

電子在徐變混成晶體或合金中的等効韓彌爾頓理論

Effective Hamiltonian Theory of Electrons in Graded Mixed Crystal or Alloy

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Abstract — Using unitary transformation method to remove the interband matrix elements successively, we can formulate the problem of an electron moving in a periodic potential with slowly varying envelop. The effective quantum mechanical Hamiltonian operator $\epsilon(\vec{p}, \lambda(\vec{r}))$ is derived and compared with that obtained by kq-representation method. And the hermitianized procedure of the effective Hamiltonian is given.

I. Introduction

For homogeneous mixed crystals of A and B that have the same structure and lattice constants, a useful concept is that of the virtual crystal. In the virtual crystal approximation [1] [2] [3], which consists of replacing the actual potential centered on each lattice site by a weighted average, $fU_p(\vec{r})$ is the perturbation on system A, where f is the fraction of B and $U(\vec{r})$ is the difference in the potentials due to B and A.

$$H = H_A + fU_p(\vec{r})$$

$$H_A = -\hbar^2 \frac{\nabla^2}{2m_a} + V_A(\vec{r})$$

$$U_p(\vec{r}) = V_B(\vec{r}) - V_A(\vec{r})$$

The perturbation $fU_p(\vec{r})$ is periodic with the same periodicity as the components A and B. This problem is solved explicitly in two-band model [4], and they show that the band gap varies linearly with f due to diagonal matrix elements of $U_p(\vec{r})$, and with higher powers of f due to interband elements. And this result agree with most experimental facts of II-VI compounds. Along this line, we would like to consider the inhomogeneous mixed crystal, i.e., the graded mixed crystal, having a composition which varies continuously along some direction. We then define the perturbation as $\lambda(x)U_p(\vec{r})$, where $\lambda(x)$ is the composition factor and is assumed to vary slowly compared to a unit cell, x is the direction of grading. This perturbation therefore is equivalent to assume a slowly varying virtual crystal. The purposed of this paper is to derive the effective Hamiltonian theory for the graded mixed crystal or graded alloy. The author has dealt with this problem by kq-representation [5], and here we try to derive this result by a method of successive removal of interband elements similar to that used to treat the dynamics of crystal electrons in perturbed periodic fields [6].

II. Unitary Transformation and Effective Hamiltonian

Let us consider the following model Hamiltonian:

$$H(\vec{p}, \vec{r}) = H_0(\vec{p}, \vec{r}) + W(\vec{r})$$

(1)

where $W(\vec{r})$ is the perturbed Hamiltonian, we write

$$W(\vec{r}) = \lambda(\vec{r}) U_p(\vec{r})$$

$H_0(\vec{p}, \vec{r})$ and $U_p(\vec{r})$ are both periodic with the same periodicity. $\lambda(\vec{r})$ is the slowly varying dimensionless function of \vec{r} . For a compositionally graded alloy or inhomogeneous mixed crystal, by using virtual crystal approximation or coherent potential approximation [7], the local disordered Hamiltonian can be replaced by an effective periodic Hamiltonian plus a nonperiodic perturbation of the form (1) where $\lambda(\vec{r})$ is given by the local concentration.

Let us first write the Hamiltonian (1) in the representation of the normalized Bloch-like eigen-functions of H_0 ,

$$\psi_{n\vec{k}}(\vec{r}) \equiv \langle \vec{r} | n\vec{k} \rangle = U_{n\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

where n is the band index and \vec{k} is the Bloch wave number, $U_{n\vec{k}}(\vec{r})$ is a periodic function of lattice length.

$\psi_{n\vec{k}}(\vec{r})$ is normalized in an unit cell with the unperturbed eigen energies, $\epsilon_n^0(\vec{k})$, we have

$$\langle n\vec{k} | H | n'\vec{k}' \rangle = \epsilon_n^0(\vec{k}) \delta_{nn'} \delta_{\vec{k}\vec{k}'} + \langle n\vec{k} | W | n'\vec{k}' \rangle$$

By the closure property of $|n\vec{k}\rangle$ and the periodicity of U_p , we then have

$$\langle n\vec{k} | W | n'\vec{k}' \rangle = \sum_{n''} \langle n\vec{k} | \lambda(\vec{r}) | n''\vec{k}'' \rangle \langle n''\vec{k}'' | U_p | n'\vec{k}' \rangle \quad (2)$$

and

$$\begin{aligned} \langle n\vec{k} | \lambda(\vec{r}) | n''\vec{k}'' \rangle &\equiv \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} U_{n\vec{k}}^*(\vec{r}) \lambda(\vec{r}) U_{n''\vec{k}''}(\vec{r}) e^{i\vec{k}'' \cdot \vec{r}} \\ &= \int e^{-i(\vec{k} - \vec{k}'') \cdot \vec{r}} \lambda(\vec{r}) U_{n\vec{k}}^*(\vec{r}) U_{n''\vec{k}''}(\vec{r}) d\vec{r} \end{aligned}$$

where $U_{n\vec{k}}^*(\vec{r}) U_{n''\vec{k}''}(\vec{r})$ is a periodic function, hence it can be written as

$$U_{n\vec{k}}^*(\vec{r}) U_{n''\vec{k}''}(\vec{r}) = \sum_m B_m(\vec{k}\vec{k}'') e^{-i\vec{K}_m \cdot \vec{r}}$$

where \vec{K}_m is the reciprocal lattice vector. Therefore,

$$\begin{aligned} \langle n\vec{k} | \lambda(\vec{r}) | n''\vec{k}'' \rangle &= \sum_m B_m(\vec{k}\vec{k}'') \int d\vec{r} e^{i(\vec{k} - \vec{k}'' + \vec{K}_m) \cdot \vec{r}} \lambda(\vec{r}) \\ &= (2\pi)^3 \sum_m B_m(\vec{k}\vec{k}'') F(\vec{k} - \vec{k}'' + \vec{K}_m) \end{aligned} \quad (3)$$

$F(\vec{k})$ is the Fourier transform of the function $\lambda(\vec{r})$. Since $\lambda(\vec{r})$ is a slowly varying gentle function, only the term with $m=0$ in (3) need be kept. The reason for this is the following. The solution of our problem with this assumption leads to values of \vec{k} and \vec{k}' much smaller than any \vec{K}_m with $m \neq 0$, hence the terms in (3) with $m \neq 0$ contain much higher Fourier components than those with $m=0$, and are thus much smaller. Therefore, we have

$$\langle n\vec{k} | \lambda(\vec{r}) | n''\vec{k}'' \rangle \approx (2\pi)^3 B_0(\vec{k}\vec{k}'') F(\vec{k} - \vec{k}'')$$

$$= \delta_{nn'} \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle \tag{4}$$

Since $\langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle = \int e^{-i\vec{k} \cdot \vec{r}} \lambda(\vec{r}) e^{i\vec{k}' \cdot \vec{r}} d\vec{r}$, it is negligible except for $\vec{k} \approx \vec{k}'$, we obtain $B_0^{(kk')}$ by its definition $\approx \frac{1}{(2\pi)} \delta_{nn'}$.

Thus, equation (2) becomes

$$\langle n\vec{k} | W | n'\vec{k}' \rangle = \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle \langle n\vec{k}' | U_p | n'\vec{k}' \rangle$$

Now, let us separate W into its intra-band and inter-band components.

$$W = W_a + W_b \tag{5}$$

and we remove the interband elements to the first order by a canonical transformation T . We write this unitary transformation as

$$T = e^{iS}$$

we treat λ as formally small and write

$$S = S_1 + S_2 + S_3 + \dots$$

in ascending powers of λ , and the transformed Hamiltonian is similarly expanded in powers of λ ,

$$\begin{aligned} \tilde{H} &= T^+ H T = e^{-iS} H e^{iS} \\ &= H + i [H, S] + \frac{1}{2} [S, [H, S]] + \dots \\ &= H_0 + W_a + W_b + i [H_0, S_1] + i [H_0, S_2] \\ &\quad + i [W_a + W_b, S_1] + \frac{1}{2} [S_1, [H_0, S_1]] + \dots \end{aligned}$$

In order to eliminate the inter-band matrix elements to the first order, we must choose S_1 , such that

$$\langle n\vec{k} | W_b + i [H_0, S_1] | n'\vec{k}' \rangle = 0, \quad n \neq n' \tag{6}$$

This can be accomplished by choosing

$$\langle n\vec{k} | S_1 | n'\vec{k}' \rangle = \begin{cases} \frac{i}{\epsilon_n^0(\vec{k}) - \epsilon_{n'}^0(\vec{k}')} \langle n\vec{k} | W_b | n'\vec{k}' \rangle, & n \neq n' \\ 0, & n = n' \end{cases}$$

All higher-order terms of S can also be chosen as off-diagonal. Thus, by the fact of $\langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle$ is negligible except for $\vec{k} \approx \vec{k}'$, and by (6), we also have:

$$= \delta_{nn'} \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle \tag{4}$$

Since $\langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle = \int e^{-i\vec{k}\cdot\vec{r}} \lambda(\vec{r}) e^{i\vec{k}'\cdot\vec{r}} d\vec{r}$, it is negligible except for $\vec{k} \approx \vec{k}'$, we obtain $B_0^{(kk')}$ by its definition $\approx \frac{1}{(2\pi)} \delta_{nn'}$.

Thus, equation (2) becomes

$$\langle n\vec{k} | W | n'\vec{k}' \rangle = \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle \langle n\vec{k}' | U_p | n'\vec{k}' \rangle$$

Now, let us separate W into its intra-band and inter-band components.

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$$\begin{aligned} \tilde{H} &= T^+ H T = e^{-iS} H e^{iS} \\ &= H + i [H, S] + \frac{1}{2} [S, [H, S]] + \dots \\ &= H_0 + W_a + W_b + i [H_0, S_1] + i [H_0, S_2] \\ &\quad + i [W_a + W_b, S_1] + \frac{1}{2} [S_1, [H_0, S_1]] + \dots \end{aligned}$$

In order to eliminate the inter-band matrix elements to the first order, we must choose S_1 , such that

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All higher-order terms of S can also be chosen as off-diagonal. Thus, by the fact of $\langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle$ is negligible except for $\vec{k} \approx \vec{k}'$, and by (6), we also have:

$$\begin{aligned}
& i [W_b, S_1] + \frac{1}{2} [S_1, [H_0, S_1]] = \frac{i}{2} [W_b, S_1] \\
& \langle \vec{n}\vec{k} | \tilde{H} | \vec{n}\vec{k}' \rangle \\
& = \{ \langle \vec{n}\vec{k} | H_0 | \vec{n}\vec{k}' \rangle + \langle \vec{n}\vec{k} | W_a | \vec{n}\vec{k}' \rangle + \sum_{\vec{n}'', \vec{k}''} \frac{1}{\epsilon_n^0(\vec{k}) - \epsilon_{n''}^0(\vec{k}'')} \cdot \langle \vec{n}\vec{k} | W_b | \vec{n}''\vec{k}'' \rangle \\
& \quad \cdot \langle \vec{n}''\vec{k}'' | W_b | \vec{n}\vec{k}' \rangle + \dots \} \\
& = \{ \langle \vec{n}\vec{k} | H_0 | \vec{n}\vec{k}' \rangle + \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle \langle \vec{n}\vec{k} | U_p | \vec{n}\vec{k}' \rangle \\
& \quad + \sum_{\vec{n}'', \vec{k}''} \langle \vec{k} | \lambda(\vec{r}) | \vec{k}'' \rangle \langle \vec{k}'' | \lambda(\vec{r}) | \vec{k}' \rangle \frac{1}{\epsilon_n^0(\vec{k}) - \epsilon_{n''}^0(\vec{k}'')} \cdot \langle \vec{n}\vec{k} | U_p | \vec{n}''\vec{k}'' \rangle \\
& \quad \cdot \langle \vec{n}''\vec{k}'' | U_p | \vec{n}\vec{k}' \rangle + \dots \} \tag{7}
\end{aligned}$$

and for $n \neq n'$, we have

$$\langle \vec{n}\vec{k} | \tilde{H} | \vec{n}'\vec{k}' \rangle = 0 \tag{8}$$

Since all the momenta \vec{k} are nearly equal, we then have neglected the differences between $\epsilon_n^0(\vec{k})$ and $\epsilon_n^0(\vec{k}')$; $\langle \vec{n}\vec{k} | U_p | \vec{n}\vec{k}' \rangle$ and $\langle \vec{n}\vec{k}' | U_p | \vec{n}\vec{k} \rangle$ etc.. This approximation introduces small nonhermitian error into equation (7), but we will remove it shortly. Now the equation (7) can be written in the following form:

$$\langle \vec{k} | \tilde{H} | \vec{k}' \rangle = \epsilon^0(\vec{k}) \delta_{\vec{k}\vec{k}'} + \epsilon^{(1)}(\vec{k}) \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle + \epsilon^{(2)}(\vec{k}) \langle \vec{k} | \lambda(\vec{r}) | \vec{k}' \rangle + \dots \tag{9}$$

where we have dropped the common band index n , and $\epsilon^0(\vec{k})$, $\epsilon^{(1)}(\vec{k})$, $\epsilon^{(2)}(\vec{k})$, etc., are the zeroth, first, second terms of the perturbation energy due to a perturbation λU_p with "a pure constant λ ". According to (9), we can write to all orders in $\lambda(\vec{r})$

$$\begin{aligned}
\langle \vec{k} | \tilde{H} | \vec{k}' \rangle &= \langle \vec{k} | \epsilon^0(\vec{k}) + \epsilon^{(1)}(\vec{k}) \lambda(\vec{r}) + \epsilon^{(2)}(\vec{k}) \lambda^2(\vec{r}) + \dots | \vec{k}' \rangle \\
&= \langle \vec{k} | \epsilon(\vec{k}; \lambda(\vec{r})) | \vec{k}' \rangle \tag{9'}
\end{aligned}$$

where, for "constant λ ", $\epsilon(\vec{k}; \lambda)$ is the energy function of the corresponding Hamiltonian $H_0 + \lambda U_p$. If λ is a function of \vec{r} , then $\epsilon(\vec{k}; \lambda(\vec{r}))$ is not quite hermitian, because of the noncommunity property of \vec{r} and \vec{k} operators. In order to make it hermitian, we must symmetrize the $\epsilon(\vec{k}; \lambda(\vec{r}))$ operator by Fourier expansion. We first Fourier expand the energy function $\epsilon(\vec{k}; \lambda)$ for "constant λ ",

$$\epsilon(\vec{k}, \lambda) = \sum_{\vec{\rho}} E_{\rho}(\lambda) e^{i\vec{\rho}\vec{r} \cdot \vec{k}} \tag{9''}$$

where the $\vec{\rho}$ are the lattice vectors, then we symmetrized (9'') and then obtain the hermitianized form of (9') as:

$$\langle \vec{k} | \tilde{H} | \vec{k}' \rangle = \langle \vec{k} | \epsilon(\vec{p}; \lambda(\vec{r})) | \vec{k}' \rangle \tag{10}$$

where

$$\epsilon(\vec{p}; \lambda(\vec{r})) \equiv \frac{1}{2} \sum_{\ell} \{ E_{\ell}(\lambda(\vec{r})) e^{i\vec{R}_{\ell} \cdot \vec{p}} + e^{i\vec{R}_{\ell} \cdot \vec{p}} E_{\ell}(\lambda(\vec{r})) \} \quad (11)$$

and the \vec{p} is the familiar momentum operator whose matrix elements are $\langle \vec{k} | \vec{p} | \vec{k}' \rangle = \hbar \vec{k} \delta_{\vec{k}\vec{k}'}$, and $[p_i, r_j] = -i\hbar \delta_{ij}$.

The Hamiltonian (11) and its matrix element (10) are our final results, and (11) is our effective Hamiltonian with slowly varying envelope function $\lambda(\vec{r})$. Because $E_{\ell}(\lambda(\vec{r}))$ is a function of coordinate \vec{r} , the hermitianized procedure (11) will introduce, if any, only small error of the order of the commutator of \vec{p} and $\lambda(\vec{r})$. And the commutator is proportional to the derivative of $\lambda(\vec{r})$, therefore, it is small by the assumption of the smoothness of $\lambda(\vec{r})$. This effective Hamiltonian in coordinate representation takes the following form:

$$\epsilon(\vec{p} \rightarrow -i\hbar\vec{\nabla}, \lambda(\vec{r})) \equiv \frac{1}{2} \sum_{\ell} \{ E_{\ell}(\lambda(\vec{r})) e^{i\vec{R}_{\ell} \cdot \vec{\nabla}} + e^{i\vec{R}_{\ell} \cdot \vec{\nabla}} E_{\ell}(\lambda(\vec{r})) \} \quad (12)$$

In general, for the problem of graded mixed crystal or graded alloy, the original Schrodinger equation is given by

$$i \frac{\partial \psi}{\partial t} = H \psi \quad \text{where} \quad H = H_0 + W \quad (13)$$

by writing $\psi = T \phi = e^{iS} \phi$, we have

$$i \frac{\partial \phi}{\partial t} = (e^{-iS} H e^{iS}) \phi$$

and by the above procedure, it can be written in the effective Hamiltonian formalism:

$$i \frac{\partial \phi}{\partial t} = \epsilon(\vec{p}, \lambda(\vec{r})) \phi \quad (14)$$

To the first order if $\lambda(\vec{r})$, for example, we can obtain the stationary eigenvalue equation from (9), as follows:

$$[H_0 + \epsilon^{(1)}(\lambda(\vec{r}))] \phi = E \phi \quad (15)$$

This equation agrees with that obtained by the kq-representation method. [5]

III. Conclusions

For the problem of an electron moving in a gently graded mixed crystal or alloy, the perturbation Hamiltonian is equivalent to assuming a slowly varying virtual crystal. In the above section, we use a unitary transformation to obtain the effective Hamiltonian operator $\epsilon(\vec{p}, \lambda(\vec{r}))$; this function $\epsilon(\vec{k}, \lambda(\vec{r}))$, for fixed point \vec{r} , is the local band structure dispersion relation function near the fixed point \vec{r} . Therefore, for a fairly complicated Hamiltonian of the gentle graded inhomogeneous mixed crystal or graded alloy, the solution of the much simpler effective Hamiltonian equation (15) is the first approximation to the problem and a lot of qualitative and reasonable results of the problem can be obtained by this effective Hamiltonian theory.

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The Hamiltonian (1) and its matrix element (2) are our first results and (1) is the effective Hamiltonian with slowly varying envelope function $\chi(\mathbf{r})$. Because $\chi(\mathbf{r})$ is a function of coordinate \mathbf{r} , the hamiltonian H_{eff} (3) will introduce it only when we take the derivative of χ and χ^* . And the commutator $[H_{eff}, \chi]$ is proportional to the derivative of χ . Therefore it is small by the assumption of the smoothness of χ . This effective hamiltonian is coordinate representation and the following form:

$$H_{eff} = \frac{1}{2m} \nabla^2 + V(\mathbf{r}) + \dots \quad (11)$$

In general, for the problem of graded mixed crystal or graded alloy, the original Schrödinger equation is given by

$$H \psi = E \psi \quad (12)$$

By writing $\psi = \chi \phi$, we have

$$H \chi \phi = E \chi \phi \quad (13)$$

and by the above procedure, it can be written in the effective hamiltonian form:

$$H_{eff} \phi = E \phi \quad (14)$$

To the first order in χ , for example, we can obtain the effective hamiltonian equation from (13) as follows:

$$H_0 \chi \phi = E \chi \phi \quad (15)$$

This equation gives us the first approximation to the effective hamiltonian theory.

2. Conclusions

For the problem of an electron moving in a graded mixed crystal or alloy, the perturbation Hamiltonian is equivalent to assuming a slowly varying virtual crystal. In the above section, we use a unitary transformation to obtain the effective Hamiltonian operator H_{eff} . Therefore, for a fairly complicated hamiltonian band structure dependent relation function near the fixed point \mathbf{r} , the solution of the much simpler hamiltonian of the graded inhomogeneous mixed crystal or graded alloy, the solution of the much simpler hamiltonian equation (15) is the first approximation to the problem and a lot of qualitative and quantitative results of the problem can be obtained by the effective hamiltonian theory.

References

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