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One-Band Model for Crystal Imperfections*

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The one-band model for an impurity in a crystal is critically discussed. In this model the wave functions for low-energy states in the presence of the impurity are considered to be composed only of wave functions from the lowest conduction band. This is shown to be invalid when the potential is smaller in size than the unit cell. It is pointed out that the model can be correctly used in this case only when the strength of the potential is treated as a parameter to be fitted after the calculation and is not presumed known at the beginning.

I. INTRODUCTION

The problem of finding the effect of an impurity potential on an otherwise perfect lattice has had many approximate solutions each with certain unsatisfactory features. This paper deals with one of these solutions, namely the one-band model, which gives the appearance of being a particularly practical technique. The present form of the model which uses Wannier functions, follows the work of Koster and Slater.[1,2]

It will however be shown in this paper that the basic assumption, that only the wave functions of the lowest band are necessary to build up the impurity wave functions, is inconsistent with another simplifying assumption usually invoked: that the perturbing potential is much smaller in size than the unit cell. Provided, however, one asks only the right questions the model can still give the correct answer. Essentially one must not ask of it: What are the binding energies or wave functions of a lattice in the presence of a given, small (in linear dimensions) impurity potential $U(\mathbf{r})$? Instead the potential parameters (in particular the strength) must be regarded as parameters not given *ab initio* but to be fitted in a phenomenological sense after the one band calculation has been completed.

Before proceeding to the details of the calculation one can bring out the difficulty by a simple argument. If the lattice spacing is d, then the highest crystal momentum component in the first band is of the order of π/d. If, on the other hand, the radius of the potential is a, then any wave function in the presence of this potential will contain some momentum components at least up to order π/a. If the potential is much smaller than the atomic cell ($a<d/2$) then the wave functions from the single band cannot represent the higher components in the true wave function. The question being asked is then what effect the absence of these higher components from the wave function has on the binding energy (if there is a bound state) and on the asymptotic wave functions (expressed through the phase shifts) for the impurity potential.

This is such a wide question that it is clear that a rigorous general answer cannot be given, since the detailed potential shape is obviously important. What is done in this paper is to consider a particular model (a special shape of impurity potential well in a lattice for which the nearly free-electron approximation is good) which is exactly soluble. By means of this model it can be shown that the effect of the higher momentum components is significant, but that the correct asymptotic wave function for the given energy can be regained by using different parameters in the potential (Sec. II). It is then shown that these remarks can be generalized both to other potential shapes (Sec. III) and to crystal lattices which are not nearly free-electron-like (Sec. IV).

II. A SOLUBLE MODEL

The first part of this section is devoted to a derivation of the one-band model. The problem will then be restated somewhat to allow the details of the calculation with the soluble potential to be made clear. The only case considered will be that of three dimensions, since the one-dimensional case leads to totally misleading conclusions concerning the validity of the model. (This point will be briefly remarked upon later.)

As always in these impurity calculations one is trying to solve the Schrödinger equation

$$(-\nabla^2+V(\mathbf{r})-E_n)\psi_n(\mathbf{r})=0, \qquad (1)$$

(where $\hbar^2/2m=1$). $V(\mathbf{r})$ consists of a perfect crystal lattice part $v(\mathbf{r})$ and an additional impurity potential $U(\mathbf{r})$ centered about one of the lattice sites:

$$V(\mathbf{r})=v(\mathbf{r})+U(\mathbf{r}), \quad v(\mathbf{r}+\mathbf{l})=v(\mathbf{r}),$$

where $\mathbf{l}$ is any lattice vector. The one-band model assumes that the perfect lattice solutions ($U(\mathbf{r})=0$) are known. Instead of the Bloch functions ϕ_{nk} for this lattice the localized Wannier functions

$$W_n(\mathbf{r}-\mathbf{r}_i)=\frac{1}{N}\sum_k e^{-i\mathbf{k}\cdot\mathbf{r}_i}\phi_{nk}(\mathbf{r})$$

are used, where n is the band index and $\mathbf{r}_i$ are the lattice points. This is done to simplify the discussion of the matrix elements of $U(\mathbf{r})$, but its principal virtue is that the lattice propagator in this representation closely resembles the free-electron propagator in plane-

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[1] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

[2] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

wave representation. The usual derivation now expands ψ in terms of the Wannier functions and finds a set of difference equations for the coefficients. Since this usual set of difference equations obscures the inadequacy of the approximations to be made, it is better to keep everything in integral equation form. The propagator for the imperfect lattice satisfies

$$(-\nabla^2+V(\mathbf{r})-E-i\epsilon)G(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}')\,, \tag{2}$$

and in terms of the propagator for the perfect lattice, G_0, is given by

$$G(\mathbf{r},\mathbf{r}')=G_0(\mathbf{r},\mathbf{r}')+\int G_0(\mathbf{r},\mathbf{r}'')U(\mathbf{r}'')G(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''\,. \tag{3}$$

This equation becomes in Wannier representation

$$(ni|G|mj)=\sum_{\mathbf{k}}\frac{e^{i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_j)}}{E-E_{n\mathbf{k}}+i\epsilon}\delta_{nm}+\sum_{\mathbf{k}}\sum_{p}\sum_{l,l'}\frac{e^{i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_l)}}{E-E_{n\mathbf{k}}+i\epsilon}(nl|U|pl')(pl'|G|mj)\,, \tag{4}$$

where

$$(ni|G|mj)=(W_n(\mathbf{r}-\mathbf{r}_i)|G(\mathbf{r},\mathbf{r}')|W_m(\mathbf{r}'-\mathbf{r}_j))\,,$$

and

$$(ni|U|mj)=(W_n(\mathbf{r}-\mathbf{r}_i)|U(\mathbf{r})|W_m(\mathbf{r}-\mathbf{r}_j))\,.$$

This has an obvious similarity to the equation for the propagator of an electron in the presence of a single potential well and all the difficulties inherent in the solution of that equation will also arise when solving Eq. (4). This similarity will be fully used later on. The one-band model is now derived by writing

$$(nl|U|pl')=U_{00}\delta_{n0}\delta_{p0}\delta_{l0}\delta_{l'0}\,, \tag{5}$$

which is reached in two steps. First, since the Wannier functions are localized around the lattice sites, if the potential is restricted to be within the cell surrounding $\mathbf{r}_0$ the matrix elements with $l=0$ and $l'=0$ will dominate. In reality the Wannier functions do overlap onto neighboring sites so that even if the other matrix elements are minimized by making the impurity potential as narrow as possible, they do not become zero. Thus, the assumption that all matrix elements $l\neq 0$ or $l'\neq 0$ are zero is not a quantitatively good approximation. Qualitatively, however, this approximation is not serious, the presence of the "off-diagonal" matrix elements makes little difference. The second, and, it is suggested here, more serious assumption is to suppose that only the lowest (zeroth) band matrix element is nonzero. It is also true here that each individual matrix element after the first is small, but together they are not negligible. In the first case the neglected matrix elements become exponentially small as $\mathbf{r}_l-\mathbf{r}_0$ increases, whereas in the second case the matrix elements behave like some small power of the band energy.

To make contact with the usual formulation one observes that the wave function equation which is formally

$$\psi=\phi+G_0U\psi\,,$$

becomes in Wannier representation

$$(ni|\psi)=(ni|\phi)+\sum_{\mathbf{k}}\sum_{p}\sum_{l,l'}\frac{e^{i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_l)}}{E-E_{n\mathbf{k}}+i\epsilon}\times(nl|U|pl')(pl'|\psi) \tag{6}$$

and this with the restriction (5) is exactly the usual difference equation.

The principal feature of this paper will be to carry out the solution of Eq. (3) in the case of a lattice of extremely weak potentials, so weak in fact that the band gaps are negligible. These weak potentials merely serve the purpose of providing a scheme for defining the Wannier functions, and a length parameter. The solution of Eq. (3) can then be very well approximated by solving for the t matrix (defined by $G=G_0+G_0tG_0$) for a free electron in the presence of the potential $U(\mathbf{r})$. Thus

$$t(\mathbf{r},\mathbf{r}')=U(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')+\int U(\mathbf{r})G_0(\mathbf{r}-\mathbf{r}'')t(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''\,, \tag{7}$$

where now $G_0(\mathbf{r})$ is the free-electron propagator with Fourier transform $1/(E-k^2+i\epsilon)$. It is at this point that one becomes suspicious of the one-band model, since any practical attempt to solve (7) leads to the inclusion of high k values in the transformed propagator unless the potential itself provides the cutoff in k values by being long ranged. Physically this can be seen to arise in perturbation theory, where, even though the energy denominator behaves like k^2 for large k, so does the density of intermediate states, so the only momentum cutoff is given by matrix elements of the potential. To demonstrate this explicitly, Eq. (7) will be solved for the potential

$$U(\mathbf{r})=\lambda\delta(r-a)/a^2 \tag{8}$$

which, so far as the author is aware, is the only potential form in three dimensions for which (7) is exactly soluble. This pathological potential consists of a spherical shell of δ function at a distance a from the origin. The integral equation (7) can, for a spherical potential, be split into its angular momentum components giving[3]

$$t_l(x,y)=U(x)\frac{\delta(x-y)}{x^2}+\frac{2}{\pi}\int U(x)\frac{j_l(kx)j_l(kz)}{E-k^2+i\epsilon}\times k^2dkt_l(z,y)z^2dz\,. \tag{9}$$

For the potential (8) write $t_l(x,y)=A_l\delta(x-a).\delta(y-a)/a^4$

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[3] J. L. Beeby, Proc. Roy. Soc. (London) **A279**, 82 (1964).

so that

$$A_l=\lambda+\frac{2}{\pi}\lambda A_l\int\frac{j_l(ka)j_l(ka)}{E-k^2+i\epsilon}k^2dk$$

$$=\lambda\left[1-\frac{2}{\pi}\lambda\int_0^\infty\frac{[j_l(ka)]^2}{E-k^2+i\epsilon}k^2dk\right]^{-1}. \qquad (10)$$

The integral can be done analytically for any value of l and the zeros of the denominator will then give the bound states (or resonances) for that value of l. The wave functions for unbound states can be recovered using the formal expression $\psi=\phi+G_0t\phi$.

Since the one-band model can lead to at most a single bound state it is only necessary to consider the s-wave part of this expression, for which the integral is

$$I=\int_0^\infty\left(\frac{\sin ka}{ka}\right)^2\frac{k^2}{E-k^2+i\epsilon}dk=-\frac{1}{2a^2}\left[\frac{\pi}{2\mu}-\frac{\pi e^{-2\mu a}}{2\mu}\right], \qquad (11)$$

where $E=-\mu^2$. The integral converges because of the Bessel function part and all values of k up to order $ka=\pi$ are important. The propagator part approaches -1 as k tends to infinity, in contrast to the one-dimensional case where the volume factor k^2 is absent. Thus in one dimension the integral converges when $k\sim\sqrt{E}$ because of the propagator part alone. It is this difference which makes the one-dimensional case irrelevant. Looking ahead this is manifested by the constant difference which will appear between Eqs. (12) and (12′) not existing in one dimension.

The equivalent one-band calculation is obtained by cutting off the k integration at the top of the first band, approximately given by $k=\pi/d$. Brillouin zone shape effects are not important. In this case

$$A_l^{\text{O.B.}}=\lambda\left[1-\frac{2\lambda}{\pi}\int_0^{\pi/d}\frac{[j_l(ka)]^2}{E-k^2+i\epsilon}k^2dk\right]^{-1}, \qquad (10')$$

so that if $\pi/d<\pi/a$ the integral will be significantly wrong. The error increases as a/d decreases, i.e., the potential becomes more narrow, but is unimportant when the potential extends beyond the atomic cell $(a>d)$. To stress the error consider the case $a\ll d$ so that $\sin ka\simeq ka$ in (10′) and the integral equivalent to (11) is

$$I^{\text{O.B.}}=-\mu\left\{\tan^{-1}\frac{\pi}{d\mu}-\frac{\pi}{d\mu}\right\}. \qquad (11')$$

The bound states $(E<0)$ and the resonances $(E>0)$ are given by the singularities of the t matrix, i.e., the solutions of $I(\mu)=\pi/2\lambda$. The differences between the solutions of this equation for the values of I given by (11) and (11′) are shown for $E<0$ in Fig. 1. The half-plane $\mu>0$ corresponds to the physical sheet of the E plane and the $\mu<0$ half-plane to the unphysical sheet.[4]

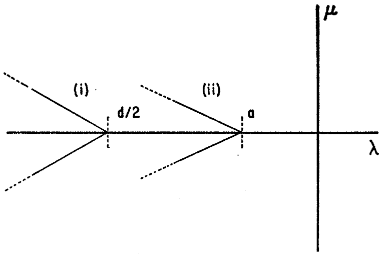

FIG. 1. Bound-state energies as functions of the potential strength: (i) one-band model, (ii) exact result.

To determine the origin of this difference in the critical potential parameter, i.e., the value of λ which is just able to bind a state, rewrite the integral in (11) into two parts

$$-I=\int_0^\infty\left(\frac{\sin ka}{ka}\right)^2dk-\mu^2\int_0^\infty\left(\frac{\sin ka}{ka}\right)^2\frac{dk}{\mu^2+k^2}$$

and consider energies so small that $\mu a\ll 1$. Then $\sin ka\simeq ka$ and

$$-I=(\pi/2a)-\mu(\pi/2). \qquad (12)$$

Thus, when $\mu\simeq 0$, which occurs when $\lambda\simeq -a$

$$\mu=(1/a)+(1/\lambda).$$

The one-band solution, on the other hand, gives

$$-I^{\text{O.B.}}=\int_0^{\pi/d}\left(\frac{\sin ka}{ka}\right)^2dk-\mu^2\int_0^{\pi/d}\left(\frac{\sin ka}{ka}\right)^2\frac{dk}{\mu^2+k^2}$$

$$=\pi/d-\mu\tan^{-1}(\pi/d\mu)\quad a/d\ll 1$$

$$=\pi/d-\mu\pi/2,\quad \mu\ll\pi/d. \qquad (12')$$

Hence one sees that $(I^{\text{O.B.}}-I)$ is virtually independent of μ for small μ. Thus

$$A_l=[(1/\lambda)-(2I/\pi)]^{-1}$$

$$=[(1/\lambda)+(1/a)-\mu]^{-1},$$

and can be written in a similar form as

$$A_l=[(1/\lambda')-(2I^{\text{O.B.}}/\pi)]^{-1}$$

provided

$$(1/\lambda)+(1/a)=(1/\lambda')+(2/d),$$

i.e., the value of the potential parameter is suitably adjusted. It is here, then, that the true value of the one-band model emerges. Provided one does not make a calculation of the parameter λ from some other source, but instead retains it as a parameter to be fitted from the final results of the calculation, then the s-wave part of the t function and thus of the propagator is correctly given. Many calculations[5] satisfy this provision.

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[4] For a discussion of these see e.g., J. L. Beeby, Proc. Cambridge Phil. Soc. **59**, 607 (1963). Note however that in that paper the ingoing propagator was used rather than the outgoing one defined by Eq. (2).

[5] See, e.g., A. M. Clogston, Phys. Rev. **125**, 439 (1962); and A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

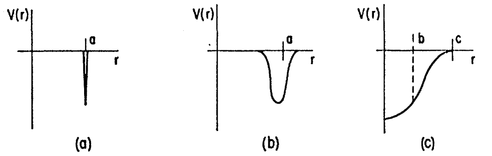

FIG. 2. The three forms of the potential.

A calculation parallel to the above was given by Koster and Slater[1] [paragraph preceding their Eq. (46)]. They extended to infinity an integral equivalent to I, as is necessary, according to the above, in order to solve for the wave function of a specific potential. However, they described the step as an insignificant change in the one-band model. This is misleading since the correct result was obtained in their example only because the one-band model was *not* used.

The potential used above can also bind p, d, states for $-\lambda$ sufficiently large. These cannot be represented by the one band model, but one extra bound state can appear for each extra band admitted to the calculation. The neglect of the overlap onto neighboring sites is not relevant to this issue, corresponding only to small additional potentials at those sites. The single, narrow potential taken above, having several bound states for large $-\lambda$, needs the consideration of more bands for a proper solution.

III. OTHER FORMS OF THE POTENTIAL

The potential used in the previous section was plainly pathological, so in this section arguments will be advanced to suggest why the form of the potential was not vital to the discussion. The free-electron-like lattice is still assumed so again the discussion will center around Eq. (9). One is trying to determine the important contributions to the k integral, rather than the detailed solution of the integral equation. Thus, one can afford to be a little sloppy in evaluating the integral provided one draws only qualitative conclusions.

The model potential of II was soluble because both the potential and its t function were localized at $r=a$ [Fig. 2(a)]. This feature is changed but little if the integral is carried out for a potential concentrated about the shell $r=a$ even if it is not of δ-function form [see Fig. 2(b)]. Thus

$$v(x)j_l(kx)\simeq v(x)j_l(ka)\,,$$
$$j_l(kz)t_l(z,y)\simeq j_l(ka)t_l(z,y)\,,$$

and the k integral is exactly that discussed before. It is here that the physical meaning of a in evaluating the integral becomes apparent. It is some sort of mean potential radius and is of the same order as any other way of defining the radius of the potential.

With this in mind one can attempt crude arguments for a more usual potential shape of the form shown in Fig. 2(c), which is zero outside some radius c. The z integral in Eq. (9) can be approximated as follows (only the case $l=0$ will be given, for simplicity):

$$\begin{aligned}L(k)&=\int_0^\infty j_0(kz)t_0(z,y)z^2dz\\&=\int_0^\infty \{1-\tfrac{1}{6}(kz)^2+\cdots\}t(z,y)z^2dz\\&=t^{(0)}-\tfrac{1}{6}k^2t^{(2)}+0(k^4)\,,\end{aligned}$$

where

$$t^{(n)}=\int_0^\infty z^{n+2}t(z,y)dz\,.$$

This can be recombined to give

$$\begin{aligned}L(k)&=t^{(0)}[1-\tfrac{1}{6}k^2b^2+\cdots]\\&\simeq t^{(0)}j_0(kb)\,,\end{aligned}\tag{13}$$

where

$$b=\{t^{(2)}(y)/t^{(0)}(y)\}^{1/2}$$

is like a mean potential radius. But to work out these $t^{(n)}$, it is necessary to take moments of Eq. (9), in doing which the right-hand side involves integrals like

$$\begin{aligned}M(k)&=\int_0^\infty v(x)j_0(kx)x^{n+2}dx\\&=v^{(n)}j_0(kb')\end{aligned}\tag{14}$$

exactly as above. Thus, finally, the k integration has the form

$$\int_0^\infty \frac{j_0(kb')j_0(kb)}{E-k^2+i\epsilon}k^2dk$$

and behaves exactly as the integral discussed in the previous section. What is important here is not the details of the approximations made to $L(k)$ and $M(k)$, which are somewhat like matrix elements of the potential, but their general behavior as a function of k. They will become small only when $kb>\pi$ where b is some radius characteristic of the potential and is in general of the same order as other mean radii of the potential. Thus if the potential is well confined within the atomic cell, $b\ll d$, more than one band must be considered (in fact d/b bands should give reasonable results).

The purpose of this section has been to give plausibility arguments to show that the results discussed in Sec. II for the pathological potential $\lambda\delta(r-a)/a^2$ are also relevant to most cases of short-range potentials. For longer range potentials (range$>d$) other considerations apply, which are not relevant here.

One final point is that the approximate treatment leading to Eqs. (13) and (14) might form a useful way of obtaining approximate analytic solutions of the t-matrix equation (9) for certain favorable potentials. In particular one would be able to carefully observe the sources of error in numerical solutions.

IV. LATTICES WHICH ARE NOT FREE-ELECTRON-LIKE

In the previous two sections, all that has been done is to analyze the problem of potential scattering. The lattice was essentially absent except for the lattice spacing parameter d. In order to discuss the effects of a real lattice on the conclusions drawn, a different approach will be necessary based on the t-matrix equation equivalent to Eq. (4):

$$(n|t|m)=(n|U|m)+\sum_p\sum_{\mathbf{k}}(n|U|p)\times\frac{1}{E-E_{p\mathbf{k}}+i\epsilon}(p|t|m), \quad (15)$$

where only the matrix elements between the Wannier functions at the impurity site are retained, and the suffix 0 corresponding to that site omitted for brevity. This equation is to be compared with the Fourier transform of Eq. (7) written for this purpose in a similar notation:

$$(\mathbf{l}|t|\mathbf{j})=(\mathbf{l}|v|\mathbf{j})+\int(\mathbf{l}|v|\mathbf{p})\frac{d\mathbf{p}}{E-p^2+i\epsilon}(\mathbf{p}|t|\mathbf{j}). \quad (16)$$

The effect of the lattice has, by use of the Wannier functions, been reduced to using average band matrix elements $(n|t|m)$ in place of the full set $(\mathbf{l}|t|\mathbf{j})$ where $\mathbf{l}$ and $\mathbf{j}$ correspond to wave functions in the nth and mth bands, respectively. The sum over discrete states in (15) can be treated as an integral, thus introducing the density of states $\eta(\mathbf{k})$:

$$(n|t|m)=(n|U|m)+\sum_p\int(n|U|p)\times\frac{\eta(\mathbf{k})}{E-E_p(\mathbf{k})+i\epsilon}d\mathbf{k}(p|t|m). \quad (15')$$

For higher bands $\eta(\mathbf{k})$ approaches 1 and $E_p(\mathbf{k})$ approaches k^2. Also $\int\eta(\mathbf{k})d\mathbf{k}=1$ for the integral over any band, so that excluding the lowest bands the parallel between Eqs. (16) and (15′) is very close. In this way the results of Secs. II and III may be transposed directly to any type of lattice. Using the first band only cannot give the correct binding energy or wave function for a potential smaller than the atomic cell. By regarding the parameters of the potential [usually only $(0|U|0)$] as free parameters and not working them out from a given potential there is little error for small energies.

One further result can be drawn from the parallel between Eqs. (16) and (15′). If matrix elements other than those at the impurity site had been retained, in particular those where both Wannier functions refer to the same site $(ri|U|mi)$, these two equations would have remained alike provided $U(\mathbf{x})$ had a small part around $\mathbf{x}=\mathbf{r}_i$. It is then obvious, as mentioned previously, that these small parts have, in general, little effect on the binding energies or wave functions. This argument can be made much more rigorous by explicitly solving Eq. (16) for such an extended potential derived from the generalization of Eq. (15′).

One might finally comment that in the one-band model the bound state is subtracted from the conduction band, in the sense that only $(N-1)$ states remain in that band. This is not generally true, for consider a potential which, after binding a state, is equivalent to a pseudopotential identical to each of the lattice potentials. Clearly in this case there is a band identical to the original band, plus the bound state, $(N+1)$ states in all. The $(N+1)$th state has actually been attracted down from the second band, a situation obviously demanding the consideration of more than one band.[6] The density-of-states curve given by the one-band model must therefore be treated with some caution.

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[6] Examples of this are given in J. Friedel, Advan. Phys. **3**, 446 (1954).