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Charge Transport in DNA with Structure of Quantum Wells and Potential Barriers

GUIQING ZHANG*, HAIQUAN HU, SHOUXIN CUI and ZENGTAO LV

School of Physics Science and Information Engineering, Liaocheng University, Liaocheng 252059, P.R. China

*Corresponding author: E-mail: zhangguiqing@lcu.edu.cn

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Based on Su-Schrieffer-Heeger model, an excess charge in DNA chain couples with lattices' distortion and appears in the form of a polaron. The four kinds of nucleotides of DNA with different on-site energy can be viewed a similar structure with quantum wells and potential barriers. Their width and depth effect on polaron motion along DNA chain will be discussed. Our calculations indicate that a polaron can go through one quantum well and more than one potential barrier under a suitable electric field. The details about charge transport are also depicted when it comes into contact with quantum wells or potential barriers in this paper.

Key Words: DNA, Su-Schrieffer-Heeger model, Quantum wells, Potential barriers, Polaron.

INTRODUCTION

Processes of charge transport along a DNA chain composed of different nucleotides are extreme interest for these are relevant to DNA damage and repair[1,2], as well as its potential application in nano-scale electronic devices[3]. Since 1993 Barton group reported that a hole transfer in DNA over a distance over 4 nanometers, a large number of experiments and theories have been advanced in the attempt to characterize the transport. However the debates about the conductivity of the DNA have never been interrupted in the past 10 years because different experimental results about the conductivity of DNA can be obtained from insulator[4,5] to well conductivity[6,7], even to super conductor[8]. Perhaps the above phenomena can be interpreted by its complex structure and different environmental conditions, such as kinds of nucleotides, solvent, polarization and temperature. In the past decade, some theoretical groups adopt model calculations to interpret the widely differential conclusions based on polaron model with modified Su-Schrieffer-Heeger (SSH) model[9-11] and Peyrard-Bishop-Holstein (PBH) model[12-17]. In these two models, the electron and lattice Hamiltonians are dealt with quantum and classic mechanics, respectively. However, the couplings between an electron with the adjacent bases deformation (in SSH model) and with hydrogen bonds stretching (in PBH model) are emphasized. The two presumed mechanisms-hopping and tunneling are also investigated and testified with these two models[18-25]. In Su-Schrieffer-Heeger model based on hole polaron carriers, some groups have investigated some certain chains made up of different bases, assumed that the chains are composed of alternate quantum wells and potential barriers[26]. However, the width and depth of quantum wells and potential barriers influences on charge transport have not been discussed.

In this paper, we will discuss the effect of the width and depth of quantum wells and potential barriers on the polaron motion along the DNA chain.

Model and calculation: The SSH model modified by Ono and Terai is adopted in our calculations[9,27,28]. In this model, the DNA double helix can be viwed as a quasi one dimensional structure showed in Fig. 1.

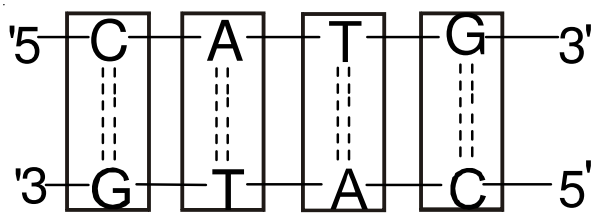


Fig. 1. DNA structure schematic diagram in our calculations.

The model Hamilton includes two parts:

$$H = H_{el} + H_{lat} \quad (1)$$

$$H_{el} = \sum_{n,s} d_n c^{+}_{n,s} c_{n,s} - \sum [t_0 - \alpha(\mu_{n+1} - \mu_n)](e^{i\gamma A} c^{+}_{n,s} c_{n+1,s} + e^{-i\gamma A} c^{+}_{n+1} c_n) \quad (2)$$

The electron Hamiltonian in period potential electric field can be acquired from (2.1)-(2.5).

$$H_{el}\psi(r) = \left[-\frac{h^2}{2m}\nabla^2 + \sum_n V(r - R_n) \right] \psi(r) = E\psi(r) \quad (2.1)$$

In which the potential field can be split into two parts:

$$\sum_n V(r-R_n) = V(r-R_n) + \sum_{n'\#n} V(r-R_{n'}) \quad (2.2)$$

We can deduce the electron Hamilton by linear combination of atomic orbitals (LCAO) and second quantization.

$$\Psi(r) = \sum_l C_l \varphi_l \quad (2.3)$$

$$\Psi(r) = \sum_l C_l \varphi_l(r) = \sum_l a_l \varphi_l(r) \quad (2.4)$$

$$\Psi^+(r) = \sum_l C_l^+ \varphi_l(r) = \sum_l a_l^+ \varphi_l(r) \quad (2.5)$$

The lattice hamiltonian can be expressed,

$$H_{lat} = \frac{k}{2}\sum_n (\mu_{n+1} - \mu_n)^2 + \frac{M}{2}\sum_n \dot{\mu}_n^2 \quad (3)$$

H_{el} and H_{lat} represent electron and lattice Hamiltonian, respectively. Here $c^+_{n,s}(c_{n,s})$ is the creation (annihilation) operator for an electron with spin s at site n. μ_n is the electron on-site energy at the site n.μn is the displacement of the lattice n from its uniform position. The transfer integral is made up of two parts: t_0 representing the transfer integral in equilibrium and a (μ_n + $_1$-μ_n) representing the change of the transfer integral by the displacement of the site (a is the electron-phonon coupling constant). γ Represents ea/hc (e, a and c are the electron charge, the lattice constant and the velocity of light in vacuum). A is the time dependent vector potential, which expresses the electric field and it satisfies the relation $E = -(1/c)(\partial A/\partial t)$. K is the elastic constant between the nearest lattice sites. M is the mass of the complementary bases at each site.

The static solution of the system Hamiltonian is,

$$y_n = -\frac{2\alpha}{k}\sum_v \phi_v'(n)\phi_v(n+1) + \frac{2\alpha}{k}\sum_m\sum_v \phi_v'(m)\phi_v(m+1) \quad (4)$$

In eqn. (4) $y_n = \mu n + 1 - \mu n$ and Σ' represents the summation over the occupied states only.

To get the properties of the dynamic polaron in an electric field, the time-dependent electron Hamiltonian and the motion equation of the lattice sites are solved separately. The time-dependent electron Hamiltonian equation is

$$i\hbar\frac{\partial\psi_v(t)}{\partial t} = H_{el}\psi_v(t) \quad (5)$$

ψ_v (t) represents the νth wave function of H_{el}. The lattice motion equation is:

$$M\ddot{y}_n(t) = -k(2y_n - y_{n+1} - y_{n-1}) + \alpha\sum\{e^{i\gamma A}[\psi_v^*(n+1)\psi_v(n+2) - 2\psi_v^*(n)\psi_v(n+1) + \psi_v^*(n-1)\psi_v(n)] + h.c.\} \quad (6)$$

ψ_n (n, t) represents the nth component of time-dependent function yn (t).

The characteristic electric-field E_0 can be calculated by the eqn. 7-8:

$$\omega_0 = (4K/M)^{1/2} \quad (7)$$

$$E_0 = \hbar\omega_0/(ea) \quad (8)$$

ω_0 is the phonon frequency and $E_0 = 5.8 \times 10^5$ V/cm. The vector potential A_0 can be acquired by the relation $A_0 t = -cE_0 t$.

In our calculations, there are 100 lattices in DNA stack and each site is occupied by a base (nucleotide). The on-site energy of four bases (Adenine: A; Cytosine: C; Guanine: G; Thymine: T) are chosen as Δ_A = 0.0 eV, Δ_C = -0.35 eV, Δ_G = -0.65 eV and Δ_T = -0.15 eV. The mass of the four kinds of bases are the same and would be 4.35×10^{-22} g, a = 3.4 Å; t_0 = 0.3 eV, α = 0.6 eV/Å; the elastic constant K = 0.85 eV/Å^2 [27].

In SSH model, there are two important parameters, which influence the static polaron: one is the electron lattice coupling constant α and the other is the electron transfer integral t_0. The two parameters effects are depicted in Fig. 2 (a) and (b). The results show that the polaron almost keeps the same profile when the parameters alter. However, the accretion of the electron lattice coupling constant a can increase the charge density and the lattice deformation at the centre of the polaron. Compared with the parameter α, the electron transfer integral t_0 has reverse influences.

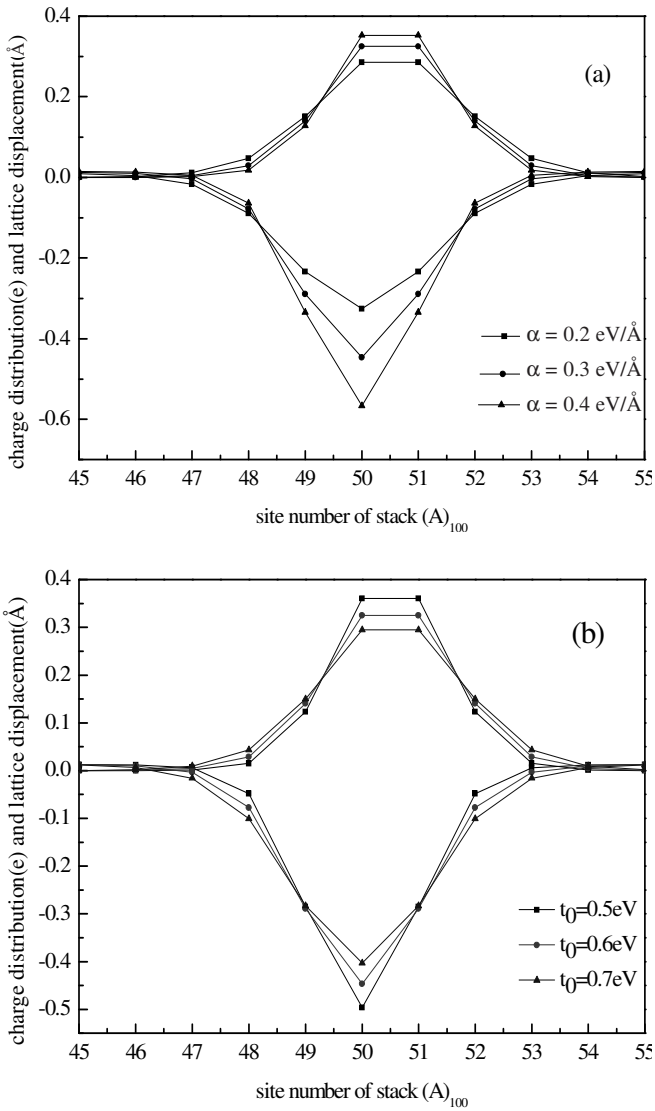


Fig. 2. Parameters of SSH model influences on the static polaron (a) the electron lattice coupling constant a influences (b) the electron transfer integral t_0 influences

The computational results testify that charge distribution and lattice displacement will couple with each other and form

a polaron when an electron is excited away. About its location, it usually localizes at the sites with lowest on-site energy or its neighborhood. However, the static polaron will appear at the sites with larger initial lattice fluctuations (in order to accelerate convergence, initial lattice fluctuations are assumed in our program), not the expected sites, *e.g.* in $(A)_{30}C(A)_{69}$, in Fig. 3. In present calculations, the lattice fluctuations reach to -0.1 Å, so the static polaron can't overcome the potential energy barriers caused by the fluctuations, then appears at the site of 50. It is speculated that these uncertain fluctuations exist reliably in real systems. This may be the reason that for this, the charge transport in DNA becomes complex and understood hardly.

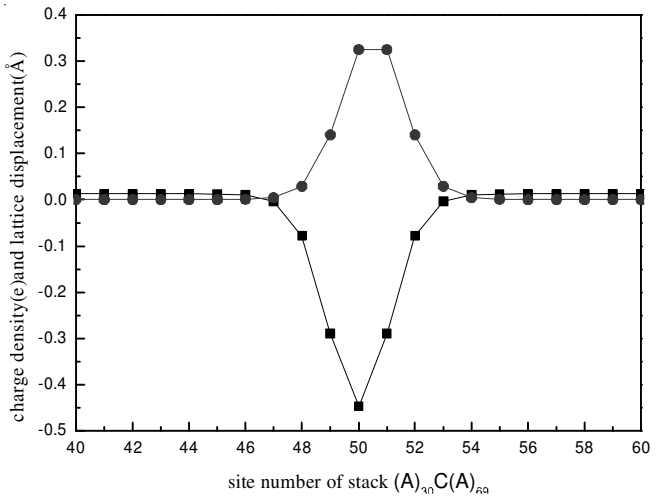
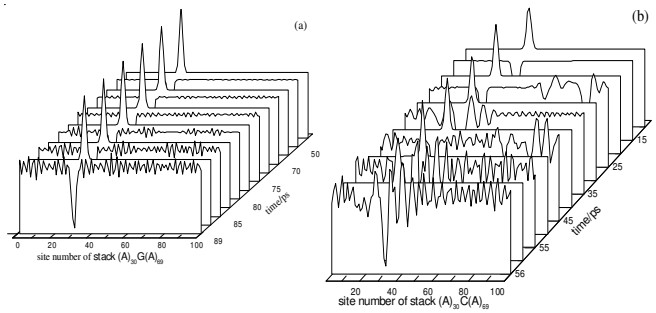


Fig. 3. Static polaron in chain $(A)_{30}C(A)_{69}$

In SSH model calculations, the hole on-site energy, *i.e.* the ionization energy, plays an important role in the dynamic behaviour of a polaron. The site with lower on-site energy will be seemed as a quantum well and the one with higher energy is a potential barrier. In our calculations, the width and depth of quantum wells and potential barriers effects are discussed in detail.

The case of single quantum well is showed in Fig. 4(a)-(c). The initial polaron will move forward along the DNA chain until reaching the quantum well under the electric field. Then the polaron runs into the quantum well and be bonded in it. Usually, the polaron can't overcome the quantum well until smearing. Only the quantum well is shallower, it can move forward as depicted in Fig. 4(c). Then the cases with two or three quantum wells are discussed. Similar to the singe well, the polaron can move into the well and smear completely, which is depicted in Fig. 4 (d)-(f) and (g)-(i).



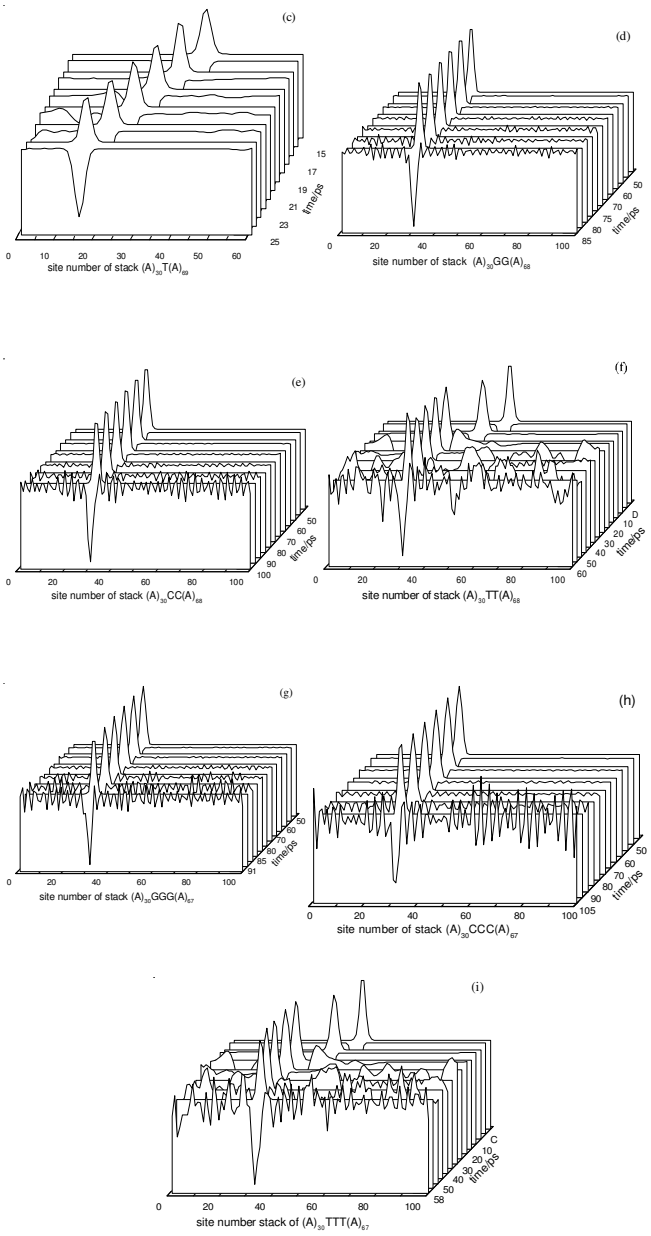


Fig. 4. Dynamic hole polaron at the chain of (a) the single-well $(A)_{30}G(A)_{69}$ (b) the single-well $(A)_{30}C(A)_{69}$ (c) the single-well $(A)_{30}T(A)_{69}$ (d) the two-well $(A)_{30}GG(A)_{68}$ (e) the two-well $(A)_{30}CC(A)_{68}$ (f) the two-well $(A)_{30}TT(A)_{68}$ (g) the three-well $(A)_{30}GGG(A)_{67}$ (h) the three-well $(A)_{30}CCC(A)67$ (i) the three-well $(A)_{30}TTT(A)_{67}$.

Then the potential barriers influences are discussed in Fig.5 (a)-(d). Single potential barriers depth effects are depicted in Fig. 5 (a)-(c). With relative potential barrier energy less, the polaron can overcome the potential barriers and move forward in the chain of $(G)_{30}A(G)_{69}$. However the polaron cannot move when the potential barriers becomes higher, such as in chain of $(G)_{30}A(G)_{69}$ and $(T)_{30}A(T)_{69}$ in Fig. 5 (a) and (b). In the chain composed of double potential barriers, part of charge can tunnel through and form a new polaron. The new small polaron can move forward until smearing and the other part remains at the barrier. Another interesting phenomenon is that the polaron can vibrate at the potential barriers depicted in Fig. 5(b). In order to make it clear, we make a new figure as in Fig. 6. It shows that the vibration of the polaron from 55 to 77ps.

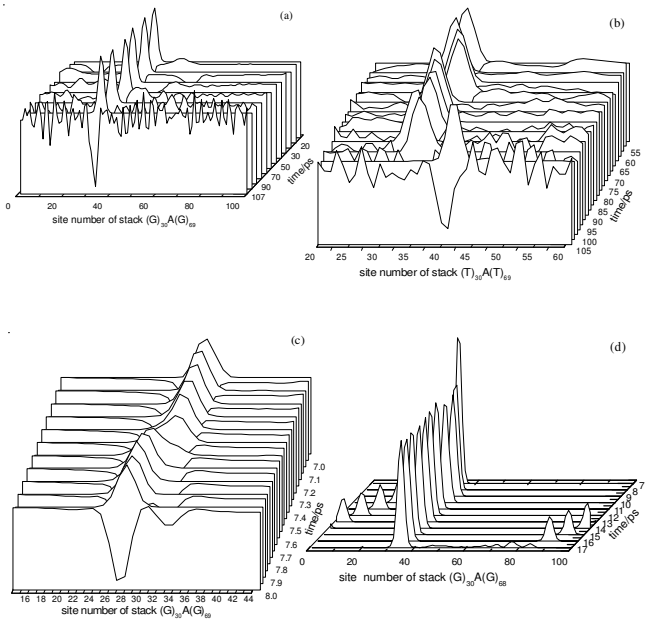


Fig. 5. Dynamic polaron at the chain of (a) the single-barrier $(G)_{30}A(G)_{69}$ (b) the single-barrier $(T)_{30}A(T)_{69}$ (c) the single-barrier $(G)_{30}A(G)_{69}$ (d) the double-barrier $(G)_{30}AA(G)_{68}$.

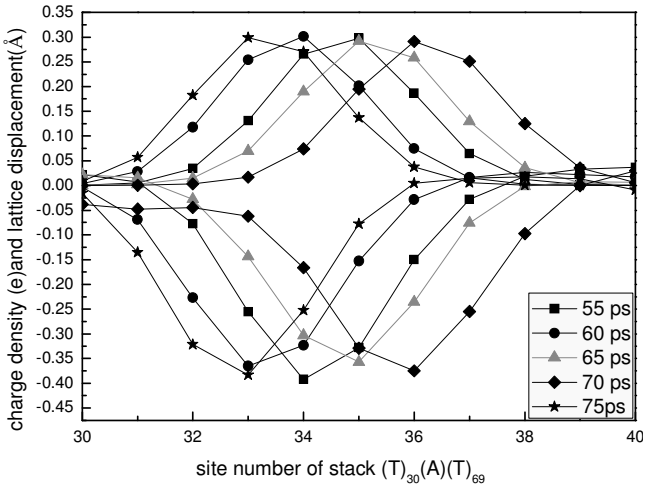


Fig. 6. Polaron of the chain $(T)_{30}A(T)_{69}$ vibrates from 55 ps to 75 ps

Conclusion

In SSH model computations of DNA, the hole polaron can move along the DNA chain composed of quantum wells and potential barriers under a suitable electric field. The following conclusions can be obtained from our calculated results:

The charge transfer integral and the coupling constant are two parameters which influences most on static polarons and its dynamic states. Increasing a will result in larger polaron: the polaron occupies fewer lattice sites with a corresponding large charge distribution and lattice displacement. However, the transfer integral t_0 has the opposite effect.

In DNA chain composed of different bases, the static polaron usually forms at the sites with lower on-site energy. But when the initial fluctuations are enough evident, the polaron will localizes at sites with large fluctuations. So fluctuations and on-site energy are the two factors, which decide the location of a polaron.

Width and depth of the quantum wells have obvious influences on hole polaron motion. The polaron can overcome the binding of quantum well after relaxing for a period time. When quantum well has larger value, the polaron will be bonded until smearing in it. Meanwhile, the quantum well width has stronger binding ability when its value becomes larger. When two or three quantum wells are plugged in the chain, the polaron always can't get rid of the binding although the electric field is raised.

In the chain with potential barriers, the hole polaron will move along the chain before it happened to potential barriers. And then it will collide with the potential barriers and begin to vibrate before it. When two potential barriers exists, the polaron will be divided into two parts: one is still at the head of the potential barriers, the other part will go through it and form a small new polaron. The new polaron will move further under the electric field until smearing. In the chain composed of three or more potential barriers, nearly no charge can get through it. It is can be testified by the corresponding experiments[29].

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REFERENCES

1. E.D.A. Stemp, M.R. Arkin and J.K. Barton, *J. Am. Chem. Soc.*, **119**, 2921 (1997).
2. B.T. Breslin, J.E. Coury, J.R. Anderson, L. McFail-Isom, Y. Kan, L.D. Williams, L.A. Bottomley and G.B. Schuster, *J. Am. Chem. Soc.*, **119**, 5043 (1997).
3. J.J. Storhoff and C.A. Mirkin, *Chem. Rev.*, **99**, 1849 (1999).
4. P.J. de Pablo, F. Moreno-Herrero, J. Colchero, J. Gómez Herrero, P. Herrero, A.M. Baró, P. Ordejón, J.M. Soler, E. Artacho, *Phys. Rev. Lett.*, **85**, 4992 (2000).
5. A.J. Storm, J.V. Noort, S.D. Vries and C. Dekker, *Appl. Phys. Lett.*, **79**, 3881 (2001).
6. H.-W. Fink and C. Schönenberger, *Nature*, **398**, 407 (1999).
7. Y. Okahata, T. Kobayashi, K. Tanaka and M. Shimomura, *J. Am. Chem. Soc.*, **120**, 6165 (1998).
8. A.Y. Kasumov, M. Kociak, S. Gueron, B. Reulet, V.T. Volkov, D.V. Klinov, H. Bouchiat, *Science*, **291**, 280 (2001).
9. W.P. Su, J.R. Schrieffer and A.J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979).
10. W.P. Su, J.R. Schrieffer and A.J. Heeger, *Phys. Rev. B*, **22**, 2099 (1980).
11. G. Zhang, P. Cui, J. Wu and C. Liu, *Physcia B*, **404**, 1485, (2009).
12. A.R. Bishop, D.K. Campbell, P.S. Lomdahl, B. Horovitz and S.R. Phillpot, *Synth. Met.*, **9**, 223 (1984).
13. T. Adams, J.M. Bishop, R. Cady, N.M. Cason, J. Gress, C. Kopp, J.M. LoSecco, J.J. Manak, A.H. Sanjari, W.D. Shephard, D.L. Stienike, S.A. Taegar, D.R. Thompson, S.U. Chung, R.W. Hackenburg, C. Olchanski, D.P. Weygand, H.J. Willutzki, S. Denisov, A. Dushkin, V. Kochetkov, I. Shein, A. Soldatov, B.B. Brabson, R.R. Crittenden, A.R. Dzierba, J. Gunter, R. Lindenbusch, D.R. Rust, E. Scott, P.T. Smith, T. Sulanke, S. Teige, Z. Bar-Yam, J.P. Dowd, P. Eugenio, M. Hayek, W. Kern, E. King, N. Shenhav, V.A. Bodyagin, A.M. Gribushin, M.A. Kostin, V.L. Korotkikh, A.I. Ostrovidov, A.S. Proskuryakov, L.I. Sarycheva, N.B. Sinev, I.N. Vardanyan, A.A. Yershov, D.S. Brown, T.K. Pedlar, K. K. Seth, J. Wise, D. Zhao, G.S. Adams, J. Napolitano, M. Nozar, J.A. Smith and M. Witkowski, *Nucl. Instr. Methods Phys. Res. A*, **368**, 617 (1996).
14. A.R. Bishop, *Synth. Met.*, **86**, 2203 (1997).
15. G. Kalosakas, S. Aubry and G.P. Tsironis, *Phys. Rev. B*, **58**, 3094 (1998).

16. S. Komineas, G. Kalosakas and A.R. Bishop, *Phys. Rev. E*, **65**, 061905(1) (2002).
17. G. Zhang, P. Cui, J. Wu and C. Liu, *Chem. Phys. Lett*., **471**, 163 (2009).
18. E.M. Conwell, *Synth. Met*., **83**, 101 (1996).
19. E.M. Conwell and D.M. Basko, *J. Am. Chem. Soc.*, **123**, 11441 (2001).
20. E.M. Conwell and D.M. Basko, *Synth. Met.*, **137**, 1381 (2003).
21. D.M. Basko and E.M. Conwell, *Phys. Rev. E*, **65**, 061902(1) (2002).
22. E.M. Conwell, J.-H. Park and H.-Y. Choi, *J. Phys. Chem. B*, **109**, 9760 (2005).
23. E.M. Conwell and S.V. Rakhmanova, *Proc. Nat. Acad Sci. USA*, **97**, 4556 (2000).
24. S.V. Rakhmanova and E.M. Conwell, *J. Phys. Chem. B*, **105**, 2056 (2001).
25. J.A. Berashevich, A.D. Bookatz and T. Chakraborty, *J. Phys.: Condens Matt.*, **20**, 5 (2008).
26. B. Zheng, J. Wu, W. Sun and C. Liu, *Chem. Phys. Lett.*, **425**, 123 (2006).
27. Y. Ono and A. Terai, *J. Phys. Soc. Jpn.*, **59**, 2893 (1990).
28. W.P. Su and J.R. Schrieffer, *Phys. Rev. Lett.*, **46**, 738 (1981).
29. D. Beratan, Yu.A. Berlin, I.V. Kurnikov, M.A. Ratner and A.L. Burin, *Topics Curr. Chem.*, **237**, 1 (2004).