A KRONIG-PENNEY MODEL OF SALTS OF DNA

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ABSTRACT **A one dimensional Kronig-Penney model for a salt like Na DNA is given. The helical periodicity is treated in a manner suggested by Tinoco and Woody. Using data on the semiconductor band gap, we estimate the strength of the potential barrier. The energy limits of the ten bands filled by 20π electrons per unit cell are calculated and exhibited in Table I.**

INTRODUCTION

The chemical structure of DNA is well-known (1) and the quantum chemistry of the base pairs has been studied by Pullman (2). Ladik and Hoffman (3) have attempted to calculate the electron band structure of DNA using the Hückel approximation. Since it is highly unlikely that the electronic structure of DNA will soon be obtainable from first principles, a good semi-empirical approach is desirable and will here be presented.

A model based on solid-state physics is required. It was found by O'Konski, Moser, and Shirai (4), that Na DNA is an intrinsic semiconductor with a band gap of 2.4 ev. Biological semiconductors have been discussed by Eley (5) and L. Brillouin (6).

In DNA we have a helical structure with a period of 34 A and a radius of 10 A superimposed on a periodicity of 3.4 A of phosphate and sugar. The crystal is almost periodic because the base pairs connecting two sugars across the helix vary from unit cell to unit cell. One would expect the phosphate group which is the only truly repeating structure and the most polar grouping to produce the largest effect on the behavior of the 20π electrons (5) which move along the axis of the molecule.

To analyze the electronic band structure of the dry salt Na DNA by solving the Schroedinger equation, we must consider the double periodicity of the molecule. We shall first study the effect of the helical structure. Tinoco and Woody (7) have introduced a simple Hamiltonian for a free particle in a helical box:

$$H = -\frac{\hbar^2}{2\mu(a_o^2 + b^2)} \frac{\partial^2}{\partial\theta^2} \tag{1}$$

where a_o is the radius and $2\pi b$ is the pitch of the helix. The angle θ is related to the distance along the axis by

$$Z = b\theta. \tag{2}$$

In terms of Z, the Hamiltonian is therefore

$$H = -\frac{\hbar^2 b^2}{2\mu(a_o^2 + b^2)} \frac{\partial^2}{\partial Z^2}. \tag{3}$$

The Hamiltonian used by Tinoco and Woody has the merit of extreme simplicity.

We now add to the Hamiltonian (Equation 3) a potential energy term which has the periodicity of the unit cell (3.4 A). This is not a simple task because the effect of the base pairs is a random function of position. A suitable function would be of the type used for random alloys (8), i.e.

$$V = \sum_{n=1}^{\infty} \gamma_n \delta(Z - na). \tag{4}$$

Here $\delta(Z - na)$ is a Dirac δ function at lattice points of strength γ_n, where γ_n has the value γ^j with probability P_j. It would be desirable to assume the potential energy (Equation 4) if we had more experimental information. Because of the lack of experimental information, we shall take δ functions of equal strength separated by the unit cell distance a, and evaluate the strength of the δ function from the energy gap data given by O'Konski et al. (4). The repeating δ-function potential energy was used by Kronig and Penney (9) as a simple model for crystalline solids. The Schroedinger equation for the case of an electron in a helical box with a Kronig-Penney potential barrier is

$$-\frac{\hbar^2}{2\mu} \frac{b^2}{(a_o^2 + b^2)} \frac{d^2\psi}{dZ^2} + V_{KP}\psi = E\psi. \tag{5}$$

The transcendental equation relating the energy and momentum hk, is given by

$$P\frac{\sin a\alpha}{a\alpha} + \cos a\alpha = \cos ka \tag{6}$$

where

$$P = \lim_{\substack{V_o \to \infty \\ b \to 0}} \frac{mV_o}{\hbar^2} b(a - b), \tag{7}$$

$$\alpha^2 = \frac{2mE}{\hbar^2}, \tag{8}$$

and $V_o\, b$ is the barrier strength. For our case, the mass is $m = \mu(a_o^2 + b^2)/b^2$ where μ is the true electron mass.

FILLED BANDS

For a crystal of length $L = aN$, where N is the number of unit cells, there are $2N$ independent states in each energy band. If the total number of π electrons is $20N$, the number of filled bands $= 20N/2N = 10$. We are therefore interested in calculating the lower and upper limits of the 10 bands as well as the lower limit of the 11th or conduction band.

For the top of the 10th band we have $\alpha a = 10\pi$. The bottom of the 11th band is given by

$$\frac{P \sin a\alpha}{a\alpha} + \cos a\alpha = 1 \tag{9}$$

with $a\alpha = 10\pi + x$. For an energy gap of 2.4 ev, we find that x must be 0.50. Using this value of x, we calculate that $P = 8.0$. With this value of P, the limits of the 10 bands are computed from Equation 6. The results are given in Table I.

TABLE I

Energy	Band
ev	
75.9	11
73.5	10
62.3	
59.9	9
49.6	
47.4	8
38.6	
36.3	7
20.9	
26.6	6
20.7	
18.5	5
13.9	
11.84	4
8.58	
6.66	3
4.63	
2.96	2
1.99	
0.74	1
0.48	

DISCUSSION AND CONCLUSION

The energy of the top of the 10th band, which is approximately 75 ev appears to be quite high. However, to see the reasonableness of the result, let us consider the problem of a π electron in a helical box or the case of P equal to zero. The energy is given by Tinoco and Woody (7). The result is

$$E_n = n^2 \frac{\hbar^2}{8\mu K^2(a_o^2 + b^2)} \tag{10}$$

where $K = L/2\pi b$. Thus

$$E_n = \frac{n^2}{L^2} \frac{h^2}{8\mu\left(\frac{a_o^2 + b^2}{b^2}\right)} . \tag{11}$$

At 0°K all the electrons would have energies below or equal to the maximum energy E_{max}. The maximum energy is obtained by substituting for n

$$n = \frac{1}{2}(20)\frac{L}{a}$$

when there are 20π electrons per unit cell. Thus

$$E_{\text{max}} = \frac{10^2 h^2}{8\mu\left(\frac{a_o^2 + b^2}{b^2}\right)a^2} . \tag{12}$$

For the Kronig-Penney model this gives the top of the 10th band.

When $P = 0$, we have sharp energy levels given by equation 10. However, when we introduce a periodic potential barrier, the simplest of which is a δ-function type, we create bands as given in Table I. It would be very useful if one were able to obtain the potential energy function that a π electron sees along the axis, by some experimental method such as electron scattering or magnetic resonance.

Some investigators may question the delocalization of π electrons to move along the axis of molecule. They assert that the motion is in the base pair plane. It is obvious that some delocalization must occur if electric field strengths are high enough. The amount of delocalization must be resolved by experiment.

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