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Vibron Self-trapped States in Biological Macromolecules: Comparison of Different Theoretical Approaches

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Abstract. We present a study of the applicability of the variational treatments based on using of the modified Lang-Firsov unitary transformation (MLF method) in the investigation of the vibron self-trapped states in biological macromolecular chains. Here we compare the values of the ground state energy predicted by MLF methods with the values of the ground state energy predicted by the standard small-polaron theory, for various values of the basic energy parameters of the system. We obtain regions in system parameter space where MLF approach gives better description of the vibron states.

1. Introduction

There exist many unresolved fundamental problems in molecular biology and biochemistry and one from them is the problem of long-distance energy transport in biological macromolecules. It is believed that the energy released by the hydrolysis of adenosine triphosphate (ATP) appears by an universal energy source allowing many biological processes. Mentioned energy released by the ATP hydrolysis may be captured by the protein molecules and excite the high-frequency amide-I vibration of a peptide group. Due to the dipole-dipole coupling between the neighbouring peptide groups the excited amide-I vibration is delocalized causing formation of the vibron state which, in turn, can move along the polypeptide chain. However, it is yet not clearly understood how this energy can be transported along macromolecule at long distances, without being dissipated or dispersed. An earlier explanation of this process is based on the soliton theory [1], [2], [3]. According to those models, a soliton arises due to the self-trapping (ST) of the amide-I quanta.

According to the general theory of ST phenomena [4], ST problem exhibits two asymptotic solutions depending on the values of three basic energy parameters of the system: the vibron bandwidth $2|J|$, the phonon characteristic frequency ω_C and the SP bending energy E_b (which is proportional to the strength of the vibron-phonon coupling). Thus, in the adiabatic limit ($2|J| > \hbar\omega_C$) lattice distortion with large inertia can not follow the exciton motion and it forms an essentially static potential well where that particle may be trapped. Depending on the value

of the mutual ratio of E_b and $\hbar\omega_C$, the spatial extent of an entity created in this way (polaron) may vary from being concentrated around one site only ($E_b \gg \hbar\omega_C$) i.e. adiabatic SP (ASP), while in the case when $E_b < \hbar\omega_C$ it is spread over the large number of lattice sites and we have adiabatic large polaron (ALP) or soliton. By contrast, in non-adiabatic limit ($2|J| < \hbar\omega_C$) the quantum nature of the phonons plays a crucial role. In such case a vibron is dressed by a virtual cloud of phonons which yields a lattice distortion essentially located on a single site and instantaneously follows the vibron motion. The vibron dressed by the virtual phonon cloud forms a small polaron (SP) whose properties are well described by performing the so-called Lang-Firsov (LF) unitary transformation [5]. As a consequence, conventional SP theories are applicable in the strong-coupling, non-adiabatic limit.

Unfortunately, the values of the basic energy parameters in biological macromolecular chains belong to non-adiabatic limit. For that reason, it has been suggested by some authors [6],[7], [8] that vibron self-trapping in hydrogen-bonded macromolecular chains might result in the formation of a small-polaron, rather than a soliton. From the other side, the values of the energy parameters indicate that the strength of vibron-phonon coupling in hydrogen-bonded macromolecules falls in the weak to intermediate limits [9]. In addition, some recent numerical [10] studies of the ST phenomena in hydrogen-bonded macromolecular chains indicate that its proper theoretical description requires an approach that goes beyond the conventional strong-coupling SP theories. Namely, according to results from [10] it seems that depending on the temperature and the values of the system parameters the abrupt transition from partially dressed (light and mobile) to self-trapped (practically immobile quasi particle) may occur. This situation can not be described in the framework of the standard SP approach (based on using of the Lang-Firsov unitary transformation) and as a consequence its theoretical investigations require the means which involve the concept of partial dressing. This concept is based on modified Lang-Firsov (MLF) unitary transformation and is applicable in a wide part of system parameter space. Such an approach is considered in a close correspondence with the supplementary variational treatment of the problem by means of the Toyozawa ansatz [11]. In our recent paper [12] we used slightly more flexible method in order to investigate the temperature dependence of the SP states character.

In this paper we consider two variational formalisms based on using of the modified Lang-Firsov approach and compare obtained results with ones predicted by the standard SP theory. The variational parameter(s) introduced here characterizes the degree in which the vibron distorts the lattice and the lattice feedback on the vibron, i.e. vibron dressing. The first variational approach (so called “ f_q -approach”) is based on the model used in [12], while the second one (“ δ -approach”) exploits the method introduced by Brown and Ivić in [7], [8] in the form used in [13]. The last approach intermediates between non-adiabatic and adiabatic limit with use of only one variational parameter. We calculate and compare the system ground state energies for various basic system parameter values in the case when vibron interacts with both optical and acoustical phonon subsystems. Our attention was restricted to the single-vibron case.

2. Theoretical methods

The system under consideration consists of single vibron excited on n -th structural element of the macromolecule which, in turn, interacts with thermal oscillations of the chain through the linear short-ranged deformation potential interaction. We suppose that vibron excitation can move along the chain from n -th to its nearest-neighbouring structural element. The corresponding Hamiltonian can be written in the following form [14],

$$H = \Delta \sum_n a_n^\dagger a_n - \sum_n J a_n^\dagger (a_{n+1} + a_{n-1}) + \sum_q \hbar\omega_q b_q^\dagger b_q + \frac{1}{\sqrt{N}} \sum_q \sum_n F_q e^{iqnR_0} a_n^\dagger a_n (b_q + b_{-q}^\dagger), \quad (1)$$

where Δ is the vibron excitation energy, $a_n^\dagger(a_n)$ describes the presence (absence) of the vibron quanta on the structural element, which is positioned on n -th lattice site, $b_q^\dagger(b_q)$ creates (annihilates) phonon quanta, and ω_q is the phonon frequency. The inter-site overlap integral J characterize the vibron transfer between neighbouring structural elements in the chain. Finally, $F_q = F_{-q}^*$ is the vibron-phonon coupling parameter which governs the character of ST states. In order to investigate the vibron self-trapping in macromolecular chains, we shall consider the following quasi particle-phonon interaction:

- (a) interaction with dispersionless optical phonon modes [14],[15], [16]

$$F_q = \chi \sqrt{\frac{\hbar}{2M\omega_q}},$$

where χ is the vibron-phonon coupling constant, which accounts the influence of the external motion of the vibron on the $(n \pm 1)$ -th structural elements and on the modulation of the vibron frequency in the n -th structural element, $\omega_q = \omega_C$ is phonon dispersion law, $\omega_C = 2\sqrt{\kappa/M}$, κ appears by the stiffness of the chain, M is the molecular group mass;

- (b) interaction with acoustic phonon modes through the short-ranged deformation potential (acoustic deformation potential, ADP) [15], [16]

$$F_q = 2i\chi \sqrt{\frac{\hbar}{2M\omega_q}} \sin qR_0,$$

with $\omega_q = \omega_C \sin |qR_0/2|$ being by phonon dispersion law, and R_0 is a lattice constant.

In order to examine the degree of the vibron dressing, we pass to the small-polaron picture using unitary transformation operator,

$$U = \exp \left\{ -\frac{1}{\sqrt{N}} \sum_q \sum_n f_q e^{-iqnR_0} a_n^\dagger a_n (b_{-q} - b_q^\dagger) \right\}.$$

Here $f_q = f_{-q}^*$ are variational parameters, while operators $a_n^\dagger(a_n)$ represent (partially) dressed vibrons. In the case of the passing to the standard small-polaron picture, parameter f_q has standard Lang-Firsov form: $f_q = \frac{F_q^*}{\hbar\omega_q}$. Operators $a_n^\dagger(a_n)$ that appear in the transformed Hamiltonian, represent the (fully) dressed quasi particle. In all cases the operators $b_q^\dagger(b_q)$ describe the new phonons in the lattice with shifted equilibrium positions of molecular groups.

Partially dressed vibron states represent the dynamically stable eigen-states of the system provided that these variational parameters correspond to the minimum energy state. Thus, we search for their optimized values minimizing the system ground-state energy. According to the method described in [17], optimization procedure will be performed in a mean-field manner, which gives better upper bound of the system free energy and consequently the better upper bound of the system ground state energy. In particular, we define (in wave number representation) an effective, mean-field Hamiltonian \tilde{H}_0 in the following way,

$$\tilde{H} = \tilde{H}_0 + \tilde{H}_{int}, \quad (2)$$

where $\tilde{H}_0 = \tilde{H}_v + \tilde{H}_{ph}$, $\tilde{H}_v = \langle \tilde{H} - \tilde{H}_{ph} \rangle_{ph}$ and $\tilde{H}_{int} = \tilde{H} - \tilde{H}_{ph} - \langle \tilde{H} - \tilde{H}_{ph} \rangle_{ph}$. The symbol $\langle \rangle_{ph}$ denotes the average over the new-phonon ensemble, which is considered in the thermal equilibrium state at the temperature T . In such a way we derive,

$$\tilde{H}_0 = \sum_k E_{SP}(k) a_k^\dagger a_k + \sum_q \hbar\omega_q b_q^\dagger b_q, \quad (3)$$

where $a_k = \frac{1}{\sqrt{N}} \sum_n e^{iknR_0} a_n$, and

$$E_{SP}(k) = \Delta - \frac{1}{N} \sum_q \left\{ (f_q + f_{-q}^*) F_q - \hbar\omega_q |f_q|^2 \right\} - 2J e^{-W(T)} \cos(kR_0) \quad (4)$$

denotes the variational energy of the small-polaron band states, while $W(T) = \frac{1}{N} \sum_q |f_q|^2 (2\bar{\nu}_q + 1)(1 - \cos(qR_0))$ denotes the vibron-band narrowing factor, which characterizes the degree of the reduction of the corresponding overlap integral or equivalently the enhancement of the polaron effective mass. For obvious reasons, they are sometimes called the "dressing fractions" or the "dressing parameters". At last, the quantity $\bar{\nu}_q$, $\bar{\nu}_q = 1/(e^{\hbar\omega_q/k_B T} - 1)$, denotes the phonon average number.

The polaron-phonon interaction term may be neglected provided that dressed vibrons represent sufficiently well eigen states of system. In such a way it cannot affect SP equilibrium properties substantially and at $T = 0$ K the further procedure simply reduces to minimization of the SP ground state energy. We note the ground-state vector of the effective Hamiltonian \tilde{H}_0 reads, $|\psi_{GS}\rangle = a_k^\dagger |0\rangle_{vib} \otimes \prod_q |0\rangle_q$, where $\prod_q |0\rangle_q$ is the phonon vacuum vector so that the ground-state energy corresponds to the lowest level of SP energy, i.e., $E_{GS} = \langle \psi_{GS} | \tilde{H}_0 | \psi_{GS} \rangle = E_{SP}(k)$. Thus, from the requirement, $\left. \frac{\partial E_{SP}(k)}{\partial f_q} \right|_{k_0} = 0$, we get,

$$f_q = \frac{F_q^*}{\hbar\omega_q + 4|J|e^{-W} (2\bar{\nu}_q + 1) \sin^2\left(\frac{qR_0}{2}\right)}. \quad (5)$$

From the Eq.(5) it follows that for each value of q there is the corresponding value of the variational parameter f_q . For that reason, the optimization procedure for this approach becomes extremely difficult problem, even numerically. Note, however, that only $k_0 = \pi/R_0$ (when $J < 0$), or $k_0 = 0$ (when $J > 0$), should be considered since it will correspond to the polaron ground state only. This case is also the most relevant for the optical spectroscopy since vibron bandwidths in these media are very narrow and its dispersion in all practical examination of optical spectra can be neglected [10], [15], [16] [18], [19].

The expressions for vibron ground state energy (normalized on the characteristic phonon energy $\hbar\omega_C$ and measured from the energy level Δ) and vibron dressing factor are obtained by the substitution of the variational parameters into (4). Performing the summation over the phonon quasi momenta q by virtue of the rule $\frac{1}{N} \sum_q \dots \rightarrow \frac{R_0}{2\pi} \int_{-\pi/R_0}^{\pi/R_0} \dots dq$ and by introducing two dimensionless parameters (that determine the system parameter space) $S = \frac{E_b}{\hbar\omega_C}$ and $B = \frac{2|J|}{\hbar\omega_C}$, we obtain,

$$\mathcal{E}_{GS} = -W - 3BWe^{-W} - Be^{-W}, \quad (6)$$

and

$$W = \frac{S}{(1 + 2Be^{-W})^{3/2}} \quad (7)$$

in the case when vibron interact with optical phonon mode, and

$$\mathcal{E}_{GS} = -\frac{W}{2} \frac{I_E}{I_W} - Be^{-W}, \quad W = 8SI_W, \quad (8)$$

when the vibron interacts with acoustic phonon modes. The quantities I_E, I_W that appear in the above relations have the integral representation,

$$I_E = \frac{1}{\pi} \int_0^{\pi/2} \cos^2 x \frac{1 + 4Be^{-W} \sin x}{(1 + 2Be^{-W} \sin x)^2} dx, \quad \text{and} \quad I_W = \frac{1}{\pi} \int_0^{\pi/2} \frac{\sin x \cos^2 x}{(1 + 2Be^{-W} \sin x)^2} dx.$$

In the case of simple “ δ -approach” we choose f_q in the form: $f_q = \frac{\delta F_q^*}{\hbar\omega_q}$, where $0 < \delta < 1$ is variational parameter. In that case, we have more simple variational technique in which we should determine only one variational parameter (δ). On the other hand, this assumption implies the equal dressing for all phonon modes. At the first sight, it looks like a very strong assumption since the whole set of variational parameters (one for each mode) is substituted by a single one. However, here we showed that predictions obtained by this approach are very close with ones, obtained by more rigorous “ f_q approach”. Repeating above described procedure we obtained condition which determines parameter δ ,

$$4J\delta W_{LF}e^{-\delta^2 W_{LF}} - 2E_b(1 - \delta) = 0, \quad (9)$$

where $E_b = \frac{1}{N} \sum_q \frac{|F_q|^2}{\hbar\omega_q}$ is small-polaron binding energy, while $W_{LF} = \frac{1}{N} \sum_q \frac{|F_q|^2}{(\hbar\omega_q)^2} (1 - \cos qR_0)$ is SP band narrowing factor calculated in the non-adiabatic, strong coupling limit (standard LF approach). Then, performing summation over phonon quasimomenta, we derive the relation for the ground state energy (in (S, B) parameter space) in the form,

$$\mathcal{E}_{GS} = -\delta(2 - \delta)S - Be^{-\delta^2 S} \quad (10)$$

in the case when vibron interact with optical phonon, and

$$\mathcal{E}_{GS} = -\delta(2 - \delta)S - Be^{-\frac{8\delta^2 S}{3\pi}}, \quad (11)$$

when vibron interact with acoustical phonons.

3. Results

According to the available literature data, the hopping constant in α -helix proteins is typically equal to, $J = 7.8 \text{ cm}^{-1}$ (in the case of the hydrogen bonds between peptide units) and $J = -12.4 \text{ cm}^{-1}$ (between different spines of hydrogen-bonded peptide units, i.e. in the case of the covalent bonds between peptide unit) [19, 20]. The mass of the peptide unit ranges between $M = 2 \cdot 10^{-25} \text{ kg}$ and $M = 5.7 \cdot 10^{-25} \text{ kg}$ [9, 19].

The above mentioned values of the system parameters in macromolecular chains indicate that adiabatic parameter in these structures ranges between $B = 0.01$ and $B = 0.5$. In the same time, coupling constant ranges between $S = 0.01$ and $S = 0.3$. The last fact indicates that these structures belong to the non-adiabatic coupling limit from weak to intermediate one.

Obtained numerical results are presented on the Figs. 1–4. The calculations obtained by “ δ -approach” are presented by full lines, the ones obtained by the “ f_q -approach” are presented by dashed lines, and the calculations obtained by the standard LF approach are presented by dotted lines. As one can remark, the results obtained by both variational approaches are strongly different compared with ones obtained by standard LF approach, for small values of coupling constant S . This difference disappears on large values of S for all values of B . For small and intermediate values of S , the difference between two variational approaches increases with increasing of B . These results are expectable, since standard LF approach is not applicable in weak coupling limit. On the other side, results obtained by both variational approaches are very similar in the whole range of S , for small values of B (non-adiabatic limit). There are significant difference only for $B > 1$ (adiabatic limit), for small and intermediate values of S .

One should be noted in addition, it is evident that both variational approaches predict a multivalued dependence of \mathcal{E}_{GS} and W on S , in certain region of S , only in the adiabatic limit. According to the variational principle, the only lowest energy value is physically meaningful. Consequently, only lower values of \mathcal{E}_{GS} (and its corresponding values of W) have physical significance and truly variational energy is presented by one line which is not smooth (at certain

value of S it have the point of cusp). In the same time, W undergoes an abrupt change. That means that vibron ST state have abrupt transition from weakly dressed to heavy dressed polaron state. Obtained results may look as a consequence of the applied variational approach. However, it seems that these results are in good agreement with some recent numerical investigations [10], where authors interpreted similar results as a coexistence of two types of SP states instead of abrupt transition from one to another quasiparticle type.

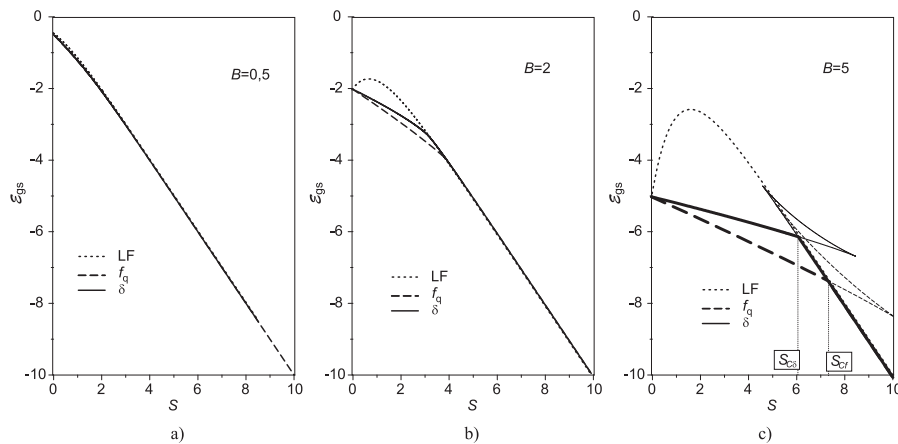


Figure 1. The dependence of the \mathcal{E}_{GS} versus S , for different values of the B . The case of vibron that interacting with optical phonon modes.

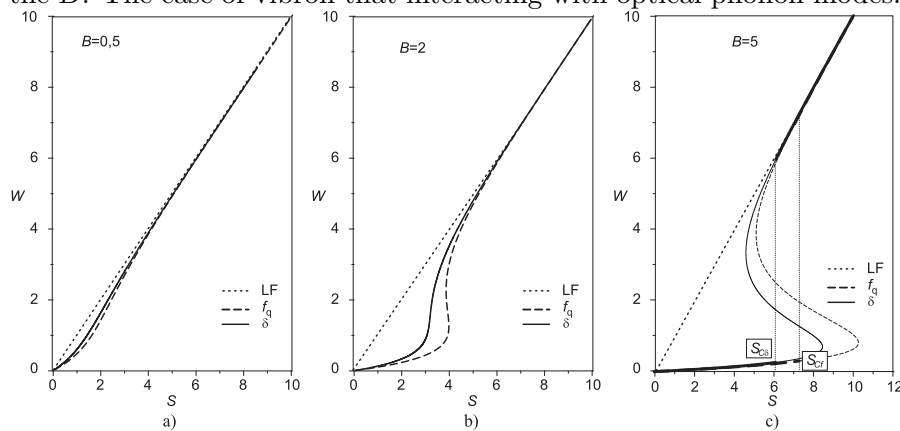


Figure 2. The dependence of the W on the S , for different values of the B . The case of vibron that interaction with optical phonon modes.

4. Conclusions

In accordance to the obtained results, one may note that both variational approaches give very similar qualitative and quantitative predictions, especially in non-adiabatic region. With the rise of the adiabatic parameter, the difference between variational approaches, as well as between variational approaches and standard small-polaron approach vanishes. In the case of the vibron interacting with the optical phonon modes, ground state energies predicted by the “ f_q -approach” are something lower than ground state energies predicted by the “ δ -approach”. But, in the non-adiabatic region of the parameter space this difference may be practically neglected, and “ δ -approach” is quite good method for the investigation of the vibron self-trapping states. Similar results are obtained in the case when vibron interacts with acoustic phonon modes.

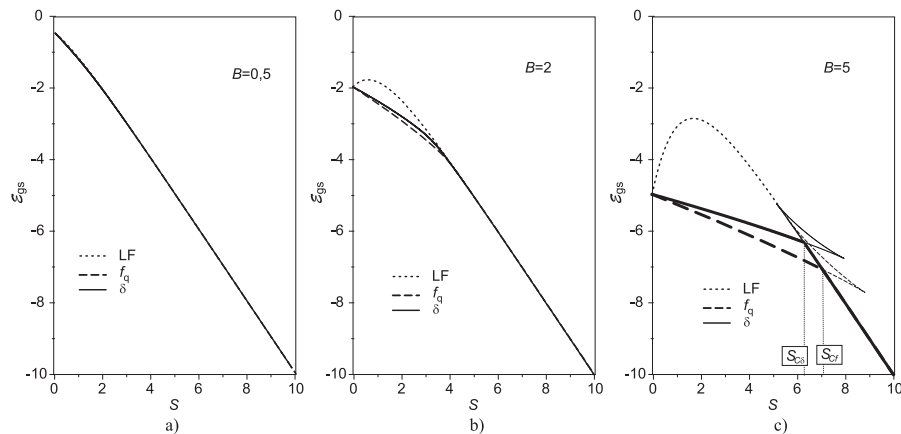


Figure 3. The dependence of the \mathcal{E}_{GS} versus S , for different values of the B . The case of vibron that interacting with acoustic phonon modes.

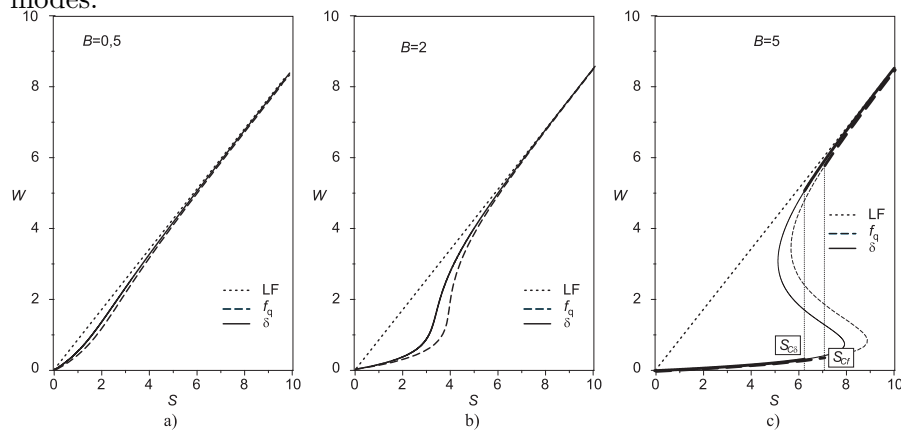


Figure 4. The dependence of the W on the S , for different values of the B . The case of vibron that interaction with acoustic phonon modes.

In the adiabatic region of the system parameter space the difference between two variational approaches is significant.

Due to the fact that practically all biological macromolecular structures belongs to the non-adiabatic, weak or intermediate coupling limit, it seems that simple “ δ -approach” may be by the hopeful method for investigations of the self-trapped vibron states in such structures.

Acknowledgments

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