Available online at www.sciencedirect.com
ScienceDirect
Physica E 40 (2008) 2736–2741
PHYSICA E
www.elsevier.com/locate/physe

Tomonaga–Luttinger liquid feature in sodium-doped quasi-one-dimensional *trans*-polyacetylene chain

Sabyasachi Sen, Swapan Chakrabarti*

Department of Chemistry, University of Calcutta, 92, A.P.C. Roy Road, Kolkata 700 009, India

Received 10 September 2007; accepted 12 December 2007
Available online 6 January 2008

Abstract

We employ density functional theoretical calculation to establish Tomonaga–Luttinger liquid (TLL) behavior of sodium-doped quasi-one-dimensional *trans*-polyacetylene chain. A study of density of states near the Fermi energy demonstrates power-law dependence at doping concentrations 8.3%, 10.0% and 12.5%. The existence of power-law behavior in density of states is the signature of TLL behavior. Related power-law scaling factors are calculated from the slopes of logarithmic density of states versus logarithmic energy relative to Fermi energy plot. Asymptotic variation of density–density correlation function also confirms the appearance of TLL.

PACS: 71.10.Pm; 71.15.Mb; 71.20.Rv

Keywords: Luttinger liquid; *Trans*-polyacetylene; Ab initio density functional calculation; Electronic structure

1. Introduction

In recent times there have been remarkable research interests on the exploration of physical and chemical properties of materials in lower dimension [1–4]. The physics of materials in lower dimension is complicated due to quantum many-body effects. It is reported that due to the strong electronic correlation effects, the metallic phase of one-dimensional (1D) or quasi-1D lattices deviates from the Fermi liquid (FL) behavior. Experimental evidences like the absence of Fermi edges in the single-particle excitation spectra probed by angle-resolved photoelectron spectroscopy also suggest that quasi-1D metals show marked deviation from the FL theory. Moreover, the FL theory fails even for apparently weak short-range repulsion between electrons in 1D or quasi-1D. The low-energy physical properties of electrons in 1D and quasi-1D are described by Tomonaga–Luttinger liquid (TLL) theory [5,6]. TLL shows unique behavior in the correlation function, momentum distribution of electrons and more significantly there is a suppression of density of states (DOS) near-Fermi energy even at 0 K which follows a power law, $n(E)\infty E^{\alpha}$, where α is an interaction-dependent exponent [7]. The elementary excitations in TLL are not the fermionic quasi-particles rather they are replaced by bosonic charge and spin density waves dispersing at different velocities. This feature of TLL is known as the spin–charge separation [8].

The issue of TLL behavior in 1D and quasi-1D systems has been addressed in numerous theoretical and experimental investigations [2–4,9–11]. TLL feature has been observed in various systems, e.g. carbon nanotube [7], charge transfer salt, like TTF-TCNQ [12], charge density wave compounds [13], Bechgaard salt [14], metallic edge of nanoclusters [15], 1D electron gas on the κ-$Al_2O_3(0\,0\,\bar{1})$ surface [13], edge of two-dimensional electron gas [16], etc. One of the major challenging aspects of the modern condensed matter physics is the designing of novel materials with TLL feature. Moreover, a great deal of research interests has also been devoted to the determination of TLL to FL transition. Recently, Rauf et al. [7] have shown that doping induced TLL to FL transition is possible in potassium-intercalated mats of single-wall carbon nanotubes (SWCNT). On the other hand FL to

---

*Corresponding author. Tel.: +91 33 25950483; fax: +91 33 23519755.
E-mail address: swapanchem@yahoo.co.in (S. Chakrabarti).

1386-9477/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physe.2007.12.009

TLL transition has also been observed at the edge of a two-dimensional electron gas in GaAs/AlGaAs system [16]. Besides this, the results of ultraviolet photoemission spectroscopic (UPS) study on heavily doped (potassium and perchlorate) *trans*-polyacetylene demonstrates that in doped *trans*-polyacetylene DOS near the Fermi level follows a power law hence the related metallic state should be associated with TLL feature [17]. Numerically the existence of TLL state in potassium-doped *trans*-polyacetylene chain has been shown by Sen and Chakrabarti [18]. Numerical simulation of TLL to FL transformation has been also reported by Sen and Chakrabarti [19] in lithium-doped *trans*-polyacetylene chain.

Pristine *trans*-polyacetylene, a prototype of all low-dimensional materials is an insulator. The hallmark feature of quasi-1D lattice of *trans*-polyacetylene is the lattice dimerization (Peierls distortion) and an associated Peierls gap opening at $\pi/2a$ (a being the lattice constant) [20]. Effect of doping results in charge injection towards the *trans*-polyacetylene chain. Consequently due to strong electron correlation, the degree of lattice dimerization as well as the Peierls gap decreases. The Peierls gap eventually disappears at certain doping concentration indicating the emergence of metallic state. The realization of metallic state in heavily doped *trans*-polyacetylene has been justified by the results of infrared spectra, Pauli spin susceptibility and measurement of high electrical conductivity in heavily doped samples [21,22]. Obvious inquisition in this context is to assess whether at all doping concentration in the metallic regime the material shows uniform TLL/FL behavior or is there any crossover between the two electron liquids.

The focus of the present study is to investigate the behavior of electron liquid in the ground state of sodium (Na)-doped quasi-1D *trans*-polyacetylene chain. First principal density functional theory (DFT) has been used as the investigating tool. The doping level at which the present calculations have been performed are 25.0%, 16.6%, 12.5%, 10.0% and 8.3%, respectively.

2. Computational details

All the calculations have been performed in the Amsterdam density functional package (ADF 2006.01) [23]. The geometry of the unit cells at different doping levels has been optimized through unconstrained relaxation search using BLYP [24]-type exchange-correlation functional and TZ2P basis set. The C–C single bond length is 1.40 Å and the corresponding C–C double bond length is 1.38 Å. From the geometry optimization of pristine *trans*-polyacetylene sample same two bond lengths are measured as 1.42 and 1.34 Å, respectively. C–Na bond distance of the doped sample is 2.52 Å. The CCC and the CCH angles are 124.5° and 119.2°, respectively, for doped samples. As evident from the geometry optimization of the unit cells, that in case of doping the dimerization amplitude varies between 0.02 and 0.03 Å. The geometry of the unit cell corresponding to the doping level of 8.3% is presented in Fig. 1. The BAND subprogram of ADF 2006.01 has been used for the calculation of band structure and evaluation of DOS. Density functional calculations have been carried out under the generalized gradient approximation (GGA) scheme. The exchange-correlation functional of Perdew and Wang (PW91) [25] has been used in GGA scheme. PW91 functional includes local correlation through the quantum Monte Carlo treatment for the homogeneous electron gas including all excitations while non-local correlation effects are incorporated through the explicit inclusion of Coulomb hole for the inhomogeneous electron gas. The basis set chosen consists of a triple zeta basis augmented with two polarization functions [TZ2P NAO + STO (basis V in the band program)]. For integration in the real space the accuracy parameter is set to three. Five symmetry unique k points are generated in the first Brillouin zone by choosing the reciprocal space integration accuracy five. Following Kohn–Sham density functional theory the Hamiltonian equation for the BAND subprogram is expressed as

$$H\psi_n(\boldsymbol{k};\boldsymbol{r}) = \{T + V_c(\boldsymbol{r}) + V_{xc}(\boldsymbol{r})\}\psi_n(\boldsymbol{k};\boldsymbol{r}) = e_n(\boldsymbol{k})\psi_n(\boldsymbol{k};\boldsymbol{r}),$$

where T is the kinetic energy operator, $V_{xc}(\boldsymbol{r})$ is the exchange-correlation potential and $V_c(\boldsymbol{r})$ is the Coulomb potential due to nuclear charges and the electron cloud. $\psi_n(\boldsymbol{k};\boldsymbol{r})$ is one electron state with wave vector $\boldsymbol{k};\boldsymbol{k}$ indicates the irreducible representations of the translational group corresponding to the Bravis lattice. The states $\psi_n(\boldsymbol{k};\boldsymbol{r})$ are

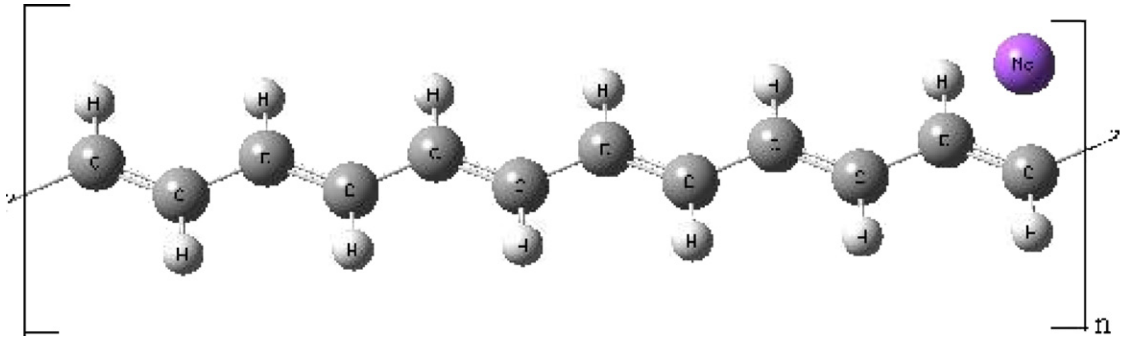

Fig. 1. Optimized unit cell of 8.3% sodium-doped *trans*-polyacetylene.