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On the Lattice Stability of Metals

II. Two Perturbation Formalisms for the Comparison of Crystals with Different Lattices

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The symmetry differences between different lattices is a main obstacle for perturbation theory. Two approaches are presented to circumvent this difficulty. The first shows how to introduce a new potential with the symmetry of the first lattice which has, for a certain number of eigenstates, the same energy and potential energy values as another potential for the second lattice. First-order perturbation theory may be used to discuss the influence of potential differences between two lattices on the band structure energy differences between these two lattices. The second shows how to transform the potential difference into one of the kinetic part of the Hamiltonian. This is achieved by a non-linear rearrangement operator. For the model of a muffin-tin potential with delta functions as atomic potentials this operator reduces to a transformation matrix. With this model the dependence of the lattice stability on the geometry of the lattices may be investigated.

Key words: Crystal – Potential differences as perturbations

1. Introduction

The band structure energy is determined as the sum of the energies of the electronic states corrected by the double counted electron–electron interaction energy [1]. If we compare the energy of those lattices which have comparable symmetry the difference in the total energy may be determined by the difference in the band structure energy. This is a well-known fact for metals [1–4]. So we may be interested in the possibility of comparing the band structure energies of different lattices. For simplicity we only discuss the cases of elements and primitive lattices. We assume that the correct energy and potential energy values of the realistic many-particle problem are presented by an approximately chosen one-particle potential $V^c(\mathbf{r})$ which satisfies the Schrödinger equation,

$$H^c \psi_n^c(\mathbf{r}) = \epsilon_n^c \psi_n^c(\mathbf{r})$$

$$H^c \equiv -\Delta + V^c(\mathbf{r}), \qquad C \equiv A, B$$

A and B characterize the two lattices to be compared. In this treatment we will neglect the double counting correction of the electronic interaction because it is the same for the potential energy as for the energy, and the electron–electron interaction is rather structure independent [1, 3, 4]. Thus we have the following criterion for the lattice stability:

$$\Delta E^{AB} \approx \Delta E_{bs}^{AB} \equiv \sum_n (\epsilon_n^A - \epsilon_n^B)$$

From this relation we will commence our consideration. In Sects. 2 and 3 we give the perturbation of the potential and the kinetic part of the Hamiltonian respectively. In Sect. 4 we discuss some further aspects of the problems involved in this work.

2. The Perturbation Treatment of the Potential

We imagine that $\bar{n}$ normalized and orthogonal functions $\psi_n^{A'}(\mathrm{r})$ belonging to the lattice A are determined by

$$\langle \psi_n^{A'} | \Delta | \psi_n^{A'} \rangle \equiv \langle \psi_n^B | \Delta | \psi_n^B \rangle; \qquad 1 \leqslant n \leqslant \bar{n}$$

$$\langle \psi_m^{A'} | \psi_n^{A'} \rangle \equiv \delta_{mn}$$

n runs through the $\bar{n}$ lowest energy states belonging to ϵ_n^B. In practice this is possible because in an Ansatz, as for example

$$\psi_n^{A'} = \sum_{m=1}^{\infty} c_{nm} \psi_n^A$$

we have many more coefficients c_{nm} than equations to be satisfied. The number of equations is

$$\bar{n} + \left(\frac{\bar{n}^2}{2} + \frac{\bar{n}}{2}\right) = \frac{\bar{n}}{2}(\bar{n} + 3)$$

and we may choose the remaining coefficients arbitrarily. This arbitrariness does not alter our result because the energy and potential energy values will not be changed. Now we imagine that we extend the set of $\bar{n}$ functions and create a complete set of orthogonal and normalized functions of the symmetry of lattice A.

We determine a Hamiltonian $H^{A'}$ and a potential $V^{A'}(\mathrm{r})$ with the spectral representation:

$$H^{A'} \equiv \sum_n |\psi_n^{A'}\rangle \epsilon_n^B \langle \psi_n^{A'}|$$

$$V^{A'}(\mathrm{r}) = H^{A'} + \Delta$$

$V^{A'}(\mathrm{r})$ given in this way is non-local. It may be determined to be local by an Ansatz

$$V_0^{A'}(\mathrm{r}) \equiv \sum_l v_l^{A'} g_l(\mathrm{r}); \qquad V^{A'}(\mathrm{r}) = \sum_{\mathrm{j}^A} V_0^{A'}(\mathrm{r} - \mathrm{j}^A)$$

with any set of localized functions $g_l(\mathrm{r})$. j^A are the lattice vectors of lattice A.

What we have gained now is a potential $V^{A'}(\mathrm{r})$ which has the property of giving the same energy (ϵ_n^B) and potential energy (V_n^B) for the n lowest energy states as the potential $V^B(\mathrm{r})$ of the lattice B. This means that we have transferred the potential $V^B(\mathrm{r})$ from the lattice B to the lattice A. Instead of comparing $V^B(\mathrm{r})$ with $V^A(\mathrm{r})$ we can compare $V^{A'}(\mathrm{r})$ with $V^A(\mathrm{r})$.

We are now able to carry out a perturbation calculation of the energies ϵ_n^B starting from the energies ϵ_n^A. The perturbation potential is $V^{A'}(\mathfrak{r}) - V^A(\mathfrak{r})$. This is hardly possible for $V^B(\mathfrak{r}) - V^A(\mathfrak{r})$ because the symmetry of A and B is different. We illustrate this using the Bloch form of the eigenfunctions [5, 6]

$$\psi_n^c(\mathfrak{r}) = e^{i\mathfrak{k}\mathfrak{w}}\, u_n^c(\mathfrak{r})$$

$$(-\Delta + \mathfrak{k}\mathfrak{p} + V^c(\mathfrak{r}))u_n^c(\mathfrak{r}) = (\epsilon_n^c - \mathfrak{k}^2)u_n^c(\mathfrak{r})$$

$u_n^c(\mathfrak{r})$ and $V^c(\mathfrak{r})$ are in the same function space. However, the function space for $C = A$ is different from that for $C = B$ because the reciprocal lattices are different. It is impossible to develop u_n^B by the set of the functions u_n^A which would be necessary for perturbation theory. A perturbation development of ψ_n^B by the ψ_n^A would connect eigenstates of different $\mathfrak{k}$ which would increase the number of involved states drastically. Being more so the stronger the potential.

We do not have to worry about perturbation theory with degeneracies because the symmetry between A and A' remains the same. But it may happen that B has large energy differences where A has vanishing differences caused by degeneracy. Therefore we may assume that the symmetry properties of the lattices are removed by an infinitesimal distortion. If it was not possible to rearrange the states of lattice B by interchanging the states of the inner part with those of the surface of the Brillouin zone the density of states would differ so strongly that a perturbation calculation would not be possible. But this is not the case for similar structures, as we may see for example in the case of the metals. The energy differences between states of bcc and fcc for lithium are smaller than about 0.01 ryd [7] and for the transition metals about 0.02 ryd [4]. The differences for the lowest valence states are 10^{-3} ryd (Γ_1) for lithium [7], and for the *d*-bands of transition metals it may be taken to be zero, as shown by Pettifor [4].

We consider the perturbation of first order:

$$\Delta E_{bs}^{BA(1)} = \sum_n \langle \psi_n^A | V^{A'}(\mathfrak{r}) - V^A(\mathfrak{r}) | \psi_n^A \rangle \approx \sum_n \langle \psi_n^{A'} | V^{A'}(\mathfrak{r}) - V^A(\mathfrak{r}) | \psi_n^{A'} \rangle$$

$$\approx \sum_n (\overline{V}_n^B - \overline{V}_n^A)$$

This holds because in first order the energy can be described with ψ_n^A and $\psi_n^{A'}$ and expresses the difference in energy and potential energy by the difference of the potentials if the first-order perturbation theory is applicable. For example, using the above relations, potential differences caused by structure differences can be discussed in the following manner: We may imagine that the regions of deep and high potential are transferred point by point from lattice B to lattice A - producing $V^{A'}(\mathfrak{r})$ - and are then compared with $V^A(\mathfrak{r})$. Thus this is nothing but a comparison of $V^B(\mathfrak{r})$ with $V^A(\mathfrak{r})$ without the mathematical difficulties caused by the different lattice symmetries.

Perturbation of first order agrees with the virial theorem [6] to within a factor of 0.5. That first-order perturbation theory may be sufficient is seen, for example, in the case of metals where the energy differences are very small as has been already mentioned. The ratio of band structure energy difference to the band structure energy of one lattice is for metals in the range of about 10^{-2} to 10^{-4} [2, 4]. Even the shift in the energy of a single state should be not larger than about 0.02 ryd, as may be seen from the density of states distribution shown by Pettifor [4]. This value has to be compared with about 0.5 ryd which is about the centre of the *d*-band. Their ratio is 0.04 and even if it were not so small, we might expect that the sign of the band structure energy difference, the trend of the lattice stability, is given correctly.

The advantage of our treatment is that we can reveal the connection between differences of the lattice potentials and the lattice stability by expressions involving low-order perturbation theory. This is hardly possible in a secular procedure. The disadvantage is that we have to determine the potential $V^{A'}(\mathfrak{r})$ by the aid of energy values and potential energies of lattice B. Therefore it would be very interesting to investigate the possibility of determining $V^{A'}(\mathfrak{r})$ entirely in terms of the potential $V^B(\mathfrak{r})$.

The simplest possibility might be the following: We divide the Wigner–Seitz cells of both lattices into spherical shells having their centres at the atom in the middle of the unit cell. We number the shells with increasing distance from the centre, there being an equal number of shells. The shells of the two lattices with the same number shall have the same volume. If the shells are cut by the surface of the cell, the remaining sections within the cell shall also have the same volume as the section or the shells with the same numbers in the cell of the other lattice.

We now calculate the mean value of the potential $V^B(\mathfrak{r})$

$$\bar{\bar{V}}_m \equiv \int_{S_m} V^B(\mathfrak{r})d\mathfrak{r}$$

within the shell S_m with the number m. We take this value as the mean value of the shell S_m of the potential $V^{A'}(\mathfrak{r})$.

3. Perturbation of the Kinetic Energy

It may happen that the potentials $V^A(\mathfrak{r})$ and $V^B(\mathfrak{r})$ differ only in their geometrical arrangement. For example, this is the case for two muffin-tin potentials with the same muffin-tin plane and the same potential within the spheres which differ only in the arrangement of the potential spheres. In such a case we define a reordering operator R^{BA} so that

$$V^B(\mathfrak{r}^B) \equiv V^A(\mathfrak{r}^A)$$

$$\mathfrak{r}^B \equiv R^{BA}\,\mathfrak{r}^A$$

If we insert these relations in the Schrödinger equation for the potential $V^B(\mathfrak{w}^B)$

$$[-\Delta_{\mathfrak{r}^B} + V^B(\mathfrak{r}^B)]\,\psi_n^B(\mathfrak{r}^B) = \epsilon_n^B\,\psi_n^B(\mathfrak{r}^B)$$

we get

$$[-\Delta_{R\mathfrak{r}^A} + V^B(R\mathfrak{r}^A)]\,\psi_n^B(R\mathfrak{r}^A) = \epsilon_n^B\,\psi_n^B(R\mathfrak{r}^A); \qquad R \equiv R^{BA}$$

$$[-\Delta_{\mathfrak{r}^A} + V^A(\mathfrak{r}^A) + K_{\mathfrak{r}^A}]\,\psi_n^{A'}(\mathfrak{r}^A) = \epsilon_n^B\,\psi_n^{A'}(\mathfrak{r}^A)$$

$$K_{\mathfrak{r}^A} \equiv \Delta_{\mathfrak{r}^A} - \Delta_{R^{BA}\mathfrak{r}^B}$$

In spite of being generated by the Laplacian, $K_{\mathfrak{r}^A}$ can be handled in a perturbation treatment as any perturbation of a potential. It generates the energies ϵ_n^B belonging to the lattice potential $V^B(\mathfrak{r})$.

There is no doubt that R^{BA} can be calculated by introducing an Ansatz

$$w_B^{(\mu)} \equiv \sum_{l,m,n} c_{lmn}^{\mu} x_A^l y_A^m z_A^n ; \qquad \begin{aligned} \mathfrak{r}^B &= \mathfrak{i} w_B^{(1)} + \mathfrak{j} w_B^{(2)} + \mathfrak{k} w_B^{(3)} \\ \mathfrak{r}^A &= \mathfrak{i} x_A + \mathfrak{j} y_A + \mathfrak{k} z_A \end{aligned}$$

in the defining equation for R^{BA} above and determining the coefficients c_{lmn}^{μ}. In general this makes R^{BA} non-linear.

The deformation of the spherical atomic potentials can be avoided if the Ansatz for R^{BA} transforms the potential shell by shell as was described at the end of the last section. That $K_{\mathfrak{r}^A}$ can really be a weak perturbation is seen by comparing empty lattices.

However, there is one case for which R^{BA} becomes linear. If the plane of a muffin-tin potential is lattice independent and the atomic potentials reduce to delta functions, R^{BA} is determined simply by

$$\mathfrak{i}^B \equiv R^{BA} \mathfrak{i}^A$$

Here R^{BA} is a simple matrix with constant elements

$$R^{BA} = (r_{\mu\nu}); \qquad 1 \leqslant \mu, \nu \leqslant 3$$

We will now obtain an explicit expression for $K_{\mathfrak{r}^A}$ for this case. With the definition

$$\mathfrak{t}_\mu \equiv \begin{pmatrix} r_{\mu 1} \\ r_{\mu 2} \\ r_{\mu 3} \end{pmatrix} \qquad 1 \leqslant \mu \leqslant 3$$

we may write

$$\frac{\partial}{\partial w_B^\mu} = \mathfrak{t}_\mu^+ \nabla_{\mathfrak{r}^A}$$

$$\Delta_{\mathfrak{r}^B} = \Delta_{R^{BA}\mathfrak{r}^A} = \sum_{\mu=1}^{3} (\mathfrak{t}_\mu^+ \nabla_{\mathfrak{r}^A})^2$$

For bcc and fcc we have

$$R^{BA} = \frac{\sqrt[3]{2}}{2} \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}; \qquad \begin{aligned} B &\equiv \text{fcc} \\ A &\equiv \text{bcc} \end{aligned}$$

For example, for the vector

$$\mathfrak{i}^{\text{bcc}} = a_0^{\text{bcc}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

we get

$$\mathfrak{j}^{\,\mathrm{fcc}} = R^{BA}\,\mathfrak{j}^{\,\mathrm{bcc}} = a_0^{\mathrm{bcc}}\,\sqrt[3]{2}\begin{pmatrix}0\\1\\1\end{pmatrix} = a_0^{\mathrm{fcc}}\begin{pmatrix}0\\1\\1\end{pmatrix}$$

a_0^{bcc} and a_0^{fcc} are the half-lattice constants of bcc and fcc respectively. The actual calculation can be carried out with the wave functions generated for lattice A using a three-dimensional de Kronig-Penny [8] like model.

4. Conclusion

Two possibilities are presented for handling the problem of comparing different structures Both can be generalized to non-primitive lattices and compounds. For example it would be very interesting to do explicit calculations for similar lattices such as Zink blende and Wurtzit. A further example would be the treatment of the metallic bond by localized orbitals as in a tight-binding treatment [7] and by perturbation theory.

Not only may $V^B(\mathfrak{r})$ be generated from $V_0^A(\mathfrak{r})$ but also the eigenfunctions of lattice B from that of lattice A, at least approximately. As is shown in [7] the tight-binding orbitals $\varphi_{\nu\mathfrak{k}}$ of a state

$$\psi_{\nu\mathfrak{k}}(\mathfrak{r}) = \frac{1}{\sqrt{N'}}\sum_{\mathfrak{j}} \epsilon^{i\mathfrak{k}\mathfrak{j}}\;\varphi_{\nu\mathfrak{k}}(\mathfrak{r}-\mathfrak{j})$$

are almost lattice independent. So it should be possible to approximately calculate energy values ϵ_n^B using only functions and a potential generated from those of lattice A.

Our rearrangement operator R^{BA} has a corresponding operator P_R for the potential $V^B(\mathfrak{r})$. From

$$V^B(R\mathfrak{r}) = V^A(\mathfrak{r}); \qquad R \equiv R^{BA}$$

it follows

$$P_R V^B(\mathfrak{r}) = V^A(\mathfrak{r})$$

Here P_R connects the functions $V^A(\mathfrak{r})$ and $V^B(\mathfrak{r})$ of the total symmetric representation of two space groups. In general there are P operators which connect the functions belonging to different representations of different groups. It would be a further interesting problem to investigate the connections arising in this way between different groups.

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