Localized electron states in a simple 1D chain with a loop

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A Green's-function method is used for calculations on the onset of localized electron states as a result of changing the connectedness of a simple 1D chain due to the formation of a loop on the chain. © *1994 American Institute of Physics.*

Since the famous paper by Kronig and Penney,[1] who derived the electron spectrum of a single-component, periodic, 1D chain, linear chains have served as an excellent model for the analysis of many properties and effects of solids.[2] The results of this research have taken on particular importance in the physics and biophysics of polymer chains.[3] In the present letter we examine the onset of a local electron state due to a special configuration of a quasi-1D chain, specifically, the formation of a loop on the chain (Fig. 1), with the result that the topology of the system is altered.

We consider the simple quasi-1D chain in Fig. 1. The Green's function of this system in the one-electron approximation, for the strong-coupling method, is

$$G^0(\bar{r},\bar{r}',\omega)=\sum_k \phi_k(\bar{r})\phi_k^*(\bar{r}')G^0(k,\omega), \tag{1}$$

where $G^0(k,\omega)=1/[\omega-A\cos(ka)]$, $\phi_k(\bar{r})$ is the wave function of an electron in the chain, given by

$$\phi_k(\bar{r})=\sum e^{ikna}\phi(|\bar{r}-\bar{a}_n|)/\sqrt{N}, \quad \bar{a}_n=a\sum_i^n \bar{e}_i,$$

e_i is a unit vector directed along segment i, $\phi(|\bar{r}-\bar{a}_n|)$ is the normalized wave function of an electron in an isolated atom in the s state near site n, $A/2$ is the resonant integral of the coupling of two neighboring atoms ($A<0$), and n is the number of atoms in the chain. The electron spectrum of this system is a band with a dispersion relation

$$\omega=A\cos(ka). \tag{2}$$

We now form a loop on the linear chain, at which the distance between the nearest atoms of the "contact" is R. As a result, there is a change in the connectedness of the

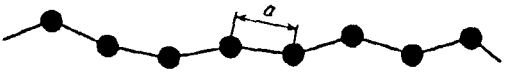

FIG. 1. Quasi-1D homoatomic chain with a period a.

system (Fig. 2). We assume $R \geqslant a$. For all distances R under consideration, the exchange interaction of the atoms of the contact outweighs other interactions. The Green's function with a loop then satisfies a Dyson equation

$$G = G^0 + G^0 \hat{V} G, \tag{3}$$

where $\hat{V}$ is the difference between the Hamiltonian of the chain with the loop and that of a rectilinear chain, given by

$$\hat{V} = \hat{H} - \hat{H}_0 = \frac{t}{2} a_p^+ a_s + \frac{t}{2} a_s^+ a_p .$$

Here the numbers p and s specify the atoms of the contact, so $|p-s|\ a = ma$ is the perimeter of the loop, and $t/2$ is the exchange integral between atoms of the contact.

We seek the Green's function of a chain with a loop in the form

$$G(\bar{r},\bar{r}',\omega) = \sum_{k,q} \phi_k(\bar{r}) \phi_q^*(\bar{r}') G(k,q,\omega). \tag{4}$$

Substituting (1) and (4) into (3), we find

$$G(k,q,\omega) = G^0(k,\omega) \left[\delta_{kq} + \sum_Q G(Q,q;\omega) V_{kQ} \right], \tag{5}$$

where V_{kQ} is the matrix element

$$V_{kQ} = \frac{t}{2} e^{ikpa} e^{-iQsa} + \frac{t}{2} e^{iksa} e^{-iQpa}. \tag{6}$$

Substituting (6) into (5), we find an equation which we first multiply, term by term, by e^{-iQpa} and then sum over k. We then repeat the procedure, multiplying by e^{-iQsa}. In this manner we obtain a system of two equations with two variables:

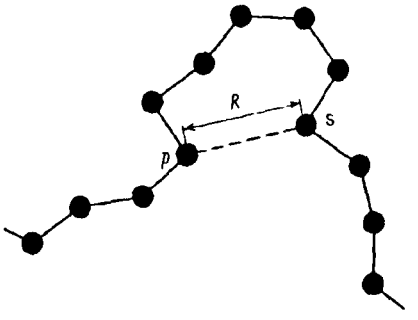

FIG. 2. Quasi-1D homoatomic chain with a self-intersection at sites p and s. The distance between the sites of the "contact" is R.

$$\begin{cases} a_1^0+Xa_1^1+Ya_1^2=0, \\ a_2^0+Xa_2^1+Ya_2^2=0, \end{cases} \tag{7}$$

where

$$X=\sum_k G(k,q;\omega)e^{-iksa}, \quad Y=\sum_k G(k,q;\omega)e^{-ikpa},$$

$$a_1^0=e^{-iqsa}G^0(q;\omega), \quad a_2^0=e^{-iqpa}G^0(q;\omega), \quad a_2^1=a_1^2=\frac{t}{2}\frac{1}{N}\sum_k G^0(k,\omega), \tag{8}$$

$$a_1^1=\frac{t}{2N_k}\sum G^0(k,\omega)e^{-ikma}-1, \quad a_2^2=\frac{t}{2N_k}\sum G^0(k,\omega)e^{ikma}-1.$$

Since bound states exist when the Green's function has an isolated pole, we restrict the discussion to the solution of system (7) [we restrict the analysis to finding $\Sigma_k G(k,q;\omega)e^{-iksa}$ and $\Sigma_k G(k,q;\omega)e^{-ikpa}$, since the poles of the latter coincide with the poles of the Green's function $G(k,q;\omega)$].

Solving system (7) for X and Y, and using (8), we can immediately state that the energy of the bound states of a chain with a loop is found from the equations

$$\left(1-\frac{t}{2}\frac{1}{N}\sum_k G^0(k,\omega)e^{-ikma}\right)\left(1-\frac{t}{2}\frac{1}{N}\sum_k G^0(k,\omega)e^{ikma}\right)$$
$$-\frac{t^2}{4}\frac{1}{N^2}\left(\sum_k G^0(k,\omega)\right)^2=0. \tag{9}$$

Since k runs over several discrete values, $k=2\pi\nu/(Na)$, where ν is an integer from the interval $-N/2<\nu<N/2$, we can replace the sum over k by an integral

$$\sum(k)\to\frac{N}{2\pi}\int_0^{2\pi} f(ka)d(ka).$$

Evaluating the resulting integrals in the region of forbidden energies, corresponding to real values of $\omega(\omega/|A|>1, \omega/|A|<-1)$, we find the following equations:

$$\left[1+\frac{|t|(-1)^m}{2(\omega^2-A^2)^{1/2}}\left(\frac{\omega-(\omega^2-A^2)^{1/2}}{|A|}\right)^m-\frac{|t|}{2}\frac{1}{(\omega^2-A^2)^{1/2}}\right]$$
$$\times\left[1+\frac{|t|(-1)^m}{2(\omega^2-A^2)^{1/2}}\left(\frac{\omega-(\omega^2-A^2)^{1/2}}{|A|}\right)^m+\frac{|t|}{2}\frac{1}{(\omega^2-A^2)^{1/2}}\right]=0 \tag{10a}$$

for $\omega/|A|>1$ and

$$\left[1-\frac{|t|(-1)^m}{2(\omega^2-A^2)^{1/2}}\left(\frac{\omega+(\omega^2-A^2)^{1/2}}{|A|}\right)^m-\frac{|t|}{2}\frac{1}{(\omega^2-A^2)^{1/2}}\right]$$

$$\times\left[1-\frac{|t|(-1)^m}{2(\omega^2-A^2)^{1/2}}\left(\frac{\omega+(\omega^2-A^2)^{1/2}}{|A|}\right)^m+\frac{|t|}{2}\frac{1}{(\omega^2-A^2)^{1/2}}\right]=0 \tag{10b}$$

for $\omega/|A|<-1$. Using the change of variable

$$\omega=|A|(y^2+1)/2y, \tag{11}$$

we can reduce Eqs. (10) to the following form under the condition $y\neq\pm 1$:

$$[y^2-1-gy+g(-1)^m y^{m+1}][y^2-1+gy+g(-1)^m y^{m+1}]=0 \quad (y>0), \tag{12a}$$

$$[y^2-1-gy-g(-1)^m y^{m+1}][y^2-1+gy-g(-1)^m y^{m+1}]=0 \quad (y<0), \tag{12b}$$

where $g=|t|/|A|$. Since we have $y>0$ and $y<0$ for each of Eqs. (12), by satisfying the latter conditions we find

$$y^2-1+gy+g(-1)^m y^{m+1}=0, \tag{13}$$

$$y^2-1-gy-g(-1)^m y^{m+1}=0. \tag{14}$$

The solutions of the latter equation are useful to classify on the basis of the parity of m. Restricting the discussion to large values of m, we find

$$y=\pm y_0+gy_0^{2k+1}/[2y_0-g-gy_0^{2k}(2k+1)]$$

for $m=2k$ and

$$y=\pm y_0\mp gy_0^{2k+2}/[2y_0-g+gy_0^{2k+1}(2k+2)]$$

for $m=2k+1$. Here $y_0=(g-\sqrt{g^2+4})/2$. Recalling that the problem has been solved for real values of the energy, for the case $g=1$, we find in the limit $m\to\infty$ that two bound states, characterized by energies $\omega=\pm|A|\sqrt{5}/2$, exist in the system.

In summary, the formation of a loop on a simple quasi-1D chain, which results in a change in the connectedness of the system, gives rise to two local states, which lie in the energy band gaps of the chain.

[1] R. de L. Kronig and W. Penney, Proc. R. Soc. **130**, 499 (1931).
[2] *Mathematical Physics in One Dimension: Exactly Soluble Models of Interacting Particles*, ed. by E. Lieb and D. C. Mattis (Academic, New York, 1966).
[3] I. B. Golovanov *et al.*, *Elementary Introduction to Quantum Biochemistry* [in Russian] (Nauka, Moscow, 1969).

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