Variational Method for Calculating Electronic Structure in Periodic Lattices

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Abstract

Walter Kohn was awarded the Buckley Prize in 1961 for his seminal contributions in "extension and elucidation of the foundations of electron theory of solid", such as the variation-iteration method and the effective mass approach. Due to space limitation, we will primarily introduce the variational method he developed for calculating the electronic structure of solids in this work. The cellular method, the earliest method used for the band structure calculation, is briefly discussed with emphasis of its shortcoming. The variation-iteration method is then elaborated on the basis of variational principles for the band structure calculation in periodic lattices (1D and 3D). Applying this method into a real material (e.g metal Li), the calculated band energies are demonstrated to be in good agreement with experiments. The derivation of variational method for periodic lattice are detailed in order to track down his contribution trajectories. At the end, some personal understandings are presented to close the topic.

1 Introduction

The band structure is one of the central problems in solid state physics. It provides the energy levels, $E_{n\mathbf{k}}$, in a crystal structure, which are characterized by the wave vector $\mathbf{k}$ and the band index n. The concept of band structure is of great importance in understanding the electronic, thermal, optical and even magnetic properties of materials, such as metals, semiconductors and insulators. The one-electron formulation was intuitively proposed to simplify the complex many-electron problems when Hartree [1] attempted to set up self-consistent field for atomic systems. In 1928, Bloch formulated a scheme that the wave function can be written

$$\psi_k(\mathbf{r}) = e^{ik\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \tag{1}$$

where, $u_{\mathbf{k}}$ is a function with the same periodicity ($\mathbf{R}$) as the crystal lattice, aka, $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$. Thus, the solution in one unit cell of the crystal shall generate all crystal orbitals. At this time, the picture of band structure was developed and later extended by Brillouin with introducing the concept of Brillouin zone in the reciprocal space. [2]

By means of this approximation, the energy dispersion of an electron in a crystal is determined by the Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{2}$$

where $V(\mathbf{r})$ is the periodic crystal potential. In order to find the the eigenfunction and eigenvalues of Eq. 2, two things we have to consider. 1) finding an equation for the periodic potential $V(\mathbf{r})$ and 2) solving the Eq. 2 for the determined potential. Unfortunately, exact solutions of this problem are in general impossible and thus many approximate methods have been developed in the past decades. The general idea behind these methods to solve Eq. 2 is that every solution can be expanded in an infinite series by using a complete basis set satisfying the boundary conditions.

$$\psi(\mathbf{r}) = \sum_{i=1}^{\infty} c_i \psi_i(\mathbf{r}) \tag{3}$$

The solution can be reached by taking a finite number of terms in the expansion to approach the exact solution. We assume that the functions of $\psi_1, \psi_2, \psi_3, ..., \psi_N$ satisfy the boundary conditions and construct the following linear combination as an approximate solution.

$$\psi(\mathbf{r}) \approx \sum_{i=1}^{N} c_i \psi_i(\mathbf{r}) \tag{4}$$

These functions should satisfy the Bloch conditions, Eq. 2. The behavior of wave functions near the lattice sites and between the sites leads to the idea that either plane or spherical functions can be used in the linear combination Eq. 4.

2 The Cellular Methods

The cellular method is the earliest approach for the band structure calculation developed by Wigner and Seitz [3], aka, WS method. By employing the Bloch relation (equivalent to Eq. 1),

$$\psi_k(\mathbf{r} + \mathbf{R}) = e^{ik\cdot r}\psi_k(\mathbf{r}) \tag{5}$$

the wave function of the entire crystal can be determined by solving the the Schrödinger equation within a single primitive cell C_0.

In order to get an acceptable wave function for the entire crystal, the following boundary conditions are imposed to ensure that $\psi(\mathbf{r})$ and $\nabla\psi(\mathbf{r})$ are continuous as $\mathbf{r}$ crosses the primitive cell boundary.

$$\psi(\mathbf{r}) = \mathrm{e}^{\mathbf{ik}\cdot\mathbf{R}}\psi(\mathbf{r} + \mathbf{R}) \tag{6a}$$

$$\frac{\partial\psi(\mathbf{r})}{\partial\hat{n}(\mathbf{r})} = -\mathrm{e}^{\mathbf{ik}\cdot\mathbf{R}}\frac{\partial\psi(\mathbf{r} + \mathbf{R})}{\partial n(\mathbf{r} + \mathbf{R})} \tag{6b}$$

where both $\mathbf{r}$ and $\mathbf{r}+\mathbf{R}$ are points on the surface of the cell and $\hat{n}(\mathbf{r})$ is the outward normal to the face of the cell. These boundary conditions introduces the wave vector $\mathbf{k}$ into the celluar solution and limit the allowed energy to only discrete set of values $\varepsilon = \varepsilon_n(\mathbf{k})$.

The Wigner-Seitz (WS) primitive cell centered on the lattice point $\mathbf{R} = 0$ is used to preserve the symmetry of the crystal. (aka, central field approximation [4]) However, the WS cell usually has a complex shape and it is almost impossible to use the above boundary conditions directly. In order to make the computations more practical, the real periodic potential $U(\mathbf{r})$ within a WS cell can be approximated by a potential $V(\mathbf{r})$ with spherical symmetry about the origin. $V(\mathbf{r})$ can be chosen to be the potential of a single ion at the origin by assuming that the contribution to the $U(\mathbf{r})$ from the neighbors of the origin is negligible.

Then the solution of the Schrödinger equation is of the form:

$$\psi_{lm}(\mathbf{r}) = Y_{lm}(\theta,\varphi)\chi_l(r) \tag{7}$$

where the radial solution is obtained from the radial equation:

$$\frac{d^2\chi}{dr^2} + \frac{2}{r}\frac{d\chi}{dr} + \frac{2m}{\hbar^2}\left(\varepsilon - V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)\chi_l = 0 \tag{8}$$

Consequently, the general solution to Schrödinger equation is:

$$\psi_\varepsilon(\mathbf{r}) = \sum_{lm} A_{lm} Y_{lm}(\theta,\varphi)\chi_{l,\varepsilon}(r) \tag{9}$$

The construction of the solution can be further simplified by fitting the boundary condition only at a finite set of points on the surface of the WS cell. This leads to a set of $\mathbf{k}$ - dependent linear homogeneous equation for the A_{lm} and the values of ε for which the determinant of these equations vanishes are the required energies $\varepsilon_n(\mathbf{k})$.

The cellular method was only good enough for the alkali metals (e.g Na, K) with s-type valence states. This is because the WS polyhedron for body-centered alkali metal does not deviate significantly from a sphere. In fact, the central field approximation, which is the foundation of the cellular method, is not nearly as good as it is in the alkali metals.

And there are perhaps two major problems [5] in celluar method: The first one is that the fairly complex polyhedral structure of the WS primitive cell lead to difficulties in computationally satisfying the exact boundary conditions. Secondly, it is a relatively crude approximation by just replacing the periodic potential by a potential representing an isolating ion. In order to overcome these disadvantages the muffin-tin potential had been developed.

3 Variational Method in 1D Lattice

Kohn and Rostoker [6, 7] proposed a convenient way of calculating electronic structure of solids on basis of the variational principles. Korringa [8] actually arrived the same conclusion from in terms of theory of lattice interference. This approach is now known as KKR method in band structure calculations. Before we discuss the the variational method for real materials, let us first take a look the derivation of the variational principle for 1D lattice, which is helpful for understanding the basic principles of 3D cases. [6] The Schrödinger equation for 1D lattice can be written as

$$H\psi = E\psi, \quad H \equiv -\frac{d^2}{dx^2} + V(x) \tag{10}$$

where $V(x)$ is the potential with a periodicity of $2a$:

$$V(x+a) = V(x-a) \tag{11}$$

By applying the Block theorem in 1D case, we arrive at the quasi-periodic condition for solution of Eq. 10.

$$\psi(x+a) = e^{2ika}\psi(x-a) \tag{12}$$

where k is real number, assuming it is between $-\pi/2a$ and $+\pi/2a$.

The quasi-periodic property Eq. 12 can then be written as the following the boundary conditions

$$\psi(a) = e^{2ika}\psi(-a) \tag{13a}$$

$$\psi'(a) = e^{2ika}\psi'(-a) \tag{13b}$$

To establish an equivalent variational principle it is natural to study the functional

$$I \equiv \int_{-a}^{a} \psi^*(H-E)\psi dx \tag{14}$$

In evaluating the first variation of I we use the Schrödinger equation Eq. 10 which is satisfied by both ψ and ψ^* and obtain

$$\delta I = \int_{-a}^{a} (\delta\psi \frac{d^2\psi^*}{dx^2} - \psi^* \frac{d^2\delta\psi}{dx^2}) dx = [\delta\psi\psi^{*\prime} - \psi^*\delta\psi']_{-a}^{a} \tag{15}$$

Thus from Eq. 15 and Eq. 13 one obtains

$$\begin{aligned} \delta I &= [\psi^{*\prime}\delta\psi(a) - \psi^{*\prime}(-a)\delta\psi(-a)] - [\psi^*\delta\psi'(a) - \psi^*(-a)\delta\psi'(-a)] \\ &= \delta\{\psi^{*\prime}(a)[\psi(a) - \psi(-a)e^{2ika}] - \psi^*(a)[\psi'(a) - \psi'(-a)e^{2ika}]\} \\ &= -\delta K_1 \end{aligned} \tag{16}$$

where K_1 can also be written as

$$K_1 = \psi^{*\prime}(a)e^{ika}[\delta\psi(a)e^{-ika} - \delta\psi(-a)e^{ika}] - \psi^*(a)e^{ika}[\delta\psi'(a)e^{-ika} - \delta\psi'(-a)e^{ika}] \tag{17}$$

We therefore have $\delta(I + K_1) = 0$, which, however, is not symmetrical in the point of a and -a. However, a similar derivation shall give an alternative results,

$$\delta I = -\delta K_2 \tag{18}$$

where

$$K_2 = \psi^*(-a)e^{-ika}[\psi(a)e^{-ika} - \psi(-a)e^{ika}] - \psi^*(a)e^{ika}[\psi'(a)e^{-ika} - \psi'(-a)e^{ika}] \tag{19}$$

We then can write down the following variational principle:

$$J(\psi, k, E) \equiv I + \frac{1}{2}(K_1 + K_2) = stationary \tag{20}$$

The above derivations demonstrate that the Schrödinger equation Eq. 10 of 1D lattice satisfy the variational principle of Eq. 20 under the boundary conditions Eq. 12 . A function satisfying the variational principle is also a solution of the Eq. 10 and Eq. 12.

Since the Imaginary part of J vanishes identically in ψ, Eq. 20 may be written in the equivalent form

$$J(\psi, k, E) \equiv Re[\int_{-a}^{a} \psi^*(H-E)\psi dx + (\psi'(-a)\psi^{*\prime}(a)e^{2ika} - \psi(a)\psi^{*\prime}(-a)e^{-2ika})] = stationary \tag{21}$$

If an approximate wave function ψ for Eq. 10 and Eq. 12 has been constructed artificially. Plug this function into Eq. 21, we will have

$$J(\varphi, k, E) = 0 \tag{22}$$

Say, the wave function is given by

$$\psi = \sum_{i}^{n} c_i \varphi_i(r), c_i \text{ is real} \tag{23}$$

Now substitute this ψ into Eq. 21 and satisfy the stationary property approximately by demanding that

$$\frac{\partial J}{\partial c_i} = 0, i = 1, 2, ...n \tag{24}$$

which produces n linear equations for the c_i. the corresponding equation has the form of

$$\Delta_n(k, E) = 0 \tag{25}$$

which defines an approximate relationship between E and k. It should be noted that E calculated for a given k with Eq 25 do not represent upper bounds to the true eigenvalues E_1, E_2 etc. This is because of the fact that variations of ψ do not satisfy the boundary conditions.

4 Variational Method for 3D Lattice

Now let us proceed to the discussion on the application of variational method into periodic lattice in solid. Within the one-electron approximation, the time independent Schrödinger equation in atomic unit is

$$\left[-\nabla^2 + V(\mathbf{r}) - E\right]\psi(\mathbf{r}) = 0 \tag{26}$$

under the boundary conditions Eq. 6 in WS cell, it can be written in the integral form

$$\psi(\mathbf{r}) = \int d\mathbf{r}' G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}') \tag{27}$$

where $G_0(\mathbf{r},\mathbf{r}')$ is the Green function for Helmholtz equation and is the solution of the equation

$$(\nabla^2 + E)G_0(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{28}$$

Eq. 27 is equivalent to the variational principle $\delta\Lambda\left[\psi\right] = 0$, where the functional Λ is given by

$$\Lambda = \int d\mathbf{r}\psi^*(\mathbf{r})V(\mathbf{r})\psi(\mathbf{r}) - \int d\mathbf{r}\int d\mathbf{r}'\psi^*(\mathbf{r})V(\mathbf{r})G_0(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}') \tag{29}$$

This variational principle can be used to find a secular equation determining the wave function. Assume the trial function with the form,

$$\psi = \sum_{j=0}^{n} a_j\phi_j, \tag{30}$$

where a_j and ϕ_j is a complex coefficient and an element of some basis set, respectively. Substitute it into Eq. 29 one obtains,

$$\Lambda = \sum_{i,j=0}^{n} a_i^*\Lambda_{i,j}aj, \tag{31}$$

where

$$\Lambda_{i,j} = \int \phi_i^* V(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} - \int\int \phi_i^* V(\mathbf{r})G_0(\mathbf{r}-\mathbf{r}')V(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r}d\mathbf{r}', \tag{32}$$

which is a Hermitian matrix. By applying the variational principle to Eq. 31,

$$\frac{\delta\Lambda}{\delta a_i} = 0, \quad i = 1, 2, ..., n, \tag{33}$$

yields the set of linear equations,

$$\sum_{j=1}^{n} \Lambda_{i,j}a_j = 0, \quad i = 1, 2, ..., n, \tag{34}$$

which has non-trivial solutions only if its determinant vanishes. This requirement will result into the secular equation,

$$\det\left|\Lambda_{ij}(E)\right| = 0, \tag{35}$$

For given ϕ_i, the Λ_{ij} are the functions of $\mathbf{k}$ and $\mathbf{E}$. Thus, Eq. 35 describes the dispersion relation between $\mathbf{k}$ and $\mathbf{E}$. Since the energy is determined from a secular equation based on a variational principle, the error in the energy will be of second order with respect to the error in the wave function.

The above derivation formally produce a solution to Eq. 26 under the boundary conditions. Nevertheless, it is still too complex to solve the problem. A simplification has to be made to $V(\mathbf{r})$ in order to numerically get the solution. It comes the approximation of muffin-tin potential for $V(\mathbf{r})$, which follows the conditions $V(\mathbf{r})$ = spherically symmetrical when $r < r_i$ = radius of inscribed sphere and $V(\mathbf{r})$ = constant, $r > r_i$. Substituting this potential into the proceeding detailed derivations, we can achieve the following secular equation

$$\det |A_{lm,l'm'} + \kappa \delta_{ll'} \delta_{mm'} \frac{n_l' - n_l L_l}{j_l' - j_l L_l}| = 0 \tag{36}$$

This equation gives the required relationship between E and k for a periodic lattice with muffin-tin potential approximation. Here $A_{lm,l'm'}$ are 'structure constant', which are characteristic for each type of lattice and could be tabulated once for all before the next calculations.

5 Remarks and Conclusion

In this paper, we have thoroughly discussed the derivation of variational principles in 1D and 3D cases for periodic lattices. The variation-iteration method is an efficient way to solve the Schrödinger under the Bloch boundary conditions. The high accuracy of energies can be obtained with only a limited trial functions. Most importantly, it avoids the numerical difficulties the Cellular method has when satisfying the boundary conditions over a complex polyhedron surface. The limitation of KKR method in band structure calculation lies in its simplified formula of potential, $V(\mathbf{r})$. Though the muffin-tin potential is appropriate for closely packed elements, the accuracy in calculating band energy levels for open structures, (e.g diamond) and high energy levels are low. Also, as the KKR method use energy-dependent basis functions, the energy eigenvalues have to be searched by searching the energy surface with the secular determinant of zero. This shortcoming was eliminated by Andersen [9] introducing the linear approximation for the basis functions.

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