

J.C. Slater and Electronic Band Theory

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1 Introduction

John Clarke Slater was an American physicist central to the development of the electronic theory of solids, molecules and atoms. I will focus on his 1934 paper *Electronic Energy Bands in Metals*, tracing a path from this oft-overlooked work to modern-day, computational packages which perform quantum mechanical calculations on periodic solids.

Perhaps best known for his determinant, Slater spent much of his career working on applications of quantum mechanics to real-world systems [1]. He obtained his doctorate in physics from Harvard in 1923 and subsequently pursued a fellowship in Europe, spending time at the University of Cambridge and the University of Copenhagen. While in Copenhagen, he published his first paper: a note to Nature on *Radiation and Atoms*. Stemming from conversations with Niels Bohr and Hans Kramers at the Institute of Theoretical Physics at the University of Copenhagen (now the Niels Bohr Institute), he wrote about what would later be called BKS theory [2]. Even though the physics community eventually rejected BKS theory (due to the lack of momentum conservation, among other things,) it served as a thought-provoking proposition that generated plenty of interest in quantum mechanics and its applications to the theory of solids [3]. This was indicative of what was to come: perhaps some of his papers were not perfect theories, but they were hugely important for the growth of physics.

Through his early efforts to calculate the band structure of certain solids, he honed the techniques that would in later years be performed by computers. His 1934 paper was a major part of this process. Armed with insights that could only be gleaned from performing the initial calculation, he developed simpler and more powerful tools over the years to study the electronic energy bands of solids, namely, the muffin-tin approximation and the augmented plane-wave method [4, 5]. Remarkably, most modern computer packages which perform quantum mechanical calculations on a lattice grew from these approximations, implying his legacy lives on most strongly, albeit quietly, in modern computing packages that solve for the electronic structure of solids.

2 Electronic energy bands in metals, 1934

2.1 Brief Overview

The main inspiration for Slater's 1934 work was Wigner and Seitz's 1933 paper, *On the Constitution of Metallic Sodium* [6]. In their paper, Wigner and Seitz aimed to determine the chemical properties (lattice constant, binding energy, compressibility, etc.) of metallic sodium by using the free electron model and a few simplifying, yet remarkably accurate, assumptions for the electric potential on a body-centered cubic lattice. They ultimately calculated several wave-functions by hand, using an approach now called the cellular (Wigner-Seitz) method. From this they obtained a plot of the ground-state electron energy level vs. the lattice constant. The distance that minimizes the energy was determined to be 4.2\AA , which matched well with experimental data. Slater's goal in 1934 was to extend it to a proper calculation of the allowed excited energies [7].

2.2 Setup

As with most problems in solid-state physics, we begin with Bloch's theorem, in its infancy at the time of the original paper, but already being applied in myriad places (see [8–10]). For an electron wave-function in a crystal lattice we have the following relation:

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi_{\mathbf{k}}(\mathbf{r}). \quad (1)$$

Simply stated, for the wave-function (labeled by wave vector \mathbf{k}) moving through the lattice by a lattice vector \mathbf{R} gives the original wave-function up to a phase factor [11].

Now, how does this apply to a body-centered cubic lattice? On the face of the Wigner-Seitz cell separating nearest neighbors (there are eight such faces corresponding to the eight nearest neighbors in bcc) we can find any number of points that satisfy the Bloch condition. Referring to Figure 1, follow the normal at the starting point to the other side of the unit cell. The vector connecting these points is a lattice vector simply shifted some amount from the origin. This is the most general form of the boundary conditions in the cellular method. When solving for the wave-function in the unit cell we will thus have an infinite number of points on each face that must satisfy Bloch's theorem, relative to points perpendicularly opposite.

To continue, we consider the potential within the unit cell. It is approximated as spherically symmetric (only depending on that cell's atom). Normally this is a cause for celebration, the only issue here being the difference in symmetries. We wish to solve a differential equation which possesses spherical symmetry subject to boundary conditions with truncated octahedral symmetry. Note, this is technically possible, but it is a complicated problem involving an infinite series of wave-functions.

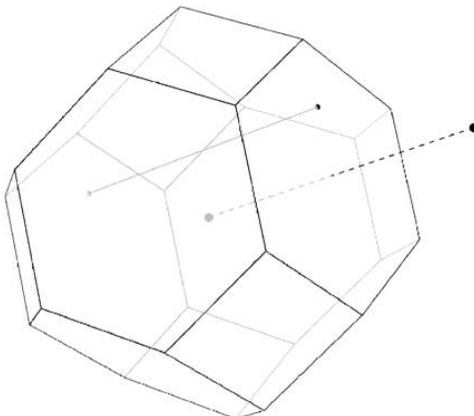


Figure 1: The Wigner-Seitz cell for a body-centered cubic lattice. One of the eight nearest neighbors is reached via the dashed vector. A pair of perpendicularly opposite points is shown on two faces of the cell. The vector connecting these is clearly the same as the dashed one.

The simplifying assumption however, is to truncate the infinite series. The number of wave-functions we must include corresponds directly to the number of boundary conditions we wish to solve. We choose to satisfy the Bloch relation at the midpoints of the lines connecting nearest neighbors. Thus, we only need eight wave-functions. The eight wave-functions are chosen to be one s , three p 's, three d 's and one f . We choose the d and f orbitals that best match the symmetries of the problem at hand: those being the xy , yz , zx ; and xyz respectively.

2.3 Calculation

Let u designate our wave-function; without loss of generality it can be written as a sum of even and odd parts, $u_g + u_u$. In this context, even and odd signify whether the function changes sign in going from one point to the opposite paired point in the unit cell. With this in mind, Eq. (1) can be rewritten as

$$\begin{aligned} u_g + u_u &= e^{i\mathbf{k}\cdot\mathbf{r}} (u_g - u_u), \\ u'_g + u'_u &= -e^{i\mathbf{k}\cdot\mathbf{r}} (u'_g - u'_u). \end{aligned} \tag{2}$$

There will be four such equations corresponding to the four pairs of points which are opposite each other. For each equation, \mathbf{r} is the vector connecting the origin to the nearest neighbor in question (dashed line in Figure 1), and u_g and u_u are evaluated at the center

of the hexagonal faces. With some algebra, we can rearrange Eq. (2) to be

$$\begin{aligned} u_g/u_u &= -i \cot(\mathbf{k} \cdot \mathbf{r}/2), \\ u'_g/u'_u &= i \tan(\mathbf{k} \cdot \mathbf{r}/2). \end{aligned} \quad (3)$$

Any solution will also be a solution if multiplied by an arbitrary constant, thus there is freedom for us to choose u_g as real, leaving u_u as pure imaginary. This further simplifies our boundary conditions to:

$$|u_u|/u_g = -u'_g/|u_u|' = \tan(\mathbf{k} \cdot \mathbf{r}/2). \quad (4)$$

Following our discussion of the eight wave-functions, we can write u_g and u_u in terms of the spherical harmonics expansion evaluated at the midpoints:

$$\begin{aligned} u_g &= As + 3(Bxy + Cyz + Dzx)d/R^2, \\ u_u &= 3^{1/2}(Ex + Fy + Gz)p/R + 3^{3/2}(Hxyz)f/R^3. \end{aligned} \quad (5)$$

Here, $R = r/2$ is half the distance to nearest neighbors, s, p, d, f are the radial parts of the corresponding spherical harmonics, evaluated at a distance R from the origin. The variables A, B, \dots, H represent the angular part of the wave-function. Note, these equations are valid for each of the eight midpoints, the only parts that will change are the x, y, z . The eight midpoints in this notation are given by $(x, y, z) = (\pm 1, \pm 1, \pm 1)R/\sqrt{3}$.

We consider the four midpoints where $\sqrt{3}/R(x, y, z)$ is (111), (11-1), (1-11), (1-1-1). At the first of these points, we have:

$$\tan(\mathbf{k} \cdot \mathbf{r}/2) = \tan\left((k_x + k_y + k_z)R/\sqrt{3}\right), \quad (6)$$

and so on for the other points. These tangent terms are denoted K, L, M, N for the respective midpoints, finally giving us our eight equations:

$$\begin{aligned} K(As + (B + C + D)d) - (E + F + G)p - Hf &= 0, \\ L(As + (B - C - D)d) - (E + F - G)p + Hf &= 0, \\ M(As - (B + C - D)d) - (E - F + G)p + Hf &= 0, \\ N(As - (B - C + D)d) - (E - F - G)p - Hf &= 0, \\ As' + (B + C + D)d' + K(E + F + G)p' + Hf' &= 0, \\ As' + (B - C - D)d' + L(E + F - G)p' - Hf' &= 0, \\ As' - (B + C - D)d' + M(E - F + G)p' - Hf' &= 0, \\ As' - (B - C + D)d' + N(E - F - G)p' + Hf' &= 0. \end{aligned} \quad (7)$$

To review: K, L, M, N contain information about the wave vector components k_x, k_y, k_z . A, \dots, H are constants determined by the angular value of the spherical harmonics. The

s, p, d, f are the radial values of the corresponding functions, and the primed versions are their derivatives.

From here, we only consider propagation in the $x - y$ plane, which enforces $K = L$, $M = N$. Following some more algebra, these reduce to:

$$\begin{aligned}
K(As + Bd) - (E + F)p &= 0, \\
M(As - Bd) - (E - F)p &= 0, \\
As' + Bd' + K(E + F)p' &= 0, \\
As' - Bd' + M(E - F)p' &= 0, \\
K(C + D)d - Gp - Hf &= 0, \\
M(-C + D)d - Gp + Hf &= 0, \\
(C + D)d' + K(Gp' + Hf') &= 0, \\
(-C + D)d' + M(Gp' - Hf') &= 0.
\end{aligned} \tag{8}$$

The strength of this form is that now A, B, E, F are entirely separate from C, D, G, H . This means we have two classes of solutions: (I) where A, B, E, F are non-zero and (II) where C, D, G, H are non-zero. Taking the determinant of the first four equations and setting it equal to zero gives an equation relating K^2 to M^2 :

$$\left(K^2 + \frac{1}{2} \frac{p}{p'} \left(\frac{s'}{s} + \frac{d'}{d} \right) \right) \left(M^2 + \frac{1}{2} \frac{p}{p'} \left(\frac{s'}{s} + \frac{d'}{d} \right) \right) = \left(\frac{1}{2} \frac{p}{p'} \left(\frac{s'}{s} - \frac{d'}{d} \right) \right)^2. \tag{9}$$

The s, p, d and their derivatives are assumed to be known—they can be calculated by fixing the energy and internuclear distance and following the work of Wigner and Seitz [6]. Finally, there is one more relation between K and M since they both depend on the wave-vector, \mathbf{k} :

$$K = \tan(k_x + k_y) R/3^{1/2}, \quad M = \tan(k_x - k_y) R/3^{1/2}. \tag{10}$$

With some trigonometry this reduces to:

$$\arctan M / \arctan K = \tan(\pi/4 - \theta), \tag{11}$$

where θ is the angle \mathbf{k} makes with respect to the x-axis. Slater proceeded to solve this equation graphically, now it can easily be done with a computer. With K and M , we can solve for A, B, E, F and the wave-function is fully determined, as long as we enforce normalization.

From here, Slater provides a plot of the wave function energies vs. internuclear distance, all calculated by hand. This is shown in Figure 2. The important takeaway is that only certain solutions are allowed at each energy, thus giving rise to the energy bands. This

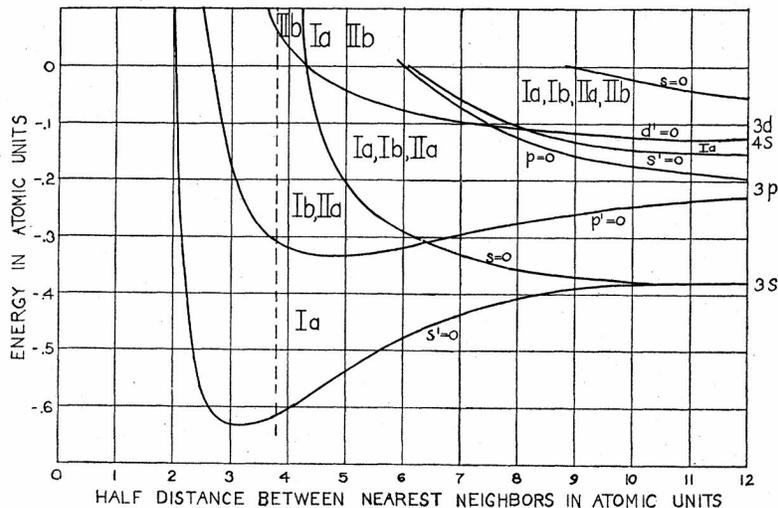


Figure 2: Energy bands for sodium, the symbols Ia-IIb represent the types of states allowed in each band. For example, Ia corresponds to one type of Class I solutions.

result can be visualized more easily if one plots the energy in the 1st and 2nd Brillouin zones. The bands can be found at the boundaries of the Brillouin zones in Figure 3, signalling forbidden energy states in this model. Slater's takeaway from this plot was that the free-electron model was an excellent approach to the problem.

Moving forward, the most important contribution that this paper had was the demonstration that the electron wave-functions appear to follow that of a free electron in between the atoms joined with a more rapidly varying function in the vicinity of the atoms. Now is also a good time to point out: clearly, this method has its flaws. Any calculations of higher energies become immensely complicated without shedding much more light on the physical processes at play. One of the most surprising results according to Slater, was that the excited energies were quite similar to those given by the crude free electron model. This was the main inspiration for his subsequent work on the muffin-tin approximation. Ultimately, the solution of this problem will look quite a bit like a free electron model superimposed on a lattice, which is precisely what he proposed in 1937.

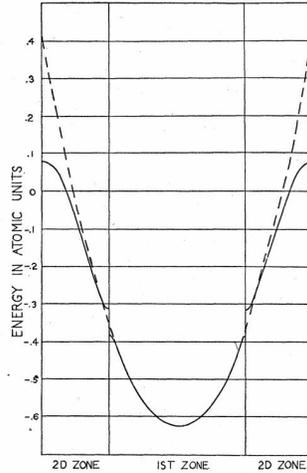


Figure 3: Energy plotted over the first two Brillouin zones where we consider a wave in the diagonal of the $x - y$ plane for simplicity. The free electron is the dashed line, the normal parabola. The solid line shows the band gaps of the metal opening up at the borders of the Brillouin zones.

3 Muffin-tin approximation and APW, 1937

3.1 History

Over the next few years, Slater continued work on calculating excited electron states in a crystal lattice. The 1934 paper was a success, but a limited one. He had calculated the excited energy levels (relatively accurately up to the p orbitals), but it required a large amount of work to get there. In order to solve for even higher energies, one must include many more terms in the expansion, leading to an equal number of boundary conditions, and an immensely complicated problem to solve. Even if performed correctly, Slater’s doctoral student, William Shockley, demonstrated that the method breaks down [12]. The truncation of the series of wave-functions makes it difficult to replicate energetic atomic-like wave-functions, thus becoming highly inaccurate for energies just beyond those that Slater worked with. Slater himself acknowledged this work, admitting that his 1934 method “converges too slowly” for any practical applications [4]. So he began work on a new method, one that was inspired by the results (and complications) of his previous work.

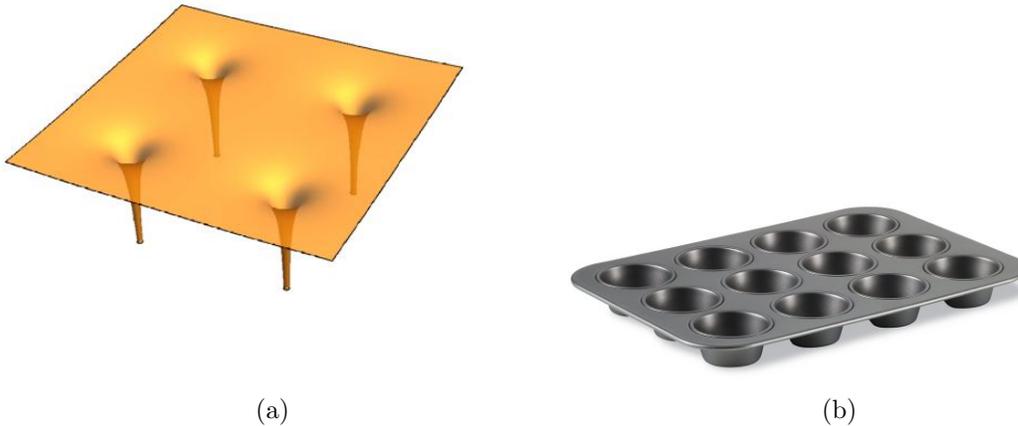


Figure 4: In (a), the shape of the muffin-tin potential plotted in two-dimensions. The potential behaves as $1/|\mathbf{r} - \mathbf{r}_n|$ within some radius R_0 of each lattice site at r_n . In (b), an actual muffin-tin to demonstrate the somewhat misleading nature of the name.

3.2 Muffin-tin

In his 1937 paper, *Wave functions in a periodic potential*, Slater described a simpler approach to the periodic potential of a lattice [4]. Near each lattice site the potential approaches that of a lone atom. In the regions between there is a constant potential (taken to be zero) connecting all of the lattice sites, thus giving rise to the “muffin-tin” shown in Figure 4a. Instead of extending the spherically symmetric potential all the way to the boundary of the unit cell and dealing with the conflicting symmetries—which becomes more difficult every time you add more points—we can simply assume the potential goes to zero fast enough to occur within the unit cell. This approximation works well because we split space into two separate regions. We can then use plane-waves in the zero potential region, and an expansion in terms of spherical harmonics in the non-zero regions.

3.3 Augmented plane-wave

Muffin-tin was the first of two insights Slater provided in this paper. The other has come to be known as the augmented plane-wave method (APW). I will explain the core of the method as presented in 1937 alongside the muffin-tin and explain the advances made by Slater and others in Section 4. The electron wave-function with wave-vector \mathbf{k} takes the form of a plane-wave in the zero-potential, *interstitial* regions, whereas it takes the form of a sum of spherical harmonics in the depressions of the potential. More specifically, if I denotes the interstitial region and S_n the region of non-zero potential around atom n , the

wave-function can be written as:

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{\mathbf{k}} v(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} & \mathbf{r} \in I, \\ \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{lm} P_l^{|m|}(\cos\theta) e^{im\phi} u_{nl}(|r-r_n|) & \mathbf{r} \in S_n. \end{cases} \quad (12)$$

Here, r_n is the position of the n th atom, and θ, ϕ are the angles about the center of said atom. $\Psi_{\mathbf{k}}$ is a function of the position (and the energy implicitly through the u_{nl}). Also, the sum for the region I is over certain, discrete wave-vectors and is only a solution if, for arbitrary k_0 , the $v(\mathbf{k})$'s satisfy the difference equations:

$$(\mathbf{k}_0 + \mathbf{K}_i)^2 v(\mathbf{k}_0 + \mathbf{K}_i) + \sum_{\mathbf{K}_j} W(\mathbf{K}_j) v(\mathbf{k}_0 + \mathbf{K}_i + \mathbf{K}_j) = v(\mathbf{k}_0 + \mathbf{K}_i) E \quad (13)$$

Here, we use units such that the energy of a free electron with wave-function $\exp(i\mathbf{k}\cdot\mathbf{r})$ is k^2 . $W(\mathbf{K}_i)$ is the integral over the unit cell of the potential energy times $\exp(i\mathbf{K}_i\cdot\mathbf{r})$ divided by the cell volume. This quantity has

With Eq. (12) in mind, we turn to the boundary conditions. We must match the plane-wave solution to the atomic-like solution at the boundaries of each atomic region, S_n . This seemingly daunting task is made exceptionally easy by an expansion of the plane-wave about r_n in terms of the spherical Bessel functions, j_l . Carrying it out,

$$\exp(i\mathbf{k}_i\cdot\mathbf{r}) = \exp(i\mathbf{k}_i\cdot\mathbf{r}_n) \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1) i^l j_l(k_i|\mathbf{r}-\mathbf{r}_n|) \quad (14)$$

$$\times \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos\theta) P_l^{|m|}(\cos\theta_i) e^{im(\phi-\phi_i)}. \quad (15)$$

The k_i, θ_i and ϕ_i denote the magnitude and direction of \mathbf{k}_i . With this expression we simply match coefficients to determine the form of the wave-function within the spheres:

$$\psi_i = \exp(i\mathbf{k}_i\cdot\mathbf{r}_n) \sum_{l=0}^{\infty} \sum_{m=-l}^l (2l+1) i^l \frac{j_l(k_i R_n)}{u_{nl}(R_n)} u_{nl}(|\mathbf{r}-\mathbf{r}_n|) \quad (16)$$

$$\times \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos\theta) P_l^{|m|}(\cos\theta_i) e^{im(\phi-\phi_i)}. \quad (17)$$

All of his work honing these numerical techniques and approximations (with no computer in sight) would ultimately pay off, thanks in part to the work of Jan Korriga and others in the '40s and '50s. They used his muffin-tin approximation in developing what is now known as the KKR method, still widely used to this day to calculate the electronic band structure of periodic solids. The APW method was also improved upon by Slater in the '50s but its applications wouldn't fully come to fruition until the advent of the computer.

4 Further improvements, 1953-

In 1953, Slater made some major improvements to the APW method, which are still used to this day in modern computing packages [13] (more on that later). The main insight was that determining the augmented plane-waves could be set up as a variation problem with constraints set by normalization and the energy of the wave [5].

Around this time, others began to recognize the power of the muffin-tin approximation. Korringa used it in his scattering theory approach to calculating the energy of electrons in a metal [14]. This was later shown to be equivalent to the variation-iteration method employed by Kohn and Rostoker in 1953, exhibiting several similarities with Slater's 1953 paper described above.

The effect these papers had on physics, chemistry, and materials science is rather hard to gauge, simply because the tools these physicists developed are so prevalent in modern research that they are not always cited. The augmented plane-wave (and its more modern cousins, linear APW and projector APW) form the foundations of the most common packages for quantum calculations on a lattice (e.g. VASP, CASTEP, WIEN2k) [15–17]. These packages are used by tens of thousands of people worldwide [17] for applications well beyond metallic sodium.

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