A tight-binding derivation of force constants : Application to covalent systems

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Résumé. — Une méthode de calcul de l'énergie électronique totale en fonction des déplacements atomiques se situant dans l'esprit de l'approximation des liaisons fortes est proposée. La somme des énergies à un électron est formellement développée au second ordre en utilisant les fonctions de Green du cristal parfait. La contribution restante est exprimée comme une somme de potentiels de paires. Une application simple au modèle moléculaire des semiconducteurs covalents est décrite. On constate qu'elle conduit déjà à des résultats assez réalistes en ce qui concerne les courbes de dispersion de phonons. La simplicité de la méthode la rend particulièrement intéressante pour l'étude des réarrangements atomiques près des défauts ou surfaces. Elle permet aussi son extension à des cas beaucoup plus compliqués tels que les systèmes amorphes, les composés tétraédriques lacunaires et même les oxydes de métaux de transition.

Abstract. — A method for calculating the total electronic energy as a function of the atomic displacements within the tight-binding approximation is presented. The sum of one electron energies is formally expanded to second order with the help of the perfect crystal Green's functions. The remaining contribution is expressed as a sum of repulsive pair potentials. A simple application to the molecular or bond orbital model of covalent semiconductors is described which already leads to fairly realistic phonon dispersion curves. The simplicity of the method thus makes it particularly suitable for the study of atomic rearrangements near defects or surfaces. It also allows its extension to much more complicated cases, such as amorphous systems, defect tetrahedral compounds and even transition metal oxides.

Introduction. — The tight-binding approximation has been applied with fair success to derive the electronic properties of covalent semiconductors [1-6]. Up to now this has mainly been done for undistorted configurations of perfect crystals, surfaces and mono-vacancies. In all these cases it has been shown that next nearest neighbour models were able to reproduce with good accuracy the predictions of much more elaborate fully selfconsistent calculations [7, 8, 9]. However these calculations will become more and more difficult to perform when the complexity of the system increases. At the moment one of the major problems currently being studied is the selfconsistent prediction of the relaxation and distortions near the vacancy in silicon [10, 11]. It is thus of great interest to devise methods for extending the tight-binding calculations to this sort of problem, the test being the confrontation with the results of the more sophisticated treatments when these become available. The major advantages of such simplified techniques lie in their computational speed which will allow their application to much more complicated problems and also in the simple physical description which they offer.

Our aim in this work is to present one possible way of extending the tight-binding approximation to the study of distorted systems. We choose for this the simplest case i.e. the perfect crystal and show how it is possible to generate the total energy of the system as a function of the atomic displacements using assumptions which are coherent with the tight-binding approximation itself. In the first part we derive a formal expression for the total energy. We write the sum of one-electron energies in terms of the matrix elements of the perturbative potential with the help of the perfect crystal Green's function and then assume for these matrix elements a given dependence on the interatomic distance. We then show that the remaining electrostatic terms can be expressed as sums of pair potentials decreasing fairly rapidly with distance. The second part treats a detailed application to the *molecular* or *bond-orbital* model [2, 3] of covalent semiconductors and

shows that it naturally leads to a simple version of the valence force field model for the phonon dispersion curves [12].

1. The total energy.

We make use of the adiabatic approximation and calculate the change in total energy in the form

$$\delta E = 2 \int_{VB} \delta n(\varepsilon) \, \varepsilon \, d\varepsilon - 1/2 \, \delta \int n(\mathbf{r}) \, V(\mathbf{r}) \, d\tau +$$

$$+ \, 1/2 \, \delta \int n_N(\mathbf{r}) \, V_N(\mathbf{r}) d\tau. \quad (1)$$

The first term represents the change in the sum of one-electron energies where $\delta n(\varepsilon)$ is the change in density of states at energy ε, the integral being performed over the valence band. The second term accounts for the electron-electron terms which have been counted twice and $n(\mathbf{r})$ is the electron density, $V(\mathbf{r})$ the electrostatic potential which it produces. The last term gives the nuclear-nuclear repulsion, $n_N(\mathbf{r})$ being the nuclei density and $V_N(\mathbf{r})$ the corresponding potential. In all cases the symbol δ means that one calculates changes in the quantities due to the atomic displacements.

Let us now describe in more details how one can express the first term in (1) in terms of the atomic displacements. The matrix elements of the perfect crystal Hamiltonian h are $\langle i\alpha \mid h \mid j\beta \rangle$ where the first index denotes the atom and the second one the atomic orbital. For the distorted configuration the Hamiltonian becomes H and the atomic states $\mid i\alpha' \rangle$ are translated from $\mid i\alpha \rangle$ in the same way as the nuclei themselves. The change in one electron energies can thus be calculated using standard perturbation theory, but with an effective perturbation potential W whose matrix elements are defined by

$$\langle i\alpha \mid W \mid j\beta \rangle = \langle i\alpha' \mid H \mid i\beta' \rangle - \langle i\alpha \mid h \mid j\beta \rangle. \quad (2)$$

This is best done using Green's functions. We thus define g the resolvent of the Hamiltonian matrix h and G the resolvent of H. If we restrict to the harmonic approximation we have to expand G to second order in W only which leads to the following expansion of Dyson's equation

$$G = g + gWG$$

$$\simeq g + gWg + gWgW + \cdots. \quad (3)$$

The first term of (1) can be expressed in terms of G and g by the following operations :

a) Integration by parts which gives

$$\int_{VB} \delta n(\varepsilon) \, \varepsilon \, d\varepsilon = - \int \delta N(\varepsilon) \, d\varepsilon \quad (4)$$

where $\delta N(\varepsilon)$ is the change in the total number of states having energy less than ε.

b) Writing the expressions :

$$\delta n(\varepsilon) = - \frac{I}{\pi} \, \mathrm{Tr} \, (G - g)$$

$$\simeq - \frac{I}{\pi} \, \mathrm{Tr} \, (gWg + gWgWg) \quad (5)$$

where I stands for the imaginary part and Tr means that one takes the trace.

Using the fact that g^2 is equal to $- \, dg/d\varepsilon$ and the cyclic property of the trace, equation (5) can be transformed into

$$\delta n(\varepsilon) = \frac{I}{\pi} \frac{d}{d\varepsilon} \, \mathrm{Tr} \, (gW + 1/2 \, gWgW). \quad (6)$$

From equations (4) and (6) the first term in (1) can finally be written

$$- 2 \int_{VB} \delta N(\varepsilon) \, d\varepsilon = -$$

$$- 2 \frac{I}{\pi} \mathrm{Tr} \int_{VB} (gW + 1/2 \, gWgW) \, d\varepsilon. \quad (7)$$

To go further it is necessary to detail the form of the selfconsistent perturbation matrix W. Any atomic displacement will induce a change in the tight-binding parameters and thus a change in the orbital populations. The electron density $n(\mathbf{r})$ of the distorted system can be viewed as the sum of a part $n_0(\mathbf{r})$ corresponding to unchanged populations on the translated orbitals and a second part $\delta n(\mathbf{r})$ resulting from the change in orbital populations. The limit $\delta n(\mathbf{r}) \to 0$ would correspond in a homopolar system to a picture of displaced neutral atoms.

The resulting perturbation matrix is thus the sum of a bare part W_b and a self consistent part δV which is due to $\delta n(\mathbf{r})$. Expression (1) can thus be rewritten :

$$\delta E = - 2 \frac{I}{\pi} \mathrm{Tr} \int_{VB} (gW + 1/2 \, gWgW) \, d\varepsilon$$

$$- 1/2 \int [n(\mathbf{r}) \, V(\mathbf{r}) - n_0(\mathbf{r}) \, V_0(\mathbf{r})] \, d\tau$$

$$- 1/2 \, \delta \int n_0(\mathbf{r}) \, V_0(\mathbf{r}) \, d\tau + 1/2 \, \delta \int n_N(\mathbf{r}) \, V_N(\mathbf{r}) \, d\tau$$

$$(8)$$

where V_0 is the electrostatic potential energy due to the density $n_0(\mathbf{r})$ and $1/2 \, \delta \int n_0(\mathbf{r}) \, V_0(\mathbf{r}) \, d\tau$ is the change in the electron-electron terms due to the displacement of the atomic orbitals when the electron populations are not modified. The second term in the right hand side of equation (8) can be transformed into

$$- 1/2 \int (n_0(\mathbf{r}) \, \delta V(\mathbf{r}) + \delta n(\mathbf{r}) \, V_0(\mathbf{r}) + \delta n(\mathbf{r}) \, \delta V(\mathbf{r})) \, d\tau$$

$$(9)$$

where the first two terms are equal which leads to :

$$- \int n_0(\mathbf{r}) \, \delta V(\mathbf{r}) - 1/2 \int \delta n(\mathbf{r}) \, \delta V(\mathbf{r}) \, d\tau \ . \quad (10)$$

One can also express (10) in terms of the Green's functions noticing that

$$\int n_0(\mathbf{r}) \, \delta V(\mathbf{r}) \, d\tau = - 2 \frac{I}{\pi} \, \mathrm{Tr} \int_{VB} g \, \delta V \, d\varepsilon$$

$$\int \delta n(\mathbf{r}) \, \delta V(\mathbf{r}) \, d\tau = - 2 \frac{I}{\pi} \, \mathrm{Tr} \int_{VB} (G - g) \, \delta V \, d\varepsilon \ . \quad (11)$$

To first order in W the difference $G - g$ occurring in (11) is equal to gWg. Injecting (11) into (8) thus gives for the total change in energy :

$$\delta E = - \frac{2 I}{\pi} \mathrm{Tr} \int_{VB} (g W_b + 1/2 \, g W g W_b) \, d\varepsilon$$

$$- 1/2 \, \delta \int n_0(\mathbf{r}) \, V_0(\mathbf{r}) \, d\tau$$

$$+ 1/2 \, \delta \int n_N(\mathbf{r}) \, V_N(\mathbf{r}) \, d\tau \ . \quad (12)$$

In (12) only one term now contains the complete self consistent potential W. In a linear screening formulation which is adequate for our purpose this one is related to W_b through the matrix relation

$$W = \varepsilon^{-1} \, W_b \quad (13)$$

where ε^{-1} is the inverse dielectric matrix in our tight-binding scheme. Here we shall not attempt to calculate it but will make the approximation of negligible screening effects, i.e. will take ε^{-1} equal to the unit matrix. This approximation is certainly less severe for diamond than for silicon and germanium where screening effects become more and more important. It will presumably be more valid for long wavelength vibrations than near the Brillouin zone limits where we shall probably miss the long-range electrostatic effects leading to the flattening of the transverse acoustic mode which is observed in Si and Ge.

With this assumption δE is still given by equation (12) where W is simply replaced by its bare part W_b. The first term in (12) then becomes simply the band structure energy of the displaced system where the electrostatic potential is due to neutral atoms. It is now interesting to separate from this band structure energy the contribution of the diagonal terms and add it to the last two terms. The expression for ΔE becomes

$$\delta E = - \frac{2 I}{\pi} \mathrm{Tr} \int_{VB} d\varepsilon (g W_b' + 1/2 \, g W_b' \, g W_b') +$$

$$+ \sum_{ij}' (f(R_{ij}) - f(R_{ij}^0)) \quad (14)$$

W_b' is the non-diagonal part of W_b and the second term corresponds to the electrostatic interaction energy of the system of neutral atoms which can be expressed as a sum of repulsive pair potentials $f(R_{ij})$ (R_{ij}^0 is the corresponding distance in the perfect crystal); $\sum'$ means that one sums over pairs.

The matrix elements of W_b' are thus the changes in the usual tight-binding resonance integrals, calculated with the potential due to neutral atoms. In the case of « s » atomic orbitals, with no directional properties these resonance integrals are smooth decreasing functions of the interatomic distance R_{ij}. For « p » or « d » orbitals however this is no longer true and the relative orientation of the orbitals with respect to the bond direction will be modified. Thus in this case $\langle i\alpha' \mid W_b' \mid j\beta' \rangle$ will have two contributions : one due to the change in interatomic distance, the other one being an angular contribution. In the following we shall simulate the change in interatomic distance by an exponential variation which is a valid procedure in a narrow range of values. The same is true for $f(R_{ij})$ which is the repulsive pair potential. All these quantities could in principle be calculated, but this would require the knowledge of the Wannier functions whose asymptotic behaviour is different from that of the free atom orbitals.

2. Application to the molecular description of covalent semiconductors.

— Equation (14) gives use the general framework to calculate the phonon dispersion curves for a given covalent system. We shall give here an illustration on a very simple but interesting example, i.e. the *molecular* or *bond orbital* description of a covalent semiconductor.

For this we first choose to work in an sp atomic basis. We retain only the nearest neighbours interactions. In the usual two centre approximation [14] we have thus only five independent parameters which can influence the band structure. One is the promotion energy $E_p - E_s$, the difference between the s and p intraatomic terms in the solid. The four other interatomic parameters are β_{ss}, $\beta_{\sigma\sigma}$, $\beta_{\sigma s}$ and $\beta_{\pi\pi}$ in the usual notation [14]. As is often done in such contexts [7, 8] we assume them to have the same exponential dependence with interatomic distance R which we write

$$\beta_{lm} = \beta_{lm}^0 \exp - p(R - R_0) \quad (15)$$

l, m standing for s, σ or π. For the moment p is an unknown parameter which we could determine by some fitting procedure. The β_{lm}^0 are the perfect crystal values which can be obtained from band structures. The fact that we take the same exponential dependence for all β_{lm} is a constraint which could be released in a more refined model, but at the expense of simplicity.

In principle (14) and (15) allow to calculate the sum of one electron energies. For the second term in (14) we choose a Born-Mayer form with

$$f(R) = f(R_0) \exp - q(R - R_0) \quad (16)$$

for nearest neighbours only. Thus we have all quantities necessary to perform a full calculation of the perfect crystal force constants. However it is quite instructive to simplify things a little more considering the *molecular* or *bond orbital* limit [2, 3]. In this case one considers only one non vanishing β^0 connecting nearest neighbour's sp^3 orbitals belonging to the same bond. This is realized if the following relationship exists for the β^0_{lm}

$$\beta^0_{ss} = -\beta^0/4; \qquad \beta^0_{\sigma s} = -\frac{\sqrt{3}}{4}\beta^0$$

$$\beta^0_{\sigma\sigma} = -\frac{3}{4}\beta^0; \qquad \beta^0_{\pi\pi} = 0 \qquad (17)$$

where β^0 is taken to be positive. One also neglects the promotion energy $E_p - E_s$. It is easy to show that the first correction to this is of order

$$\left| \frac{E_p - E_s}{\beta_0} \right|^2 .$$

In this approximation the perfect crystal Green's functions are extremely easy to calculate. To do this it is interesting to make a change of basis and work in terms of bonding $|B\rangle$ and antibonding $|A\rangle$ states at each bond, these states being just the sum and difference of sp^3 hybrids belonging to the same bond. In this basis the perfect crystal Hamiltonian becomes

$$h = -\beta^0 \left\{ \sum_B |B\rangle\langle B| - \sum_A |A\rangle\langle A| \right\} \qquad (18)$$

the sum being performed over all bonding and antibonding states. The resolvent operator g corresponding to h is thus given by

$$g = \lim_{\eta\to 0^+} \left(\sum_B \frac{|B\rangle\langle B|}{\varepsilon + \beta^0 + i\eta} + \sum_A \frac{|A\rangle\langle A|}{\varepsilon - \beta^0 + i\eta} \right). \qquad (19)$$

A straightforward application of (14) thus leads to :

$$\delta E = 2 \left[\sum_B \langle B | W'_b | B\rangle + \right.$$

$$\left. + \frac{1}{2\beta^0} \sum_{B,A} |\langle B | W'_b | A\rangle|^2 \right]$$

$$+ \sum_{ij}{}' f(R_0)\{ \exp - q(R_{ij} - R^0_{ij}) - 1 \} \qquad (20)$$

$\sum_{ij}'$ being carried out over pairs of nearest neighbours.

To go further one has now to calculate the matrix elements of W'_b and expand them to second order in the atomic displacements. For this we employ formula (2) and express the matrix elements occurring in (20) in terms of $\langle s' | W'_b | s'\rangle$, $\langle s' | W'_b | \sigma'\rangle$ .... In doing this, as we have already mentioned, care must be taken that terms such as $\langle s' | H | \sigma'\rangle$ correspond to a distorted bond and that $|\sigma'\rangle$ is not the p state along that new bond. One has then to express $|\sigma'\rangle$ in terms of the $|\sigma\rangle$, $|\pi\rangle$ ... corresponding to this new bond. The same is true for all p states.

Once this is done one can use (15) to account for changes in interatomic distances. Finally the last term in (20) can also be expanded to second order in the atomic displacements.

We do not give here the details of the second order expansion of (20) which have not much interest but simply write down the final result which turns out to be

$$\delta E = \sum_{ij}{}' (2p\beta^0 - qf(R^0)) \left(d_{ij} + \frac{u_{ij}^2 - d_{ij}^2}{2 R^0} \right) +$$

$$+ \left(\frac{q^2}{2} f(R^0) - p^2 \beta^0 \right) d_{ij}^2 + \frac{\beta^0}{4} \sum (d\theta)^2 . \qquad (21)$$

Here the notations are the following : if $\mathbf{u}_i$ and $\mathbf{u}_j$ are the displacement vectors of atoms i and j and if $\mathbf{r}_{ij}$ is the unit vector joining atom j to i, then

$$d_{ij} = (\mathbf{u}_i - \mathbf{u}_j).\mathbf{r}_{ij} . \qquad (22)$$

On the other hand u_{ij} is given by

$$u_{ij} = |\mathbf{u}_i - \mathbf{u}_j| \qquad (23)$$

finally $\sum (d\theta)^2$ is the sum over changes in the angles θ between two adjacent bonds.

Equation (21) can be applied to the calculation of the equilibrium interatomic distance. This occurs when the following condition is satisfied

$$2p\beta^0 = qf(R^0). \qquad (24)$$

Applying this to equation (21) one finds the second order expansion

$$\delta E = pq(1 - p/q) \beta^0 \sum_{ij}{}' d_{ij}^2 + \beta^0/4 \sum (d\theta)^2 . \qquad (25)$$

This is an extremely simple and attractive expression which reduces to the simplest form of the valence force field model with two force constants k_{rr} and k_θ. The positive point here is that we can predict an order of magnitude for these force constants, once the electronic structure and thus β^0 is known. It is also true that equation (25) is too naive and can only serve for order of magnitude estimates or as an illustration of our more general expansion of section 1.

A first check of the interest of expression (25) is provided by the predicted value of the elastic constants. The combination of these which requires the minimum number of electronic parameters is $C_{11} - C_{12}$ which is given by

$$C_{11} - C_{12} = \frac{3\sqrt{3}}{4} \frac{\beta^0}{R^3} . \qquad (26)$$

One can evaluate β^0 from the expressions of the electron interatomic resonance integrals given by Harrisson [5] which lead to the general relationship

$$\beta^0 = 4.37 \frac{\hbar^2}{mR^2} . \qquad (27)$$

Table I. — *Theoretical and experimental values of the elastic constant $C_{11} - C_{12}$ and the transverse acoustic mode frequency ω_{TA} at the X point.*

	$C_{11} - C_{12\,cal.}$ 10^{12} dyn/cm^2	$C_{11} - C_{12\,exp.}$ 10^{12} dyn/cm^2	$\omega_{TA}(X)_{exp.}$ 10^{12} hz	$\omega_{TA}(X)_{exp.}$ 10^{12} hz
C	7.86	9.5	27	24.1
Si	0.96	1.01	7.5	4.49
Ge	0.78	0.8	4.3	2.39

The corresponding results are given in table I and are in very good agreement with the experimental values. They are also comparable to the values of a numerical tight-binding calculation showing that our simple model gives the essential contribution to $C_{11} - C_{12}$ [15]. One can try to do the same for $\omega_{TA}(X)$ the frequency of the transverse acoustical mode at the X point of the Brillouin zone. This is given by

$$M\omega_{TA}^2(X) = \frac{6\,\beta^0}{R^2} \qquad (28)$$

and can also be determined using (27). The results are given on table I and are quite good for diamond but much less so for Si and Ge where ω_{TA} is found to be too high. However in these two cases the agreement with the results of reference [15] remains correct.

To go further it is necessary to evaluate p and q. This can be done by a fitting procedure from two experimental quantities. The first one is taken to be

$$\frac{C_{11} + 2\,C_{12}}{3} = \frac{pq(1 - p/q)\,\beta^0}{2\sqrt{3}\,R} . \qquad (29)$$

A second combination of p and q is the cohesive energy per atom which in our model is given by

$$E_{coh} = 4\,\beta^0(1 - p/q) - (E_p - E_s) . \qquad (30)$$

Here we do not neglect $E_p - E_s$ which comes as a first order correction. Taking for E_s and E_p in (30) the free atom values [16] and the experimental values of $\dfrac{C_{11} + 2\,C_{12}}{3}$ one obtains for pR, qR the results of table II. These are again extremely reasonable. One finds $pR \sim 2$ which is consistent with formula (27) as regards the logarithmic derivative. One also finds qR equal to about twice pR which should become rigourously true in the asymptotic limit.

Table II. — *Values obtained for the parameters pR_0 and qR_0.*

	C	Si	Ge
pR^0	2.55	2.31	2.08
qR^0	3.55	4.28	4.16

To end this application we have drawn on figure 1 the phonon dispersion curves in reduced units ω/ω_M

compared to the experimental values for silicon. The overall results are quite correct, the main discrepancy being the lack of flattening of the transverse acoustic modes. This certainly comes from our two major assumptions. i.e. the *molecular* approximation and also the neglect of screening effects. It would then be worth improving the model in these two directions.
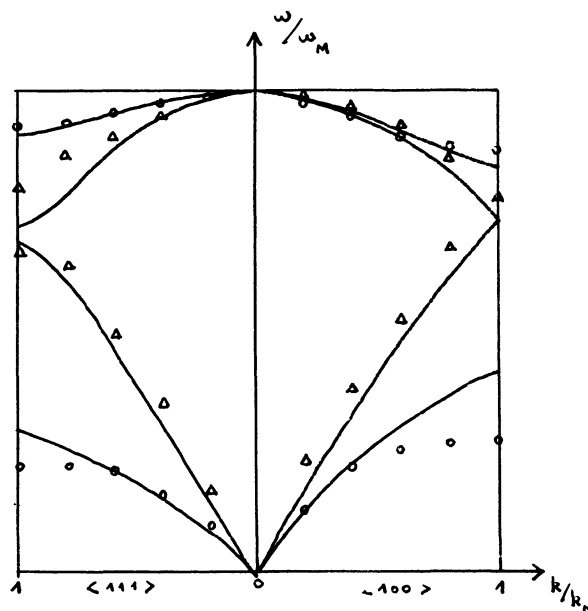

Fig. 1. — Phonon dispersion curves in reduced coordinates. The O and $\triangle$ are the Si experimental values.

3. **Conclusion.** — We have derived a systematic method of calculating the total energy in the tight-binding approximation as a function of the atomic displacements. We have worked out an application to the *molecular* or *bond orbital* limit where we obtain the most simple version of the valence force field model for phonons. We obtain correct order of magnitudes for the parameters but the model as it stands fails to describe the flattening of the transverse acoustic phonon frequencies a fact which was expected in view of our neglect of screening effects. It then seems that an extension of this work is worth pursuing to improve the model with the aim of applying it to the problem of atomic rearrangements near defects or surfaces and to more complicated systems.

It is to be noted that a similar technique has already been used for transition metals but using a method of moments restricted to the second moment [17-19]. Within this context angular terms such as described here are absent but should appear in a complete Green's function treatment of the d orbitals. It should then be worth reinvestigating this problem taking these terms into account.

Note : At the time this paper was just written an analysis of the relaxation and reconstruction near semiconductor surfaces based on similar ideas was published [20]. This consists in a direct numerical calculation using a nearest neighbours' approximation and does not involve Green's functions.

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