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Xin Sun, Chang-qin Wu, Rouli Fu, Duo Liang Lin and Thomas F. George

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What is the effect of the electron interaction on the lattice instability of one-dimensional systems with strong electron correlation is a controversal problem. One side believes the electron interaction enhances the instability; but the other side declares the instability is reduced by the electron interaction. The origin of this controversy is analysed in this paper, and we find that the range of the electron interaction plays a decisive role. When the range is long, the electron interaction enhances the lattice instability, whereas, if the range is short, the electron interaction reduces the instability. Based on this conclusion, we can clarify the dispute about the effect of the electron interaction on the dimerization of the conducting polymers.

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STRONGLY COUPLED ONE-DIMENSIONAL SYSTEM AND THE POLYMER

Xin SUN * Chang-qin WU *. Rouli FU §. Duo Liang LIN †. and Thomas F. GEORGE †

* Lab for Solid State Microstructure. Nanjing University. Nanjing 210008; and Department of Physics. Fudan university. Shanghai 200433. China [a]
§ Lab for Infrared Physics. Academia Sinica. Shanghai 200081. China
† Department of Physics and Astronomy. State University of New York at Buffalo. Buffalo. New York 14260

What is the effect of the electron interaction on the lattice instability of one-dimensional systems with strong electron correlation is a controversal problem. One side believes the electron interaction enhances the instability; but the other side declares the instability is reduced by the electron interaction. The origin of this controversy is analysed in this paper, and we find that the range of the electron interaction plays a decisive role. When the range is long, the electron interaction enhances the lattice instability, whereas, if the range is short, the electron interaction reduces the instability. Based on this conclusion, we can clarify the dispute about the effect of the electron interaction on the dimerization of the conducting polymers.

1. INTRODUCTION

For a one-dimensional system, due to the electron-lattice interaction, a proper modulation of the lattice can always make the boundary of the Brillouin zone coincide with the Fermi surface. Then, a gap is opened on the Fermi surface. This gap will lower the energy, and a lattice distortion results from such modulation. It is the so-called Peierls instability, which is the peculiarity of one-dimensional systems. If the band is half filled, this instability will cause the dimerization, which produces the bond alternation of the polymers. In many one-dimensional systems, such as the conducting polymers, the electron correlation is strong. Then, an important question is asked: is the lattice instability enhanced or reduced by the electron-electron interaction? It has attracted considerable attention.[1-6] So far the extended Hubbard model

$$H_H = U\sum_{i,\sigma} n_{i,\sigma}n_{i,-\sigma} + V\sum_{i,\sigma,\sigma'} n_{i,\sigma}n_{i-1,\sigma'} \qquad (1)$$

is used to describe the electron interaction. And many different techniques, such as the renormalization group.[1] Gutzwiller variational calculation.[2] Monte Carlo simulation.[3] valence bond method.[4] etc., have been used to investigate the effect of electron interaction on the dimerization. These studies reach the same result that the dimerization is greatly enhanced by electron interaction. Furthermore, they conclude that the main origin of the dimerization is the electron-electron interaction rather than the electron-lattice interaction.

2. DISPUTE

However, this conclusion is challenged recently by Kivelson, Su, Schrieffer and Heeger (KSSH),[7] who argue that the repulsive interaction between electrons should be unfavorable to deviate from the uniform structure. Then they declare an opposite opinion that the electron interaction has to reduce the dimerization. KSSH point out that the extended Hubbard model only contains site-charge repulsion, which is the diagonal part of the Coulomb interaction, missing the bond-charge repulsion

$$W C^{+}_{i,s} C_{i+1,s} C^{+}_{i,s'} C_{i+1,s'} \quad , \tag{2}$$

which is one of the off-diagonal terms of the Coulomb interaction. By adding such W term to the extended model, they show the dimerization can be suppress by the electron interaction. But the other side presents opposite Comments on KSSH's theory and insists the original opinion.[8]

Obviously, the divergence of these two sides lies in the different descriptions of the electron interaction. One side only takes the diagonal terms U, V of Coulomb interaction, and the other side adds one more term W. Since the site-charge repulsion U, V and the bond-charge repulsion W are some terms of Coulomb interaction, the full interaction between electrons contains many other terms also. Therefore, in order to clarify this dispute, we should start the study from a general electron interaction — the screened Coulomb potential

$$v(r) = \frac{U_0}{\sqrt{1+(r/a)^2}} \exp(-\beta r/a) \quad , \tag{3}$$

where U_0 and β are the strength and the screening factor of the interaction. This general interaction includes all diagonal and off-diagonal terms. Actually, in the second quantized representation, the interaction (3) can be written as

$$H' = \sum_{i,j,l,m,s,s'} V(i,j,l,m) C^{+}_{i,s} C^{+}_{j,s'} C_{l,s'} C_{m,s} \quad , \tag{4}$$

$$V(i,j,l,m) = \int dx \int dx' \phi^{*}_{i}(x) \phi^{*}_{j}(x') v(x-x') \phi_{l}(x') \phi_{m}(x) \quad . \tag{5}$$

It is easy to see that $V(i,i,i,i) = U$, $V(i,j,j,i) = V$, and $V(i,j,i,j) = W$. So, the extended Hubbard model and the KSSH's model are different approximations of the interaction (3), and the general interaction (3) can give a reliable answer to the dispute.

3. CORRELATED BASIS FUNCTIONS (CBF) THEORY

The key quantity of a many-electron system is the electron correlation function $g(1,2)$, from which the energy and other properties, including the dimerization u of the system can be obtained. A powerful method to get the correlation function is the CBF theory.[10]

Let us denote the non-interacting electron orbit as $\phi_k(x)$, hen, the ground state of the interacting system can be written as

$$\Psi(1,2,\ldots,N) = D[\phi_k] \cdot \exp[u(1,2,\ldots,N)] \quad , \tag{6}$$

where $D[\phi_k]$ is the Slater determinant and $u(1,2,.....N)$ is the correlation factor, which can be determined by the variational principle. In the case of a half-filled band, each atom has only one electron, and the electron density is not high. Meanwhile, there is no electron condensation due to the repulsion between electrons. Then, it is rare for three or more electrons to be gathered closely, and the two-body correlation factor u_{ij} is dominant. In such a case, the correlation function $g(1,2)$ can be calculated by solving the following equations[9]

$$g(1,2/\xi) = g(1,2/0)\exp\int_0^{\xi} d\xi' K(1,2/\xi') \ , \tag{7}$$

$$K(1,2/\xi) = [u_{12} + \alpha(1,2) + \alpha(2,1) + \int d3P(3)h_{12}\alpha(2,3)] \cdot[\delta(1,2) + \delta(2,1) + \varsigma(1,2) + \gamma(1,2)]/g(1,2) \ , \tag{8}$$

$$h_{12} = g(1,2) - 1 \ , \qquad \alpha(1,2) = \int d3P(3)h_{13}u_{23} \ , \tag{9}$$

$$\delta(1,2) = \int d3P(3)h_{13}h_{23}[u_{12} + \alpha(1,3) + \alpha(3,1) + \int d4P(4)h_{14}\alpha(3,4)] \ , \tag{10}$$

$$\varsigma(1,2) = \int d3P(3)h_{13}\delta(3,2) \ , \tag{11}$$

$$\gamma(1,2) = \int d3P(3)h_{13}h_{23}\int d4P(4)[u_{34}g(3,4) + \alpha(3,4)(1 + h_{34}/2)h_{34}\int d5P(5)h_{45}(u_{45} + \alpha(4,5)/2)]. \tag{12}$$

4. RESULTS AND CONCLUSIONS

By using the variational principle and the obtained $g(1,2)$, we can get the dependence of the dimerization $u(U_0)$ on the interaction strength U_0 for different screening factors β. Our results show there exists a critical value β_c:

1. if $\beta < \beta_c$, the dimerization is initially enhanced by the electron-electron interaction.
2. if $\beta > \beta_c$, the dimerization is reduced by the electron-electron interaction.

In other words, the effect of the electron-electron interaction on the lattice instability depends on the interaction range $\Lambda = a/\beta$. The long-ranged interaction will enhance the instability, but the short-ranged interaction will suppress it. For the conducting polymers, $\beta_c \sim 2$.

It is not difficult to understand why the interaction range is the decisive factor to determine the behavior of the lattice instability. First, let us look at the dependence of the ratio W/V on the screening factor β, which is shown in the following table. The ratio W/V monotonically

β	1.0	3.0	5.0	7.0
W/V	0.02	0.10	0.26	0.43

increases with increasing β. Therefore, when the interaction range Λ is long (β is small), the off-diagonal terms are very small and can be neglected. Then the extended Hubbard model is valid, so the dimerizasion is enhanced by the electron-electron interaction. In the opposite case, Λ is

short (β is big), the off-diagonal terms become important, and the extended Hubbard model fails. hen the bond-charge repulsion and other off-diagonal terms make the dimerization reduced. For the polyacetylene. it can be estimated from the optical gap that its screening factor $\beta_{PA} = 1.7$. Since $\beta_{PA} < \beta_c$. the dimerization of the polyacetylene is enhanced about 25% by the electron interaction.

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REFERENCES

(*a*) The permanent address.

1. G.W. Hayden and E.J. Mele, Phys. Rev. B34 (1986) 5484.
2. D. Baeriswyl and K. Maki, Phys. Rev. B31 (1985) 6633.
3. J.E. Hirsch. Phys. Rev. Lett. 51 (1983) 296; D.K. Campbell. T. DeGrand and S. Mazumdar. Phys. Rev. Lett. 52 (1984) 1717.
4. Z. Soos and S. Ramasesha. Phys. Rev. Lett. 51 (1983) 2374; S. Mazumdar and S. N. Dixit. Phys. Rev. Lett. 51(1983) 292; P. Tavan and K. Schulten. Phys. Rev. B36 (1987) 4337.
5. S. Kivelson and D.Heim. Phys. Rev. B26 (1982) 4278; H. Fukutome and M. Sasai. Prog. Theor. Phys. 61 (1983) 1.
6. W. Wu and S. Kivelson. Phys. Rev. B33 (1986) 8546.
7. S. Kivelson. W.P. Su. J.R. Schrieffer and A.J. Heeger. Phys. Rev. Lett. 58 (1987) 1899.
8. D. Baeriswyl. P. Horsch and K. Maki. Phys. Rev. Lett. 60 (1988) 70; J. Gammel and D.K. Campbell. Phys. Rev. Lett. 60 (1988)71.
9. C. Wu. X. Sun and K. Nasu. Phys. Rev. Lett. 59 (1987) 831.
10. E. Feenberg. *Theory of Quantum Fluids* (Academic. New York. 1969); S. Chakravarty and C.W. Woo. Phys. Rev. B13 (1976) 4815.

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