

## A New Look at the Structural Polymer Transitions: 'Bridging the Quantum Gap' through Non-Radiative Processes

G. Keković<sup>1,a</sup>, D. Raković<sup>1,b</sup> and D.M. Davidović<sup>2,3,c</sup>

<sup>1</sup> Faculty of Electrical Engineering, Belgrade, Serbia

<sup>2</sup> Vinca Institute of Nuclear Sciences, Belgrade, Serbia

<sup>3</sup> School of Electrical and Computer Engineering, RMIT, Melbourne, Australia

<sup>a</sup>astra678@yahoo.com, <sup>b</sup>rakovicd@etf.bg.ac.yu, <sup>c</sup>davidd@vin.bg.ac.yu

**Keywords:** Structural Polymer Transitions, Q1D Nonlinear Excitations, Non-Radiative Quantum Resonance, Cascade Resonant Transitions, Kinetics of Photochemical Reactions of Isomer Polymer Transitions

**Abstract.** Structural polymer transitions, caused by non-radiative processes, are considered in the frameworks of both nonlinear solitonic excitations as well as the non-radiative quantum resonance. Our results show that the latter approach provides a much better description of cascade transport phenomena of double CC bonds in non-saturated hydrocarbons, kinetics of photochemical reactions of the isomer polymer transitions and some related phenomena. This fact clearly demonstrates that for a deeper understanding and insight into these processes the fully quantum description is indispensable.

### Introduction

Various structural transformations of Q1D-molecular chains are characterized by local rearrangements of atoms between neighbor unit cells, with supposed significant role of low-frequency skeletal vibrations and their higher overtones; namely, neighbor atoms are approaching each other thus increasing probability density for finding charged particles within chemical bonds, which might result in migrations of conjugated chemical bonds along Q1D- molecular chain as well as proton transfer from a carbon atom to its second neighbor, as it is the case for linear conjugated hydrocarbons [1].

In this context non-radiative structural polymer transitions are considered, firstly in the framework of nonlinear solitonic excitations which can describe cascade transport phenomena of double CC bonds in non-saturated hydrocarbons, and secondly in the framework of quantum-mechanical non-radiative resonance which can provide better understanding of kinetics of photochemical reactions of the isomer polymer transitions.

### Nonlinear Solitonic Excitations and Non-Radiative Structural Polymer Transitions

As excited double CC bond migrates gradually along conjugated Q1D atomic chain, which passes through corresponding isomeric forms, this resembles on solitonic directive transport of charged particles (electrons and protons) along the chain.

Having this in mind, as well as that interatomic distance is a dominant parameter, the starting point of our theoretical treatment is the equation for longitudinal oscillations of Q1D atomic chain in the field of many-electron energy-configuration hypersurface:

$$M \frac{d^2 u_n}{dt^2} = k(u_{n+1} - 2u_n + u_{n-1}) + F_{pot}, \quad (1)$$

where  $M$  is the atomic mass,  $u_n$  is the displacement of  $n$ -th atom from its equilibrium position, while  $F_{pot} = -dE_e(x)/dx$  is the potential force of the chain coupling with the many-electron energy-configuration hypersurface  $E_e(x)$ .

Also, as minima of the many-electron energy-configuration hypersurface  $E_e(x)$  correspond to maxima of probability density of the electronic subsystem  $|\Psi_e(r, x, t)|^2$ , we can formulate this by variational equation with the varying Lagrange multiplier ( $\lambda$ ):

$$\frac{dE_e(x)}{dx} + \lambda \frac{d|\Psi_e(r, x, t)|^2}{dx} = 0. \quad (2)$$

Dynamics of Q1D chain, described by Eqs. 1 and 2, can be reduced into the well known closed system of Davydov equations [2] (see Eqs. 10 below), what implies that the classical approach is roughly speaking only 'a half of the story', so that for realistic description quantum properties of the system must be taken into account!

Indeed, combining Eqs. 1 and 2 with the development:

$$u_{n\pm 1} = u_n \pm \frac{du_n}{dx} R_0 + \frac{1}{2} \frac{d^2 u_n}{dx^2} R_0^2 + \dots \quad (3)$$

gives

$$\frac{d^2 u_n}{dt^2} = c^2 \frac{d^2 u_n}{dx^2} + \frac{\lambda}{M} \frac{d|\Psi_e(r, x, t)|^2}{dx} \quad (4)$$

where  $c = R_0 \sqrt{k/M}$  is the velocity of sound in the medium, while  $R_0$  is the interatomic distance. In the above equation there are two unknown variables, and it is necessary to include into analysis also Schrodinger equation of the electronic subsystem, which has the following form in the Born-Openheimer adiabatic approximation:

$$i \frac{\partial \Psi_e(r, x, t)}{\partial t} = (\hat{T}_e + V_{ei} + V_{ee} + V_{ii} + V_{rez}) \Psi_e(r, x, t) \quad (5)$$

(in  $m_e = \hbar = 1$  unit system), with included operators of the kinetic energy of electronic subsystem ( $\hat{T}_e$ ) and all Coulomb interactions of electrons and ions/atomic nuclei (electron-ion ( $V_{ei}$ ), electron-electron ( $V_{ee}$ ), and ion-ion ( $V_{ii}$ )), while the phenomenologically introduced term ( $V_{rez}$ ) represents resonant interaction with most probable isomer forms. It is well known that exact solution of the Eq. 5 does not exist, but in a first approximation this equation is solved without electron-electron interaction, which later appears as a correction in the Hartree-Fock or other approximations [1].

As we are here interested in transport phenomena, then electron(vibron)-phonon interaction has most significant role and so we can neglect electron-electron interaction; also we suppose that some excitation appears only on the  $n$ -th molecular lattice site. Then, due to atomic non-equilibrium displacements there is an increased overlap of electronic wavefunctions centered on the nearest molecular lattice sites, which significantly increases the excitation probability to appear on these neighbour sites within the approximation of nearest neighbours. The coupling of these excitations and collective oscillations of the molecular chain can result in migration of double CC bond gradually along conjugated chain of unsaturated hydrocarbons [1], which passes through corresponding isomeric forms [3], so that local chain deformations reflect themselves on the change of wavefunctions of the electronic subsystem.

Therefore, it is completely legitimate to "decouple" in Hamiltonian the electron-ion Coulomb interactions regarding  $n$ -th term and the others:

$$V_{ei} \Psi_e(r, x, t) = \left( -\sum_{\substack{j\alpha \\ \alpha \neq n}} \frac{Ze^2}{r_{j\alpha}} - \sum_{jn} \frac{Ze^2}{r_{jn}} \right) \Psi_e(r, x, t) = (V_{ei}^{j\alpha} + V_{ei}^{jn}) \Psi_e(r, x, t). \quad (6)$$

In accordance with the previous assumption, the displacement of the  $n$ -th molecular lattice site will change the Coulomb potential energy of the electrons localized on this site, which can be presented by the development [2]:  $V_{ei}^{jn} \cong V_{ei}^0 - \chi(u_{n+1} - u_{n-1}) = V_{ei}^0 - 2\chi R_0 du_n / dx$ , where  $V_{ei}^0$  is a constant; besides, the rest of Coulomb potential energy ( $V_{ei}^{j\alpha}$ ,  $V_{ii}$ ,  $V_{ee}$ ) remains approximately constant, which is reasonable if the excitation is localized on only one molecular lattice site [1].

Also, an action of the operator of the resonant interaction can be defined, if most probable isomeric transitions of unsaturated hydrocarbons with fulfilled  $\Delta x = \pm R_0$  are known i.e.:

$$\hat{V}_{rez} \Psi_e(r, x, t) = -J(\Psi_e(r, x + R_0, t) + \Psi_e(r, x - R_0, t)) \quad (7)$$

where  $J$  is the energy of resonant interaction with equally probable states  $\Psi_e(r, x \pm R_0)$ , while negative sign appears due to energy balance.

By combining Eqs. 5 - 7 it follows:

$$i \frac{\partial \Psi_e(r, x, t)}{\partial t} = (\varepsilon_0 + V - 2\chi R_0 \frac{du_n}{dx}) \Psi_e(r, x, t) - J(\Psi_e(r, x + R_0, t) + \Psi_e(r, x - R_0, t)) \quad (8)$$

where  $\varepsilon_0 = -\sum_j \Delta_j / 2$  and  $V = (V_{ei}^0 + V_{ei}^{j\alpha}) + V_{ii} + V_{ee}$ . The obtained Eq. 8 can be further transformed by applying the continuum approximation:

$$\Psi_e(r, x \pm R_0, t) = \Psi_e(r, x, t) \pm R_0 \frac{d\Psi_e(r, x, t)}{dx} + \frac{R_0^2}{2} \frac{d^2\Psi_e(r, x, t)}{dx^2} + \dots \quad (9)$$

Finally, Eqs. 8, 9 and 4, together with formally adopted Lagrange multiplier in the form  $\lambda = 2\chi R_0$ , result into well known closed system of Davydov equations [2]:

$$i \frac{\partial \Psi_e(r, x, t)}{\partial t} = (\varepsilon_0 + V - 2J - JR_0^2 \frac{d^2}{dx^2} - 2\chi R_0 \frac{du}{dx}) \Psi_e(r, x, t), \quad (10)$$

$$\frac{d^2 u}{dt^2} = c^2 \frac{d^2 u}{dx^2} + \frac{2\chi R_0}{M} \frac{d|\Psi_e(r, x, t)|^2}{dx},$$

which describe the *soliton* nonlinear excitations.

The properties of the solutions of Eqs. 10, based on the classification of nonlinear charged autolocalized excitations in Q1D systems [4], were explored recently in the case of non-saturated hydrocarbon polymers, where it was shown that migration of double CC bond can be described by *adiabatic large polarons – solitons*, with optical phonons of the conjugated chains having major role in skeletal chain deformations during soliton-like cascade non-radiative resonant structural transitions *via* close intermediate participating isomeric states [5].

## Quantum-Mechanical Resonance and Non-Radiative Structural Polymer Transitions

In the framework of the non-radiative structural polymer transitions described above, the phenomenon of quantum-mechanical resonance (*via* degenerate excited electronic-vibrational states of the close isomer forms) is especially interesting, as it points out indispensable role of quantum approach to description of these transitions. An explanation of this experimentally established phenomenon [6] was given by Gribov in his monograph [1]. Simply stated, by exciting polymer (thermally, irradiating...) there appears significant overlap of the electronic-vibrational wavefunctions of the two degenerate electronic-vibrational states (1) and (2) belonging to the close isomer forms of the polymer, which gives rise to periodical oscillation back-and-forth between these two close structural polymer states.

In this approach, the (quasi)classical problem of many-electron energy-configuration hypersurface  $E_e(x)$ , not adiabatically well-defined when traversing between two adjacent local minima (1) and (2), is replaced by better defined problem of the two (virtually intersecting) isomeric many-electron hypersurfaces (hyperparaboloids) serving as potential hypersurfaces for the two vibrational (isomeric) problems. Then, by *external perturbation* of the isomers, at this very intersection the conditions for electronic-vibrational non-radiative resonant transitions between the two isomers (1) and (2) are achieved: these resonance electronic-vibrational states of two isomers are transformed from the corresponding (nonperturbed) products of electronic and vibrational stationary wavefunctions  $(\phi_e^{(1)}(r, x)\phi_v^{(1)}(x), \phi_e^{(2)}(r, x)\phi_v^{(2)}(x))$  into (perturbed) symmetrized stationary superpositions  $(\phi_e^{(1)}(r, x)\phi_v^{(1)}(x) \pm \phi_e^{(2)}(r, x)\phi_v^{(2)}(x))/\sqrt{2}$ , and their (nonperturbed) energies from resonating (equal) superpositions of the ground electronic energies of corresponding minima of many-electron energy-configuration hypersurface and vibrational energies of higher excited states  $(E_e^{(1)} + E_v^{(1)} = E_e^{(2)} + E_v^{(2)})$  into (perturbed) slightly split energy doublet  $(E_e^{(1)} + E_v^{(1)} + \frac{1}{2}\Delta E, E_e^{(2)} + E_v^{(2)} - \frac{1}{2}\Delta E)$ , with  $\Delta E = 2(E_e^{(1)} + E_v^{(1)})S_{ev}^{(1,2)}$  (where electronic-vibrational overlap integral between the two resonating isomeric states (1,2) is  $S_{ev}^{(1,2)} = \iint \phi_e^{(2)}(r, x)\phi_v^{(2)}(x)\phi_e^{(1)*}(r, x)\phi_v^{(1)*}(x)drdx \approx S_v^{(1,2)}S_e^{(1,2)}$ , while  $S_v^{(1,2)}$  and  $S_e^{(1,2)}$  are corresponding overlap integrals of vibrational and electronic components).

To describe the temporal aspect of this quantum-mechanical resonance correctly, we start from the nonstationary Schrodinger equation,

$$i\hbar \frac{\partial \Psi_{ev}(r, x, t)}{\partial t} = (\hat{H}_0 + \Delta H)\Psi_{ev}(r, x, t), \quad (11)$$

where  $\Delta H$  is a nondifferential step-like perturbation operator. Then the solution of the Eq. 11 is sought in the form [1]

$$\Psi_{ev}(r, x, t) = a(t)\Psi_{ev}^{(1)}(r, x, t) + b(t)\Psi_{ev}^{(2)}(r, x, t), \quad (12)$$

where

$$\Psi_{ev}^{(1)}(r, x, t) = \frac{1}{\sqrt{2}}(\phi_e^{(1)}(r, x)\phi_v^{(1)}(x) + \phi_e^{(2)}(r, x)\phi_v^{(2)}(x))\exp(-i\omega t) \quad (13)$$

$$\Psi_{ev}^{(2)}(r, x, t) = \frac{1}{\sqrt{2}}(\phi_e^{(1)}(r, x)\phi_v^{(1)}(x) - \phi_e^{(2)}(r, x)\phi_v^{(2)}(x))\exp(-i\omega t)(\cos \Delta\omega t - i \sin \Delta\omega t)$$

are the solutions of the nonstationary Schrodinger equation without perturbation,

$$i\hbar \frac{\partial \Psi_{ev}(r, x, t)}{\partial t} = \hat{H}_0 \Psi_{ev}(r, x, t), \quad (14)$$

with  $\omega = (E_e^{(1)} + E_v^{(1)})/\hbar \sim 10^{15}$  Hz and  $\Delta\omega = \Delta E/\hbar = 2(E_e^{(1)} + E_v^{(1)})S_{ev}^{(1,2)}/\hbar \sim 10^9$  Hz [1], while  $a(t)$  and  $b(t)$  are time-dependent functions, which can be determined by insertion of Eq. 12 into Eq. 11 (having in mind that electronic-vibrational wavefunctions of Eqs. 13 are solutions of Eq. 14), so that we get two differential equations,  $i\hbar\partial a/\partial t = a\Delta H$  and  $i\hbar\partial b/\partial t = b\Delta H$ , with the solutions  $a(t) = b(t) = \exp(-i\Delta H t/\hbar)/\sqrt{2}$  (fulfilled for the initial condition  $|\Psi_{ev}(r, x, 0)|^2 = |\phi_e^{(1)}(r, x)\phi_v^{(1)}(x)|^2$ , when  $a(0) = b(0) = 1/\sqrt{2}$ ). By inserting Eqs. 13 and solutions for  $a(t)$ ,  $b(t)$  into Eq. 12, with some algebraic manipulation the time-dependent probability density of the electronic-vibrational wavefunction of the system is obtained:

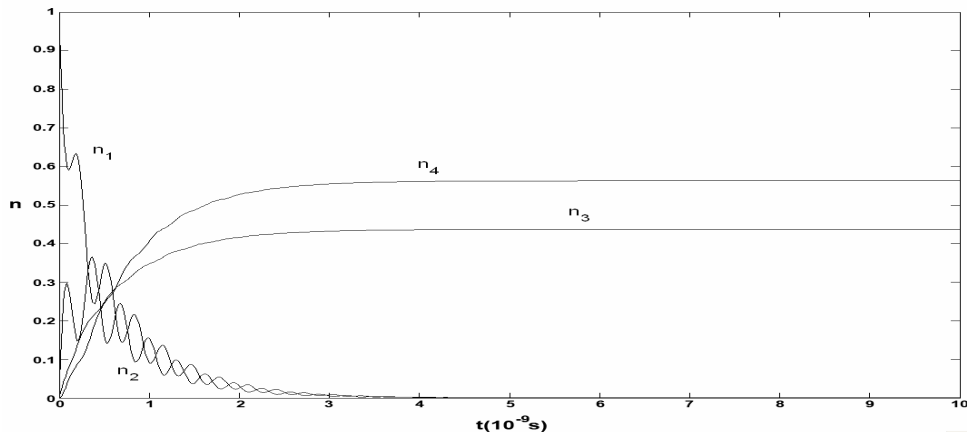
$$|\Psi_{ev}(r, x, t)|^2 = |\phi_e^{(1)}(r, x)|^2 |\phi_v^{(1)}(x)|^2 \cos^2 \frac{\Delta\omega}{2} t + |\phi_e^{(2)}(r, x)|^2 |\phi_v^{(2)}(x)|^2 \sin^2 \frac{\Delta\omega}{2} t. \quad (15)$$

On the basis of Eq. 15, it can be concluded that system alternatively excites two isomer-conformational states with periodicity  $\tau = 1/\Delta\omega \sim 10^{-9}$  s, which is macroscopically manifested as a temporal change in concentration of the two isomers in the two-isomer polymer solution. Thus obtained probability of finding temporal evolution of the resonating doublet state of such a system, served to Gribov and colleagues [7,8] as a basis to explore the kinetics equations for populated polymer electronic-vibrational levels in photochemical reactions of isomer transitions.

In particular, we shall here consider the model photochemical reaction of isomer transitions for two-isomeric polymer system with four energy levels, where the system is initially excited by some external optical perturbation  $\Delta H$ , from the first-isomer ground energy state (3) into its excited energy state (1). This causes an intense overlap of the wavefunctions of the two excited isomer forms (1) and (2), which exhibit resonant fluctuating back-and-forth chemical-isomer transitions (1) $\leftrightarrow$ (2) (defined by corresponding time-dependent probabilities  $w_{12} = w \cos^2 \Delta\omega t$  and  $w_{21} = w \sin^2 \Delta\omega t$ , cf. Eq. 15), also accompanied by spontaneous isomer deexcitations (1)  $\rightarrow$  (3) and (2)  $\rightarrow$  (4) into corresponding isomer ground states (defined by time-independent probabilities  $w_{13}$  and  $w_{24}$ , respectively). Accordingly, we easily obtain the system of kinetics equations describing these processes:

$$\begin{aligned} \frac{dn_1}{dt} &= -w_{13}n_1 - wn_1 \cos^2 \Delta\omega t + wn_2 \sin^2 \Delta\omega t ; \\ \frac{dn_2}{dt} &= -w_{24}n_2 + wn_1 \cos^2 \Delta\omega t - wn_2 \sin^2 \Delta\omega t ; \\ \frac{dn_3}{dt} &= w_{13}n_1 ; \\ \frac{dn_4}{dt} &= w_{24}n_2 . \end{aligned} \quad (16)$$

with concentrations  $n_j$  ( $j = 1, \dots, 4$ ) of polymers occupying these four electronic-vibrational levels. By solving numerically the above system of equations (with model-adopted probabilities  $w = 0.7$ ,  $w_{13} = 0.1$ ,  $w_{24} = 0.2$ , resonant frequency  $\Delta\omega = 10^9$  Hz of fluctuating back-and-forth photochemical-isomer transitions (1) $\leftrightarrow$ (2), time scale in  $10^{-9}$  s, and polymer isomer concentrations in relative units  $n_j \in (0,1)$ ), graphical temporal dependance of the four relative polymer concentrations is obtained, cf. Fig. 1.



**Fig.1.** The kinetics of the time dependent polymer concentrations  $n_j$  (in relative units) in the model photochemical reaction of isomer transitions, for two-isomeric polymer system with each isomer in possible ground and excited electronic-vibrational states (see Eq. 16 and the text for details).

Inspecting this graph, one can see that the effect of the quantum-mechanical resonance between the first-isomer excited state (1) and the second-isomer excited state (2) (equally probable due to quantum-mechanical resonance), and subsequent external spontaneous deexcitation of the second-isomer excited state (2) into its ground state (4) increases the saturated population  $n_4$  with respect to  $n_3$ . [The silent assumption here is that the bottom of the energy-configuration hypersurface  $E_e(x)$  of the second-isomer ground state (4) is lower than the first-isomer ground state (3), i.e.  $E_{ev}^{(4)} < E_{ev}^{(3)}$ , and consequently  $E_v^{(2)} > E_v^{(1)}$  measured with respect to the corresponding minima of the vibrational potential wells. In combination with Maxwell-Boltzman distribution applied in saturation limit for equally populated vibrational levels  $E_v^{(2)}$  and  $E_v^{(1)}$ ,  $n_4 \exp(-E_v^{(2)} / kT) = n_3 \exp(-E_v^{(1)} / kT)$ , this gives  $n_4 > n_3$ .]

## Conclusion

Non-radiative structural polymer transitions were considered in this work within the two approaches, firstly in the framework of nonlinear solitonic excitations which can describe cascade transport phenomena of double CC bonds in non-saturated hydrocarbons, and secondly in the framework of quantum-mechanical non-radiative resonance. The comparison of the results obtained shows that the latter approach provides a much better description of the kinetics of photochemical reactions of the isomer polymer transitions. This fact clearly demonstrates that for a deeper understanding and insight into these processes quantum approach is indispensable.

## References

1. L. A. Gribov, From Theory of Spectra Towards Theory of Chemical Transformations, URSS, Moscow (2001), in Russian.
2. A. S. Davydov, Solitons in Molecular Systems, Naukova Dumka, Kiev (1984), in Russian.
3. L. A. Gribov, Izv. Akad. Nauk, Ser. Him. **N 2**, 213 (2002), in Russian.
4. Ž. Pržulj, D. Kostić, Z. Ivić, Solid State Phenomena, **61-62**, 291 (1998), and references therein; G. Keković, Consideration of a Possible Contribution of Large Polarons (Solitons) in the Neutron Scattering on the Quasi-One-Dimensional Molecular Crystals, M.S. Thesis, Faculty of Electrical Engineering, Belgrade (2000), in Serbian.
5. G. Keković, D. Raković, D. Davidović, Mater. Sci. Forum, **555**, 119 (2007).
6. P. M. Felker, A. H. Zewail, Chem. Phys. Lett., **102**, 113 (1983).
7. V. I. Baranov, L. A. Gribov, Zh. Prikl. Spekr., **71(4)**, 421 (2004).
8. V. I. Baranov, F. A. Savin, L. A. Gribov, J. Appl. Spectr., **71(3)**, 320 (2004).