

ELECTRONIC STRUCTURE OF A ONE DIMENSIONAL DISORDERED SYSTEM

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RESUMEN

El método de las superceldas y la aproximación local propuestos por Butler y Kohn dan lugar a singularidades de Van Hove en la densidad de estados. Estas singularidades provienen del carácter periódico de la teoría y deben ser tratadas correctamente. Con este objetivo se escoge como test un modelo unidimensional con potenciales delta. En el trabajo se muestra que el método converge rápidamente una vez que las singularidades son correctamente alisadas sin destruir las estructuras existentes en la densidad de estados de la aleación.

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ABSTRACT

The supercell method and local approximation proposed by Butler and Kohn gives rise to Van-Hove singularities in the density of states. In order for this method to work these singularities, which arises from the periodic nature of the theory, must be treated correctly. To this end a one-dimensional delta function model was chosen. We show that, once the singularities are properly smoothed so as not to interfere with the existing structure in the density of states the supercell method converges rapidly, as a functions of the unit cell size.

I. INTRODUCTION

Theorists have always been fascinated with problems in one dimension, due to their simplicity, analyticity and solubility [1].

In the case of electronic structure the well-known treatment of Kronig and Penney [2,3] and their replacement of the scattering potentials by delta fraction forms, contains all the necessary physics. Kramers, Saxon and Hunter [4,5] were the first to consider disordered structures, and Luttinger [6] gave a proof of the Saxon and Hunter conjecture on the disjointness of the special function. Dyson's solution of the characteristic function for the linear chain problem, led directly to the elegant and compact treatment of Schmidt [7]. With

the numerical work of Dean [8], the discussion of Lifschitz [9], and the localization theorem of Mott and Tuose [10], the essential features of the problem were largely completed.

Our main reason for re-examination this problem is, that neither Schmidt's method nor Deans' treatment is readily generalizable to considering electronic structure in three dimensions. In our discussion of Ni-Cu alloys [11], we showed that the local approximation of Kohn et al. [12,13], yielded a rapidly convergent treatment of the Ni-Cu system. Such a transition metal alloy system is, however, yet sufficiently complex that we wished to apply the same detailed approach to the well studied one dimensions, are Kohn and Butler to further illuminate the local approximation. Inter alia we have found that Schmidt's method does not yield either a simpler or faster computational algorithm. In fact, near the extremes of the concentration regime (whose difficulty was explicitly pointed out in Schmidt's paper) the convergence near the extremes becomes logarithmic. Agacy and Borland [14], have considered A B alloys of concentration $x=0,5$ using Schmidt's method.

Their main focus was to show that the electronic spectra of the A B disordered alloy was as spectrally rich using Schmidt's method as Dean had found by numerical methods in the case of the linear chain.

They found it difficult to give a detailed description of the convergence of the Schmidt method - but an examination of their results shows sufficient convergence to unambiguously identify the existence of spectral richness.

An outline of our presentation is as follows. In section two, we briefly review for completeness the supercell model and local approximation of Kohn et al. This is followed in section three by the mathematical techniques developed for the study of the one-dimensional model, the numerical solutions of which are presented in section four. In section five we present our conclusions.

II. Model

For completeness, we review briefly the supercell model as originally proposed by Butler and Kohn. The basis for the supercell approximation is that in a disordered system, the physical properties depend only on the conditions in a small neighborhood $|\vec{r}' - \vec{r}| < R$, where R is of the order of the mean free path. The effects of the environment at larger distances fall off exponentially with distance. Thus the properties of an infinite disordered system can be calculated by averaging over an ensemble of small neighborhoods. In order to implement this idea we choose a unit cell of N atoms and repeat

this cell periodically as if we have a perfect crystal. In the binary case, each site of the unit cell is populated with either an A or B type atom, repeated periodically to form a crystal and a density of states (DOS) for this configuration D_c is calculated. After all possible configurations have been calculated, the final DOS for the disordered system is approximated by the average over all configurations.

The Hamiltonian for such an ensemble of delta function potentials is

$$\hat{H} = \sum_{\alpha=-\infty}^{\alpha=\infty} V_{\alpha} \delta(y - \alpha a) - \frac{d^2}{dy^2} \quad (1)$$

where 'a' is the lattice constant and V_{α} is an arbitrary potential which is equal to V_A or V_B .

Following the above prescription the DOS for the alloy is taken to be

$$D(E) = \lim_{N \rightarrow \infty} \sum_c W_c D_c(E) \quad (2)$$

where D_c is the DOS for a particular configuration c , containing N atoms/cell. The statistical weight W_c for a binary system for which all configurations are equally probable is

$$W_c = x^N (1-x)^{N-N_A} \quad (3)$$

where x is the concentration and N_A is the number of A atoms.

Equation (2) is to be solved for N large enough such that $D(E)$ is no longer affected by the unit cell size.

In the next section, we describe a method used for obtaining an analytic solution of Schrodinger's equation for each configuration and the DOS associated with it.

III. Analytical solutions

A) Wave function

Let us choose a one-dimensional crystal with a unit cell of length l containing N equidistant atoms a distance 'a' apart with constant potential of amplitude V_n ($n=1,2,\dots,N$) at each site (see fig. 1). For this system, we know the following:

1. The wave function can be written as [7]

$$\Psi(y) = A_n e^{i\epsilon y_n} + B_n e^{-i\epsilon y_n} \quad (4)$$

for $(n-1)a < y < na$ and where

$$y_n = y - a(n - \frac{1}{2}) \quad (5)$$

$$\epsilon = |E|$$

2. There exists a relation between the coefficients A_n , B_n corresponding to the solution of the wave function to the left and right of each delta function, of the form

$$\begin{pmatrix} B_{n+1} \\ A_{n+1} \end{pmatrix} = M_n \begin{pmatrix} B_n \\ A_n \end{pmatrix} \quad (6)$$

where

$$M_n = \begin{pmatrix} \left(1 + \frac{V_n}{2\epsilon}\right) e^{-\epsilon a} & \frac{V_n}{2\epsilon} \\ -\frac{V_n}{2\epsilon} & \left(1 - \frac{V_n}{2\epsilon}\right) e^{\epsilon a} \end{pmatrix} \quad (7)$$

and where $V_n < 0$. For the case where $V_n > 0$ it suffices to replace all $\epsilon \rightarrow i\epsilon$ and change the sign of V_n .

Once any two of the coefficients are known say A_1 and B_1 the wave function (eq. 4) can be found at any point y . Using the boundary conditions

$$\Psi_1(0) = 1 \quad (8)$$

$$\frac{d\Psi_1}{dy}(0) = 0$$

we get

$$\begin{aligned} A_1 &= \frac{1}{2} e^{i\epsilon a/2} \\ B_1 &= \frac{1}{2} e^{-i\epsilon a/2} \end{aligned} \quad (9)$$

On the other hand, if the wave function satisfies the boundary conditions

$$\Psi_2(0) = 0 \quad (10)$$

$$\frac{d\Psi_2}{dy}(0) = 1$$

we get

$$A_1 = \frac{1}{2i\epsilon} e^{i\epsilon a/2} \quad (11)$$

$$B_1 = -\frac{1}{2i\epsilon} e^{-i\epsilon a/2}$$

B) Energy bands

Following Kramers [4] the energy bands for a one dimensional system, having an arbitrary potential can be expressed as

$$\cos(k\ell) = \mu(E) \quad (12)$$

where k is the wave vector, ℓ the length of the unit cell and $\mu(E)$ is of the form

$$\mu(E) = \frac{1}{2} \left\{ \Psi_1(E, \ell) + \frac{d}{dy} \Psi_2(E, \ell) \right\} \quad (13)$$

Using equations 4, through 11 leads us to the following relation:

$$\mu(E) = \frac{1}{2} \text{Sp} m_N \quad (14)$$

where

$$m_N = M_N M_{N-1} \dots M_2 M_1 \quad (15)$$

For one atom/cell eq. (14) reduces to the familiar

Kronig-Penney equation [2]

$$\cos(ka) = \cos(\epsilon a) + \frac{V}{2\epsilon} \sin(\epsilon a) \quad (16)$$

Furthermore, it can be shown that eq. (15) can be written in a more compact form which facilitates the calculation when the number of atoms increases. We have.

$$m_N = \begin{pmatrix} \sum_{\alpha=-N}^N Q_{\alpha}^N e^{\alpha\epsilon a} & \sum_{\alpha=-N}^N S_{\alpha}^N e^{\alpha\epsilon a} \\ \sum_{\alpha=-N}^N R_{\alpha}^N e^{\alpha\epsilon a} & \sum_{\alpha=-N}^N T_{\alpha}^N e^{\alpha\epsilon a} \end{pmatrix} \quad (17)$$

where the coefficients satisfy the following recurrence relations

$$Q_{\alpha}^P = Q_{\alpha-1}^{P-1} + \frac{V_P}{2\epsilon} \left[Q_{\alpha-1}^{P-1} + R_{\alpha}^{P-1} \right]$$

$$R_{\alpha}^P = R_{\alpha+1}^{P-1} - \frac{V_P}{2\epsilon} \left[Q_{\alpha}^{P-1} + R_{\alpha+1}^{P-1} \right]$$

$$S_{\alpha}^P = S_{\alpha-1}^{P-1} + \frac{V_P}{2\epsilon} \left[S_{\alpha-1}^{P-1} + T_{\alpha}^{P-1} \right]$$

$$T_{\alpha}^P = T_{\alpha+1}^{P-1} - \frac{V_P}{2\epsilon} \left[S_{\alpha}^{P-1} + T_{\alpha+1}^{P-1} \right] \quad (18a)$$

and where $2 \leq P \leq N$, $-N \leq \alpha \leq N$. The initial values as defined by $m_1 = M_1$ (see eq. 7) are

$$Q_{-1}^1 = 1 + \frac{V_1}{2\epsilon} \quad Q_0^1 = 0 \quad Q_1^1 = 0$$

$$R_{-1}^1 = 0 \quad R_0^1 = -\frac{V_1}{2\epsilon} \quad R_1^1 = 0 \quad (18b)$$

$$S_{-1}^1 = 0 \quad S_0^1 = \frac{v_1}{2\varepsilon} \quad S_1^1 = 0$$

$$T_{-1}^1 = 0 \quad T_0^1 = 0 \quad T_1^1 = 1 - \frac{v_1}{2\varepsilon}$$

Again eqs. (17) and (18) can be written for $v_n > 0$ simply by letting $\varepsilon \rightarrow -i\varepsilon$ and changing the sign of v_n .

C) Density of states (DOS)

In general, the DOS in one-dimension can be written as

$$D(E) = \frac{2}{\pi} \frac{dk}{dE} \quad (19)$$

or in terms of the Green function

$$D(E) = -\frac{1}{\pi} \text{Im} G(E) \quad (20)$$

Equation (19) takes into account a factor of 2 for spin degeneracy and another factor of 2 for time-reversal symmetry ($E(-k) = E(k)$).

Substituting equation (12) into equation (19) gives us directly in terms of $\mu(E)$ without having to calculate the energy bands. We have

$$D(E) = \text{Re}[F(E)] \quad (21a)$$

where

$$F(E) = -\frac{2}{\pi l} \frac{\mu'(E)}{\sqrt{1-\mu^2(E)}} \quad (21b)$$

The right hand side of equation (21a) is always positive as can be seen from the following argument. Rewriting $F(E)$, and again making use of equation (12) gives

$$F(E) = -\frac{2}{\pi l} \frac{\mu'(E)}{\sin(\arccos(\mu(E)))} \quad (21c)$$

$$= -\frac{2}{\pi l} \frac{\mu'(E)}{\sin(k(E)l)} \quad (21d)$$

Each time we pass from one band to the next the $\sin(k(E)l)$ changes sign, as well as the derivate of μ such that the product is always positive. This is because each energy band is defined to within a multiple of π .

$F(E)$ gives us the density of states for the allowed energies ($-1 \leq \mu(E) \leq 1$) and becomes imaginary for the forbidden energies. At the zone boundaries where $\mu(E) = \pm 1$, we obtain the Van-Hove singularities which are infinite.

It is of physical interest to show the relation between the function $F(E)$ and the Green function of our system, that is that equation (20) is satisfied rigorously. We show in detail in appendix A that

$$G(E) = -i \pi F(E) \quad (22)$$

with $F(E)$ as defined by equation (21b).

D) Treatment of singularities

These singularities, which are due to the periodic approximation of the supercells, are not present in the

real alloy and must be treated in a manner such that the real structure if it exists in the DOS can be extracted correctly. To this end we have convolved D with a Lorentzian, which gives rise to a "smoothed density of states" D_s . The width of the Lorentzian γ must be chosen such that the infinite Van-Hove singularities become small and finite but that the detail in D is not washed out. The calculation of the Lorentzian convolution

$$D_s(E) = \frac{\gamma}{\pi} \int_{-\infty}^{\infty} \frac{D(E')}{(E'-E)^2 + \gamma^2} dE' \quad (23)$$

can be simplified, by taking into account the analytic properties of $F(E)$. We have used that equation (23) can be replaced by

$$D_s(E) = R_e [F(E + i\gamma)] \quad (24)$$

E) Schmidt's Solution

For completeness we briefly review the Schmidt's method (which we have programmed) and for which in the limit of an infinite chain of delta function potentials gives exactly the integrated DOS $D_{int}(E)$.

$$D_{int}(E) = \lim_{n \rightarrow \infty} W^{(n)}(-\pi) \quad (25)$$

where

$$W^{(n)}(\varphi) = \frac{1}{n+1} \sum_{i=0}^n W_i(\varphi) \quad (26)$$

$$W_{i+1}(\varphi) = \sum_j p^{(j)} W_i(T_j^{-1}(\varphi)) - W_i(-\pi) \quad (27)$$

and $W_0(\varphi)$ is any function which satisfies

$$W_0(\varphi + 2\pi) = W_0(\varphi) + 1 \quad (28)$$

$$W_0(0) = 0$$

$W_0(\varphi)$ is monotonically nondecreasing in φ

T_j^{-1} is the operator defined by

$$T_j^{-1}(\varphi) = 2 \operatorname{arctg} \left\{ 2\alpha_j - \frac{1}{\operatorname{tg}(\varphi/2)} \right\} \quad (29)$$

$$T_j^{-1}(0) = -\pi \quad (30)$$

$$\alpha_j = -\cosh(\epsilon a) + \frac{V_j}{2\epsilon} \sinh(\epsilon a) \quad (31)$$

and $p^{(j)}$ is the concentration of the j^{th} potential.

Starting with the value $W_0(\varphi) = \varphi/2\pi$ we have solved these equations, the result and convergence of which will be discussed in the next section.

IV. Results

We have programmed equation (24) using the formalism of the previous section. The numerical error in the program was of the order of 10^{-14} . This was the r.m.s. difference in D between the results for 8 atoms/cell and 1 atom/cell for the pure system ($V_A = V_B$). In all of our calculations we have restricted ourselves to the first band.

Plot of $E(k)$ for $N = 1, 2, 3$ identical atoms/cell is shown in figure (2). As the size of the cell in real space

is enlarged, the size of the Brillouin zone is reduced inversely giving rise to new planes of symmetry. At these planes the bands become degenerate as they are folded back towards Γ . When the potentials V_A and V_B are different many of these bands are split resulting in new Van-Hove singularities. There exists a maximum of 2^N singularities for each band. For $V_n > 0$, the upper band boundaries are independent of the potential strength while for $V_n < 0$ the lower band boundaries are independent of the potential strength.

The DOS was calculated for the following pairs of potentials $V_A = 2$, $V_B = 3\pi$, $V_A = 2$, $V_B = -4$ and $V_A = 2V_B = 2$. The potential $V_A = 3\pi$ corresponds to the value used by Kronig-Penney, while the potentials of second case correspond to those of Butler and Kohn. The values of γ (smoothing factor) chosen were $\gamma = 5.10^{-2}$, 10^{-2} , 10^{-1} . These values cover the range of spacings between successive singularities, 10^{-2} Ryd for $N=6$, 10^{-3} Ryd for $N=8$. This value for $N=6$ also coincides with the average distance of 10^{-2} Ryd between two successive structure values in the integrated DOS of Schmidt.

We have calculated the DOS for chains up to 13 atoms/cell.

In figure (3) we show the DOS for 1, 3 and 10 atoms/cell.

We have used equation (25) to obtain the integrated DOS as proposed by Schmidt. In figure (4) we show a plot

of the integrated DOS at two different energies as a function of n , the number of iterations used in equation (25). In order to estimate the convergence of this method in the limit of large n we have fit the last four points (10-13) in a least square sense

$$\text{r.m.s.} = \sum_{n=10}^{13} \left[D_n - D \left(1 - \frac{1}{n+1} \right) \right]^2 \quad (32)$$

since we expect a $1/n$ convergence. Minimizing the r.s.m. difference with respect to D

$$D = \frac{\sum_{n=10}^{13} D_n \left(1 - \frac{1}{n+1} \right)}{\sum_{n=10}^{13} \left(1 - \frac{1}{n+1} \right)^2} \quad (33)$$

produced a 2 % error for $E = 0.01$ Ryd and 0.5 % for $E = 3.0$ Ryd. The solid lines of figure (4) show the r.m.s. curve obtained in this manner.

Our analysis of the data generated for all cases was divided as follows. As a function of the number of atoms/cell and for a fixed value of γ we calculated the correlation matrix.

$$C_{NN'} = \frac{\int_{E_1}^{E_2} D_S^{(N)}(E) D_S^{(N')}(E) dE}{\left[\int_{E_1}^{E_2} D_S^{(N)}(E)^2 dE \cdot \int_{E_1}^{E_2} D_S^{(N')}(E)^2 dE \right]^{1/2}} \quad (34)$$

were E_1 and E_2 are the upper and lower band limits. In figure (5) we have plotted the coefficient $C_{\theta N}$ as a function of N .

Secondly, we calculated the moments to high precision (10^{-15}) using the following formula

$$\mu_P^N = \int_{E_1}^{E_2} L_P(\alpha E - \beta) D_S^{(N)}(E) dE \quad (35)$$

where L_P are the Legendre polynomials and where

$$\alpha = \frac{2}{E_2 - E_1} \quad ; \quad \beta = \frac{E_2 + E_1}{E_2 - E_1} \quad (36)$$

(see fig. 6)

Thirdly, we calculated

$$\sigma_N = \int_{E_1}^{E_2} |D_S^{(N)}(E) - D_S^{(N-1)}(E)| dE \quad (37)$$

(see fig. 7)

We have presented only the results for the concentration 50 %, however these results hold for all concentrations for $V_n > 0$.

The rapid decrease in σ_N (fig. 7) shows the power of this method. It is interesting to compare this result with the case of nearly free electrons. In appendix B we show that the change in the DOS for a system of

nearly free electrons (nor exactly our case) as a function of a perturbing potential $V(r')$ a distance R away from the center of the supercell varies as

$$\frac{\delta D_S(E)}{\delta V(r')} = - \frac{\pi^2}{32 R^2} \sin(2V R) e^{-2uR} \quad (38)$$

where

$$u = \left[\frac{(\gamma^2 + E^2)^{\frac{1}{2}} - E}{2} \right]^{\frac{1}{2}}$$

An estimation of the convergence can be seen by examining the three limiting cases:

$$E = 0 \quad , \quad u = \sqrt{\frac{\gamma}{2}} \quad (39)$$

$$E \ll -\gamma \quad , \quad u = \sqrt{|E|} \quad (40)$$

$$E \gg \gamma \quad , \quad u = \frac{\gamma}{2\sqrt{E}} \quad (41)$$

where γ is the width of the Lorentzian.

Using our values of $5 \cdot 10^{-2}$ for γ and 6 for R we obtain a convergence of the order of $5 \cdot 10^{-3}$ for $E > 0$ and 10^{-15} for $E < 0$.

The rate of convergence can also be estimated from our moment calculation (see fig. 6). For all N the first moment is converged to 7 decimal places. With a supercell of 6 atoms the 8th moment is converged to two decimal places.

Likewise the curve (5) of correlation coefficients shows that the DOS converges as the number of atoms is increased ($C_8 = 0.96$) and secondly that there is a higher correlation between supercells of larger numbers of atoms.

Let us now compare the supercell method with that of Schmidt. The results of figure (4) indicates that we would need at least 200 iterations to obtain milliryberg accuracy in the integrated DOS. This precision is needed if we are to differentiate numerically to obtain a DOS accurate to within a hundredth of milliryberg. The computer time on a very fast machine (IBM 370/168) is of the order 50 secs for 13 iterations as compared to 1.5 secs for a 6 atom/cell supercell calculation, both these times being for a fixed energy. Since we have to differentiate in the Schmidt case to obtain the DOS we need to calculate many more points than for the supercell. Moreover the Schmidt calculation has to be repeated for each concentration, whereas in the supercell model, once all the configurational DOS are calculated, it is a matter of milliseconds to obtain the DOS for any concentration. Thus the supercell method is more desirable in terms of the work required to achieve a given precision in the DOS, a result also verified in the work of Butler and Kohn, where for the integrated DOS a supercell of 6 atoms/cell was also sufficient.

Finally a few words should be mentioned about the choice of γ when smoothing. The larger the value of γ the more rapid the convergence. However if γ is larger than the minimum distance between any two singularities in the structure, a part of the existing structure in the DOS will be wiped out. The hump formed about the infinite singularities after smoothing should be considered as a part of the actual DOS since in the real solid there are local regions which resemble the periodic supercell and thus make large contributions to D at certain energies.

V. Summary. Concluding remarks

The properties of an infinite crystal with substitutional disorder can be understood by considering periodic crystals built up out of large cells with a fixed configuration of atoms inside each cell. For given concentrations of the constituents, each possible configuration inside the supercell has associated with it a weight, giving the frequency of the configuration in an infinite disordered crystal. By taking a weighted average over all possible configurations, a density of states (DOS) can be defined for each cell size. In principle, it is clear that in the limit of large cell sizes one will obtain the DOS for the disordered system, but the practicability of the method will be determined by the rate of convergence.

To investigate the rate of convergence for one dimensional systems, we have calculated the averaged density

of states for chains of up to 13 atoms. The potential was taken as a sequence of equidistant delta-functions, spaced by one atomic unit and with strengths of $V_A = 2V_B = 3\pi$, $V_A = 2V_B = -4$, $V_A = 2V_B = 2$ Rydberg. The effect of a single delta-function on the wave function is described by an energy dependent 2x2 transfer matrix and the whole chain of N atoms by a product of N matrices. The energy spectrum of the periodic crystal made up out of identical chains is given by the trace of the resulting matrix. Depending on the value of the trace, the energy either lies in a band gap or the trace can be used to calculate a real Bloch-vector k. The density of states is then calculated by differentiation.

After averaging over the possible configurations, the integrated DOS and the DOS result, shown in fig. 3 for chains of 1, 3 and 10 atoms for a concentration of 0,5; these contain 2, 4 and 78 contributions, respectively. To determine the rate of convergence, we have also calculated the norm of the difference between successive approximations, defined as the integral over the absolute value of the difference between the integrated DOS, fig. 7. The result is a slow convergence of 1/n. This can be understood in two ways. First, the averaged DOS for chains of N atoms has a structure of N-1 smeared out gaps, clearly because each contribution has N-1 band gaps. The oscillatory behavior has the slow convergence as a consequence. Second, it is known that in one dimension all states

eventually become localized and that the true DOS is a sum of delta-functions, but convergence towards a delta-function is of the 1/n type. This suggests that in three dimensions one should expect similar behavior for localized states, but better convergence for extended states in the continuous part of the band.

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Appendix A

In order to show the relationship between the Green function G(E) and our function F(E) we begin with the following expression for G(E).

$$G(E) = \frac{2}{\pi} \lim_{\gamma \rightarrow 0^+} \int_0^{\infty} \frac{dk}{E - E'(k) + i\gamma} \quad (A1)$$

where a factor of 2 for spin and a factor of 2 due to Kramers degeneracy ($E^*(-k) = E^*(k)$) have been included.

Upon changing variables we obtain an integral over allowed energies of the form

$$G(E) = \frac{2}{\pi} \lim_{\gamma \rightarrow 0^+} \int_{E' \text{ allowed}} dE' \frac{dk}{dE'} [E - E' + i\gamma]^{-1} \quad (A2)$$

Recalling the definition of $F(E)$ and separating into real and imaginary parts we write

$$F(E) = \frac{2}{\pi} \frac{dk}{dE} = F_1(E) + i F_2(E) \quad (A3)$$

As stated in section III, $F(E)$ is real for the allowed energies and purely imaginary for the forbidden energies which allows us to rewrite equation (A2) as

$$G(E) = \lim_{\gamma \rightarrow 0^+} \int dE' F_1(E') [E - E' + i\gamma] \quad (A4)$$

Using the identity

$$\lim_{\gamma \rightarrow 0^+} \frac{1}{E - E' + i\gamma} = P \frac{1}{E - E'} - i \pi \delta(E - E') \quad (A5)$$

we arrive at

$$G(E) = P \int_{-\infty}^{\infty} dE' F_1(E') [E - E']^{-1} + \pi F_2(E) \quad (A6)$$

We now invoke the Kramers-Kronig relations between the real and imaginary parts of $F(E)$ giving

$$G(E) = -i \pi F(E) \quad (A7)$$

Appendix B

Let us call the actual density of states D , and the partition function

$$Z(\beta) = \int_{-\infty}^{\infty} dE D(E) e^{-\beta E} \quad (B1)$$

where $\beta = \hbar / (2mk_B T)$

The Lorentz smoothed density of states is then defined as

$$D_s(E) = \frac{\gamma}{\pi} \int_{-\infty}^{\infty} dE' \frac{D(E')}{(E - E')^2 + \gamma^2} \quad (B2)$$

Using the Laplace transform for

$$\frac{1}{E^2 + \gamma^2} = \frac{1}{\gamma} \int_0^{\infty} d\beta \sin(\gamma\beta) e^{-\beta E} \quad E > 0 \quad (B3)$$

we rewrite (B2) as

$$D_s(E) = \frac{1}{\pi} \int_0^{\infty} d\beta \sin(\gamma\beta) e^{\beta E} Z(\beta) \quad (B4)$$

The same thing can be done for the local density of states and partition function giving:

$$D(E, r) = \sum_n |\psi_n(r)|^2 \delta(E - E_n) \quad (B5)$$

and

$$z(\beta, r) = \langle r | e^{-\beta H} | r \rangle = \sum_n |\psi_n(r)|^2 e^{-\beta E_n} = \int dE D(E, r) e^{-\beta E} \quad (B6)$$

According to Butler and Kohn, if we perturb a free electron gas by a small perturbation $\delta V(r')$, the change in the local partition function is given by

$$\frac{\delta Z(\beta, r)}{\delta V(r')} = \frac{\pi^{5/2}}{16\beta^{3/2}R} e^{-\frac{R^2}{\beta}} \quad (B7)$$

implying

$$\frac{\delta D_s(E, r)}{\delta V(r')} = \frac{\pi^{3/2}}{16R} \int_0^\infty d\beta \frac{\sin(\gamma\beta)}{\beta^{3/2}} e^{\beta E} e^{-\frac{R^2}{\beta}} \quad (B8)$$

where $R = |r - r'|$

We calculate this expression for negative energies and continue it analytically for positive E.

Setting $E = -\epsilon$, changing variables and using the result [15]

$$\int_0^\infty dx e^{-\left(\beta x^2 + \frac{\gamma}{x^2}\right)} \sin(ax^2) = \frac{1}{2} \sqrt{\frac{\pi}{a^2 + \beta^2}} e^{-2a\sqrt{\gamma}} \quad (B9)$$

we evaluate equation (B8) giving

$$\frac{\delta D_s(E, r)}{\delta V(r')} = -\frac{\pi^2}{32R^2} \sin(\gamma R) e^{-2\mu R} \quad (B10)$$

where the exponent

$$u = \frac{\sqrt{E^2 + \gamma^2} - E}{2} \quad (B11)$$

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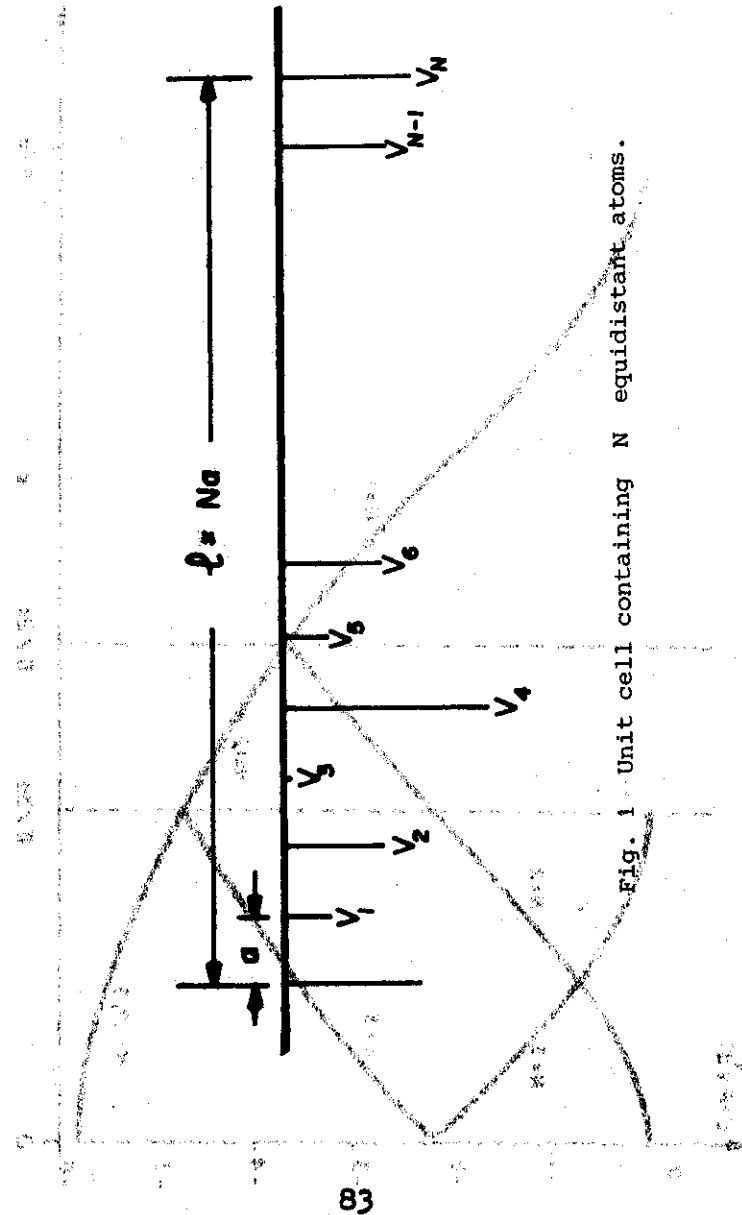


Fig. 1 Unit cell containing N equidistant atoms.

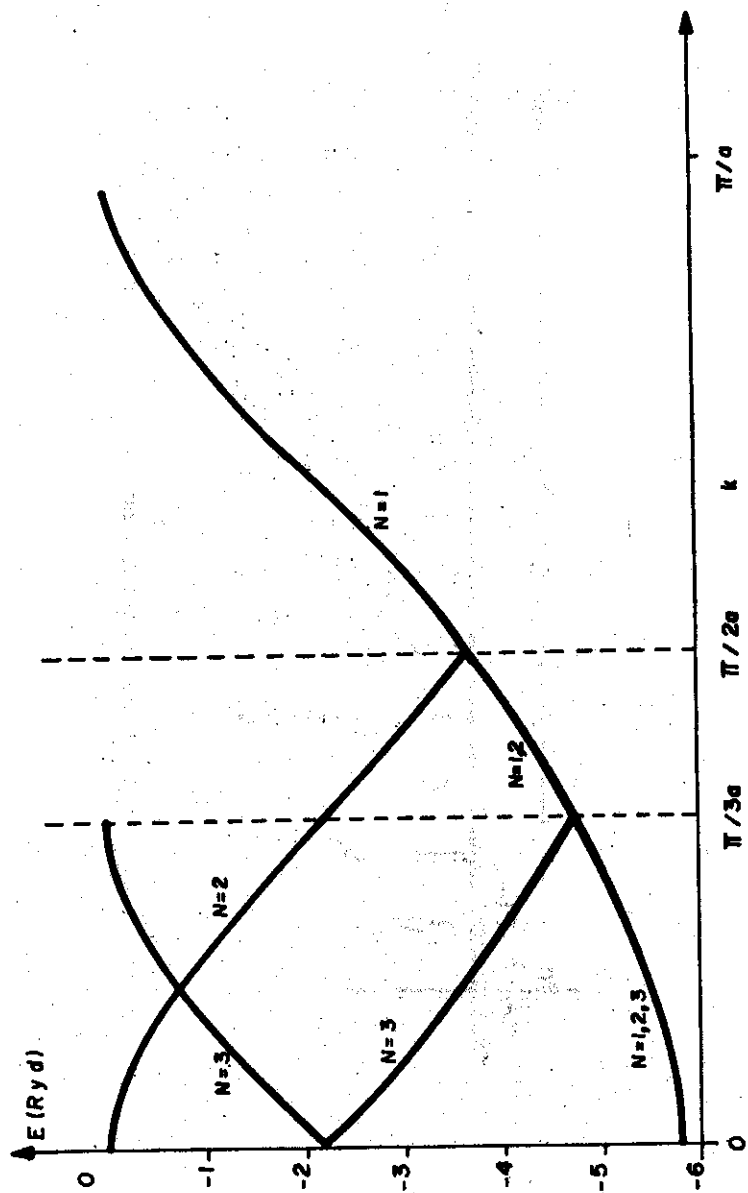


Fig. 2 Lowest energy bands for $V_A = V_B = -4$ as calculated for $N = 1, 2, 3$ atoms/cell.

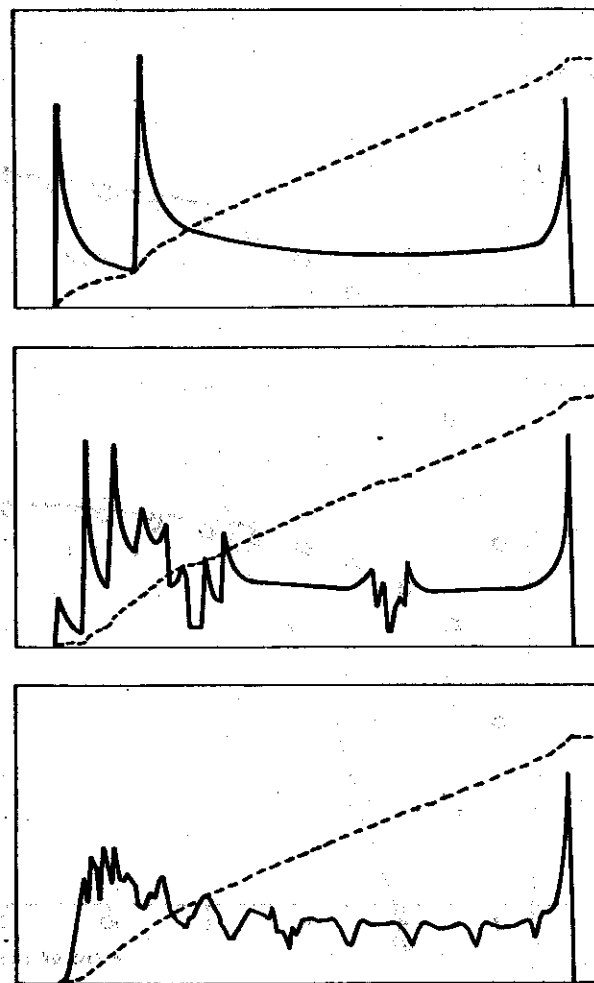


Fig. 3 Density of states for 1, 3 and 10 atoms/cell.

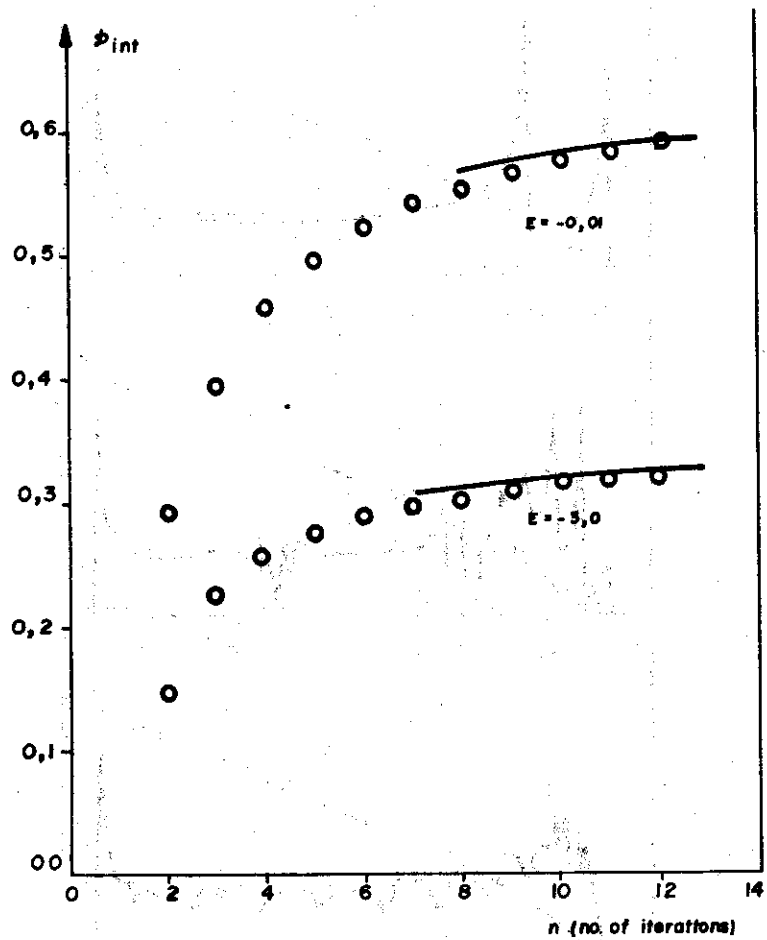


Fig. 4 Integrated DOS $D_{int}(E)$ as a function of the number iterations for two different energies using the method of Schmidt.

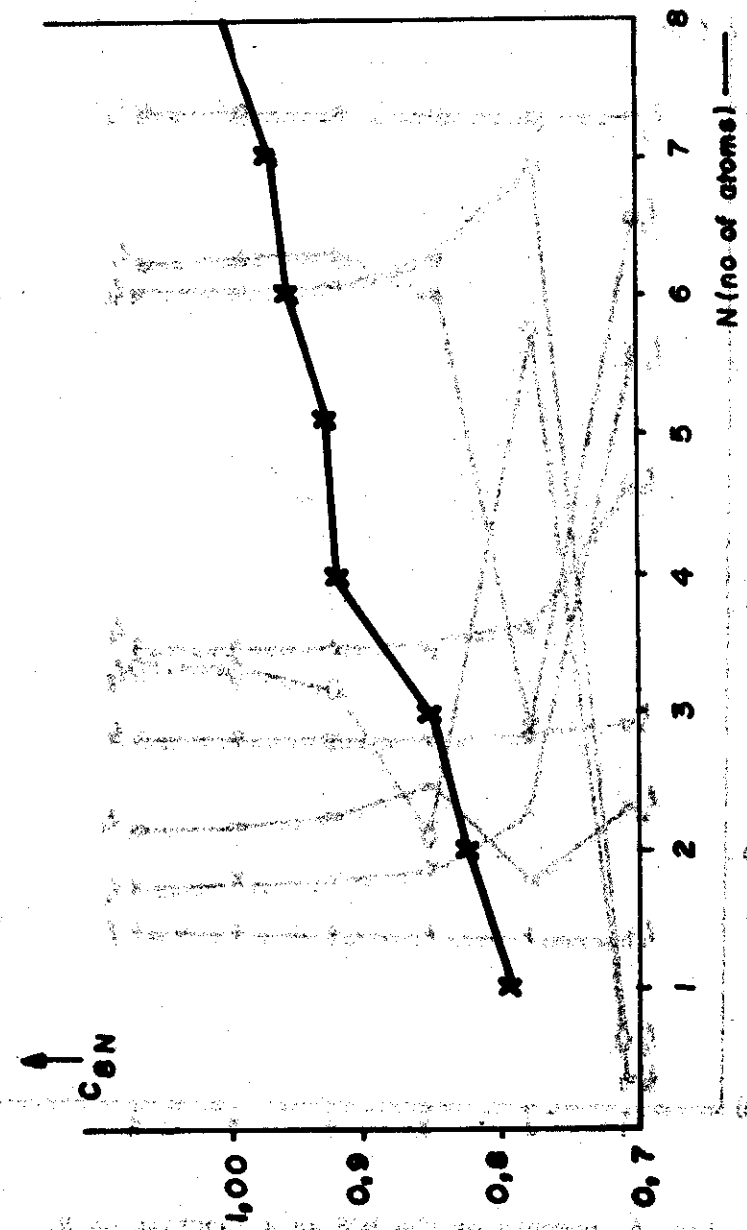


Fig. 5 Correlation coefficient C_{BN} as a function of N.

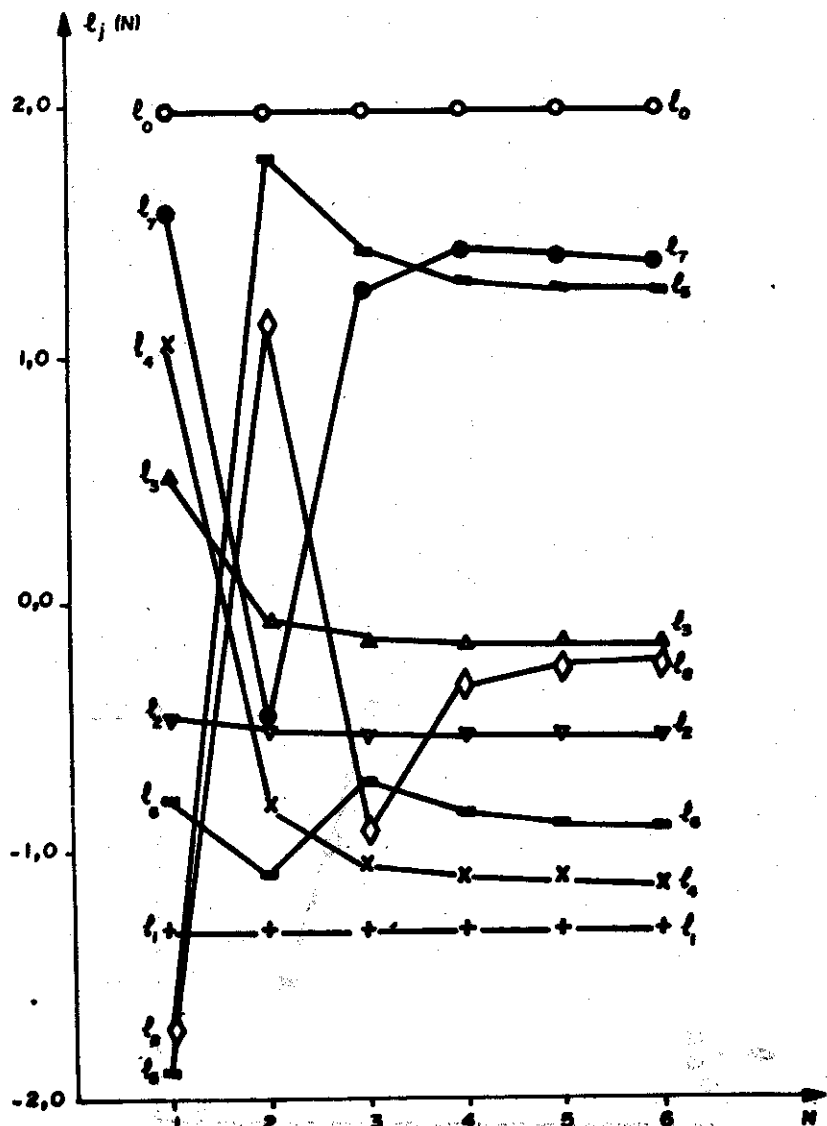


Fig. 6 Moments of the DOS as a function of N .

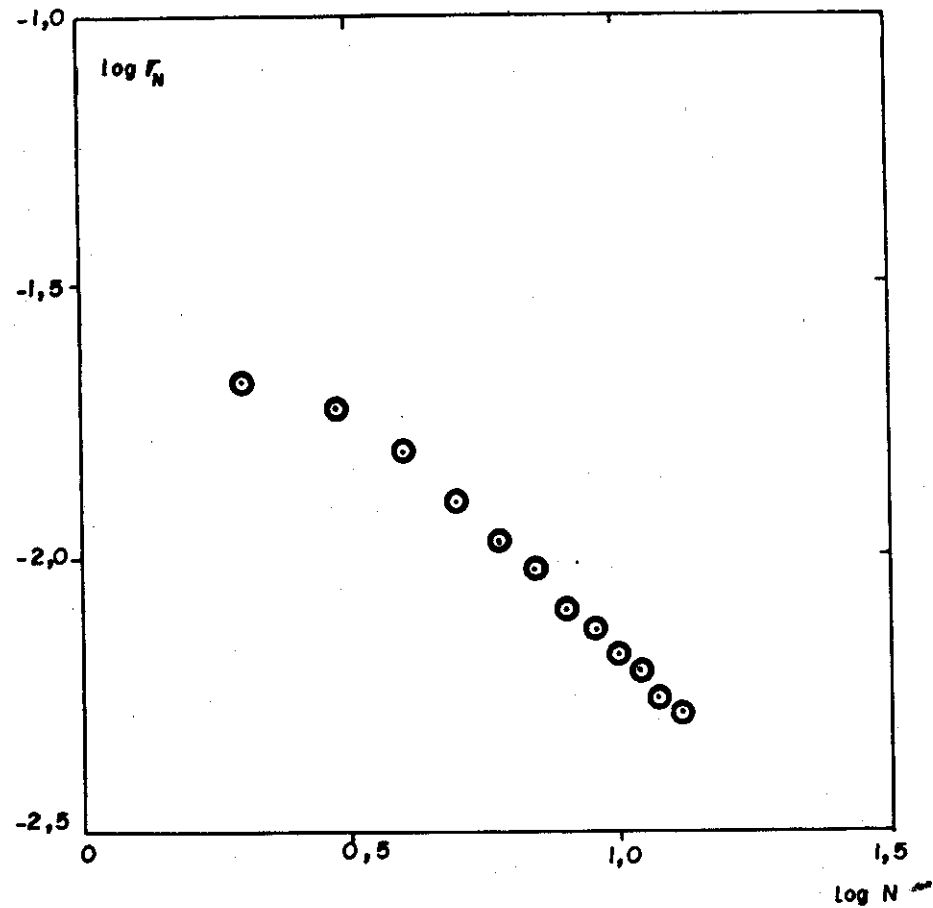


Fig. 7 σ_N