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16.Summary/Notes

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IMPROVED EFFECTIVE MASS APPROXIMATION FOR IMPURITY LEVELS IN INSULATORS †

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We present a variational expression for the energy eigenvalues of an inpurity in an insulating matrix. Our variational expression may yield better results than those of the effective mass approximation because, in our method the smoothly varying potential hypothesis is not needed

On présente une expression variationelle des valeurs propres de l'energie d'une impureté dans un crystal isolant. Cette expression variationelle nous permet d'obtenir des meilleurs résultats par rapport à l'approximation de la masse effective parce que, dans notre cas, l'hypothèse du potential faiblement variable est abandonnée.

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We consider the problem of an impurity in an insulating matrix, where we want to determine the impurity levels in the forbidden band. This problem was largerly studied in the past and is well solved in the two limiting cases:

1. For shallow impurity levels, the effective mass approximation[1] stands as a neat way to determine the levels. These shallow levels have wave functions with spreads much larger than the lattice parameter, in which case the approximation becomes very good.

2. For deep impurity levels, techniques such as those developed by Parada[2], and the Multiple-Scattering method for clusters[3], are being used with success. In the case of deep levels, the spread of the impurity wave functions is small and a large cluster is not needed.

In this article, we intend to show how to treat the intermediate cases, that is, those of impurity wave functions which have a spread large enough to exclude their treatment by the multiple-scattering method, and yet small enough to raise the question of the validity of the effective mass approximation.

Consider a crystal potential in the form

$$V(\vec{r}) = V_o(\vec{r}) + U(\vec{r}) \tag{1}$$

where $V_o(\vec{r})$ is the potential of the pure crystal and $U(\vec{r})$ is the impurity perturbation potential. Let $\vec{k}_o$ be a point in the Brillouin where the band have extrema. The Bloch functions $b_n(\vec{r})$ at $\vec{k}_o$ satisfy the equation

$$\left[-\nabla^2 + V_o(\vec{r})\right] b_n(\vec{r}) = E_n b_n(\vec{r}) \tag{2}$$

where E_n is the energy of the n-th band at $\vec{k}_o$.

The wave function for the impurity may be written as the following sum[1]:

$$\psi(\vec{r}) = \sum_n F_n(\vec{r}) b_n(\vec{r}) \tag{3}$$

Inserting this expression into

$$\left[-\nabla^2 + V_o(\vec{r}) + U(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \qquad (4)$$

we obtain

$$\sum_n \{ \left[E_n - E + U(\vec{r})\right] F_n(\vec{r}) b_n(\vec{r}) +$$

$$+ b_n(\vec{r}) \; (-\nabla^2) F_n(\vec{r}) -$$

$$- 2\nabla F_n(\vec{r}) \cdot \nabla b_n(\vec{r}) \} = 0 \cdot \qquad (5)$$

Here E is the energy eigenvalue we are looking for.

Now, for a given translational symmetry, the set b_n is complete. Thus, we write

$$\frac{\nabla}{i} b_n(\vec{r}) = \sum_m \vec{p}_{mn} b_m(\vec{r}) \qquad (6)$$

where $\vec{p}_{mn} = \langle b_m \left| \frac{\nabla}{i} \right| b_n \rangle$ (7)

is the momentum matrix element.

Inserting (6) into (5) one finds the following solutions:

$$\left[-\nabla^2 + U + E_n - E\right] F_n(\vec{r}) +$$

$$+ \sum_m 2\vec{p}_{nm} \cdot \frac{\nabla}{i} F_m(\vec{r}) = 0 \qquad (8)$$

In the effective mass approximation, at this point, we make the hypothesis that among all F_n, only one, say E_o, is large. Further, we assume that E is near E_o, that U is small, and that F_n and U are slowly varying. Then, from (8) one obtains that the small F_n are given in terms of F_o by

$$F_n = \frac{\vec{p}_{no} \cdot \frac{\nabla}{i} F_o}{E_o - E_n} \qquad (9)$$

If one wants to go beyond the effective mass approximation we must eliminate its assumptions and treat the set of Eqs. (8) as coupled differential equations. An exact treatment of Eqs. (8) is, of course, impossible, thus we resort to a variational expression for E, given by

$$E = \frac{\sum_n \langle F_n | -\nabla^2 + U + E_n | F_n \rangle + \sum_{n,m} 2\vec{p}_{nm} \cdot \langle F_n | \frac{\nabla}{i} | F_m \rangle}{\sum_n \langle F_n | F_n \rangle} . \tag{10}$$

It can be readily checked that Eq. (10) is truly a variational expression for E, in the sense that upon an arbitrary variation of F_n the resulting variation in E is null if F_n obeys Eq. (8).

Thus our method is based on the variational expression (10). The function F_n are chosen in the form

$$F_n(\vec{r}) = C_n \phi_n(\vec{r}) . \tag{11}$$

where C_n are variational parameters and the $\phi_n(\vec{r})$ form a conveniently chosen basis set, also dependent on variational parameters. Later on we present some suggestions on how to construct the basis set ϕ_n.

Inserting (11) into (10) and varying C_n so that E is an extreme, we obtain the secular equation

$$\sum_m \{ [H_n + (E_n - E) S_n] \delta_{n,m} + 2\vec{g}_{n,m} \cdot \vec{p}_{n,m} \} C_m = 0 \tag{12}$$

where $\vec{p}_{n,m}$ is defined by Eq. (7), and

$$S_n = \langle \phi_n | \phi_n \rangle ; \tag{13a}$$

$$H_n = \langle \phi_n | -\nabla^2 + U | \phi_n \rangle ; \tag{13b}$$

$$\vec{g}_{n,m} = \langle \phi_n | \frac{\nabla}{i} | \phi_m \rangle . \tag{13c}$$

When choosing the set ϕ_n one is oriented by two principles:

1. The rotational symmetry of the impurity state - Usually one is looking for an impurity state with a definite symmetry. Since the

symmetries of the Bloch functions b_n in Eq. (3) are known, the F_n must also have definite symmetries so that their product with b_n leads to a function ψ with the symmetry of the impurity state.

2. The effective mass approximation - This approximation establishes the relation (10) between a function F_o with the others. Thus, when constructing the set ϕ_n one may begin by setting the ϕ_n proportional to the gradient of a given ϕ_o.

To illustrate the method and the guidelines of the preceding paragraph for the construction of the set $\phi_n(\vec{r})$, we consider the donor level in the semiconducting III-V and II-VI compounds. We assume we have a zinc blende semiconductor, the conduction band minimum being located at Γ (center of the zone). Then the conduction state has a Γ_1 symmetry, while the highest valence state is of the Γ_{15} symmetry. Let us consider an impurity state of the Γ_1 symmetry. In the effective mass approximation, the function F in Eq. (3) corresponding to the conduction state would be of the form

$$e^{-\lambda r}$$

Thus we adopt the following set

$$\phi_{\Gamma_1} = e^{-\lambda r} \tag{14a}$$

for all Γ_1 states,

$$\phi_{\Gamma_{15}} = Y_{1,m}(\hat{r})\ e^{-\lambda r} \tag{14b}$$

for all Γ_{15} states, because these are the gradient of ϕ_{Γ_1}, and, by analogy,

$$\phi_{\Gamma_{12}} = Y_{2,m}(\hat{r})\ e^{-\lambda r} \tag{14c}$$

for all Γ_{12}. In Eqs. (14), λ is a variational parameter chosen so that the solution E of Eq. (12) is an extreme, and $Y_{\ell,m}(\hat{r})$ are symmetrized combinations of spherical harmonics with angular momentum ℓ.

Despite of the fact that the construction of the trial functions is based on the effective mass approximation, the present method should

yield better results because no assumption is made on the smoothness of the perturbing impurity potential.

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