On the Electron Spectrum of Crystalline Superstructures

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Abstract

Electron spectrum is analysed for the crystal that can be represented as a system of two ordered structures nested one into the other. Intercalated layered crystals, crystalline systems with the spin, charge, deformation or dipole ordering, the adsorbent-adsorbate systems and the superstructures may be relevant examples. The detailed consideration of the structures with incommensurable parameters of their lattices is presented. It is pointed to a unique possibility for essential change in the electron spectrum, in particular for the case of ferroelectrics.

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Introduction

Owing to modern technologies in the field of semiconductor materials, physical parameters of the latter have been allowed to meet the highest requirements of microelectronics. In particular, molecular beam epitaxy is capable of creating artificial layered structures with designed parameters of their layers, the so-called superstructures. These structures built on the basis of broad classes of semiconductors, e.g., the classical semiconductors of group IV and the $A_{II}B_{VI}$ or $A_{III}B_{V}$ materials, are featured by a number of unique electric and optical properties [1]. It is the reason for their wide applications in the modern electronic engineering.

Crystal structures obtained with introducing foreign atoms into a crystalline matrix may be considered as superstructures, too. Under certain conditions, the atoms may form an ordered structure. As a result, we would have a system “crystal in crystal”. If the lattice parameters of the crystals are multiples, a structure is distinguished as commensurate. Contrary, if the parameters are incommensurable to each other (this may be peculiar of one, two or three crystallographic directions), a structure is called incommensurate.

Intercalated layered crystals [2,3] may exemplify such the superstructures. Introducing one or another impurity atoms into van der Waals gap of a crystalline matrix of the layered crystal and varying their amounts, one can obtain crystals with different properties. At certain concentrations of intercalated atoms, ordering of intercalation complexes into the superlattice structures has been observed at low temperatures [2,3]. There has been a number of studies confirming such the ordering, e.g., the staged ordering of intercalates in graphite and transition metal dichalcogenides [2,3] or the intercalate ordering in van der Waals gap. In particular, the diffuse X-ray scattering experiments in [4] have shown that there exist the superlattices in Li_xTiS_2 at x=1/4 and x=1/2. The study [5] has confirmed the existence of $\sqrt{3}a\times\sqrt{3}a$ superlattice at x=1/3. Some other references dealing with the ordering of various types in the intercalated layered crystals may be found in [2]. Adsorbate-adsorbent systems may be referred to as quasi two-dimensional superstructures. Then the adsorbate forms sometimes the ordered structure, which can be both commensurable and incommensurable with respect to the crystalline matrix (see [6]).

A principal difference from the superstructures mentioned above seems to be significant. Here a role of foreign atoms inserted into the crystalline matrix is played by the charge or spin density waves, dipole ordering in ferroelectrics below the critical temperature, etc. Then the charge, the spin densities or the dipole momentum may be considered as the sites in some lattice-"pseudo-lattice". Such the system "lattice + pseudo-lattice" may be both commensurate and incommensurate. Below we shall show that peculiarities of the superstructures give rise to essential change in their electron spectra.

Description of the incommensurate structures differs fundamentally from that of translation-invariant structures, since the momentum in the former does not represent a quantum number. Seemingly, the common diffraction methods for structural studies would have been useless in this case. But it is just the diffraction methods that have discovered the ordering in the incommensurate structures. For example, the additional Bragg reflexes (the so-called anomalous satellites), which point to a structural ordering, have been found in the radiographic, neutron diffraction and the electron-microscope studies of ferroelectrics (see, e.g., [7]). On the other hand, even distorted crystal structures possess the properties caused by characteristics of ideal crystalline structure, such as the forbidden gap [8].

Therefore, while describing superstructure theoretically, it is possible to consider it as a combination of two ordered structures nested one into another. Then if, e.g., the electron spectrum of each structure is known, the spectrum of the superstructure should be determined by the electron spectra of the substructures themselves and their interaction. Electronic spectra of the commensurate structures may be considered with the traditional methods. This has been confirmed by the investigations of electronic spectra of superlattices in the direct-bandgap $A_{II}B_{VI}$ and $A_{III}B_V$ semiconductors with perfectly matched lattice parameters [9]. In this case, the effect of the superstructure has been revealed to result in modification of the electron behaviour, due to additional potential V_{S-L} acting along the growth axis of the superstructure created with the molecular-beam epitaxy. The electron characteristics in the layer plane remain the same as those of the initial structures. When the lattice parameters are not matched (the case of the incommensurable structure), the problem of electron spectrum becomes more complicated. Then the distortions of single-electron potential in the plane of contacting structures should be taken into account.

In this paper we analyse, in framework of the suggested model, quantitative changes in the electron spectrum imposed by the incommensurate structure.

Theoretical Model

Let us consider incommensurable crystalline lattices, one of which is enclosed in the other. Let the single-electron potentials of the structures be V_1 and V_2, respectively, where the index α (*f*) denotes the site in the first (or second) structure. Then the Hamiltonian of the system is

$$H=-\frac{\hbar^2}{2m}\nabla^2+V_1(\vec{r})+V_2(\vec{r}). \qquad (1)$$

Suppose that we know the wave functions of the first ($\Psi_{\alpha\sigma}(\vec{r})$) and second ($\varphi_{f\sigma}(\vec{r})$)

structures (σ being the spin index). We may expand the wave function $\phi_\sigma(\vec r)$ of the system described by Eq. (1) in a series in these functions:

$$\phi_\sigma(\vec r) = \sum_\alpha c_{\alpha\sigma}\Psi_{\alpha\sigma}(\vec r) + \sum_f a_{f\sigma}\varphi_{f\sigma}(\vec r) \qquad (2)$$

Let us transform Hamiltonian (1) to the site representation:

$$\begin{gathered} H = \sum_{\alpha\alpha'\sigma} H_1(\alpha\alpha')c^+_{\alpha\sigma}c_{\alpha'\sigma} + \sum_{\alpha\alpha'\sigma} V_2(\alpha\alpha')c^+_{\alpha\sigma}c_{\alpha'\sigma} + \sum_{ff'\sigma} H_2(ff')a^+_{f\sigma}a_{f'\sigma} + \\ \sum_{ff'\sigma} V_1(ff')a^+_{f\sigma}a_{f'\sigma} + \sum_{\alpha f\sigma}\left[V_1(\alpha f)c^+_{\alpha\sigma}a_{f\sigma} + h.c.\right] + \sum_{\alpha f\sigma}\left[V_2(f\alpha)a^+_{f\sigma}c_{\alpha\sigma} + h.c.\right] \end{gathered} \qquad (3)$$

where $c^+_\alpha, c_\alpha, a^+_f, a_f$ mean the common creation and destruction operators. Here

$$H_1(\alpha\alpha') = \int \Psi^*_\alpha(\vec r)(T + V_1(\vec r))\Psi_{\alpha'}(\vec r)d^3r, \qquad (4)$$

$$H_2(ff') = \int \varphi^*_f(\vec r)(T + V_2(\vec r))\varphi_{f'}(\vec r)d^3r \qquad (5)$$

are the matrix elements (protoplasts of the dispersion laws of the first and second sublattices, respectively) and $V_2(\alpha\alpha')$ concerns electron scattering at the lattice with the sites α by the potential of the other lattice V_2 (the term $V_1(ff')$ has a similar meaning). The last two terms in Eq. (3) describe scattering of electron at V_1 and V_2 with its transitions between the different lattices. It may be shown that mixing among the states localized at the sites in the same sublattice, scattered by potential of the other sublattice, is much less than that among the sites of different sublattices, i.e., $V_1(ff'), V_2(\alpha\alpha') << V_1(\alpha f), V_2(f\alpha)$. This is why we shall neglect $V_1(ff')$ and $V_2(\alpha\alpha')$ further on.

After passing to the momentum representation, Hamiltonian (3) takes the form

$$\begin{gathered} H = \sum_{\vec k\sigma}\varepsilon(\vec k)c^+_{\vec k\sigma}c_{\vec k\sigma} + \sum_{\vec q\sigma}E(\vec q)a^+_{\vec q\sigma}a_{\vec q\sigma} + \\ + \sum_{\vec k\vec q}\left[V(\vec k\vec q)c^+_{\vec k\sigma}a_{\vec q\sigma} + h.c.\right] \end{gathered}, \qquad (6)$$

where

$$\varepsilon(\vec k) = \sum_\alpha H_1(\alpha\alpha')\exp\left[i\vec k(\vec R_\alpha - \vec R_{\alpha'})\right], \qquad (7)$$

$$E(\vec q) = \sum_{ff'} H_2(ff')\exp\left[i\vec q(\vec R_f - \vec R_{f'})\right], \qquad (8)$$

$$\begin{gathered} V(\vec k\vec q) = \sum_{\alpha f}\left[V_1(\alpha f) + V_2(f\alpha)\right]\times \\ \times\exp(-i\vec k\vec R_\alpha)\exp(i\vec q\vec R_f) \end{gathered}. \qquad (9)$$

Eqs. (7) and (8) represent the dispersion laws of the first and second sublattices, and $\vec k$ and $\vec q$ respectively the momenta for them.

Calculation Technique and Solutions

We shall use the retarded double-time Green's functions. Equation of motion for the Green's functions $\langle\langle a_{\vec q\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle$ takes the form

$$\begin{gathered} \omega\langle\langle a_{\vec q\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle = \delta_{\vec q\vec q_2} + E(\vec q)\langle\langle a_{\vec q\sigma} | a^+_{q_2\sigma}\rangle\rangle + \\ \sum_{\vec k} V^*(\vec k\vec q)\langle\langle c_{\vec k\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle \end{gathered}. \qquad (10)$$

The same for $\langle\langle c_{\vec k} | a^+_{\vec q_2}\rangle\rangle$, which appears in Eq. (10), is as follows:

$$\begin{gathered} \omega\langle\langle c_{\vec k\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle = \varepsilon(\vec k)\langle\langle c_{\vec k\sigma} | a^+_{q_2\sigma}\rangle\rangle + \\ + \sum_{\vec q_1} V(\vec k\vec q_1)\langle\langle a_{\vec q_1\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle \end{gathered}. \qquad (11)$$

Starting from the set of Eqs. (10) and (11), one obtains

$$\begin{gathered} \langle\langle a_{\vec q\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle = \frac{\delta_{\vec q\vec q_2}}{\omega - E(\vec q)} + \frac{1}{\omega - E(\vec q)}\times \\ \times\sum_{\vec k\vec q_1}\frac{V^*(\vec k\vec q)V(\vec k\vec q_1)}{\omega - \varepsilon(\vec k)}\langle\langle a_{\vec q\sigma} | a^+_{q_2\sigma}\rangle\rangle \end{gathered}. \qquad (12)$$

Therefore the Green's function $\langle\langle a_{\vec q\sigma} | a^+_{\vec q_2\sigma}\rangle\rangle$ is a solution of Eq. (12), which represents a secondkind integral equation or the Fredholm's integral equation [10].

Let us now analyse the cases, when the potential $V(\vec{k}\vec{q})$ (i.e., the kernel of the integral equation (12)), is degenerated, i.e., $V(\vec{k}\vec{q}) = F_1(\vec{k})F_2(\vec{q})$ (below we shall also consider a more general class of $V(\vec{k}\vec{q})$). Then Eq. (12) takes the form

$$\left\langle\left\langle a_{\vec{q}\sigma} \middle| a^{+}_{\vec{q}_2\sigma} \right\rangle\right\rangle = \frac{\delta_{\vec{q}\vec{q}_2}}{\omega - E(\vec{q})} + \frac{1}{\omega - E(\vec{q})} \sum_{\vec{k}\vec{q}_1} \frac{\left|F_1(\vec{k})\right|^2 \left|F_2(\vec{q})\right|^2}{\omega - \varepsilon(\vec{k})} \Phi_1 , \qquad (13)$$

where

$$\Phi_1 = \sum_{\vec{q}_1} F_2(\vec{q}_1) \left\langle\left\langle a_{\vec{q}_1\sigma} \middle| a^{+}_{\vec{q}_2\sigma} \right\rangle\right\rangle .$$

After multiplying Eq. (13) by $F_2(\vec{q})$ and adding it to $\vec{q}$, we get equation for Φ_1. Substituting its solution into Eq. (13), one yields at $\vec{q} = \vec{q}_2$ the relation

$$\left\langle\left\langle a_{\vec{q}\sigma} \middle| a^{+}_{\vec{q}_2\sigma} \right\rangle\right\rangle = \frac{1}{\omega - E(\vec{q})} + \frac{\left|F_2(\vec{q})\right|^2}{\left[\omega - E(\vec{q})\right]^2} F(\omega) , \qquad (14)$$

where $F(\omega) = \dfrac{\dfrac{\left|F_1(\vec{k})\right|^2}{\omega - \varepsilon(\vec{k})}}{1 - \sum\limits_{\vec{k}} \dfrac{\left|F_1(\vec{k})\right|^2}{\omega - \varepsilon(\vec{k})} \sum\limits_{\vec{q}} \dfrac{\left|F_2(\vec{q})\right|^2}{\omega - E(\vec{q})}}$. (15)

Finally, after performing transformations in Eq. (14) and taking Eq. (15) into account, this may be written as

$$\left\langle\left\langle a_{\vec{q}\sigma} \middle| a^{+}_{\vec{q}_2\sigma} \right\rangle\right\rangle = \frac{\prod\limits_{p}(\omega - \varepsilon_p)\prod\limits_{r \neq q}(\omega - E_r) - \sum\limits_{i}\left|F_1(i)\right|^2 \prod\limits_{p \neq i}(\omega - \varepsilon_p) \sum\limits_{r}\left|F_2(r)\right|^2 \prod\limits_{f \neq r,q}(\omega - E_f)}{\prod\limits_{p}(\omega - \varepsilon_p)\prod\limits_{r}(\omega - E_r) - \sum\limits_{i}\left|F_1(i)\right|^2 \prod\limits_{p \neq i}(\omega - \varepsilon_p) \sum\limits_{r}\left|F_2(r)\right|^2 \prod\limits_{f \neq r}(\omega - E_f)} . \qquad (16)$$

Here we use the notations $E_r \equiv E(r)$ and $\varepsilon_p \equiv \varepsilon(p)$, where r and p are the moments referred to the different sublattices. The poles of the Green's function (16) describe the spectrum of the problem under consideration.

Let us analyse some special cases of this problem.

(a) Case of commensurable sublattices:

Then $V(\vec{k}\vec{q}) = \delta_{\vec{k}\vec{q}} V(\vec{k})$ and it follows from Eq. (12) that

$$\left\langle\left\langle a_{\vec{q}\sigma} \middle| a^{+}_{\vec{q}\sigma} \right\rangle\right\rangle = \frac{1}{\omega - E(\vec{q}) - \dfrac{\left|V(\vec{q})\right|}{\omega - \varepsilon(\vec{q})}} . \qquad (17)$$

We have therefore

$$\omega_{1,2} = \frac{1}{2}\left[E(\vec{q}) + \varepsilon(\vec{q}) \pm \sqrt{\left(E(\vec{q}) - \varepsilon(\vec{q})\right)^2 + 2\left|V(\vec{q})\right|^2}\right] . \qquad (18)$$

In other words, the problem has been reduced to a two-band model within the limits of superstructure. It can be seen that the mixing integral between the bands tends to “repulse” their positions, thus reminding the results known for the two-level problem [11].

(b) Case of incommensurable sublattices:

As an example of this case, let us consider a hypothetical structure with two states in every sublattice. Then the pole of the Green's function (16) is given by

$$\begin{gathered}(\omega - \varepsilon_1)(\omega - \varepsilon_2)(\omega - E_1)(\omega - E_2) - \\ - \left[\left|F_1(1)\right|^2(\omega - \varepsilon_2) + \left|F_1(2)\right|^2(\omega - \varepsilon_1)\right] \times \\ \left[\left|F_2(2)\right|^2(\omega - E_1) + \left|F_2(1)\right|^2(\omega - E_2)\right] = 0\end{gathered} . \qquad (19)$$

In this model problem, $\varepsilon_1(E_1)$ and $\varepsilon_2(E_2)$ are respectively the bottom and the top first "bands" of the sublattices (see Eq. (2)). The analysis shows that the "bands" are “repulsed” if $V(\vec{k}\vec{q})$ is taken into account. If $\varepsilon_1 \langle E_1 \langle \varepsilon_2 \langle E_2$ (i.e., the "bands" are overlapped), taking $V(\vec{k}\vec{q})$

into account causes pushing aside of bottom of the lower "band" and the top of the upper one. The top of the lower "band" can be “pulled” down or up, depending on whether the relation $\frac{|F_2(2)|^2(\varepsilon_2 - E_1)}{|F_2(1)|^2(E_2 - \varepsilon_2)}$ is larger or smaller than unity. Similarly, the bottom of the upper "band" would tend downwards or upwards, depending on whether $\frac{|F_1(1)|^2(\varepsilon_2 - E_1)}{|F_1(2)|^2(E_1 - \varepsilon_1)}$ becomes smaller or larger than unity. In other words, the bandwidth can be increased or decreased, depending on the position of the levels and the magnitude of the "interband" overlapping.

We stress also that the presented technique is applicable to the problems with a more common class of kernels in Eq. (12), when compare with a degenerate one used above. According to [10], any uniform-continued kernel may be approximated with a desirable accuracy by degenerate kernels. One of the methods is expanding $V(\vec{k}\vec{q})$ in a Taylor series at a certain point $(\vec{k}\vec{q})$. For the sake of concreteness, let it be the point (0,0). Then we have

$$V(\vec{k}\vec{q}) = V(00) + a_1 k + b_1 q + a_2 k + ckq + ..., \quad (20)$$

where *a, b* and *c* are the expansion coefficients.

Substituting Eq. (20) into Eq. (12), one obtains

$$\left\langle\left\langle a_{\vec{q}\sigma} \middle| a^{+}_{\vec{q}_2\sigma} \right\rangle\right\rangle = \frac{\delta_{\vec{q}\vec{q}_2}}{\omega - E(\vec{q})} + \frac{1}{\omega - E(\vec{q})} \left\{ \sum_k \frac{\left|V(00) + a_1 k + a_2 k^2\right|^2}{\omega - \varepsilon_k} \sum_{q_1} \left\langle\left\langle a_{q_1\sigma} \middle| a^{+}_{q_2\sigma} \right\rangle\right\rangle + \right.$$

$$\left. \sum_k \frac{A_1(k)}{\omega - \varepsilon_k} \sum_{q_1} q_1 \left\langle\left\langle a_{q_1\sigma} \middle| a^{+}_{q_2\sigma} \right\rangle\right\rangle + \sum_k \frac{A_2(k)}{\omega - \varepsilon_k} q_1^2 \left\langle\left\langle a_{q_1\sigma} \middle| a^{+}_{q_2\sigma} \right\rangle\right\rangle + ... \right\}$$

where

$$A_1 = \left[\left(V(00) + a_1 k + a_2 k^2\right)^* (b_1 + ck) + h.c. \right],$$

$$A_2 = \left\lfloor b_2^* \left(V(00) + a_1 k + a_2 k^2\right) + \left|b_1 + ck\right|^2 + h.c. \right\rfloor.$$

The latter equation may be rewritten as

$$\omega \left\langle\left\langle a_{\vec{q}\sigma} \middle| a^{+}_{\vec{q}_2\sigma} \right\rangle\right\rangle = \frac{\delta_{\vec{q}\vec{q}_2}}{\omega - E(\vec{q})} + \frac{1}{\omega - E(\vec{q})} \sum_{n=0}^{\infty} R_n \Phi_n ,$$

where $\Phi_n = \sum_{q_1} q_1^n \left\langle\left\langle a_{q_1\sigma} \middle| a^{+}_{q_2\sigma} \right\rangle\right\rangle$ and R_n are coefficients.

Repeating the procedure for eliminating Φ_n mentioned above, we get the equation similar to Eq. (14).

Conclusions

In this work the technique for solving the stationary Schrodinger equation for crystalline systems is represented, where the single-electron potential include the two terms. They both describe the ordered structures, generally with the different lattice parameters. In case of the commensurable parameters ($a_i = mb_i$, with a_i and b_i being the lattice parameters, m an integer and *i = x, y, z*), the technique leads to the known equation describing electron behaviour in a crystalline lattice with a basis. The major outcome of the present work is application of this technique to the problem of electron spectrum in the systems with incommensurable lattice parameters. Dependence of the bands on the magnitude of the mutual electronic mixing is illustrated on a rather simple example. It is shown that in the case of overlapped bands, the degree of overlapping can increase or decrease, depending on the magnitude of the mixing. Nonetheless, the distance between the bottom of the lower band and the top of the upper one increases in any case. We have analysed the problem of the interband interaction potential, too. It is revealed that the superstructure (especially the incommensurate one) has fundamentally different properties of the electron spectrum (or the density of electron states), if compare with the properties of basic structures forming the superstructure. It is worthwhile to point at a unique possibility for varying the electron spectrum in the case of “lattice + pseudo-lattice”. For example, a ferroelectric phase transition between the paraelectric and ferroelectric states gives rise to appearance of such the pseudo-lattice, and so to essential change in the electron spectrum.

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