa_3}(x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + \tau_3 \mathbf{a}_3) = f_{n,k_1,k_2,\kappa_3}(x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + (\tau_3 + N_3) \mathbf{a}_3) = 0. \]

Therefore \( \hat{\psi}_{n,j_3}(\hat{\mathbf{k}}, x; \tau_3) \) defined in (9) are continuous functions satisfying (5) and (6) with eigenvalues given by

\[ \hat{\Lambda}_{n,j_3}(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2) = \lambda_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + \kappa_3 \mathbf{b}_3) \]  

Each eigenvalue \( \hat{\Lambda}_{n,j_3}(\hat{\mathbf{k}}) \) for this case, is a function of \( N_3 \), the film thickness. But they all do not depend on the film boundary \( \tau_3 \). The eigenvalues \( \hat{\Lambda}_{n,j_3}(\hat{\mathbf{k}}) \) of the electronic states in the film (11) map the band structure of the bulk \( \lambda_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3) \) exactly.

However, for many crystals such as important semiconductors with diamond structure or zinc-blend structure, in general (8) is not true. Thus we do not have (11) for general \( k_1 \) and \( k_2 \). We have to treat each film case separately. In the following we treat FCC (001) films and FCC (110) films as two examples.

We discuss the FCC (001) films first. The primitive vectors can be chosen as \( \mathbf{a}_1 = a/2 \ (1, -1, 0) \) and \( \mathbf{a}_2 = a/2 \ (1, 1, 0) \), \( \mathbf{a}_3 = a/2 \ (1, 0, 1) \) and thus \( \mathbf{b}_1 = 1/a \ (1, -1, -1) \),
$b_2 = 1/a (1, 1, -1)$, and $b_3 = 1/a (0, 0, 2)$. Three Cartesian components of the wavevector $k$ can be obtained as $k_x = (k_1 + k_2)/a$, $k_y = (-k_1 + k_2)/a$ and $k_z = (-k_1 - k_2 + 2k_3)/a$.

In general, we do not have (8) for FCC crystals. Nevertheless, due to the high symmetry of the FCC band structures, we are still able to obtain an analytical expressions for the electronic states in FCC (001) films, similar to (11).

In fact, we can have many different ways to choose the primitive vectors. For example, we can choose a new primitive vector system as $a'_1 = a_1$, $a'_2 = a_2$, $a'_3 = m_1a_1 + m_2a_2 + a_3$, here $m_1$ and $m_2$ are integers. The new primitive vectors in $k$ space are $b'_1 = b_1 - m_1b_3$, $b'_2 = b_2 - m_2b_3$, $b'_3 = b_3$. In principle, the primitive vector systems given by $a_i$ and $a'_i$ are equivalent. The wavevector $k$ can be expressed as either $k_1b_1 + k_2b_2 + k_3b_3$ or $k'_1b'_1 + k'_2b'_2 + k'_3b'_3$ and $k_1 = k'_1$, $k_2 = k'_2$, $k_3 = -m_1k'_1 - m_2k'_2 + k'_3$. Thus for a specific wavevector $k$, in two different primitive vector systems used here, both $k_1$ and $k_2$ are unchanged.

In FCC (001) films we have $\hat{b}_1 = 1/a(1, -1, 0)$ and $\hat{b}_2 = 1/a(1, 1, 0)$, $\hat{k}_1 = k_1$ and $\hat{k}_2 = k_2$. Our purpose is to find $\Lambda_{n,j_3}(\hat{k})$ for different $\hat{k}$.

For FCC crystals we have $\lambda_n(k_x, k_y, k_z) = \lambda_n(k_x, k_y, -k_z)$ for any $k_x$ and $k_y$. We have also that $k_x = (k_1 + k_2)/a$, $k_y = (-k_1 + k_2)/a$, $k_z = (-k_1 - k_2 + 2k_3)/a = -(2m_1 + 1)k_1 - (2m_2 + 1)k_2 + 2k_3/a$. If for two specific $k_1$ and $k_2$, we can find two $m_1$ and $m_2$, to make

$$(2m_1 + 1)k_1 + (2m_2 + 1)k_2 = 0,$$  

then in the primitive vector system specifying by $a'_3 = m_1a_1 + m_2a_2 + a_3$, we have

$$\lambda_n(k_1b'_1 + k_2b'_2 + k_3b'_3) = \lambda_n(k_1b'_1 + k_2b'_2 - k_3b'_3)$$

and thus

$$\Lambda_{n,j_3}(k_1\hat{b}_1 + k_2\hat{b}_2) = \lambda_n(k_1b'_1 + k_2b'_2 + \kappa_3b'_3).$$

This in fact is[3]

$$\Lambda_{n,j_3}(k_1\hat{b}_1 + k_2\hat{b}_2) = \lambda_n(k_1\hat{b}_1 + k_2\hat{b}_2 + \kappa_3b_3),$$  

(13)

where $\kappa_3 = j\pi/N_3$, $j_3 = 1, 2,...N - 1$. Note (13) does not depend on $m_1$ and $m_2$ any more.
There are some pairs of \( k_1 \) and \( k_2 \) for which the condition (12) can not be true. Nevertheless, in a small circle centered in an any specific pair \( k_1 \) and \( k_2 \), there are always infinite number of pairs \( k_{1,c} \) and \( k_{2,c} \), which can be as close to \( k_1 \) and \( k_2 \) as needed, for each pair we can find two integers \( m_1 \) and \( m_2 \), to make \((2m_1 + 1)k_{1,c} + (2m_2 + 1)k_{2,c} = 0\). Thus (13) will be true for each such pair \( k_{1,c} \) and \( k_{2,c} \). Because both \( \hat{\Lambda}_{n,j_3}(k_1\hat{b}_1 + k_2\hat{b}_2) \) and \( \lambda_n(k_1\hat{b}_1 + k_2\hat{b}_2 + \kappa_3\hat{b}_3) \) are continuous functions of \( k_1 \) and \( k_2 \), therefore (13) must be true for any \( k_1 \) and \( k_2 \). The corresponding eigenfunction can be written as \( \hat{\psi}_{n,j_3}(\kappa, \mathbf{x}; \tau_3) \).

In the Cartesian system, Eq. (13) for (001) films can be written as:

\[
\hat{\Lambda}_{n,j_3}(k_x, k_y) = \lambda_n(k_x, k_y, 2\kappa_3)
\]  

(14)

for any \( k_x \) and \( k_y \), where \( \kappa_3 = j_3\pi/N_3 \).

Eqs. (13) and (14) can be used for Si (001) films. Zhang and Zunger calculated the electronic structure in thin Si (001) films using a pseudopotential method. Their results for the even number \( N_f \) of monolayer can be directly compared with our general analytical results: Our \( N_3 \) is equal to their \( N_f/2 \). Their "central observation" is that the energy spectrum of electronic states in Si quantum films \((N_f = 12)\) maps the energy band structure of Si approximately. The equation (9) in [7], which Zhang and Zunger obtained from their numerical results, is a special case of Eq. (14) when \( k_x = k_y = 0 \). Therefore Eq. (14) is a more general result obtained analytically.

The FCC (110) films can be very similarly discussed.

The primitive vectors can be chosen as \( \mathbf{a}_1 = a (0, 0, 1) \) and \( \mathbf{a}_2 = a/2 (1, -1, 0) \), \( \mathbf{a}_3 = a/2 (0, 1, 1) \). Corresponingly we have \( \mathbf{b}_1 = 1/a (-1, -1, 1) \), \( \mathbf{b}_2 = 1/a (2, 0, 0) \), \( \mathbf{b}_3 = 1/a (2, 2, 0) \), and \( \hat{\mathbf{b}}_1 = 1/a(0, 0, 1) \), \( \hat{\mathbf{b}}_2 = 1/a(1, -1, 0) \). By using very similar argument as we obtain Eq. (13) for FCC (001) films, but using that for FCC crystals \( \lambda_n(k_3 + k_2, k_3 - k_2, k_1) = \lambda_n(-k_3 + k_2, -k_3 - k_2, k_1) \) is true for any \( k_1 \) and \( k_2 \), we can obtain that for the electronic states in the \( N_3 \) layers of FCC (110) films, \( \hat{\Lambda}_{n,j_3}(k_1\hat{b}_1 + k_2\hat{b}_2) = \lambda_n(k_1\hat{b}_1 + k_2\hat{b}_2 + \kappa_3\hat{b}_3) \) for any \( k_1 \) and \( k_2 \). Here \( \kappa_3 = j_3\pi/N_3 \), \( j_3 \) is the sub-band index: \( j_3 = 1, 2, ..., N_3 - 1 \). This is exactly the same as Eq. (13). Thus Eq. (13) is correct for both FCC (001) films and FCC (110) films. The difference lies on that \( \hat{\mathbf{b}}_1, \hat{\mathbf{b}}_2 \) and \( \mathbf{b}_3 \) are different in two cases. For FCC (110) films, Eq. (13) can also be written as

\[
\hat{\Lambda}_{n,j_3}(k_1\hat{b}_1 + k_2\hat{b}_2) = \lambda_n((2\kappa_3 - k_2)/a, (2\kappa_3 + k_2)/a, k_1/a)
\]  

(15)
In the cases where $k_1 = k_2 = 0$, we have $\hat{\Lambda}_{n,j_3}(0) = \lambda_n(j_3/N_3 \cdot 2\pi/a, j_3/N_3 \cdot 2\pi/a, 0)$. This is what Zhang and Zunger\cite{7} obtained from their numerical results on Si (110) films due to that our $N_3$ is equal to their $N_f$ in (110) films.

Much previous work also indicates that the eigenvalues of Bloch states in films map closely the dispersion relations of the unconfined Bloch waves\cite{8}. Now we understand that the mapping in fact is general and exact in the cases treated here.

Franceschetti and Zunger\cite{9} investigated the $\Gamma - X$ transition in GaAs free standing (110) films, quantum wires and quantum dots. According to Eq. (15) we have analytically that for (110) films

$$E_{\Gamma}^{\text{film}} = \frac{\hbar^2}{2m} \lambda_c(1/N_3 \cdot 2\pi/a, 1/N_3 \cdot 2\pi/a, 0), \quad E_{X}^{\text{film}} = \frac{\hbar^2}{2m} \lambda_c(1/N_3 \cdot 2\pi/a, 1/N_3 \cdot 2\pi/a, k_{\text{min}}),$$

where $c$ denotes the lowest conduction band, $k_{\text{min}}$ is the location of the ”X” valley on the $k_z$ axis and $N_3$ is the number of mono-layers.

Each $\hat{\psi}_n(\mathbf{k}, x; \tau_3)$ defined in (7) is an electronic state in the film whose energy $\hat{\Lambda}_n(\mathbf{k}; \tau_3)$ is dependent on the film boundary $\tau_3$ but independent of the thickness of the film $N_3$. In one-dimensional crystals of finite length\cite{2} the energy bands $\lambda_n(k)$ do not overlap and a $\tau$-dependent eigenvalue is either inside the band gap or at the band edge. In films the energy bands $\lambda_n(k)$ usually overlap and $\hat{\Lambda}_n(\mathbf{k}; \tau_3)$ is either above or at the highest energy of the Bloch function with that $n$ and that $\hat{\mathbf{k}}$.

If in Eq. (4) $\hat{\lambda}_n(\mathbf{k}; \tau_3) = \lambda_n(\mathbf{k})$, $\hat{\Lambda}_n(\mathbf{k}; \tau_3)$ is equal to the highest energy for that energy band and that $\hat{\mathbf{k}}$. It means that the corresponding eigenfunction of (3) $\hat{\phi}_n(\mathbf{k}, x)$ is a Bloch function $\phi_n(\mathbf{k}, x)$. Examples of this case were observed, for example, in numerical results in the Fig. 3 and Fig. 4 of [7], such as the one of the double degenerated $X_1$ state in the valence band, the constant energy confined band edge state at the top of valence band, etc. Other examples are the constant energy confined band edge states at the top of the valence band observed in numerical calculations for Si (110) films\cite{7} and GaAs (110) films\cite{11} etc. This case happens when the corresponding Bloch function $\phi_n(\mathbf{k}, x)$ with $\hat{\mathbf{k}}$ has a ”zero surface” at $x_3 = \tau_3$ and thus has ”zero surfaces” at $x_3 = \tau_3 + j$, where $j = 1, 2, ......N_3$.

In the cases where $\hat{\lambda}_n(\mathbf{k}; \tau_3) > \lambda_n(\mathbf{k})$, none of the Bloch function $\phi_n(\mathbf{k}, x)$ with that $n$ and that $\hat{\mathbf{k}}$ has a ”zero surface” at $x_3 = \tau_3$. Then $\hat{\psi}_n(\mathbf{k}, x; \tau_3)$ could be a surface state. In
ideal one dimensional crystals of finite length we have proved that there is at most one surface state in each band gap\[2\]. Eq. (4) shows, there is at most one surface energy band \( \hat{\Lambda}_n(\hat{k}, \tau_3) \) for each bulk energy band \( \lambda_n(k) \), even a film always has two surfaces. Nevertheless, due to that in three dimensional crystals below the major band gap there are several energy bands overlapping, such as the energy bands \( n = 1, 2, 3 \) in Si or GaAs etc, thus in the major band gap there could be more than one surface energy bands. However, for the band gap inside the valence band of III-V and II-VI semiconductors between the band \( n = 0 \) and the band \( n = 1 \), we predict that there is at most one surface energy band \( \hat{\Lambda}_0(\hat{k}; \tau_3) \) for a perfectly even (001) or (110) film, as a direct consequence of Eq. (4).

In summary, we have demonstrated that for interesting free standing films, such as ideal FCC (001) films and FCC (110) films, exact and general results on the eigenvalues of the electronic states in the film can be obtained: For the film bounded between \( \tau_3a_3 \) and \( (N_3 + \tau_3)a_3 \), there are \( N_3 - 1 \) electronic states \( \hat{\psi}_{n,j3}(\hat{k}, x; \tau_3) \) for each energy band \( n \) and each two dimensional wavevector \( \hat{k} \), whose energy \( \hat{\Lambda}_{n,j3}(\hat{k}) \) is dependent on the thickness of the film \( N_3 \) but not on the film boundary \( \tau_3 \). The eigenvalues of these electronic states in the film map the energy bands \( \lambda_n(k) \) exactly; There is one electronic state \( \hat{\psi}_n(\hat{k}, x; \tau_3) \) in the film for each \( n \) and \( \hat{k} \) whose energy \( \hat{\Lambda}_n(\hat{k}; \tau_3) \) is dependent on the film boundary \( \tau_3 \) but not on the film thickness \( N_3 \).

This approach can be further extended to obtain exact and general results on electronic states in quantum wires and quantum dots\[10\]. For example, it is found that for a quantum dot which are formed by FCC (001) or (110) films further truncated in two more directions and thus bounded between \( \tau_1a_1 \) and \( (\tau_1 + N_1)a_1 \) and \( \tau_2a_2 \) and \( (\tau_2 + N_2)a_2 \) and \( \tau_3a_3 \) and \( (\tau_3 + N_3)a_3 \), for each energy band there are \( (N_1 - 1)(N_2 - 1)(N_3 - 1) \) bulk states, \( (N_1 - 1)(N_2 - 1) + (N_2 - 1)(N_3 - 1) + (N_3 - 1)(N_1 - 1) \) surface states, \( (N_1 - 1) + (N_2 - 1) + (N_3 - 1) \) "side states" and one "conner state" in spite of that the crystal has six faces, twelve sides and eight corners.
Appendix

The Eq. (4) in the text is essentially an extension of the theorem (6.3.1) in [4] and its proof is similar, with some differences.

We choose \( \phi_n(k,x) \) to be normalized over \( A \): \( \int_A \phi_n(k;x) \phi^*_n(k;x) dx = 1 \).

We denote \( F \) as the set of all complex-valued functions \( f(x) \) which are continuous in \( A \) and have piecewise continuous first-order partial derivatives in \( A \). The Dirichlet integral \( J(f,g) \) in three dimensions is defined by

\[
J(f,g) = \int_A \{ \nabla f(x) \cdot \nabla g^*(x) + v(x)f(x)g^*(x) \} dx
\]

(A.1)

for \( f(x) \) and \( g(x) \) in \( F \). If in (A.1) \( g(x) \) also has piecewise continuous second-order partial derivatives in \( A \), from Green’s theorem we have

\[
J(f,g) = \int_A f(x)\{-\nabla^2 g^*(x) + v(x)g^*(x)\} dx + \int_{\partial A} f \frac{\partial g^*}{\partial n} dS,
\]

(A.2)

where \( \partial A \) denotes the boundary of \( A \), \( \partial/\partial n \) denotes derivative along the outward normal to \( \partial A \), and \( dS \) denotes an element of surface area of \( \partial A \).

If \( f(x) \) and \( g(x) \) satisfy the conditions Eq. (2) in the text, the integral over \( \partial A \) is zero because the integrals over opposite faces of \( \partial A \) cancel out. In particular, when \( g(x) = \phi_n(k,x) \), (A.2) gives

\[
J(f,g) = \lambda_n(k) \int_A f(x)\phi^*_n(k,x) dx.
\]

Thus \( J(\phi_m(k,x),\phi_n(k,x)) = \lambda_n(k) \) if \( m = n \) and \( J(\phi_m(k,x),\phi_n(k,x)) = 0 \) if \( m \neq n \).

Now we consider the function set \( \hat{\phi}(\hat{k},x;\tau_3) \) which satisfy the conditions (3) in the text. We also choose \( \hat{\phi}(\hat{k},x;\tau_3) \) to be normalized over \( A \): \( \int_A \hat{\phi}(\hat{k},x;\tau_3)\hat{\phi}^*(\hat{k},x;\tau_3) dx = 1 \).

Note if \( f(x) = \hat{\phi}(\hat{k},x;\tau_3) \), and \( g(x) = \phi_n(k,x) \), the integral over \( \partial A \) in (A.2) is also zero because the integral over two opposite faces of \( \partial A_1 \) and \( \partial A_2 \) cancel out due to that \( (k - \hat{k}) \cdot \mathbf{a}_i = 0 \) for \( i = 1, 2 \) and the integral over each face of \( \partial A_3 \) is zero, due to that \( f(x) = 0 \) when \( x \in \partial A_3 \).

Thus

\[
J(\hat{\phi}(\hat{k},x;\tau_3),\phi_n(k,x)) = \lambda_n(k)f_n(k)
\]
where
\[ f_n(k) = \int_A \hat{\phi}(k; x; \tau_3) \phi_n^*(k, x) dx, \]
and
\[ \sum_{n=0}^{\infty} |f_n(k)|^2 = 1. \]

An important property of the function \( \hat{\phi}(k, x; \tau_3) \) defined by (3) in the text is

\[ J(\hat{\phi}(k, x; \tau_3), \hat{\phi}(k, x; \tau_3)) \geq \sum_{n=0}^{\infty} \lambda_n(k) |f_n(k)|^2. \] (A.3)

To prove (A.3), we assume \( v(x) \geq 0 \) first. Then \( J(f, f) \geq 0 \) from (A.1) for any \( f \) in \( F \). Thus for any positive integer \( N \) we have

\[ J(\hat{\phi}(k, x; \tau_3) - \sum_{n=0}^{N} f_n(k) \phi_n(k, x), \hat{\phi}(k, x; \tau_3) - \sum_{n=0}^{N} f_n(k) \phi_n(k, x)) \geq 0. \]

That is

\[ J(\hat{\phi}(k, x; \tau_3), \hat{\phi}(k, x; \tau_3)) \geq \sum_{n=0}^{N} \lambda_n(k) |f_n(k)|^2. \]

\( N \) can be as large as it needs, therefore

\[ J(\hat{\phi}(k, x; \tau_3), \hat{\phi}(k, x; \tau_3)) \geq \sum_{n=0}^{\infty} \lambda_n(k) |f_n(k)|^2. \] if \( v(x) \geq 0 \) (A.4)

To prove (A.3) without the assumption that \( v(x) \geq 0 \), let \( v_0 \) be a constant which is sufficient large to make \( v(x) + v_0 \geq 0 \) in \( A \). Then Eq. (1) in the text can be written as

\[ -\nabla^2 y(x) + [V(x) - \Lambda] y(x) = 0 \] (A.5)

where \( V(x) = v(x) + v_0 \) and \( \Lambda = \lambda + v_0 \). Since in (A.5) \( V(x) \geq 0 \), due to (A.4) we have

\[ \int_A \{ \nabla \hat{\phi}(k; x; \tau_3) \cdot \nabla \hat{\phi}^*(k; x; \tau_3) + [v(x) + v_0] \hat{\phi}(k; x; \tau_3) \hat{\phi}^*(k; x; \tau_3) \} dx \]

\[ \geq \sum_{n=0}^{\infty} (\lambda_n(k) + v_0) |f_n(k)|^2 \]

That is

\[ \int_A \{ \nabla \hat{\phi}(k; x; \tau_3) \cdot \nabla \hat{\phi}^*(k; x; \tau_3) + v(x) \hat{\phi}(k; x; \tau_3) \hat{\phi}^*(k; x; \tau_3) \} dx \geq \sum_{n=0}^{\infty} \lambda_n(k) |f_n(k)|^2 \]
This is (A.3). On the basis of (A.3) we can prove Eq. (4) in the text.

We consider

\[ \hat{\phi}(\hat{k}, \hat{x}; \tau_3) = c_0 \hat{\phi}_0(\hat{k}, \hat{x}; \tau_3) + c_1 \hat{\phi}_1(\hat{k}, \hat{x}; \tau_3) + \ldots + c_n \hat{\phi}_n(\hat{k}, \hat{x}; \tau_3) \]

and choose \( n + 1 \) constants \( c_i \) to make

\[ \sum_{i=0}^{n} |c_i|^2 = 1 \]

and

\[ f_i(k) = \int_A \hat{\phi}(\hat{k}, \hat{x}; \tau_3) \phi_i^*(k, x) dx = 0 \quad i = 0, 1, \ldots, n - 1 \quad (A.6) \]

Eq. (A.6) corresponds to \( n \) homogeneous algebraic equations for \( n+1 \) constants \( c_0, c_1, \ldots, c_n \). A choice of such \( c_i \)'s is always possible. Therefore

\[ \lambda_n(\hat{k}; \tau_3) \geq \sum_{i=0}^{n} |c_i|^2 \lambda_i(\hat{k}; \tau_3) = J(\hat{\phi}(\hat{k}, \hat{x}; \tau_3), \hat{\phi}(\hat{k}, \hat{x}; \tau_3)) \]

\[ \geq \sum_{i=0}^{\infty} |f_i(k)|^2 \lambda_i(k) = \sum_{i=n}^{\infty} |f_i(k)|^2 \lambda_i(k) \geq \lambda_n(k) \sum_{i=n}^{\infty} |f_i(k)|^2 = \lambda_n(k) \]

This is Eq. (4) in the text.
References

[1] See for example, A. D. Yoffe, Adv. Phys. 42, 173 (1993); A. D. Yoffe, Adv. Phys. 50, 1 (2001); M. Kelly, Low Dimensional Semiconductors: Materials, Physics, Devices and Applications, Oxford University Press, Oxford (1996); Peter Y. Yu and Manuel Cardona, Fundamentals of Semiconductors, Physics and Materials Properties, Springer Verlag, Berlin (1999).

[2] S. Y. Ren, "Electronic states in one dimensional crystals of finite length", submitted for publication. A special case of the results obtained has been published in [3].

[3] S. Y. Ren, Phys. Rev. B64, 035322 (2001).

[4] M. S. P. Eastham, The Spectral Theory of Periodic Differential Equations, Scottish Academic Press, Edinburgh (1973) and references therein.

[5] For a free standing film with a boundary at \( x = \tau_3 \mathbf{a}_3 \), in general we have neither a reason to require that \( \tau_3 \) to be a constant nor a reasonable way to assign \( \tau_3(x_1, x_2) \) beforehand. However, \( \tau_3 = \tau_3(x_1, x_2) \) must be a periodic function of \( x_1 \) and \( x_2 \):

\[
\tau_3 = \tau_3(x_1, x_2) = \tau_3(x_1 + 1, x_2) = \tau_3(x_1, x_2 + 1).
\]

Otherwise the film will not have the two dimensional translational invariance.

[6] Because

\[
\lambda_n(k_1 b_1' + k_2 b_2' + \kappa_3 b_3') = \lambda_n(k_1(b_1 - m_1 b_3) + k_2(b_2 - m_2 b_3) + \kappa_3 b_3)
\]

\[
= \lambda_n(k_1 \mathbf{b}_1 - k_1(2m_1 + 1)/2 || \mathbf{b}_3 + k_2 \mathbf{b}_2 - k_2(2m_2 + 1)/2 || \mathbf{b}_3 + \kappa_3 \mathbf{b}_3) = \lambda_n(k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + \kappa_3 \mathbf{b}_3).
\]

Eq. (12) is used in the last step.

[7] S. B. Zhang and A. Zunger, Appl. Phys. Lett. 63, 1399 (1993).

[8] For example, Z. V. Popovic, H. J. Trodahl, M. Cardona, E. Richter, D. Strauch and K. Ploog, Phys. Rev. B40, 1202 (1989); Z. V. Popovic, M. Cardona, E. Richter, D. Strauch, L. Tapfer and K. Ploog, Phys. Rev. B40, 1207 (1989); Z. V. Popovic, M. Cardona, E. Richter, D. Strauch, L. Tapfer and K. Ploog, Phys. Rev. B40, 3040 (1989); P. Malinasmata and M. Cardona, Superlattices and Microstructures 10, 39 (1991).
[9] A. Franceschetti and A. Zunger, Appl. Phys. Lett. 68, 3455 (1996).

[10] S. Y. Ren, ”Electronic states in ideal quantum wires and quantum dots”, to be published.