Self-Consistent Band Theoretic Models of DNA

John Altieri and John E. Krizan

Department of Physics
University of Vermont
Burlington, Vermont 054041

ABSTRACT. Previously investigated models are further elaborated here, with particular application to DNA. Accepting the premise that DNA may be characterized as an intrinsic semiconductor with a band gap energy of approximately 2 eV, a self-consistent method reveals term energies of reasonable magnitude. The treatment also determines that the mobilities are of the order of 10 to 10^2 cm^2/V sec, indicating delocalization of the electrons with respect to the base pairs.

I. Introduction

In this paper we compare two models which have been hitherto considered by Rosen[1] and Krizan[2] as semiempirical approaches to the complex problem posed by periodic biomolecules such as DNA. Other approximation schemes have been exhaustively applied to organic molecules by Pullman and Pullman[3] and Ladik and Hoffman,[4] and many others; such calculations, although differing somewhat in their results at present, may well contain the germ for a more complete understanding of the role of electronic structure in complex biomolecules.

For the present, however, we continue to investigate the problem of the exact determination of band structure for simplified one-dimensional models, and apply the calculations to DNA. The Kronig-Penney model was first applied by Rosen[1] to the problem; here we re-examine this model and the Harmonic Potential model.[2] While our treatment is exact as far as the band structure is concerned, we do introduce the effective mass approximation, in a self-consistent procedure. This has the effect of producing term energies which have quite realistic values. As in previous work,[1,2] we accept the premise that biomolecules such as DNA may be treated as intrinsic semiconductors.[5-9] We would note that Rosen[10] has recently shown how a model involving electron exchange can lead to very

Source	Form	σ_0 $(\Omega^{-1}cm^{-1})$	E_g (eV)	Reference
Calf thymus	solid gel	6×10^2	2.44	15
Calf thymus	solid gel	4×10^4	1.27	15
Calf thymus (denatured)	fibers	3.2×10^3	2.42	16
Calf thymus	fibers	5×10^7	2-2.2	17
Chicken erythrocyte	fibers	10^6	1.9	17
Calf thymus Salmon sperm	dry fibers	10^2	2.36	18
Herring sperm	oriented films	3.5×10^3 to 3.5×10^4	2.18	5
Calf thymus	compressed	4×10^3	2.4	7
Salmon sperm	films and compressed tablets		2.43	19

*in part from Vasilescu[20]

narrow band widths, suggesting contact with models which treat energy exchange between monomers in terms of excitons.[11,12] The band widths obtained here are larger than those of Rosen[10] and this is possibly more consistent with the mechanism of intrinsic semiconduction. We also obtain mobilities which are of the order of magnitude of those estimated by Suhai.[13]

II. Band Gap Energy

Organic molecular crystals and macromolecules such as DNA exhibit a dc conductivity which varies according to the relation*

$$\sigma = \sigma_0 e^{-W/kT} \qquad (1)$$

where σ_0 is a constant, and W is the experimentally determined activation energy. The equations (with classical statistics) for intrinsic semi-conductors are assumed to apply and so $E_g = 2W$ is the band gap energy: this is the minimum energy an electron must acquire if it is to make a transition from the valence band to the conduction band. Many researchers have measured the resistance of DNA as a function of temperature and have determined that E_g lies between 2 and 2.4 ev, but there is a large variation in the value for σ_0 because of the difference in the water content of the samples. Table I is a compilation of some of the experimental results.

*For detailed aspects of conduction in polymers, see the paper by Pohl.[14]

The conductivity measurements are usually made on samples which are in the form of dried films, microcrystalline powders, or compressed tablets so that the native two-stranded complementary structure may not be present. However, O'Konski[7] reasons that

> "a substantial portion of the hydrogen bonded structure is probably restored upon cooling the solution, even if a complementary rematching of the strands over the entire lengths is not possible under the experimental conditions. Although separated from its complement, a given polynucleotide chain can apparently fold back upon itself and find complementary sections intramolecularly, perhaps with the formation of additional short loops consisting of one or more bases which cannot match the opposite chain."

The models presented here take into account the double periodicity of DNA in the sense of Refs. 1 and 2. That is although the unit cell is defined according to the base periodicity, the helical periodicity is treated implicitly by means of a coordinate transformation, according to Tinoco and Woody.[21] The effect of the parameter associated with the helix pitch is, however, suppressed in what follows due to the use of a self-consistent effective mass approximation.

The order of bases in the macromolecule is assumed to have no effect on the band structure. Carrier motion is postulated to take place by tunneling between the bases, or by conduction along the sugar phosphate backbone.

III. The Model

The dispersion relation for the energy as a function of wave number was obtained in Ref. 2. This relation holds in general for any periodic, symmetric potential form. In particular it was applied to a periodic harmonic potential, for which the Schrödinger fundamental solutions were confluent hypergeometric functions. In general however, in the notation of Ref. 2,

$$F(z^+) = +1 + 2(y_1'y_2)_z+ = -1 + 2(y_1y_2')_z+ \qquad (2)$$

where y_1, y_2 are the fundamental solutions of the Schrödinger equation, for any symmetric potential. The relation could also be used for the Kronig-Penney model; however, care would have to be taken not to actually pass to the limit of infinitely high and infinitesimally thin barrier, since continuity of function and derivative were assumed in derivation of (2).

The function $F(z^+)$ is restricted to lie between the values ± 1. This restriction determines the band edges. In Ref. 2 only a single filled band was plotted analytically for the Harmonic Potential model. In the present paper we apply the above relation to a DNA realization with nine filled

bands, where the calculation has been extended with the aid of a computer.[†] According to the above, the zeroes of y_1, y_2' and y_2, y_1' determine the locations of the bands.

The band gap energy is chosen as 2.4 eV. (See Table I) for use in both the Harmonic Potential model and in the Kronig-Penney Potential model, and the band structure is found by means of a self-consistent method where the bandwidth of the conduction band determines the effective mass of the electron.

The location of the zero set associated with the 10th (conduction) band and the upper limit of the 9th (valence) band was determined by requiring that the band gap be fixed at 2.4 eV. The width of the conduction band in turn is related to the effective mass, according to a relation given by Shockley,[22] $m^*_e = h^2/8\ell^2\delta\xi$, where h is Planck's constant, ℓ is the unit cell lattice constant and $\delta\xi$ is the width of the conduction band (this may be obtained by assuming a parabolic density of states for the thin band). A similar relation can be developed from the Uncertainty Principle, namely $m_e^* = \pi\hbar^2/\ell^2\delta\xi$. Either form may be used without changing the final results very much and we will use the former expression for the effective mass. The procedure is self-consistent since the value of $\delta\xi$ is used to generate the parameter z^+ in equation (2) and one proceeds iteratively until the parameter group consisting of z^+, $\delta\xi$, m_e^*, and the band gap edges form a self-consistent set.

At this point we comment on the choice of a number of bands: based on the results of Subertova and Drobnik[5] and Ladik and Hoffman[4] there are an average of 18 π electrons in each base pair, so there are nine filled bands. While the actual number of π electrons is 12 for adenine and thymine, 14 for guanine and 10 for cytosine, Subertova's values for the band gap of 2 to 2.2 eV indicate that 17 to 19 π electrons per base pair form the valence bands. Ladik's HMO-LCAO calculations on G-C and A-T show that when the base pairs are in close proximity (as in DNA) some of the energy levels coalesce to form a single energy band, resulting in 9 valence bands. In fact, however, our results do not differ very markedly if one assumes 10, rather than 9, filled bands (for comparison we include term energies for both cases).

By incorporating the 18 electrons per base pair, the effective mass relation and the band gap energy of 2.4 eV into two computer programs, the band structure given in Table II results. The self-consistent procedure was followed for the Kronig-Penney model by passing to the delta function limit and using the well-known relation,[1] rather than Eqn. (2). Without the effective mass relation, and simply using the Tinoco-Woody[21]

[†]For computational details, see J. Altieri, University of Vermont, M.S. thesis, 1974 (unpublished).

TABLE II

Energy Band Edges for the Harmonic Potential and Kronig-Penney Potential Models.

Band	Harmonic Potential		Kronig-Penney Potential	
	Nine Filled Bands (eV)	Ten Filled Bands (eV)	Nine Filled Bands (eV)	Ten Filled Bands (eV)
11		30.19		17.51
		29.57		16.87
10	27.91	27.17	16.46	14.47
	27.21	26.94	15.73	13.94
9	24.81	24.26	13.33	11.72
	24.55	24.18	12.74	11.29
8	21.83	21.38	10.53	9.26
	21.75	21.36	10.06	8.92
7	18.90	18.53	8.06	7.09
	18.88	18.52	7.70	6.83
6	15.98		5.92	5.21
	15.98	15.67	5.66	5.02
5	13.08	12.82	4.11	3.62
			3.93	3.48
4	10.17	9.97	2.63	2.32
			2.51	2.28
3	7.27	7.13	1.48	1.30
			1.41	1.25
2	4.36	4.28	0.66	0.58
			0.63	0.56
1	1.45	1.43	0.17	0.15
			0.16	0.14
m_e^*/m	4.67	5.26	4.49	5.10
m_h^*/m	12.46	13.96	5.50	6.14

transformation, we get the same values as Rosen in his paper (apart from an apparent typographical error: the bottom of his seventh band should read 29.0 eV). Both the Kronig-Penney and Harmonic Potential models, with self-consistent effective mass approximation, appear to be good representations of the band structures of DNA inasmuch as reasonable term values are obtained. Note that Pullman and Pullman (see also Rosen[10]) obtain an energy difference of about 28 eV between the lowest and highest π electron energies (see Table II); our corresponding π energy values, particularly for the Harmonic Potential model, give surprising approximate agreement. Without such a self-consistent approach Rosen[1]

found the energy difference between the top of the 10*th* valence band and the bottom of the first valence band to be 73 eV (assuming ten filled bands), while Ladik and Hoffman determined this energy difference to be only 10 eV (for nine filled bands). For both the models the conduction band widths are of the order of tenths of an electron volt, which indicates that the electrons are relatively mobile. The top of the potential barrier in the Harmonic Potential model is 19.6 eV which is below both the conduction band and the 9*th* valence band, and this also implies mobile charge carriers.

IV. Mobilities

For biological materials, there may be several ways of defining mobilities, and these frequently do not agree with each other.[14] Here we estimate the ohmic mobility after making several assumptions and approximations for the charge carriers in the Harmonic and Kronig-Penney Models. The ohmic mobilities are smaller than the local mobility for electrons in DNA as estimated by Suhai[13] but are larger than the drift mobilities measured for anthracene.[24,25] The local mobility, $\mu_\varrho = v_\varrho/E$ is the mobility of a charge carrier in a single crystallite, whereas the drift mobility, $\mu_d = v_d/E$, is the mobility of a charge carrier in a macroscopic polycrystalline sample. The distinction is necessary, of course, because in a measurement of the drift mobility the charge carriers undergo intermolecular motion and may be scattered by structural defects or impurities, or may be influenced by the surface of the sample. The ohmic mobility μ_0, may be estimated from the conductivity data given in Table I, since $\mu_0 = \sigma/nq$. The following expression also then results if one assumes DNA to be an intrinsic semi-conductor[23]

$$\sigma_0 = 2q(\mu_e + \mu_h)\left(\frac{2\pi kTm}{h^2}\right)^{3/2}\left(\frac{m^*_e m^*_h}{m^2}\right)^{3/4} \tag{3}$$

where q is the electron charge, μ_e and μ_h are the electron and hole mobilities, and m is the rest mass of the electron. For calculating μ_0 we here take as a reasonable experimental estimate O'Konski's value of $\sigma_0 = 4\times10^3$ ohm^{-1}cm^{-1}. The "constant" σ_0 is a function of temperature, but a calculation for σ_0 at 300°K differs from one at 400°K by only a factor of 1.5 which is small compared to the uncertainty in σ_0 of an order of magnitude or more. The effective masses m^*_e and m^*_h taken from Table II are found through the Shockley relation and are the effective masses of the charge carriers within a single crystal of DNA. However, here we will assume they are reasonable approximations of the carriers' effective masses anywhere within the DNA sample. Making a final assumption

that the electron and hole mobilities are equal, then the mobilities for the two models are $\mu_0 = 24$ cm^2/V sec for the Harmonic Potential and $\mu_0 = 45$ cm^2/V sec for the Kronig-Penney Potential.

Few organic semiconductor mobilities have been measured, but typically they are very small compared to those of semiconductors like Si and Ge. The drift mobilities for anthracene lie in the range of 10^{-2} to 10 cm^2/V sec and an estimate of the local electron mobility in DNA has been made by Suhai from O'Konski's ac conductivity data. Suhai reasons that the ac conductivity levels off at 10^8 Hz because motions of the electrons are totally confined to the molecules. They make no intermolecular jumps, so they are not impeded by intermolecular barriers and are not scattered by structural defects or impurities. Suhai notes that this value is only approximate since the lengths of the molecules are not accurately known. The calculations presented here show that the models do not give unreasonable values for the ohmic mobility, but because of the uncertainty in σ_0, because of the number of approximations, and because of the lack of experimental data on μ_0 there is some doubt in the validity of the calculations.

V. Summary

We have applied simplified models to the problem of the determination of term energies in DNA. Similar calculations may be carried out for other molecules for which periodicity may be exploited. No perturbation approximations have been employed in the π electron calculation here although an effective mass has been defined. This effective mass arises in a self-consistent manner, where the physical band gap is assumed given by the experimental data. While admittedly the effective mass approximation seems crude compared to an approach from first principles, it does bring in the fact that the electrons may exchange energy with the lattice and with other electrons (albeit in a phenomenological way). In any event, the concept of effective mass does continue to be a useful one in diverse solid state applications.

The model calculations show that the conducting electrons are relatively mobile and that the conduction widths are of the order of tenths of an electron volt. The mobilities are high and better comparison will have to await more exact and reproducible measurements. The term energies compare favorably with those obtained by more complicated approximations.

Acknowledgment

References

[1] P. Rosen, *Biophys. J.*, 8 (1968) 391.

[2] J. Krizan, *Biophys. J.*, 13 (1973) 1.

[3] B. Pullman and A. Pullman, *Prog. Nuc. Acid Res. Mol. Biol.*, 9 (1969) 327.

[4] T. A. Hoffman and J. Ladik, *The Structure and Properties of Biomolecules and Biological Systems*, ed. by J. Duchesne (J. Wiley and Sons, New York, 1964).

[5] E. Subertova, V. Prosser and J. Drobnik, *Biopolymers*, 8 (1969) 421.

[6] L. Brillouin, *Wave Mechanics and Molecular Biology*, ed. by L. de Broglie (Addison-Wesley, Reading, Mass., 1966).

[7] C. T. O'Konski, P. Moser, and M. Shirai, *Quantum Aspects of Polypeptides and Polynucleotides*, ed. by M. Weissbluth (J. Wiley and Sons, New York, 1964).

[8] D. D. Eley, *Horizons in Biochemistry*, ed. by M. Kasha and B. Pullman (Academic Press, New York, 1962).

[9] J. Avery, J. Parker, J. Ladik and G. Biczo, *J. Mol. Spect.*, 29 (1969) 194.

[10] P. Rosen, *J. Biol. Phys.*, 1 (1973) 244.

[11] W. Rhodes, *J. Chem. Soc.*, 83 (1961) 3609.

[12] M. Weissbluth, *Quart. Rev. Biophys.*, 4 (1971) 1.

[13] S. Suhai, *J. Chem. Phys.*, 57 (1972) 5599.

[14] H. A. Pohl, *J. Biol. Phys.*, 2 (1974) 113.

[15] R. S. Snart, *Trans. Faraday Soc.*, 483 (1963) 755.

[16] D. D. Eley and D. I. Spivey, *Trans. Faraday Soc.*, 58 (1962) 411.

[17] D. Vasilescu, Doctoral thesis (1964), Lyon; G. Mesnard and D. Vasilescu c.r. hebd. Seanc. Acad. Sci., Paris, 257 (1963) 4177.

[18] M. E. Burnell, D. D. Eley and V. Subramangan, Ann. N. Y. Acad. Sci., 158 (1969) 191.

[19] C. Y. Liang and E. G. Scalco, *J. Chem. Phys.*, 40 (1964) 919.

[20] D. Vasilescu, *Physico-chemical Properties of Nucleic Acids, VI*, ed. by J. Duchesne (Academic Press, New York, 1973).

[21] I. Tinoco and R. W. Woody, *J. Chem. Phys.*, 40 (1964) 160.

[22] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand, New York, 1966).

[23] C. Kittel, *Introduction to Solid State Physics*, 4th ed. (J. Wiley and Sons, New York, 1971).

[24] O. H. Leblanc, *J. Chem. Phys.*, 33 (1960) 626.

[25] R. G. Kepler, *Phys. Rev.*, 119 (1960) 1226.