ONE-DIMENSIONAL HARMONIC MODEL FOR BIOMOLECULES

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ABSTRACT Following in spirit a paper by Rosen, we propose a one-dimensional harmonic model for biomolecules. Energy bands with gaps of the order of semiconductor gaps are found. The method is discussed for general symmetric and periodic potential functions.

INTRODUCTION

There is some current interest in the solution of one-dimensional problems as a possible guide to the understanding of more realistic three-dimensional models. In relation to biophysics, one-dimensional systems have obvious physical realizations in biopolymers and in layered structures. In a recent paper (1), Rosen put forward a one-dimensional Kronig-Penney model for the salts of DNA. While the delta-function potential used in this calculation is somewhat artificial, it is, as Rosen points out, a good starting point for a semiempirical approach.

Here we present a one-dimensional model calculation which involves a periodic harmonic well configuration. The model thus gives an example of a more complicated (if still idealized) interaction which leads to a band structure. The estimate of lattice parameter and binding (coupling) parameter leads to energy gaps which are of the order of a fraction of an electron volt, and thus in the semiconductor range (2, 3). The model may be used for comparison with the band structure of DNA salts by determining the coupling parameter from the known band gap (4) as in reference 1. Thus the harmonic "force constant" in each "cell" may be determined. In this paper we only make qualitative conclusions and the model is offered as one with potential application for biomolecular systems.

The development given in One-Dimensional Model is actually applicable to any symmetric one-dimensional potential $V = \sum_i v(x_i)$, where $v(x_i + nl) = v(x_i)$ (l is the lattice parameter and n is an integer). In particular the Kronig-Penney relation between energy and $\hbar k$ would be obtained if appropriate solutions were used in the dispersion form given there.

ONE-DIMENSIONAL MODEL

The electrons, $2N$ in number, move in one dimension and interact with an harmonic potential array involving N fixed sites. The hamiltonian for the system is

$$H = -\sum_i (\hbar^2/2M)d^2/dx_i^2 + \beta \sum_{i,j} \theta_j^i\,(x_i - jl)^2, i = 0, 1, \ldots, 2N-1, j = 0, 1, \ldots, N-1. \quad (1)$$

The boundaries of the jth cell are given by the condition that $\theta_j^i = \theta_j(x_i) = 1$ if

$$d_j^- \leq x_i \leq d_j^+, \quad (2)$$

and is zero otherwise. The limits are defined such that

$$d_j^\pm = jl \pm l/2, \quad (3)$$

and the total range for the ith electron is given by

$$d_0^- \leq x_i \leq d_{N-1}^+. \quad (4)$$

We also assume that the N cells are connected into a ring, such that $d_{N-1}^+ = d_0^-$. Thus "periodic" boundary conditions are assumed.

Equation 1 leads to the Schroedinger equation:

$$H\Psi = (\sum_i H_i)\sum_P (-1)^P \pi_i \psi(Px_i)/\sqrt{2N!} = E\Psi, \quad (5)$$

where

$$H_i = -(\hbar/2M)d^2/dx_i^2 + \beta \sum_j \theta_j^i (x_i - jl)^2, \quad (6)$$

over the domain given by equation 4. The wave function above is written in the uncoupled, antisymmetrized form. In equation 5 the sum is taken over all permutations of the configuration coordinates and spin (the spin index is not explicitly shown here or elsewhere in the paper); the product of the single wave functions for a given permutation P is shown, together with the normalizing factor for the $2N$ identical particles.

In equations 5,

$$E \equiv \sum_i \epsilon_i, \quad (7)$$

where ϵ_i is the eigenvalue of the single particle equation

$$H_i\psi(x_i) = \epsilon_i\psi(x_i). \quad (8)$$

Denoting by $\psi_j(x_i)$ the wave function as defined over the jth cell the problem from equation 6 becomes one of solving

$$[(\hbar^2/2M)d^2/dx_i^2 + \beta(x_i - jl)^2]\psi_j(x_i) = \epsilon_i\psi_j(x_i), \tag{9}$$

subject to the conditions of continuity of wave function and its derivative at the cell boundaries in equation 3; the wave function is also required to satisfy the periodic boundary condition

$$\psi_j(x_i) = \psi_{j+N}(x_i + Nl), \tag{10}$$

(this is easily seen to be required by the ring configuration).

(The problem may be converted to a form suitable for use in the helical variables introduced by Tinoco and Woody [5]. Thus, as in the treatment of Rosen, the one-dimensional form [equation 9] may be applied to DNA, for example, by the replacement

$$\frac{\hbar^2}{2M}\frac{d^2}{dx^2} \rightarrow \frac{\hbar^2 b^2}{2M(a_0^2 + b^2)}\frac{d^2}{dZ^2}, \tag{11}$$

where $Z = b\theta$, $2\pi b$ is the pitch of the helix and a_0 is its radius. The potential accordingly becomes $v = v(Z)$.)

The solution to equation 9 is written (suppressing the index i)

$$\psi_j = \psi_j(0)y_1 + \psi_j'(0)y_2, \tag{12}$$

where the fundamental set y_1, y_2 is defined such that

$$\begin{aligned} y_1(0) &= 1, & y_2(0) &= 0, \\ y_1'(0) &= 0, & y_2'(0) &= 1, \end{aligned} \tag{13}$$

and $\psi_j(0)$ and $\psi_j'(0)$ are constants.

Defining further

$$\begin{aligned} z^2 &\equiv [(x - jl]/\lambda]^2, \\ \lambda^2 &\equiv \hbar/2(2M\beta)^{1/2}, \end{aligned} \tag{14}$$

and

$$E_0 \equiv 2\hbar\beta^{1/2}/(2M)^{1/2}, \tag{15}$$

and writing

$$\epsilon = (m + \tfrac{1}{2})E_0, \tag{16}$$

the Schroedinger equation 9 has the dimensionless form

$$d^2y/dz^2 + (m + \tfrac{1}{2} - z^2/4)y = 0. \tag{17}$$

Equation 16 defines the number m in anticipation of the limiting case of large lattice parameter, where the harmonic oscillator case with integer m emerges.

A fundamental set of solutions 13 to 17 is given by (6, 7)

$$y_1(z) = \exp(-z^2/4)F\left(-\frac{m}{2}\bigg|\frac{1}{2}\bigg|\frac{z^2}{2}\right),$$

and

$$y_2(z) = z\exp(-z^2/4)F\left(-\frac{m}{2}+\frac{1}{2}\bigg|\frac{3}{2}\bigg|\frac{z^2}{2}\right), \qquad (18)$$

where F is a confluent hypergeometric function, and y_1 and y_2 have even and odd symmetry in z, respectively.

At the point separating the jth and j'th cells:

$$\psi_j(z^+) = \psi_{j'}(z^-), \qquad (19)$$

and

$$\psi_j'(z^+) = \psi_{j'}'(z^-), \qquad (20)$$

where $z^+ \equiv l/2\lambda$ (see equations 14 and 3) and $z^+ = -z^-$.

Using the symmetry and antisymmetry in equation 18 and applying equation 19 to eliminate $\psi_{j'}'(0)$ we obtain for the condition 20, between the jth and $j+1$st cells,

$$\psi_j(0)[y_1(z^+)y_2'(z^+) + y_2(z^+)y_1'(z^+)] + 2\psi_j'(0)y_2'(z^+)y_2(z^+) = \psi_{j+1}(0)W, \quad (21)$$

where $W = y_1y_2' - y_2y_1'$ is the wronskian of the independent solutions. Similarly between the j-1st and jth cells we have

$$\psi_j(0)[y_1(z^+)y_2'(z^+) + y_2(z^+)y_1'(z^+)] - 2\psi_j'(0)y_2'(z^+)y_2(z^+) = \psi_{j-1}(0)W. \quad (22)$$

Adding equations 21 and 22 and using the fact that $W = 1$ for the fundamental solutions of any one-dimensional Schroedinger equation, we get (8) (the following two forms are equivalent)

$$2\psi_j(0)\left\{\pm 1 + 2\begin{bmatrix} y_1'(z^+)y_2(z^+) \\ y_1(z^+)y_2'(z^+) \end{bmatrix}\right\} = \psi_{j-1}(0) + \psi_{j+1}(0). \qquad (23)$$

As pointed out earlier, the form 23 will hold for any periodic potential which is symmetric. If appropriate harmonic functions y_1 and y_2 are used, then the Kronig-Penney transcendental relation follows.

QUALITATIVE BEHAVIOR AND ENERGY GAPS

Defining $\psi_j(0) = \phi_j(0)f$, where f is a common factor for all cells, we write equation 23 as

$$2F\phi_j(0) = \phi_{j-1}(0) + \phi_{j+1}(0). \tag{24}$$

In equation 24 we have also defined

$$F = F(z^+) = \pm 1 + 2\begin{bmatrix} v_1'v_2 \\ v_1v_2' \end{bmatrix}_{z^+}. \tag{25}$$

From the boundary condition 10

$$\phi_j(0) = \phi_{j+N}(Nl) \equiv \phi_{j+N}(0), \tag{26}$$

and so equation 24 will be satisfied if

$$\phi_j(0) = e^{i2\pi js/N} \tag{27}$$

where s is an integer. Inserting equation 27 into equation 24 gives

$$2F\phi_j(0) = 2\cos(2\pi s/N)\phi_j(0); \tag{28}$$

thus

$$F = \cos 2\pi s/N, \tag{29}$$

and consequently

$$-1 \leq F \leq 1. \tag{30}$$

The above defines bounds which determine the band edges. The allowed energies within a given band are generated by letting s vary.

The F vs. m curves for two values of z^+ are shown in Fig. 1. Taking the value $\beta \sim 10^6$ erg/cm^2 as an atomic-binding estimate, and thus from equation 14, taking

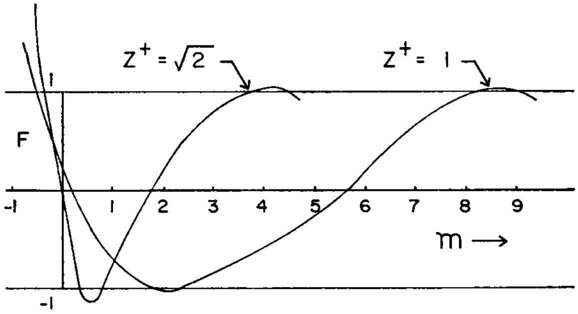

FIGURE 1 Two curves of F vs. m.

$\lambda \sim 10^{-8}$ cm, we get values in the neighborhood of the parameter choices shown. The band edges are located at the points where $F = \pm 1$. The roots of the confluent hypergeometric functions (6, 7) in equation 25 occur in pairs that are relatively close. For $z^+ = 1$, the first gap occurs between the root $y_1 = 0$ at $m = 2$ and the zero $y_2' = 0$, which occurs at 2.1. The next gap will occur at $m \sim 9$, where y_2 has a zero, and so on. If $z^+ = \sqrt{2}$ then the first roots of $y_1 y_2' = 0$ occur at the points $m \sim 0.3$ and $m \sim 0.6$. From equations 15 and 16, these gap widths are of the order of fractions of an electron volt, or they are in the semiconductor range.

For large values of m we obtain the following qualitative behavior (6, 7):

$$y_1 \underset{m \to \infty}{\longrightarrow} \cos \sqrt{(2m + 1)/2}\, z^+, \tag{31}$$

and

$$y_2 \underset{m \to \infty}{\longrightarrow} \sin \sqrt{(2m + 1)/2}\, z^+/\sqrt{m + 1}. \tag{32}$$

Thus

$$F \underset{m \to \infty}{\longrightarrow} 1 - 2 \sin^2 \sqrt{m}\, z^+ = \cos 2 \sqrt{m}\, z^+, \tag{33}$$

and the curve oscillates between $F = \pm 1$; the distance between the zeros of F for large m is given asymptotically by $\Delta m \sim 4 \sqrt{m}\, z^+/\pi$. This follows from equation 33 where $\sqrt{m} = r\pi/4z^+$ and r is an odd integer. Thus the curve abscissa intercepts increase as $\sqrt{m}$.

In the limit of large m (for fixed β) the electrons become quasi-free. Then according to equations 15 and 16, as $\epsilon \to (k\hbar)^2/2M$, $\sqrt{m}\, z^+ \to kl$. The dispersion relation 23 then becomes, from equation 33

$$2\psi_j(0) \cos kl = \psi_{j-1}(0) + \psi_{j+1}(0), \tag{34}$$

the known free particle result.

From the curves there is a shift in the gap toward lower energies as z^+ increases; this corresponds to increased binding at the fixed lattice parameter l.

The limit of large l (or large β) corresponds to the asymptotic approach of the bands in Fig. 1 to single lines. Thus for large z

$$F(a \mid c \mid z^{+2}/2) \sim [\Gamma(c)(z^{+2})^{a-c}/\Gamma(a)] \exp (z^{+2}/2). \tag{35}$$

In equation 35 there will be divergent behavior unless the gamma function $\Gamma(a) \to \infty$ in the limit. This is assured if m takes on even and odd integer values, since (9)

$$\Gamma(a) = \pi/\Gamma(1 - a) \sin (a\pi). \tag{36}$$

Thus $F \to \pm 1$ in equation 25 in this limit and the bands degenerate to single energies.

DISCUSSION

The harmonic model is presented here as an example of a type of periodic potential calculation which can be applied to systems such as biomolecules (both open ended and cyclic). The harmonic potential represents a somewhat more realistic situation than the delta function Kronig-Penney model. Thus a force constant can be obtained by comparison with band gap data. On the other hand, the analysis here has only been carried out graphically for a single filled band. Of course the problem can be easily generalized to $2cN$ electrons (where c is an integer) with a corresponding extension of the graphical analysis to c bands (for DNA $c = 10$) (1).

The treatment here can be used for any symmetric periodic potential energy function, the only possible limitation being the availability of tables of functions of solutions to the one-dimensional Schroedinger equation, or availability of computing facilities to calculate the dispersion curves.

The assumption of delocalization of electrons, which allows the electrons to move across the lattice, is a question of experimental determination, as has been pointed out by Rosen. In the present model, however, the tight-binding limit is also implied as a limiting case, and so, even if motion is restricted to the neighborhood of the sites (base planes in the case of DNA), the model should be applicable.

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REFERENCES

1. Rosen, P. 1968. *Biophys. J.* **8**:391.
2. Szent-Gyorgyi, A. 1941. *Nature* (*Lond.*). **148**:157.
3. Brillouin, L. 1966. *In* Wave Mechanics and Molecular Biology. L. de Broglie, editor. Addison-Wesley Publishing Co., Inc., Reading, Mass. 170.
4. O'Konski, T. T., P. Moser, and M. Shirai. 1964. *In* Quantum Aspects of Polypeptides and Polynucleotides. M. Weissbluth, editor. Wiley-Interscience Div., John Wiley and Sons, Inc., New York. 479.
5. Tinoco, I., and R. W. Woody. 1964. *J. Chem. Phys.* **40**:160.
6. Abramowitz, M., and L. A. Stegun. 1964. Handbook of Mathematical Functions. National Bureau of Standards Applied Mathematical Series. **55**:686.
7. Slater, L. J. 1960. Confluent Hypergeometric Functions. Cambridge University Press, London.
8. Montroll, E. W. 1970. *J. Math. Phys.* **11**:635.
9. Whittaker, E. T., and G. N. Watson. 1963. *In* Course in Modern Analysis. Cambridge University Press, London. 239.