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THE METHOD OF MOMENTS FOR SEMI-CONDUCTORS 
AND LOCALIZED STATES

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Résumé. — On montre comment approximer des courbes de densité d’états par des modèles composés de fonctions delta vérifiant un certain nombre de moments de la courbe réelle. On applique ceci au cas de l’approximation des liaisons fortes. La méthode donne des expressions analytiques pour l’énergie de cohésion des semi-conducteurs dans l’approximation de Hartree, la position des états liés dus à des défauts ainsi que des renseignements sur la population des états. Dans les modèles les plus simples l’erreur relative sur les résultats obtenus varie entre un et dix pour cent. Les modèles présentés peuvent se généraliser facilement et être appliqués à d’autres problèmes tels que l’étude des états de surface et des états localisés de vibration dus à des impuretés.

Abstract. — It is shown how to approximate density of states curves by delta function models fitted to a few moments of the true curve. Application is made to the tight-binding approximation. The method gives analytical expressions for the cohesive energy of semi-conductors in the Hartree approximation, the position of bound states due to defects and also information about the population of the states. In the simplest models the results are obtained with a relative error in the range from one to ten per cent. The models presented here can be generalized easily and applied to other problems such as the study of surface states and localized vibrational states due to impurities.

Introduction. — The aim of this work is to develop simple analytical models for physical quantities of interest in the study of solids.

Use is made of the tight binding approximation which gives by far the most simple results but the models can be extrapolated to the study of phonons in a straightforward manner. It is even possible to extend some of them to the case of more sophisticated methods such as OPW and so on, but in those cases we partly lose the analytical simplicity and some numerical computation is needed.

The basis of the study is the use of the moments of the density of states to derive approximate expressions of the physical quantities. We restrict ourselves to the first three or four moments and fit simple models to this limited number of moments. These models are all built of delta functions. In this way the cohesive energy of perfect semi-conductors in the Hartree approximation can be evaluated with a good precision (a few per cent). We can also derive very simply the energy of localized states with a precision of the same order.

Furthermore such models can be very helpful in the study of the electronic density and we apply them to the case of bonding and antibonding states in elemental semi-conductors and also to the problem of the charge density around a vacancy in these materials.

It is to be noted at this point that we use the most simple form of the tight-binding method with only one resonance integral. This allows us to compare easily the approximate results to the exact numerical values. However the models are not modified when using more resonance integrals and we plan to employ them in more elaborate descriptions.

In a first part, the formalism of the moments is derived. Then we apply it to the calculation of energies (mean energies-bound states). The problem of charge densities will be considered in the last section.

II. General considerations. — We first recall the definition of the moments of the density of states. It is then applied to the study of an imperfection and finally extended for charge densities.

1. DEFINITION OF THE MOMENTS. — The moments of a density of states curve \( n(E) \) are given by

\[
\mu_0 = \int n(E) \, dE \\
\mu_1 = \frac{1}{\mu_0} \int n(E) \, E \, dE \\
\mu_k = \frac{1}{\mu_0} \int n(E) \, (E - \mu_1)^k \, dE \quad k \geq 2.
\]

(1)

Using the fact that \( n(E) \) is defined by

\[
n(E) = \text{Tr} \, \delta(E - H_0)
\]

(2)
we can write them as
\[ \mu_1 = \frac{1}{\mu_0} \text{Tr} \mathcal{H}_0, \quad \mu_k = \frac{1}{\mu_0} \text{Tr} \mathcal{H}^k \] (3)
where \( \mathcal{H} = \mathcal{H}_0 - \mu_1 I, I \) being the unit operator.

If we use a tight binding approximation the calculation of the moments can be done by a walk counting technique [1], [2].

In general the first moments can be derived easily. They are analytic functions of the resonance integrals.

One proceeds in the following way: Let us call \( \phi_{nj} \) the \( m \)th basis function associated to the \( j \)th cell of the lattice. When the overlap integrals are neglected the \( \phi_{mj} \) are atomic orbitals, but if they are taken into account the \( \phi_{nj} \) are combinations of the atomic orbitals given by Löwdin's orthogonalization technique.

From translational invariance the moments reduce to
\[ \mu_0 = nN \]
\[ \mu_1 = \frac{1}{n} \sum_{m=1}^{n} \langle \phi_{m0} | \mathcal{H}_0 | \phi_{m0} \rangle \] (4)
\[ \mu_k = \frac{1}{n} \sum_{m=1}^{n} \langle \phi_{m0} | \mathcal{H}^k | \phi_{m0} \rangle \]

\( N \) is the number of primitive cells and \( n \) the number of basis functions associated to one primitive cell.

The first moments can easily be evaluated in terms of the resonance integrals.

2. CASE OF AN IMPERFECTION. — Here we have to determine the change \( \delta n(E) \) of the total density of states due to the presence of the imperfection, i.e. to evaluate the change of the moments.

We define them by
\[ \delta \mu_k = \int \delta n(E) (E - \mu_1)^k \, dE \quad \text{for every } n. \] (5)

Here we have taken the first moment of the perfect crystal as the origin of energies because such a procedure usually simplifies the calculation of the moments.

A common basis set \( \{ \phi_i \} \) can be used for the perfect and imperfect crystal, and this gives
\[ \delta \mu_k = \sum_i \langle \phi_i | (\mathcal{H} + V)^k - \mathcal{H}^k | \phi_i \rangle \] (6)
where \( V \) is the perturbative potential.

3. CHARGE DENSITY. — If \( \psi(r, E) \) is a solution of energy \( E \) for the perfect or imperfect crystal and if \( \{ \phi_i \} \) is the basis set, we may write
\[ \psi(r, E) = \sum_i C_i(E) \phi_i \] (7)
and then
\[ |\psi(r, E)|^2 = \sum_{i,j} C_i^*(E) C_j(E) \phi_i \phi_j. \] (8)

If one knows the terms \( C_i^*(E) C_j(E) \) for all values of \( E \) one exactly knows the charge density. To do this, let us define
\[ n_{ij}(E) = \sum_k C_i^*(E_k) C_j(E_k) \delta(E - E_k) \] (9)
where \( E_k \) are the energies of the system. For \( E = E_k \), \( n_{ij}(E) \) reduces to \( C_i^*(E_k) C_j(E_k) \). The functions \( n_{ij}(E) \) are partial densities of states. We shall use for them the method of moments and define the \( k \)th moment.
\[ \mu_{ij}^k = \int n_{ij}(E) (E - \mu_1)^k \, dE. \] (10)

From the definition of \( n_{ij} \), we can easily see that this reduces to
\[ \mu_{ij}^k = \langle \phi_i | \mathcal{H}^k | \phi_j \rangle. \] (11)

For a given problem we can calculate and use these moments as for the total density of states. It is then possible to derive approximate values for the charge densities and this is important if one wants to do self consistent calculations.

Finally we can notice the following identity
\[ n(E) = \sum_{ij} n_{ij}(E). \] (12)

III. Evaluation of the energies. — The moments have been used to approximate density of states curves [1], [2]. This was done by fitting a curve (Gaussian or combination of two Gaussian curves) to a restricted number of moments. Here we shall proceed in a different way, using delta functions.

1. PERFECT SEMI-CONDUCTORS : COHESIVE ENERGY (Hartree approximation). — For elemental semi-conductors in the tight binding method, the valence and conduction bands contain equal number of atomic states \( 4N \) (\( N \) being the number of primitive cells), the atomic states being sp\(^3\) hybrid orbitals. The evaluation of the cohesive energy is mainly a problem of determining the mean energy of the valence band. For this we use the simple model of figure 1. The valence and conduction bands are averaged each by a delta function. If the density of states is normalized to unity, the weight of the delta function must be \( \frac{1}{2} \) for each band.

\[ \text{FIG. 1. — Delta functions model for a two-band system.} \]
We have two unknowns which are the energies $E_1$, $E_2$ of the delta functions. These energies must satisfy the right number of lower moments. As $\mu_0$ is already fitted, we must write

$$E_1 + E_2 = 0$$
$$\frac{E_1^2}{2} + \frac{E_2^2}{2} = \mu_2 .$$

Note that the origin of the energies is taken at the first moment $\mu_1$. The solution of this system is straightforward

$$E_2 = - E_1 = \sqrt{\mu_2} .$$

Now the cohesive energy per atom is easily written down as

$$E_{\text{coh}} = -4E_1 + E_f - 4\mu_1$$

where $E_f$ is the energy of the $s^2 p^2$ state of the free atom, i.e.

$$E_f = 2(E_s + E_p)$$

$E_s$, $E_p$ being the atomic s and p energies.

Finally we find

$$E_{\text{coh}} = 2(E_s + E_p) - 4\mu_1 + 4\sqrt{\mu_2} .$$

We have applied this analytic expression to the simplest model of covalent semi-conductors, with only one resonance integral between sp$^3$ hybrids pointing towards each other. In this model let us define the promotion energy $4\varepsilon$ as

$$4\varepsilon = E_p - E_s$$

and introduce the resonance integral $\lambda$ between two sp$^3$ orbitals pointing towards each other.

We can write (17) as shown in Appendix A.1

$$E_{\text{coh}} = 4\sqrt{\lambda^2 + 3\varepsilon^2} - 4\varepsilon .$$

Numerical application gives the same value as the computed one within the limits of accuracy of the last one (a few per cent).

We can evaluate the relative error introduced by such a model (Appendix A.1). It proves to be :

$$\left(1 - \frac{V_2 + C_2}{2\mu_2}\right)^{-1/2} - 1$$

where $V_2$ and $C_2$ are the second order moments of the valence and the conduction bands with respect to their center of gravity. This error is smaller when the gap becomes large compared to the bandwidth. The model is also favoured when the density of states presents one main peak inside one band, which seems to be the case for covalent solids.

2. Bound state for a one band system. — Let us now consider the problem of a bound state issued from a band and due to an imperfection. We treat the case where the total number of states is not changed by the imperfection, i.e. where $\delta\mu_0$ vanishes.

As one state must be lost in the band the simplest model would be that of figure 2 with two delta functions, one with weight 1 for the localized state, the other with weight $-1$ in the band.

![Fig. 2. — Model for a bound state. $E_L$ is the energy of the bound state.](image)

We have two unknowns $E_1$ and $E_L$; two equations are needed

$$-E_1 + E_L = \delta\mu_1$$
$$-E_1^2 + E_L^2 = \delta\mu_2 .$$

The result is

$$E_L = \frac{\delta\mu_2 + \delta\mu_1^2}{2\delta\mu_1} .$$

We have checked this model for a cubic s band in the tight-binding approximation, with only one resonance integral between nearest neighbours. The perturbation was assumed to be an intraatomic term $\alpha$ on the central atom. This problem can be solved exactly by the Green's operator method. When comparing the exact value of $E_L(\alpha)$ to the approximate one, which in this case turns out to be (Appendix A.3)

$$E_L = \alpha$$

we find that, in the less favorable case, i.e. when $E_L$ is just at the limit of the band the relative error on its value is about 0.28, but when $E_L$ is at twice this distance from the center of the band this error becomes of the order of 0.04.

To improve the agreement one can go a little further and use the three delta functions model of figure 3, where two delta functions are located at distances $+\Delta$ and $-\Delta$ from $\mu_1$. 
The equations are

\[ A_1 + A_2 + 1 = 0 \]
\[ (A_2 - A_1) A + E_L = \delta \mu_1 \]
\[ - A^2 + E_2^2 = \delta \mu_2 \]
\[ (A_2 - A_1) A^3 + E_3^2 = \delta \mu_3 . \]  
(24)

The solution for \( E_L \) is

\[ E_L = - \frac{\delta \mu_3}{2 \delta \mu_1} \pm \frac{1}{2} \left[ \left( \frac{\delta \mu_3}{\delta \mu_1} \right)^2 + 4 \left( \frac{\delta \mu_3}{\delta \mu_1} + \delta \mu_3 \right) \right]^{1/2} . \]

(25)

The sign to choose will depend on the particular problem we are treating. For a repulsive potential, the + sign has to be used in order that \( E_L \) tends to infinity when \( \delta \mu_1, \delta \mu_2, \delta \mu_3 \) tend to plus infinity.

This applied to the same problem gives very good agreement with a relative precision of 0.07 at the limit of the band which is the less favorable case. The formula obtained is for a repulsive potential (Appendix A. III)

\[ E_L = - \frac{\alpha}{2} + \frac{3 \alpha}{2} \sqrt{1 + \frac{2}{\alpha^2}} \quad \alpha > 0 \]

(26)

where the energy is written in units of \( 2 \lambda \), \( \lambda \) being the resonance integral between nearest neighbours.

3. VACANCY IN COVALENT SOLIDS. — We shall consider here the semiconductor in terms of bonding and antibonding orbitals. To create a vacancy in the diamond lattice for instance, we must break four bonding and four antibonding orbitals. Then roughly speaking one must loose four bonding states (i.e. four valence band states), and four antibonding states (i.e. four conduction band states). As we must find four bound states on the free atom (one at energy \( E_s \) and three at \( E_p \)) it is necessary, in order to keep the total number of states constant, to find four other states. When these fall in the gap they are bound states. If not they become resonant states.

To solve this problem it is useful to classify the states by their symmetry properties. They belong to the \( A_1 \) and \( T_2 \) representations of \( T_D \) (s and p states on the central atom). Formally four similar problems have to be solved (one for \( A_1 \) and 3 identical for \( T_2 \)).

To determine the energy of the localized or resonant states the simplest possible model is that of figure 4 which concerns the \( A_1 \) representation. One state is lost at an average energy \( E_1 \) for the valence band, \( E_2 \) for the conduction band. We find a bound state at the known energy \( E_s \) (free atom) and a localized or resonant state at energy \( E_L \). We have three unknowns and then must solve equations using \( \delta \mu_1, \delta \mu_2, \delta \mu_3 \). One finds (Appendix A. IV) for the \( A_1 \) state:

\[ E_L = \frac{\delta \mu_3 + \delta \mu_1^2 + \frac{3}{2} \delta \mu_1 \delta \mu_2 - \frac{3}{4} (\delta \mu_2 + \delta \mu_3) E_s}{\frac{3}{2} (\delta \mu_2 + \delta \mu_3^2 - 3 E_s \delta \mu_1)} \]

(27)

and a similar formula for the threefold degenerate state \( T_2 \).

Now with the simple tight binding method of Leman and Friedel [3] the problem can be solved numerically [4], [5] by the Green's operator method. In this simple case \( E_L \) reduces to (Appendix A. IV):

\[ E_L = 0 \]

(28)

for \( A_1 \), as for \( T_2 \).

We must recall here that the origin of the energy is taken at \( \mu_1 \), which is distant from the center of the gap.
III. Study of the charge densities. — Here similar models will be used for partial densities of states $n_{ij}(E)$ in order to evaluate the charge densities. This technique is applied to the case of covalent solids in the tight-binding approximation. First we treat the bonding and antibonding states of the perfect crystal and then the change in charge density due to the creation of a vacancy.

1. Bonding and antibonding states in covalent solids. — If the promotion energy defined in I tends to zero we can say that the valence band is built completely with bonding states and the conduction band with antibonding states in the simple model of Leman and Friedel [3]. Now in the real case where $4\varepsilon$ does not vanish, it is necessary to know the weight of bonding and antibonding states in the valence band. Such a result will also give informations about the charge density.

For this purpose we define as in (9)

$$n_B(E) = \sum_k \langle \Phi_B | \psi_k \rangle^2 \delta(E - E_k)$$

(29)

$n_B(E)$ is the bonding density of states per bond and $\Phi_B$ is one of the bonding orbitals. In the same way, for antibonding states

$$n_A(E) = \sum_k \langle \Phi_A | \psi_k \rangle^2 \delta(E - E_k).$$

(30)

As in I.3 the moments of these curves can be defined

$$\mu^k_B = \langle \Phi_B | \chi^k | \Phi_B \rangle,$$

$$\mu^k_A = \langle \Phi_A | \chi^k | \Phi_A \rangle.$$

We shall use here the simplest possible model. First the total density of states is related to $n_A$ and $n_B$

$$n(E) = \frac{n_B(E) + n_A(E)}{2}$$

(32)

and it is important to satisfy

$$\int_{bv} \frac{1}{2} [n_A(E) + n_B(E)] \, dE = \frac{1}{2}.$$  

(33)

The quantities to be determined here are

$$\int_{bv} n_A(E) \, dE \quad \text{and} \quad \int_{bv} n_B(E) \, dE.$$

For this, taking (32) into account, we have only to approximate $n_B(E) - n_A(E)$, and this is done with the two delta-functions model of figure 5. It requires the calculation of the first four moments $\mu^k_B - \mu^k_A$ with $k = 0, 1, 2, 3$. Using the model of Leman and Friedel [3] we find (Appendix B.1)

$$\int_{bv} n_A(E) \, dE = \frac{1}{2} \frac{\lambda}{2 \sqrt{\lambda^2 + \varepsilon^2}}.$$  

(34)

$$\int_{bv} n_B(E) \, dE = \frac{1}{2} \frac{\lambda}{2 \sqrt{\lambda^2 + \varepsilon^2}}.$$  

In the limit where $\varepsilon/\lambda$ vanishes the antibonding character is of order $\varepsilon^2/\lambda^2$. This is similar to the result found directly by Leman [3], but we do not find the same coefficient for the $\varepsilon^2/\lambda^2$ term. The reason for this is that the error introduced by our simple model is just of the same order.

We can conclude that our model is not very accurate for the calculation of the bonding and antibonding character of C, Si, Ge in the description of Leman. However it must be noticed that the absolute error introduced is still of a few per cent, but it is done on a quantity of the same order of magnitude. In cases where the antibonding character becomes important, especially for III-V and II-VI semiconductors, we expect to have the same absolute precision and the model will become meaningful.

In order to test the precision we have done the exact calculation for a two-band linear chain [see 4].

The bonding and antibonding characters are given by elliptic integrals. The absolute error introduced by our model is of maximum order 0.07 in a case where the energy gap is small compared to the bandwidth.

We have done another test by estimating the s and p characters in the valence band by a quite similar method (Appendix B. II). The computed value of the s character was 1.6 and our approximate value was 1.56.

2. Charge density around a vacancy. — We shall again have a look at the problem of the vacancy in covalent solids in the simple tight-binding description. Such a problem was solved by the Green’s operator method [4], [5].
Let us first give some details about the atomic orbitals around the vacancy. As in (II.3) we use states which are basis functions for irreducible representations of $T_d$. In terms of the hybrid orbitals shown on figure 6, these states contain:

- $s(A_1)$ and $p(T_2)$ on the vacancy atom.
- $v(A_1)$ and $t_x, t_y, t_z(T_2)$ on the first neighbours, built from the four sp$^2$ hybrids $a, b, c, d$ pointing towards the vacancy atom. They are defined precisely in [4].

![Fig. 6. — The vacancy and its four nearest neighbours in the diamond lattice.](image)

Let us consider only the symmetrical representation: the calculations would be similar for $T_2$. First we have worked out in (II.3) an approximate model for the change $\delta n_A(E)$ of the symmetric density of states due to the creation of the vacancy.

We want to evaluate the change in charge density on the neighbours of the vacancy. For this we work again with partial densities of states. Let us define $\delta n_{s}(E)$ as the change in the s density on the vacancy atom and $\delta n_{A_1}(E)$ by

$$\delta n'_{A_1}(E) = \delta n_{A_1}(E) - \delta n_{s}(E).$$

Then $\delta n'_{A_1}(E)$ represents the change in the symmetrical density of states due to all the neighbours of the vacancy. The knowledge of this quantity gives information about the overall change of charge density on the neighbours of the vacancy.

Again we can use a delta function model to evaluate $\delta n_{s}(E) - \delta n'_{A_1}(E)$ because we know the sum of these two quantities. Detailed calculation, which will not be given here, shows that one looses in the valence band about 0.7 s state on the vacancy atom and 0.3 symmetric state on other atoms. However as there was 0.8 s state on the vacancy atom before breaking the bonds we must loose all of it. This gives us a direct measure of the accuracy of that particular model. One sees that it gives a relative precision of 0.12 only.

In this case the model will have to be refined, but the essential thing we wanted to show was that it is possible to derive approximate values for the population of the states on the neighbours of a vacancy. The accuracy depends on the number of moments we include in the model. We intend to use such a procedure to do self-consistent calculations for the different charge states of the vacancy.

Let us end up by noticing the following point: the last model used for the vacancy included moments up to the third one and in this approximation only the population of the $v, t_x, t_y, t_z$ orbitals is affected. This is equivalent to the use of a molecular model for the vacancy [6], [7].

**Conclusion.** — Simple analytical models have been developed to evaluate energies and charge densities for semi-conductors and bound states. Their basis is the following: one approximates the density of states by a few delta functions which fit a limited number of moments. These crude models give the physical results with good accuracy owing to their simplicity.

We plan to extend this preliminary work to the following cases.

a) The study of perfect semi-conductors: for this we should like to follow the work of Phillips [8] who has redefined the ionicity in compounds on the basis of a two parameters phenomenological approach. His model bears a strong resemblance with what is obtained in (III.1) when using moments up to $\mu_2$ for the density of states. We plan to extend Coulson's tight binding work [9] by including overlap integrals and hope to be able to reconcile to some extent Coulson's and Phillip's definitions of ionicity.

b) The study of vacancies in semi-conductors: we want to obtain approximate self-consistency for the calculation of charge densities around a vacancy. This will be carried out by two methods: the Green's function approach and the moments.

We also hope to include the distortions of the system in the calculations.

c) The study of localized states of vibration, for which the models of (III.2) seem particularly interesting. Such a preliminary work has been done for Rayleigh waves in a simple case and we were able to find the dispersion curve with quite good accuracy. We plan to extend the same considerations to more real cases and also try to study localized states of vibrations due to defects in solids.

It should be emphasized that the models used in that work are the simplest we could find. Of course it is possible to take account of one or two higher moments and get in that way a greatly enhanced precision; preliminary work already shows that two more moments give a quite better value for the cohesive energy (I.1). However it seems desirable to keep the analyzity of the results.
APPENDIX A

1. Moments for covalent semi-conductors. — In the model of Leman if \( N \) is the number of primitive cells in the crystal, as we have two atoms per unit cell and four orbitals per atom, we find

\[
\mu_0 = 8 N \tag{A.1}
\]

Let us now call \( \alpha \) one of the sp\(^3\) hybrids. The non-vanishing matrix elements of the Hamiltonian between sp\(^3\) hybrids are

\[
\begin{align*}
\langle \alpha | \mathcal{H} | \alpha \rangle &= \frac{E_s + 3 E_p}{4} \epsilon_m \\
\langle \alpha | \mathcal{H} | \alpha' \rangle &= -\epsilon \\
\langle \alpha | \mathcal{H} | \beta \rangle &= -\lambda
\end{align*}
\tag{A.2}
\]

\( \alpha' \) being one of the three other sp\(^3\) hybrids centered on the same atom as \( \alpha \), \( \beta \) being the nearest neighbour's hybrid pointing towards \( \alpha \).

From this and (3) we derive easily

\[
\begin{align*}
\mu_1 &= \epsilon_m \\
\mu_2 &= \langle \alpha | \mathcal{H}^2 | \alpha \rangle = \lambda^2 + 3 \epsilon^2
\end{align*}
\tag{A.3}
\]

Combining (A.2) and (17) we find (18) for the cohesive energy per atom.

II. Evaluation of the error for the cohesive energy. — Let \( \varepsilon_1 \) and \( \varepsilon_2 \) be the exact centers of gravity of the valence and conduction bands, with the origin of energies taken at \( \mu_1 \). If \( n(E) \) is normalized to unity, we first can write

\[
\int n(\varepsilon) \varepsilon \, d\varepsilon = \frac{1}{2} (\varepsilon_1 + \varepsilon_2) = 0 \tag{A.4}
\]

For \( \mu^2 \) we have

\[
\int n(\varepsilon) \varepsilon^2 \, d\varepsilon = \mu_2 \tag{A.5}
\]

Let us consider the contribution of the valence band to this integral

\[
\int_{Bv} n(\varepsilon) \varepsilon^2 \, d\varepsilon = \int_{Bv} n(\varepsilon) (\varepsilon - \varepsilon_1)^2 + \varepsilon_1^2 / 2 \tag{A.6}
\]

\[
= \frac{1}{2} (V_2 + \varepsilon_1^2)
\]

where \( V_2 \) is the second moment of the valence band with respect to its center of gravity. If \( C_2 \) is the similar quantity for the conduction band, the exact equations are

\[
\varepsilon_1 + \varepsilon_2 = 0
\]

\[
\frac{1}{2} (\varepsilon_1^2 + \varepsilon_2^2) = \mu_2 - \frac{(V_2 + C_2)}{2}
\tag{A.7}
\]

which have to be compared to (13). The absolute error is then

\[
\Delta = E_1 - \varepsilon_1 = \sqrt{\mu_2} \left( 1 - \sqrt{1 - \frac{V_2 + C_2}{2 \mu_2}} \right) \tag{A.8}
\]

which leads to the relative error of (20).

III. Bound state for a s band. — We have to treat a cubic system with one s orbital per atom. If the mean energy of the s orbital is taken as the origin of energies, we have only one parameter \( \lambda \), the resonance integral between nearest neighbours. In such a case the first moment \( \mu_4 \) of the perfect system vanishes and the band is symmetric with respect to zero.

If we introduce a perturbation \( V \) on the perfect crystal Hamiltonian \( H \) which has only one non-vanishing matrix element \( \alpha \) on the impurity, we immediately obtain from (6)

\[
\begin{align*}
\delta \mu_0 &= 0 \\
\delta \mu_1 &= \text{Tr} \, V = \alpha \\
\delta \mu_2 &= 2 \text{Tr} \, \mathcal{H} V + \text{Tr} \, V^2 = \alpha^2 \\
\delta \mu_3 &= 3 \text{Tr} \, \mathcal{H} V^2 + 3 \text{Tr} \, \mathcal{H}^2 V + \text{Tr} \, V^3 \\
&= \alpha^3 + 18 \lambda^2 \alpha
\end{align*}
\tag{A.9}
\]

Now, inserting these values into (22) and (25) and expressing the localized state energy \( E_L \), in units of \( 2 \lambda \), we finally obtain (23) and (26).

IV. Vacancy in covalent solids. — The set of equations corresponding to figure 4 is:

\[
\begin{align*}
- E_1 - E_2 + E_S + E_L &= \delta \mu_4 \\
- E_1^2 - E_2^2 + E_S^2 + E_L^2 &= \delta \mu_2 \\
- E_1^3 - E_2^3 + E_S^3 + E_L^3 &= \delta \mu_3
\end{align*}
\tag{A.10}
\]

We take as auxiliary unknowns the sum \( S \), the product \( P \) of \( E_1 \) and \( E_2 \), and \( S' \), \( P' \) for \( E_S \) and \( E_L \)

\[
\begin{align*}
- S + S' &= \delta \mu_1 \\
- S^2 + 2 P + S'^2 - 2 P' &= \delta \mu^2 \\
- S(S^2 - 3 P) + S'(S'^2 - 3 P') &= \delta \mu_3
\end{align*}
\tag{A.11}
\]

From the two first equations \( S \) and \( P \) can be determined in terms of \( S' \) and \( P' \). Injecting these values into the third relation we obtain

\[
\frac{1}{2} (\delta \mu_2 + \delta \mu_1^3) S' - 3 \delta \mu_1 P' = \delta \mu_3 + \frac{1}{2} \delta \mu_1^3 + \frac{1}{2} \delta \mu_1 \delta \mu_2
\tag{A.12}
\]
Now for the $A_1$ case we can write the matrices

\[ \mathcal{J} = \begin{bmatrix} -3\epsilon & -\lambda & \cdots \\ -\lambda & 0 & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}, \quad \mathcal{U} = \begin{bmatrix} 0 & \lambda \\ \lambda & 0 \end{bmatrix} \]  

(A.13)

where $\mathcal{J}$ and $\mathcal{U}$ are respectively the perfect crystal and the perturbation matrices, in the basis of all the $A_1$ combinations of the sp$^3$ hybrids. The two functions of interest here are $s$ and $v$ defined in (III.2) (for more detailed considerations see [4]).

Calculating the $\delta\mu_b$ as in (A.9) we easily find

\[ \begin{align*}
\delta\mu_2 &= 0 \\
\delta\mu_3 &= -2\lambda^2 \\
\delta\mu_5 &= 9\epsilon\lambda^2.
\end{align*} \]  

(A.14)

With these values and (27) $E_1$ vanishes in this case. The calculation is similar for $T_2$ replacing $-3\epsilon$ by $\epsilon$ and gives the same final result.

APPENDIX B

I. Bonding and antibonding characters.

We shall not detail the calculation of the moments which is straight-forward. We obtain

\[ \begin{align*}
\mu_0^b &= 1 \\
\mu_0^a &= 1 \\
\mu_1^b &= -\lambda \\
\mu_1^a &= +\lambda \\
\mu_2^b &= \lambda^2 + 3\epsilon^2 \\
\mu_2^a &= \lambda^2 + 3\epsilon^2 \\
\mu_3^b &= -9\epsilon - \lambda^2 - 6\epsilon^3 \\
\mu_3^a &= \lambda^3 + 6\epsilon^2 \lambda - 6\epsilon^3.
\end{align*} \]  

(B.1)

The model of figure 5 must fit the differences

\[ \mu^{(k)} = \mu^b_k - \mu^a_k. \]

First we may write, for the weights of the delta functions

\[ A_1 = -A_2 = -A. \]  

(B.2)

From this three equations can be derived

\[ \begin{align*}
A(E_2 - E_1) &= \mu^{(1)} \\
A(E_2^3 - E_1^3) &= \mu^{(2)} \\
A(E_2^3 - E_1^3) &= \mu^{(3)}.
\end{align*} \]  

(B.3)

Using the sum $S$ and product $P$ of $E_1$ and $E_2$ we obtain

\[ S = \frac{\mu^{(2)}}{\mu^{(1)}}, \]

\[ S^2 - P = \frac{\mu^{(3)}}{\mu^{(1)}}. \]  

(B.4)

From this

\[ A = \frac{\mu^{(1)}}{\sqrt{S^2 - 4P}} = \frac{\mu^{(1)}}{\sqrt{4\frac{\mu^{(3)}}{\mu^{(1)}} - 3\left(\frac{\mu^{(2)}}{\mu^{(1)}}\right)^2}}. \]  

(B.5)

We have then only to study the quantity

\[ n_s(E) - n_p(E) \]

(B.8)

for which we use the same model as in (B.1).

The moments are:

\[ \begin{align*}
\mu_0^s &= 1 \\
\mu_0^p &= 1 \\
\mu_1^s &= -3\epsilon \\
\mu_1^p &= \epsilon \\
\mu_2^s &= \lambda^2 + 9\epsilon^2 \\
\mu_2^p &= \lambda^2 + \epsilon^2 \\
\mu_3^s &= -3\epsilon(2\lambda^2 + 9\epsilon^2) \\
\mu_3^p &= \epsilon(\epsilon^2 + 2\lambda^2).
\end{align*} \]  

(B.9)

From (B.7, 8 and 9) the s character is given by:

\[ m(E) = \frac{1}{4}\left[ n_s(E) + 3n_p(E) \right]. \]

(B.7)

(B.10)

which, with the numerical values of Leman gives 0.78 and then 1.56 when the spin degeneracy is taken into account.
Bibliographie


