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The Specific Heat Caused by Solitons in the Protein Molecules*

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The property of specific heat caused by the solitons excited in the protein molecules has been discussed in terms of the equations of motion of operators for the excitons and the phonons in our theory. The values of specific heat arisen from the solitons are consistent completely with the experimental data. The results obtained show fully that the soliton is existent indeed and biologically relevant in the protein molecules.

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In the 1970s Davydov proposed a soliton model for the bio-energy transport.[1] Since then this theory and the "Davydov soliton" have been extensively studied and applied in many works.[2-8] However, a lot of studies show that the soliton is instable at 310 K, its lifetime is too short (about $10^{-12} - 10^{-13}$s) to be useful in biological processes.[5-6] The reason for this is that the theory is applied without modification on the protein molecule rather than the general one-dimensional molecules which had been studied since 1969, but the former is some different from the latter, in which the collective excitation resulted from the fluctuation and the deformation of structure caused by the energy released in ATP hydrolysis in the protein has the coherent feature, and so on.[9] In view of the weakness of the Davydov theory and the properties of this collective excitation, recently we proposed a new theory[10,11] to study the features of soliton motion and energy transport in the protein. A new Hamiltonian and new coherent wavefunction are given in our theory. Thereupon, the equations of motion and the properties of the soliton are different from that of the Davydov soliton. The results obtained show that our theory is preferable and more justifiable to the protein compared with the Davydov theory.[10] I find, after studying the thermal stability and the lifetime,[12] that it is quite stable and its lifetime is on the order of 10^{-8}s at 310 K, which shows that the soliton is completely useful in biological processes. The purpose of this paper is to calculate the specific heat caused by the soliton in terms of the equations of motion of operators for excitons and phonons in our theory in order to demonstrate the existence of the soliton in the protein. Therefore, we should study such protein molecular system with the temperature $T \neq 0$, or speaking, which is contacted with a thermal reservior at temperature $T \neq 0$ because the temperature will affect the states and features of the quasi-particles excited in the protein, or speaking, the values of parameters in the equations of motion.[13] This influence can be discussed in terms of the equations of

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motion of operators for excitons and phonons because the thermal fluctuation may be expressed by the fluctuation of the number of phonons.[13]

The Hamiltonian in our theory is of the form[10,11]

$$H = \frac{1}{2m}\sum_i p_i^2 + \frac{1}{2}m\omega_0^2\sum_i r_i^2 - \frac{1}{2}m\omega_1^2\sum_i r_i r_{i+1} + \frac{1}{2M}\sum_i P_i^2 + \frac{1}{2}\beta\sum_i (R_i - R_{i-1}) + \frac{1}{2}\sum_i m\chi_1(R_{i+1} - R_{i-1})r_i^2 + \sum_i m\chi_2(R_{i+1} - R_i)r_i r_{i+1} , \tag{1}$$

In the second quantized representation Eq.(1) becomes

$$H = \sum_i (\varepsilon_0 + \frac{1}{2})b_i^+ b_i - J\sum_i (b_i^+ b_{i+1} + b_{i-1}^+ b_i) + \sum_q \hbar\omega_q (a_q^+ a_q + \frac{1}{2}) + \sum_{i,q}\Big(g(q)(b_i^+ b_i + b_i b_i^+) + g_1(q)(b_i^+ b_{i+1} + b_i^+ b_{i-1})\Big)(a_q + a_{-q}^+)e^{jir_0 q} , \tag{2}$$

where $g(q) = (\frac{\hbar}{2MN\omega_q})^{\frac{1}{2}}(\frac{\hbar\chi_1}{4\omega_0})(e^{jr_0 q} - e^{-jr_0 q})$, $g_1(q) = (\frac{\hbar}{2MN\omega_q})^{\frac{1}{2}}(\frac{\hbar\chi_2}{4\omega_0})(e^{jr_0 q} - 1)$, $\varepsilon_0 = \hbar\omega_0$, $J = \frac{\hbar\omega_1^2}{2\omega_0}$, $b_i^+(b_i)$ and $a_q^+(a_q)$ are the creation (annihilation) operator of the intramolecular excitation (exciton) and the phonon, respectively.

Due to the fact that the protein is a sort of bio-self-organization system and that the collective excitation in this system has coherent feature,[9] the wavefunction describing this excitation should be our coherent wavefunction,[10,11] instead of the Davydov wavefunction.[1] When the protein is at the specified temperature it is of the form:

$$|\Psi_\nu\rangle = \Big(\frac{1}{\lambda}\sum_i \Big(1 + \psi_i(t)b_i^+\Big)|0\rangle_{\rm ex}\Big)\Big(\exp\Big[\sum_q(\beta_{iq}^* a_q - \beta_{iq}a_q^+)\Big]\prod_q \frac{a_q^+ {}^{\nu_q}}{(\nu_q!)^{1/2}}|0\rangle_{\rm ph}\Big) . \tag{3}$$

Inserting Eq.(2) and (3) into the Heisenberg equations of motion of operators b_i and a_q and a_{-q}^+ and again calculating the thermal average of every term, then yield

$$j\hbar\dot{\psi}_i = \varepsilon_0\psi_i - J(e^{-W_{i,i+1}}\psi_{i+1} + e^{-W_{i,i-1}}\psi_{i-1}) + \sum_q\Big(2g(q)\psi_i + g_1(q)(\psi_{i+1} + \psi_{i-1})\Big)(\beta_{iq} + \beta_{i-q}^*)e^{jir_0 q} , \tag{4}$$

$$j\hbar\dot{\beta}_{iq} = \hbar\omega_q\beta_{iq} + \sum_i\Big(2g(q)|\psi_i|^2 + g_1(q)(\psi_i^*\psi_{i+1} + \psi_i^*\psi_{i-1})\Big)e^{-jir_0 q} , \tag{5}$$

$$j\hbar\dot{\beta}_{i-q}^* = j\hbar\langle\Psi_\nu|\dot{a}_q^+|\Psi_\nu\rangle = -\hbar\omega_q\beta_{i-q}^* - \sum_i\Big(2g(q)|\psi_i|^2 + g_1(q)(\psi_i^*\psi_{i+1} + \psi_i^*\psi_{i-1})\Big)e^{-jir_0 q} , \tag{6}$$

We here think approximately the thermal average of $W_{i,i+1}$ to be same version as $\bar{W}_i$, and the approximate value of the $\bar{W}_i$ has been given by Davydov[4]

$$W_{i,i\pm1} = \sum_q -(1 + \bar{\nu}_q)\beta_{qi\pm1}\beta_{qi}^* - \bar{\nu}_q\beta_{qi\pm1}^*\beta_{qi} + (\bar{\nu}_q + \frac{1}{2})(|\beta_{qi}|^2 + |\beta_{qi\pm1}|^2) \approx \bar{W}_i = \frac{1}{2}r_0\delta_0|\psi_i|^2 BF(T) , \tag{7}$$

where $\delta_0 = \dfrac{2(\chi_1+\chi_2)^2}{8r_0\beta(1-s^2)J\omega_0^2}$, $B = \dfrac{\pi r_0(\chi_1+\chi_2)^2}{4\omega_0^2\beta V_0\hbar(1-s^2)}$, $F(T) = \dfrac{r_0}{\pi N}\sum_q(2\bar{\nu}_q+1)|q|$. (8)

From Eqs. (5) and (6), we may get

$$(\dot{\beta}_{iq}+\dot{\beta}^*_{i-q}) = -\omega_q(\beta_{iq}+\beta^*_{i-q}) - \sum_i\left(\frac{4g(q)\omega_q}{\hbar}|\psi_i|^2 + \frac{2g_1(q)\omega_q}{\hbar}(\psi_i^*\psi_{i+1}+\psi_i^*\psi_{i-1})\right)e^{-jir_0q}. \quad (9)$$

In the region where $|\psi_i|^2 \neq 0$, the distances between the peptide groups decrease and this is defined by the function: $\langle\beta_i|(R_i - R_{i-1})/r_0|\beta_i\rangle$, with account taken of Eq. (9), and in the long wave-length approximation and the continuum limit, then the function $Q(x,t)$ satisfies the equation:

$$\frac{\partial^2}{\partial t^2}Q(\chi,t) - v_0^2\frac{\partial^2}{\partial\chi^2}Q(\chi,t) = \frac{\hbar(\chi_1+\chi_2)r_0}{M\omega_0}\frac{\partial^2}{\partial\chi^2}|\psi|^2, \quad (10)$$

where we take $\omega_q = v_0 q$. Meanwhile, Eq. (14) becomes approximately as

$$\begin{aligned} j\hbar\frac{\partial}{\partial t}\psi \approx{}&(\varepsilon_0 - 2J)\psi(\chi,t) - Jr_0^2\frac{\partial^2}{\partial\chi^2}\psi(\chi,t) \\ &+ \left(\frac{\hbar(\chi_1+\chi_2)r_0}{\omega_0}Q(\chi,t) + r_0\delta_0 BF(T)|\psi(\chi,t)|^2\right)\psi(\chi,t), \end{aligned} \quad (11)$$

Assuming $\zeta = x - vt$ and inserting the solution of Eq. (10) into Eq. (11), we can get

$$j\hbar\frac{\partial}{\partial t}\psi(\chi,t) = (\varepsilon_0 - 2J)\psi(\chi,t) - Jr_0^2\frac{\partial^2}{\partial\chi^2}\psi(\chi,t) - G(T)|\psi(\chi,t)|^2\psi(\chi,t), \quad (12)$$

where $G(T) = \dfrac{\hbar^2(\chi_1+\chi_2)^2r_0^2}{M\omega_0^2v_0^2(1-s^2)}\left(1 - \dfrac{1}{4}BF(T)\right)$.

Applying the boundary conditions, the soliton solution of Eq. (12) is

$$\psi(\chi,t) = \left(\frac{G}{\delta J}\right)^{\frac{1}{2}}\operatorname{sech}\left[\frac{G}{2J}(\chi - \chi_0 - vt)\right]\exp\left[j\frac{\hbar v}{2Jr_0^2}(\chi-\chi_0) - E_{\rm sol}t/\hbar)\right]. \quad (13)$$

Thus the displacement $\bar{\beta}(x,t)$ of the molecule from its equilibrium is of the form similar Eq. (13)

$$\bar{\beta}(\chi,t) = -\frac{\hbar(\chi_1+\chi_2)r_0^2}{Mv_0^2\omega_0(1-s^2)}\tanh\left[\frac{G}{4J}(\chi-\chi_0-vt)\right] \quad \left(\text{here } Q(\chi,t) = \frac{d\bar{\beta}(\chi,t)}{d\chi}\right). \quad (14)$$

In the rest coordinate system the energy of the above soliton (involving the deformation energy of the protein molecular system) in this case is also of similar form

$$E_{\rm sol} = \int_{-\infty}^{\infty}\left[Jr_0^2|\frac{\partial\psi}{\partial\chi}|^2 + (\varepsilon_0 - 2J)|\psi|^2 - G(T)|\psi|^2\psi\right]d\zeta + \frac{1}{2}\int_{-\infty}^{\infty}\left[M(\frac{\partial\bar{\beta}}{\partial t})^2 + \beta(\frac{\partial\bar{\beta}}{\partial\chi})^2\right]d\zeta, \quad (15)$$

Substituting Eqs. (13) and (14) into Eq. (15), we can obtain

$$E_{\rm sol} = (\varepsilon_0 - 2J) + \frac{1}{2}mv^2 - \frac{\hbar^4(\chi_1+\chi_2)^4(1-5s^2)}{24\omega_0^4\beta^2J(1-s^2)^3}\left[1 - \frac{B}{4}F(T)\right]^2 = E_0 + \frac{1}{2}M_{\rm sol}v^2. \quad (16)$$

The energy of the soliton depends on the temperature ($T \neq 0$) of this molecular system and decreases with increasing temperature. Therefore the specific heat arisen from the motion of the soliton can be calculated from Eq. (16) i.e.,

$$C_v = \frac{dE}{dT} = \frac{\hbar^4(\chi_1+\chi_2)^4B(1-5s^2)}{48\omega_0^4\beta^2J(1-s^2)^3}\left(1 - \frac{1}{4}BF(T)\right)\frac{dF(T)}{dT}. \quad (17)$$

From Eq.(8), we can find approximately out the value of $F(T)$. At high temperature, $F(T) \approx \frac{2K_B r_0 T}{\hbar v_0 \pi}$. Thus $C_v = K_B(A + B'T)$. We here take $J = 1.55 \times 10^{-22}$ J, $\beta = 13$ N/m, $\chi_1 = \hbar\chi_1/2\omega_0 = 62$ PN, $\chi' = \hbar\chi_2/2\omega_0 = (2-4)$ PN, $r_0 = 4.5$ Å, $M = 114\, m_p$ (m_p is a proton mass), thus $A = 5.15$, B'=0.0199 K^{-1}. This specific heat value is in agreement with the experimental result: $C_v = K_B(a + rT)$, which is measured by Mrevlishvil[14] from various biopolymers including protein. In order to compare further with the experimental data given by Goldanskii *et al.*[15] the linear specific heat C_1 is defined as $C_1 = B'K_B N'/M_0 \sim 10^4$ erg/gK^2, where $M_0 = 114$ gmol^{-1} is the molar weight of the protein and N' is the Avogadro constant. Above value of C_1 is in agreement with the experimental value.[15] This result obtained shows that this linear dependence for the specific heat of the protein is resulted basically from the heat excitation and the motion of the solitons. It shows that there is indeed the soliton in the protein and our theory is correct and successful.

When the temperature of the protein is lower, namely $K_B T \ll \hbar w_q$, the expression of $F(T)$ can be found out from Eq.(8) to be $F(T) = 1/2 + (\pi^2 K_B^2 T^2)/(3\hbar^2 v_0^2 q^2)$, thus $C_v = CT + DT^3$. where $C = 5.54 \times 10^{16}$ erg/gK^2, $D = 0.68 \times 10^{-20}$ erg/gK^4. This new result obtained is very surprising for us because the specific heat resulted from the thermal excitation of the solitons in the protein is very similar to the one in solid state matters. A possible reason is that this sort of soliton is also the intramolecular excitation (exciton) motion together with the local chain deformation.

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