

Theory of a Wave Function within a Band and a New Process for Calculation of the Band Energy*

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Derived from the first principle, a dynamical theorem in form of an operator equation is proved for a wave function within a band and its inverse theorem is also proved. New process is devised for the calculation of the band energy in analytic form in terms of crystal momentum. Further we have shown that this new process is an \hbar -independent process. The effective mass is derived as a dynamical variable (an observable) from the above theorems and regarded as an intrinsic quantity correct only within a band. Finally, we apply the theory to calculate the band energies of free electron, hydrogen atom and hydrogen solid.

I. INTRODUCTION

CURRENT methods of calculating the band energy of a crystal are greatly dependent on the techniques of computation. The purpose of the present note is to get an extended theory from the current theory via the first principle. We conclude our theory in a theorem and its inverse theorem in Sec. II. From these theorems, a new process is devised for calculating the **analytic** expression of the band energy. The prior knowledge of this new process of calculation is similar to the current theory, i.e. (i) the effective crystal potential for which the one electron wave equation is to be solved, and (ii) an approximate Bloch function. In this new process, we need a wave function not necessarily an (approximate) Bloch function. We need only a wave function belonging to a wider class of wave function, called **a wave function within the band**, describing the electron believed to be inside a given band. But our result is much more general than the result obtained from the current theory. That is, in the current theory, we assume a known wave function at a given point (or line at most) (high symmetry usually). Only at this given point (or line), we can calculate our band energy value. But in the present suggested process, if we know the wave function which has the only assumption, i.e., to be inside a band (much wider class of functions than that in the current theory), we are able to calculate the analytic expression of band energy of this band as a function of the crystal momentum over all possible values of the crystal momentum.

From the result of this new process of calculations, we have shown in this note that the **underline principle** of calculation process is \hbar -independent. That means, the whole theory reported in this note is valid both in quantum mechanics and in classical dynamics. Further development from the derived theorems, the dynamical properties of the electron give a new sense for the effective mass, i.e. the effective mass is derived from the equation of motion as an observable and intrinsic quantity of the electron and a direct result of the band energy.

In Sec. VI, applications of the new process to free electron (which usually is a test of a new

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band theory), hydrogen atom and hydrogen solid are given. For hydrogen solid case, the effective mass has been calculated to be anisotropic in general.

II. THEORY

For the periodic potential $V(\mathbf{r})$ the Bloch function $b_n(\mathbf{k}, \mathbf{r})$ satisfies

$$H_0 b_n(\mathbf{k}, \mathbf{r}) = E_n(\mathbf{p}) b_n(\mathbf{k}, \mathbf{r}), \quad (\text{II-1})$$

where the energy eigenvalues $E_n(\mathbf{p})$ is a function of the band index n and the crystal momentum $\mathbf{p} \equiv \hbar \mathbf{k}$ where we have used \mathbf{p} instead of \mathbf{k} for convenience. The Hamiltonian has been given in the form

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}). \quad (\text{II-2})$$

Transforming the Bloch function representation to the Wannier function representation by defining the Wannier function in the n -th band⁽¹⁾

$$W_n(\mathbf{r}-\mathbf{R}) \equiv N^{-1/2} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} b_n(\mathbf{k}, \mathbf{r}), \quad (\text{11-3})$$

we can easily obtain⁽¹⁾

$$\begin{aligned} H_0 W_n(\mathbf{r}-\mathbf{R}) &= N^{-1/2} \sum_{\mathbf{k}} E_n(\mathbf{p}) e^{-i\mathbf{k}\cdot\mathbf{R}} b_n(\mathbf{k}, \mathbf{r}) \\ &= \sum_j N^{-1} \sum_{\mathbf{k}} E_n(\mathbf{p}) e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R})} W_n(\mathbf{r}-\mathbf{R}_j). \end{aligned} \quad (\text{11-4})$$

The Wannier function in (II-4) is displaced by a translation operator and (11-4) **becomes**

$$\begin{aligned} H_0 W_n(\mathbf{r}-\mathbf{R}) &= \sum_j \sum_{\mathbf{k}} N^{-1} E_n(\mathbf{p}) e^{i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R})} e^{i(\mathbf{R}-\mathbf{R}_j)\cdot(i\nabla+\mathbf{K})} W_n(\mathbf{r}-\mathbf{R}) \\ &= \sum_{\mathbf{k}} E_n(\mathbf{p}) N^{-1} \sum_j e^{i(\mathbf{k}+i\nabla+\mathbf{K})\cdot(\mathbf{R}_j-\mathbf{R})} W_n(\mathbf{r}-\mathbf{R}) \\ &= E_n(\mathbf{p}_{op}) W_n(\mathbf{r}-\mathbf{R}), \end{aligned} \quad (\text{11-5})$$

where the operator \mathbf{p}_{op} inside $E_n(\mathbf{p}_{op})$ is given as

$$\mathbf{p}_{op} \equiv -i\hbar \nabla + \hbar \mathbf{K}' \quad (\text{11-6})$$

for arbitrary reciprocal vector \mathbf{K}' and the function form of $E_n(\mathbf{p}_{op})$ in terms of \mathbf{p}_{op} is the same as that of $E_n(\mathbf{p})$ in terms of \mathbf{p} . Here we have used the identity

$$N^{-1} \sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j} = \delta_{\mathbf{k}, \mathbf{K}}$$

in the last equality of (II-5).† It is noted that two operators H_0 and $E_n(\mathbf{p}_{op})$ on both sides of (11-5) are independent of \mathbf{R} which appears in $W_n(\mathbf{r}-\mathbf{R})$. In other words, (11-5) is valid for all $W_n(\mathbf{r}-\mathbf{R})$ specified by \mathbf{R} , but given n . Naturally, we consider the set of functions $\{W_n(\mathbf{r}-\mathbf{R})\}$ as well as $\{b_n(\mathbf{k}, \mathbf{r})\}$ for given n , forming a subspace M_n for the n -th band of the electron states. Further inside M_n , we define an arbitrary wave function $f_n(\mathbf{r})$ which is, of course, a linear combination of the complete set of basis functions of M_n , here the set $\{W_n(\mathbf{r}-\mathbf{R})\}$ or $\{b_n(\mathbf{k}, \mathbf{r})\}$. Since every

(1) G. Wannier, Phys. Rev. 52, 191 (1937); Joseph Callaway, "Energy Band Theory" (Academic Press, N. Y. 1964) and the references therein. The notations in this note follow essentially the Callaway's notations.

† In (II-5), since $W_n(\mathbf{r}-\mathbf{R})$ is periodic across the entire crystal, we can expand $W_n(\mathbf{r}-\mathbf{R}) \equiv \sum_{\mathbf{k}} w_n(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}$.

Then the last equality of (II-5) is obtained as

$$\begin{aligned} H_0 W_n(\mathbf{r}-\mathbf{R}) &= \sum_{\mathbf{k}} \sum_{\mathbf{k}'} E_n(\mathbf{p}) N^{-1} w_n(\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{K})\cdot(\mathbf{R}_j-\mathbf{R})} e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{R})} \\ &= \sum_{\mathbf{k}} \sum_{\mathbf{k}'} E_n(\mathbf{p}) w_n(\mathbf{k}') \delta_{\mathbf{k}-\mathbf{k}', \mathbf{K}} e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{R})} = E_n(\mathbf{p}_{op}) \sum_{\mathbf{k}} w_n(\mathbf{k}') e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{R})} = E_n(\mathbf{p}_{op}) W_n(\mathbf{r}-\mathbf{R}) \end{aligned}$$

$f_n(\mathbf{r})$ in terms of $W_n(\mathbf{r}-\mathbf{R})$ satisfies (II-5), therefore we can conclude this equality as a theorem in the following:

Theorem: $f_n(\mathbf{r})$ satisfies the operator equation

$$H_0 f_n(\mathbf{r}) = E_n(\mathbf{p}_{op}) f_n(\mathbf{r}) \quad (11-7)$$

with $\mathbf{p}_{op} \equiv -i\hbar\nabla + \mathbf{K}$.

Furthermore, we are able to get the inverse theorem of the above theorem. Let us start with the momentum representation[@] of the Bloch function,

$$b_n(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{K}} M_{\mathbf{k}+\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}, \quad (11-8)$$

and obtain an eigen equation for $m \neq n$

$$E_m(\mathbf{p}_{op}) b_n(\mathbf{k}, \mathbf{r}) = E_n(\mathbf{p}) b_n(\mathbf{k}, \mathbf{r}), \quad (11-9)$$

since the operator \mathbf{p}_{op} is only determined up to an arbitrary reciprocal vector $\hbar\mathbf{K}'$. Then, let us consider a general equation

$$H_0 f(\mathbf{r}) = E_n(\mathbf{p}_{op}) f(\mathbf{r}) \quad (11-10)$$

with the periodic boundary condition on $f(\mathbf{r})$, i.e. $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}_G)$ across the entire crystal \mathbf{R}_G . After multiplying a bra $b_m(\mathbf{k}, \mathbf{r})$ on the left side of (II-10), we get

$$[E_m(\mathbf{p}) - E_n(\mathbf{p})] \langle b_m(\mathbf{k}, \mathbf{r}) | f(\mathbf{r}) \rangle = 0.$$

Thus $f(\mathbf{r})$ has non-vanishing components[‡] only if

$$E_m(\mathbf{p}) - E_n(\mathbf{p}) = 0. \quad (II-11)$$

That is, $f(\mathbf{r})$ must be one of $\{f_m(\mathbf{r})\}$ in M_n for suitably chosen subspace M_n . Carefulness must be taken for choosing M_n because in (II-11) we may have overlapped bands. The way to choose M_n is as follows. If there are band interactions, for example, $E_m(\mathbf{p}_1) = E_n(\mathbf{p}_1)$, then $b_m(\mathbf{k}_1, \mathbf{r})$ and $b_n(\mathbf{k}_1, \mathbf{r})$ are degenerate energy eigenfunctions. In this case, M_n should be chosen suitably at these values of \mathbf{p}_1 . Linear combinations of $b_m(\mathbf{k}_1, \mathbf{r})$ and $b_n(\mathbf{k}_1, \mathbf{r})$, $b'_m(\mathbf{k}_1, \mathbf{r})$ and $b'_n(\mathbf{k}_1, \mathbf{r})$ say, always solve the problem,⁽³⁾ i.e. we are able to make $\langle b'_m(\mathbf{k}_1, \mathbf{r}) | f(\mathbf{r}) \rangle = 0$ and $\langle b'_n(\mathbf{k}_1, \mathbf{r}) | f(\mathbf{r}) \rangle \neq 0$. Conclusively, we obtain the inverse theorem as follows:

Inverse Theorem: The operator equation

$$H_0 f(\mathbf{r}) = E_n(\mathbf{p}_{op}) f(\mathbf{r}) \quad (11-12)$$

with $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}_G)$ determines a wave function $f(\mathbf{r}) = f_n(\mathbf{r})$ within the n -th band for suitable choice of the subspace M_n .

III. METHOD OF CALCULATING BAND ENERGY

From the first principle, two equations (11-7) and (11-12) have been proved in the last section. We are going to devise new process to calculate the band energy. Before going to describe the new

(2) J. C. Slater: "Electronic Structure of Solids: The Energy Band Method", Tech. Rept. -4, Solid State and Molecular Theory Group, MIT July 15, 1953. Or H. B. Callen: "The Energy Band Theory of Solids" in "Handbook of Physics," ed. by Condon and Odishow (McGraw-Hill, N. Y. 1958).

(3) A detailed discussions of the general properties, cf. Der-Ruenn Su, Report to the National Science Council, Republic of China, July 26, 1969. (unpublished).

‡ Since m may or may not equal to n , we see that the theory here is a "many band" theory. Of course, we assume that the set $\{b_m(\mathbf{k}, \mathbf{r})\}$ for all m and \mathbf{k} forms a complete orthonormal basis in the Hilbert space.

process, we review the current relevant procedure of calculating band energy first. In the current calculations, we shall first assume that the effective crystal potential for which the one-electron wave equation is to be solved is known. Then, we assume a physical reasonable wave function which includes the considerations of the symmetric properties of the potential at a given point (or line at most). Of course, the appropriate boundary conditions are taken into consideration. Thus the band energy is calculated at this given symmetric point (or line). Mostly, only the band energy at this point (or line) is obtained.

Now a new process is devised to calculate the band energy $E_n(\mathbf{p})$. The prior known materials to calculate $E_n(\mathbf{p})$ are the effective crystal potential and a general wave function $f_n(\mathbf{r})$ believed to be entirely within the n-th band (in the subspace M_n). Then we can obtain the analytic expression of the band energy $E_n(\mathbf{p})$ for all values of \mathbf{p} . Of course, if we have known the rigorous wave function $f_n(\mathbf{r})$, our result for the expression $E_n(\mathbf{p})$ is also exact. On the other hand, an approximate $f_n(\mathbf{r})$ will give an approximate expression for $E_n(\mathbf{p})$. Apart from that we can get an analytic expression of $E_n(\mathbf{p})$, we have another advantage of this new process, i.e. we can choose the general wave function $f_n(\mathbf{r})$ as any wave function within the band, such as Bloch function of any one \mathbf{k} , Wannier function at any one \mathbf{R} or any other functions in usual band energy calculations. Furthermore, what we need to calculate analytic expression of $E_n(\mathbf{p})$ for all \mathbf{p} is only one function $f_n(\mathbf{r})$, e. g. the wave function at a high symmetric point.

The basic idea of this new process comes from the Schrödinger's original formalism of the wave mechanics⁽⁴⁾ together with the idea of the classical correspondence.^(5,6) The usual treatment of the classical limit of a quantum system is to take the limiting process $\hbar \rightarrow 0$.

We shall point out two equivalent processes in the following. First, let us consider rigorously a function $f_n(\mathbf{r})$ believed to be entirely within the n-th band.⁽⁷⁾ Then this function $f_n(\mathbf{r})$ can be expressed in the form

$$f_n(\mathbf{r}) \equiv A(\mathbf{r})e^{iS(\mathbf{r})/\hbar} \quad (\text{III-1})$$

with two real functions $S(\mathbf{r})$ and $A(\mathbf{r})$. Further we assume that $A(\mathbf{r})$ is a reasonably slowly varying function of \mathbf{r} as we can expect in most quantal systems. Applying the formula

$$e^{-iS(\mathbf{r})/\hbar}(-i\hbar\nabla)e^{iS(\mathbf{r})/\hbar} = -i\hbar\nabla + \nabla S(\mathbf{r})$$

to $f_n(\mathbf{r})$ in (III-1), we obtain from (11-7) with $H_0 = H_0(\mathbf{p}, \mathbf{r}) = \mathbf{p}^2/2m + V(\mathbf{r})$,

$$H_0(-i\hbar\nabla + \nabla S, \mathbf{r})A(\mathbf{r}) = E_n(-i\hbar\nabla + \nabla S)A(\mathbf{r}). \quad (\text{III-2})$$

Here the term $\hbar\mathbf{K}'$ in \mathbf{p}_{op} has been arbitrarily put to be zero without any loss of the generality. Now let us put $\hbar \rightarrow 0$. Eq. (III-2) becomes

$$H_0(\nabla S, \mathbf{r}) = (\nabla S)^2/2m + V(\mathbf{r}) = E_n(\nabla S). \quad (\text{III-3})$$

The above process, putting $\hbar \rightarrow 0$, did not introduce any approximations to the result, although this process is exactly the same one as finding the classical limit of a quantum system. The exactness of this process will be proved in the next section. Now we eliminate \mathbf{r} from the following equations:

$$\begin{cases} \mathbf{p} = \nabla S(\mathbf{r}) \\ V = V(\mathbf{r}), \end{cases} \quad (\text{III-4})$$

which result the potential function

$$V = \tilde{V}(\mathbf{p}). \quad (\text{III-5})$$

(4) For simplicity, cf. E. Schrödinger, "Collected Papers on Wave Mechanics" (Blackie & Son, London 1928) p. 1 and p. 13.

(5) cf. e.g. P. A. M. Dirac, "Principles of Quantum Mechanics" (Oxford Univ. Press, 1958) 4th ed. p. 121.

(6) Der-Ruenn Su, Intern. J. Theoret. Phys. 4, 171 (1971).

(7) cf. e.g. J. Callaway, "Electron Energy Bands in Solids" in "Solid State Physics" vol. 7, ed. by Seitz and Turnbull (Academic Press, N.Y. 1958).

The result (III-5) is essential. Substituting (III-5) to (III-3), together with (III-4), we get finally

$$E_n(\mathbf{p}) = \mathbf{p}^2/2m + V(\mathbf{p}). \quad (\text{III-6})$$

From (III-6), we can understand that the elimination of \mathbf{r} from (III-4) to get (III-5) is an important and hard procedure.

The second process is similar to the above one, but instead of $S(\mathbf{r})$ above, we use another function⁸ defined as

$$\phi(\mathbf{r}) \equiv -i\hbar \ln f_n(\mathbf{r}), \quad (\text{III-7})$$

which yields

$$E_n(\nabla\phi) = H_0(\nabla\phi, \mathbf{r}) \quad (\text{III-8})$$

after putting $\hbar \rightarrow 0$. Similar procedure as above, we eliminate \mathbf{r} from

$$\begin{cases} \mathbf{p} = \nabla\phi(\mathbf{r}), \\ V = V(\mathbf{r}), \end{cases} \quad (\text{III-9a})$$

$$(\text{III-9b})$$

which result

$$V = \tilde{V}(\mathbf{p}). \quad (\text{III-10})$$

Then we get

$$E_n(\mathbf{p}) = \mathbf{p}^2/2m + \tilde{V}(\mathbf{p}). \quad (\text{III-11})$$

Similar to the above case, the procedure, putting $\hbar \rightarrow 0$, does not affect the exactness of the above result as will be shown in the next section.

IV. A-INDEPENDENCE OF THE THEORY

In Sec. III above, we have claimed that the procedure, putting $\hbar \rightarrow 0$, does not introduce any approximations to the final result. Now we shall show this statement by proving that the result (III-11) together with (III-9a) and (III-9b), after putting $\hbar \rightarrow 0$, is still an exact result. Let us start with choosing $f_n(\mathbf{r})$ to be Bloch function and using the Bloch theorem,

$$f_n(\mathbf{r}) = b_n(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_n(\mathbf{k}, \mathbf{r}). \quad (\text{IV-1})$$

Eq. (III-9a) implies

$$\begin{aligned} \mathbf{p} &= \hbar\mathbf{k} = \nabla[-i\hbar \ln f_n(\mathbf{r})] \\ &= \hbar\mathbf{k} - i\hbar \frac{\nabla u_n(\mathbf{k}, \mathbf{r})}{u_n(\mathbf{k}, \mathbf{r})}, \end{aligned}$$

or

$$\nabla u_n(\mathbf{k}, \mathbf{r}) = 0. \quad (\text{IV-2})$$

It is noted that in this process, we need not take $\hbar \rightarrow 0$ inside the function $u_n(\mathbf{k}, \mathbf{r})$ although we have put $\hbar \rightarrow 0$ in order to obtain (III-11). Thus we get

$$u_n(\mathbf{k}, \mathbf{r}) = C_{\mathbf{k}} = \text{constant}, \quad (\text{IV-3})$$

(8) The classical and semiclassical meanings of $\phi(\mathbf{r})$ are discussed clearly in the WKB method in ordinary quantum mechanics.

which is a periodic function of \mathbf{r} (since $u_n(\mathbf{k}, \mathbf{r}) = u_n(\mathbf{k}, \mathbf{r} + \mathbf{R})$)⁽⁹⁾ in terms of \mathbf{k} . To express $u_n(\mathbf{k}, \mathbf{r})$ in (IV-3) in the momentum representation^(*) we have

$$u_n(\mathbf{k}, \mathbf{r}) = C_{\mathbf{k}} = \sum_{\mathbf{K}} M_{\mathbf{k}+\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} \quad (\text{IV-4})$$

which corresponds to (III-Ya). Furthermore, it is easy to get

$$C_{\mathbf{k}} = M_{\mathbf{k}} \quad (\text{IV-4a})$$

since (IV-4) is valid for all values of \mathbf{r} .

To use (III-Yb), we also express $V(\mathbf{r})$ in the momentum representation (since $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$)

$$V = V(\mathbf{r}) = \sum_{\mathbf{K}} V_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} \quad (\text{IV-5})$$

Combining (IV-4), (IV-4a) and (IV-5), an equation is obtained,

$$\begin{aligned} VM_{\mathbf{k}} &= \sum_{\mathbf{K}} \sum_{\mathbf{K}'} V_{\mathbf{K}} M_{\mathbf{k}+\mathbf{K}'} e^{i(\mathbf{K}+\mathbf{K}')\cdot\mathbf{r}} \\ &= \sum_{\mathbf{K}} V_{\mathbf{K}} M_{\mathbf{k}-\mathbf{K}}, \end{aligned}$$

where the last equality is due to the fact that the first equality is valid for all values of \mathbf{r} , or

$$V = M_{\mathbf{k}}^{-1} \sum_{\mathbf{K}} V_{\mathbf{K}} M_{\mathbf{k}-\mathbf{K}}$$

which corresponds to (III-lo). Hence the band energy (III-II) is obtained as

$$\begin{aligned} E_n(\mathbf{p}) &= \frac{\mathbf{p}^2}{2m} + \tilde{V}(\mathbf{p}) \\ &= \frac{\mathbf{p}^2}{2m} + M_{\mathbf{k}}^{-1} \sum_{\mathbf{K}} V_{\mathbf{K}} M_{\mathbf{k}-\mathbf{K}}. \end{aligned}$$

In order to compare with the exact result, we get

$$E_n(\mathbf{p})M_{\mathbf{k}} = -\frac{\hbar^2 \mathbf{k}^2}{2m} M_{\mathbf{k}} + \sum_{\mathbf{K}} V_{\mathbf{K}} M_{\mathbf{k}-\mathbf{K}}. \quad (\text{IV-6})$$

which is exactly the Schrodinger equation in the momentum representation.⁽²⁾

What we have shown above in this section is that our result (IV-6), or equivalent to (III-11), is still exact although we have already put $\hbar \rightarrow 0$ in (III-11). In other words, our theorems and the procedure, putting $\hbar \rightarrow 0$, do not influence the exactness of the theory. Therefore this theory is an \hbar -independent theory. That means, although we have put $\hbar \rightarrow 0$ a procedure similar to the classical limit, this theory is valid in the quantum mechanical considerations as well as in the classical dynamic considerations.

V. EFFECTIVE MASS THEORY

A basic equation (11-7) corresponding to the time-independent Schrödinger equation has been derived in Sec. II, if we consider from the principles of quantum mechanics. Then the dynamical properties of the electron can be discussed from usual quantum mechanical consideration.⁽³⁾ The subject which we have already had in the current band theory is the effective mass. The current theory of the effective mass is treated together with an imperfect crystal or in an external field. It is the reason why we call it the "effective" mass. From the above theorem, we shall show that the effective mass is an observable and intrinsic dynamical quantity of the electron independent of any external perturbations.

Restricting the electron moving in the n -th band, i.e. neglecting the interband transitions, we

(9) Der-Ruenn Su, Chinese J. Phys. 7, 76 (1969); 8, 16 (1970).

need consider the wave function of the electron only inside the subspace M_n . Inside M_n , we have a relation between the momentum and the coordinate as

$$H_0(\mathbf{p}, \mathbf{r}) = E_n(\mathbf{p} + \hbar\mathbf{K}). \quad (\text{V-1})$$

Then the equation of motion of the electron can be deduced as

$$\begin{aligned} \frac{d\mathbf{r}}{dt} &= \frac{1}{i\hbar} [\mathbf{r}, H_0] = [\nabla_{\mathbf{p}}, H_0] \\ &= (\nabla_{\mathbf{p}} H_0) = [\nabla_{\mathbf{p}} E_n(\mathbf{p})], \end{aligned}$$

where (V-1) has been used in the last equality. It is noted that $[\nabla_{\mathbf{p}} E_n(\mathbf{p})]$ is a c-number and does not operate on the wave functions. The acceleration operator thus becomes

$$\begin{aligned} \frac{d^2\mathbf{r}}{dt^2} &= \frac{d}{dt} [\nabla_{\mathbf{p}} E_n(\mathbf{p})] \\ &= \frac{d\mathbf{p}}{dt} \cdot \nabla_{\mathbf{p}} [\nabla_{\mathbf{p}} E_n(\mathbf{p})] \equiv \frac{d\mathbf{p}}{dt} \cdot \frac{1}{m^*}. \end{aligned} \quad (\text{V-2})$$

The effective mass dyadic m^* is obtained easily and obviously as

$$\frac{1}{m^*} \equiv \nabla_{\mathbf{p}} [\nabla_{\mathbf{p}} E_n(\mathbf{p})]. \quad (\text{V-3})$$

The equation defining m^* , i.e. (V-2) is entirely followed from classical Newtonian idea. Thus it is an intrinsic property or the "inertia" of the electron. This result is not trivial because our treatment has emphasized the wave function describing the electron to be inside M_n only. In other words, only for the state within a single band, we can have (V-1), a relation between dynamical variables. Thus we can conclude that the effective mass theory is only an one band approximation as expected. As a remark here, the correct result (V-3) for the effective mass is derived from (V-1) which comes from our theorems in Sec. II. This is a success of our theorems.

VI. APPLICATIONS TO PHYSICAL SYSTEMS

As discussed above, (III-6) or (III-II) gives an exact band energy. But to find the function $V = \tilde{V}(\mathbf{p})$, we need to treat the problem carefully. In this section, we treat two extreme cases first, then try to solve the band energy of hydrogen solid.

The two extreme examples we are going to treat are (i) free electron case, usually a test of any new band theory, in which the interactions between electrons are considered to be extremely weak, and (ii) hydrogen atom case in which the interaction is so strong that the bound states of electron are formed.

(i) free electron case: We choose

$$f_n(\mathbf{r}) = (2\pi)^{-3/2} e^{i\mathbf{k} \cdot \mathbf{r}},$$

then, (111-4) becomes

$$\begin{aligned} \mathbf{p} &= \nabla S = \hbar\mathbf{k} \\ V &= 0. \end{aligned}$$

The band energy is obtained as

$$E_n(\mathbf{p}) = \mathbf{p}^2 / 2m$$

which is expected.

(ii) hydrogen atom bound states: We have already had (for infinite lattice spacing)

$$f_{nlm}(\mathbf{r}) \equiv \psi_{nlm}(\mathbf{r}) = N_{nlm} r^l e^{-r/a_0} L_{n-l-1}^{2l+1} Y_{lm}(\theta, \varphi).$$

Let us introduce a quantity

$$\beta \equiv \frac{a_0}{\hbar} = \frac{\hbar}{me^2} = m\alpha,$$

where α is the fine structure constant. Using (III-7), we have

$$\phi_{nlm} = \frac{\hbar}{i} \ln [N_{nlm} r^l L_{n-l-1}^{2l+1} Y_{lm}(\theta, \varphi)] + \frac{ir}{n\beta}.$$

Putting $\hbar=0$, we have

$$\mathbf{p} = \nabla \phi_{nlm}(\mathbf{r}) = \frac{i}{n\beta} \frac{\mathbf{r}}{r} = \frac{i}{n\beta} \hat{\mathbf{r}},$$

$$V = -\frac{e^2}{r} = -\frac{\hbar}{m\beta} \frac{1}{r} = 0.$$

Then the "band" energy becomes

$$E_{nlm} = \frac{\mathbf{p}^2}{2m} + \bar{V}(\mathbf{p})$$

$$= \frac{(\nabla \phi_{nlm})^2}{2m} = -\frac{1}{2mn^2\beta^2} = -\frac{me^4}{2n^2\hbar^2}$$

which is exactly the H-atom energy. Since $E_{nlm}(\mathbf{p})$ is independent on \mathbf{p} , we conclude that the "band" is actually a single level only! As a remark here, many authors⁽¹⁰⁾ believe that there are limits to be a band for the band model for very narrow bands. From the example of the H-atom above, we see that our result is not in agreement to their arguments since in the above band treatment even for zero width band, we can apply the band theory to get the correct result.

Now, the hydrogen solid^(7,11) (or impurity bands⁽¹²⁾) is considered. We adopt the tight-binding approximation which seems to be appropriate for this case. Let us use the 1s state to be the ground state of hydrogen atom, then

$$f_{1s}(\mathbf{r}) \equiv b_{1s}(\mathbf{k}, \mathbf{r})$$

$$= N^{-1/2} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} N_{100} e^{-|\mathbf{r}-\mathbf{R}|/a_0}.$$

Using (IV-3), we obtain

$$u_{1s}(\mathbf{k}, \mathbf{r}) = C_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} b_{1s}(\mathbf{k}, \mathbf{r})$$

$$= N_{100} N^{-1/2} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r})} e^{-|\mathbf{R}-\mathbf{r}|/a_0}$$

$$\equiv (N\nu)^{-1/2} \sum_{\mathbf{K}} A_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} \quad (\text{VI-1})$$

with the Fourier component

$$A_{\mathbf{K}} = \frac{N_{100}}{\nu^{-1/2}} \frac{4\pi a_0^3}{[1 + (\mathbf{k} + \mathbf{K})^2 a_0^2]^2}, \quad (\text{VI-2})$$

where ν is the volume of the unit cell of the crystal. Thus we get an equation

$$\frac{1}{(1 + k^2 a_0^2)^2} = \sum_{\mathbf{K}} \frac{e^{i\mathbf{K}\cdot\mathbf{r}}}{[1 + (\mathbf{k} + \mathbf{K})^2 a_0^2]^2}. \quad (\text{VI-3})$$

(10) N.F. Mott, Proc. Phys. Soc. (London) A62, 416 (1949); H. Fröhlich, Proc. 10th Solvay Conf. p. 255 (1955); H. Fröhlich, "Limits of the Band Model and Transition to the Metallic State" in "Quantum Theory of Atoms, Molecules and the Solid State" ed. by P. Löwdin (Academic Press, N. Y. 1966) p. 465.

(11) E. Wigner and H.B. Huntington, J. Chem. Phys. 3, 764 (1935).

(12) F. Stern and R. M. Talley, Phys. Rev. 100, 1638 (1955).

A collection of H-atoms which form the hydrogen solid seems reasonably to have the periodic coulombic potential

$$V(\mathbf{r}) = \sum_{\mathbf{R}} \frac{-e^2}{|\mathbf{R} - \mathbf{r}|}, \quad (\text{VI-4})$$

which can be expanded as

$$V(\mathbf{r}) \equiv V_{\mathbf{k}=0} + \sum_{\mathbf{K} \neq 0} V_{\mathbf{K}} e^{i\mathbf{K} \cdot \mathbf{r}} \quad (\text{VI-5})$$

with the Fourier component

$$V_{\mathbf{K}} = -\frac{4\pi e^2}{v\mathbf{K}^2} \quad (\text{VI-6})$$

for $\mathbf{K} \neq 0$. $V_{\mathbf{k}=0}$ is undetermined which is reasonably physically because $V_{\mathbf{k}=0}$ determines only the reference zero potential point and it can be compensated by the background positive charge distributions. Eqs. (VI-3) and (VI-5) give

$$V \frac{1}{(1 + \mathbf{k}^2 a_0^2)^2} = \sum_{\mathbf{K}} \sum_{\mathbf{K}'} \frac{V_{\mathbf{K}'} e^{i(\mathbf{K} + \mathbf{K}') \cdot \mathbf{r}}}{[1 + (\mathbf{k} + \mathbf{K})^2 a_0^2]^2}$$

or

$$V = V_{\mathbf{k}=0} - \frac{4\pi e^2}{v} \sum_{\mathbf{K} \neq 0} \frac{(1 + \mathbf{k}^2 a_0^2)^2}{\mathbf{K}^2 [1 + (\mathbf{k} + \mathbf{K})^2 a_0^2]^2}. \quad (\text{VI-7})$$

Thus the band energy is obtained as

$$E_{1s}(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V_{\mathbf{k}=0} - \frac{4\pi e^2}{v} \sum_{\mathbf{K} \neq 0} \frac{(1 + \mathbf{k}^2 a_0^2)^2}{[1 + (\mathbf{k} + \mathbf{K})^2 a_0^2]^2 \mathbf{K}^2}.$$

The expression of the effective mass m^* is lengthy, but as $\mathbf{k} \rightarrow 0$

$$\left(\frac{1}{m^*} \right)_{\mathbf{k}=0} = \frac{1}{m} \left[1 - \frac{16\pi a_0^3 e^2}{v} \sum_{\mathbf{K} \neq 0} \frac{(1 + \mathbf{K}^2 a_0^2) \mathbf{K}^2 \sum_i \ell_i \ell_i + 6\mathbf{K}\mathbf{K}}{(1 + \mathbf{K}^2 a_0^2)^4 \mathbf{K}^2} \right]$$

where ℓ_i is the unit vector along i -th axis. From this equation we see that the effective mass is anisotropic in general.