THE DYNAMICAL MODEL OF THE HYDROGEN BOND.
THE GREEN FUNCTION METHOD

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The Green function method is adopted to the recently developed dynamical model of hydrogen bond. The lowering in the energy of the hydrogen bond, resulting from the attractive interaction of the non-bonding electrons, located at opposite sides of hydrogen bridge via chemical bond valence electrons and proton stretching vibration is obtained. The result is similar to that of Witkowski, but allows for the unique definition of the zero of energy and shows additional stabilization of hydrogen bond via non-bonding electron's chemical potential changes during the formation of this bond.

1. Introduction

In the two subsequent papers [1, 2] the dynamical model of a hydrogen bond was presented, in which a special attention was paid to the physical nature of this phenomenon and not to numbers. Witkowski [1] has shown that the dynamical interaction between non-bonding and valence electrons in the molecular fragment X–H...Y leads to the attraction between the non-bonding electrons located on the X and Y atoms, and owing to the simultaneous screening of the Coulomb repulsion by the proton, it results in the lowering of energy of the total system. We can say, therefore, that such interaction is, at least, partly responsible for the stabilization of a hydrogen bond, and play a very important role in hydrogen bonds, which are not very strong. Such hydrogen bonds are the most interesting ones, as they are present in all biologically active macromolecules. In that paper a special role of the almost spherical symmetry of non-bonding electrons excited states was also pointed out. In the subsequent paper of the present author [2] a main attention was paid to the role of the X–H bond stretching vibration. It was shown that the polarization of the non-bonding electrons by the vibrating proton leads also to the attraction between non-bonding electrons, and, therefore, the hydrogen bond binding energy possesses part of a vibrational origin. There was the paper of Anderson and Lippincott [3] in which it was pointed out, for the first time, that the hydrogen bond phenomenon cannot be fully understood on the basis of pure electronic interactions only. In paper [2]

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also the explanation of the great enchancement of the infrared absorption intensity in the region of the X–H stretching vibration, as well as shifting of the gravity centre of this absorption toward lower energies, was presented. Also the term responsible for the unusual change in the total infrared absorption intensity after deuteration, arises in a natural way from the dynamical model of the hydrogen bond.

The aim of this paper is to present the Green function application to the recently formulated model. It is shown that this method leads to a very similar results, however, it allows for the unique definition of the zero energy in a very simple form, and shows an additional stabilization of the hydrogen bond via change in the non-bonding electron chemical potential during the formation of the hydrogen bond. For simplicity of notations only the case of symmetrical hydrogen bond will be investigated.

2. Application of the Green function method

Let us assume, for simplicity, that the hydrogen bond is symmetrical. Witkowski [1] has shown that the assymetry of hydrogen bond play a very important role in the stabilization of this bond and in the existence of permanent dipole moment. However, for the ground state energy, the assymetry leads only to a redefinition of the quantity Δ, which determines this energy. As we are interested only in the ground state energy, we can assume that the hydrogen bond is symmetrical, as equations resulting in this case are much simpler, and only replace, in the final expression, Δ for $(\Delta^2 + \eta_0^2)^{1/2}$ (notations from [1] are used here). In such a case we can drop in the Hamiltonian (25) of [1] all terms which are expressed by the $\hat{t}_i$ operators, as the ground state energy belongs, in the case of symmetrical hydrogen bond ($\eta_k = 0$), to the Hilbert subspace spaned on S_i operators only. Therefore, the Hamiltonian of the hydrogen bond can be written in the following form [1, 2].

$$H = \sum_k \overline{\mathscr{E}}_k(a_k^+ a_k + c_k^+ c_k) + \sum_{k,k_1} V(k, k_1)a_k^+ c_k^+ c_{k_1}a_{k_1}, \tag{1}$$

where $\overline{\mathscr{E}}_k = \mathscr{E}_k - \mu$, $\mathscr{E}_k$ being the energy of the k-th excited state of non-bonding electrons, μ is the chemical potential for these electrons, and a_k^+, a_k; c_k^+, c_k are the creation, annihilation operators of the non-bonding electrons located on the opposite sides of the hydrogen bond. According to [2], the matrix element $V(k, k_1)$ is given by

$$V(k, k_1) = -\frac{2|V_{k_1k}|^2\omega}{(\mathscr{E}_k - \mathscr{E}_{k_1})^2 - \omega^2} + \sum_n \frac{|V_{kk_1}^{0n}|^2\omega_n}{(\mathscr{E}_k - \mathscr{E}_{k_1})^2 - \omega_n^2}. \tag{2}$$

ω is the X–H stretching vibration frequency, ω_n is the excitation energy of the n-th excited state of the chemical bond X–H, summation goes over all valence electron's excited state, and the matrix elements are expressed as follows:

$$V_{k_1k} = \alpha \left(\frac{\hbar}{2M\omega}\right)^{1/2} \langle k|\hat{x}_A|k_1\rangle_{x_A, x_B} \tag{3a}$$

$$V_{kk_1}^{0n} = \frac{1}{m} \langle 0|\hat{p}_A|n\rangle_{x_B}\langle k|\hat{p}_A|k_1\rangle_{x_A}. \tag{3b}$$

Here α is the non-bonding electrons — proton vibration interaction constant, x_A, p_A, x_B, p_B denote the coordinates and momenta of non-bonding; valence electrons, respectively. For $\omega < (\mathscr{E}_k - \mathscr{E}_{k_1}) < \omega_n$ the interaction (2) is an attractive one. As for the ground state calculation we will need matrix elements $V(k, 0)$ the above mentioned inequality will be satisfied. The chemical potential μ in (1) should be calculated from the requirement of the constant number of non-bonding electrons, i. e. from the equation:

$$\sum_k \langle a_k^+ a_k \rangle = \sum_k \langle c_k^+ c_k \rangle = 1, \tag{4}$$

the averaging being performed over the ground state of the system.

Let us now introduce the following Green's functions [4]:

$$G_k^{(a)}(t) = -i\theta(t) \langle [a_k(t), a_k^+(0)]_+ \rangle,$$

$$G_k^{(c)}(t) = -i\theta(t) \langle [c_k(t), c_k^+(0)]_+ \rangle,$$

$$G_{kl}^{(ca)}(t) = -i\theta(t) \langle [c_k^+(t) c_l(t) a_l(t), a_k^+(0)]_+ \rangle,$$

$$G_{kl}^{(ac)}(t) = -i\theta(t) \langle [a_k^+(t) a_l(t) c_l(t), c_k^+(0)]_+ \rangle. \tag{5}$$

The Fourier transforms of these functions satisfy the following set of equations of motion:

$$(\Omega - \overline{\mathscr{E}}_k) G_k^{(a)}(\Omega) = (2\pi)^{-1} + \sum_{k_1} V(k, k_1) G_{kk_1}^{(ca)}(\Omega), \tag{6a}$$

$$(\Omega - \overline{\mathscr{E}}_k) G_k^{(c)}(\Omega) = (2\pi)^{-1} + \sum_{k_1} V(k, k_1) G_{kk_1}^{(ac)}(\Omega), \tag{6b}$$

$$(\Omega - 2\overline{\mathscr{E}}_{k_1} - \overline{\mathscr{E}}_k) G_{kk_1}^{(ca)}(\Omega) = (2\pi)^{-1} \delta_{kk_1} \overline{n}_k^{(c)} + \sum_l V(k_1, l) \langle\!\langle c_k^+(1 - c_{k_1}^+ c_{k_1}) c_l a_l; a_n^+ \rangle\!\rangle_\Omega$$

$$- \sum_l V(k_1 l) \langle\!\langle a_{k_1}^+ a_{k_1} c_k^+ c_l a_l; a_k^+ \rangle\!\rangle_\Omega + \sum_l V(l, k) \langle\!\langle a_l^+ c_l^+ c_{k_1} a_{k_1} a_k; a_k^+ \rangle\!\rangle_\Omega, \tag{6c}$$

$$(\Omega - 2\overline{\mathscr{E}}_{k_1} - \overline{\mathscr{E}}_k) G_{kk_1}^{(ac)}(\Omega) = (2\pi)^{-1} \delta_{kk_1} \overline{n}_k^{(a)} + \sum_l V(k_1, l)$$

$$\times \langle\!\langle a_k^+(1 - a_{k_1}^+ a_{k_1}) a_l c_l; c_k^+ \rangle\!\rangle_\Omega - \sum_l V(k, l) \langle\!\langle c_{k_1}^+ c_{k_1} a_k^+ a_l c_l; c_k^+ \rangle\!\rangle_\Omega$$

$$+ \sum_l V(l, k) \langle\!\langle c_l^+ a_l^+ a_{k_1} c_{k_1} c_k; c_k^+ \rangle\!\rangle_\Omega. \tag{6d}$$

Here we have put

$$\langle\!\langle A; B \rangle\!\rangle_\Omega = (-\theta(t) \langle [A(t), B(0)]_+ \rangle)_\Omega, \tag{7a}$$

$$\overline{n}_k^{(a)} = \langle a_k^+ a_k \rangle, \quad \overline{n}_k^{(c)} = \langle c_k^+ c_k \rangle, \tag{7b}$$

and $(\ldots) \Omega$ means the Fourier transformation with respect to time.

Now we cut the infinite chain of motion's equations by the following approximation of the higher order Green's functions:

$$\langle\langle c_k^+(1-c_{k_1}^+c_{k_1})c_la_l; a_k^+\rangle\rangle_\Omega \simeq (1-\bar{n}_{k_1}^{(c)})G_{kl}^{(ca)}(\Omega), \tag{8a}$$

$$\langle\langle a_{k_1}^+a_{k_1}c_k^+c_la_l; a_k^+\rangle\rangle_\Omega \simeq \bar{n}_{k_1}^{(a)}G_{kl}^{(a)}(\Omega), \tag{8b}$$

$$\langle\langle a_l^+c_l^+c_{k_1}a_{k_1}a_k; a_k^+\rangle\rangle_\Omega \simeq B_{lk_1}G_k^{(a)}(\Omega), \tag{8c}$$

$$B_{lk_1} = \langle a_l^+c_l^+c_{k_1}a_{k_1}\rangle. \tag{8d}$$

Such an approximation is equivalent to inclusion of correlations between electron pairs only, and is similar to that in the BCS theory of superconductivity [4]. In that theory it is assymptotically correct. Of course, such a situation does not appear in our problem. It introduces some error to the ground state energy of the hydrogen bond, but we believe that electron pair correlations are the most important, and that this type of aproximation allows us to get the main part of the ground state energy. We will see below, that it leads to a similar result as that obtained by Witkowski [1] by a totally different method. A similar approximation must be done for Green's functions appearing in Eq. (6d). As we are concerned with the symmetrical hydrogen bond, we have $\bar{n}_k^{(a)} = \bar{n}_k^{(c)}$, and also $G_k^{(a)}(\Omega) = G_k^{(c)}(\Omega)$, $G_{kl}^{(ac)}(\Omega) = G_{lk}^{(ca)}(\Omega)$. Therefore, we can neglect the labels a, c as both types of Green's functions satisfy the same equation

$$(\Omega-2\bar{\mathscr{E}}_{k_1}-\bar{\mathscr{E}}_k)G_{kk_1}(\Omega) = (2\pi)^{-1}\delta_{kk_1}\bar{n}_k+(1-2\bar{n}_{k_1}),$$

$$\sum_l V(k_1, l)G_{kl}(\Omega) + \sum_l V(l, k)B_{l,k_1}G_k(\Omega). \tag{9}$$

Equation (9) is formally similar to the equation appering in the Zuburev paper [4], of course its physical meaning is here different.

Let us put now

$$B_{lk_1} = A_lA_{k_1}, \quad G_{kk_1}(\Omega) = g_k(\Omega)A_{k_1}, \tag{10}$$

where the quantities A_l satisfy the equation

$$2\bar{\mathscr{E}}_{k_1} + \frac{1-2\bar{n}_{k_1}}{A_{k_1}} \cdot A_{k_1} = 0, \tag{11}$$

with

$$A_{k_1} = \sum_l V(k_1, l)A_l, \tag{12}$$

then from Eqs. (6a) and (9), one gets

$$(\Omega-\bar{\mathscr{E}}_k)G_k(\Omega)-A_kg_k(\Omega) = (2\pi)^{-1}, \tag{13a}$$

$$(\Omega+\bar{\mathscr{E}}_k)g_k(\Omega)-A_kG_k(\Omega) = 0. \tag{13b}$$

In Eq. (13b) we droped the term with δ_{kk_1}, as in Eqs (6a, b) only term with $k \neq k_1$ play a role ($V(k, k) = 0$).

From Eqs. (13) and (10) we obtain

$$G_k(\Omega) = \frac{1}{4\pi}\left[\left(1 + \frac{\overline{\mathscr{E}}_k}{\Omega_k}\right)\frac{1}{\Omega - \Omega_k} + \left(1 - \frac{\overline{\mathscr{E}}_k}{\Omega_k}\right)\frac{1}{\Omega + \Omega_k}\right], \tag{14}$$

$$G_{kl}(\Omega) = A_l \Delta_k (4\pi\Omega_k)^{-1}[(\Omega - \Omega_k)^{-1} - (\Omega + \Omega_k)^{-1}], \tag{15}$$

where

$$\Omega_k = (\overline{\mathscr{E}}_k^2 + \Delta_k^2)^{1/2}. \tag{16}$$

Now, we have

$$\overline{n}_k = \int\limits_{-\infty}^{\infty} I_k(\Omega)d\Omega, \tag{17}$$

where $J_k(\Omega)$ is the spectral density of the function $G_k(\Omega)$ defined by

$$-i(e^{\frac{\Omega}{kT}} + 1)I_k(\Omega) = G_k(\Omega + i\varepsilon) - G_k(\Omega - i\varepsilon); \quad \varepsilon = +0. \tag{18}$$

Therefore, from Eqs. (13a), (17) and (18) we get

$$\overline{n}_k = \frac{1}{2}\left(1 - \frac{\overline{\mathscr{E}}_k}{\Omega_k}\operatorname{th}\frac{\Omega_k}{2kT}\right) \approx \frac{1}{2}\left(1 - \frac{\overline{\mathscr{E}}_k}{\Omega_k}\right), \tag{19}$$

as $\Omega_k \gg kT$. Similarly, we can get A_k from the spectral density of the function $g_k(\Omega)$. One can write, according to Eq. (10)

$$\langle a_l^+(t_1)c_l^+(t)c_{k_1}(t)a_{k_1}(t)\rangle = A_{k_1}A_l(t - t_1) = A_{k_1}\int\limits_{-\infty}^{\infty}\tilde{I}_l(\Omega)e^{i\Omega(t - t_1)}d\Omega, \tag{20}$$

where $\tilde{I}_k(\Omega)$ satisfy the equation identical to Eq. (18) with $I_k(\Omega)$ and $G_k(\Omega)$ replaced by $\tilde{I}_k(\Omega)$ and $g_k(\Omega)$, respectively. Therefore, we get

$$A_l = \int\limits_{-\infty}^{\infty}\tilde{I}_l(\Omega)d\Omega = -\frac{\Delta_l}{2\Omega_l}\operatorname{th}\frac{\Delta_l}{2kT} \approx -\frac{\Delta_l}{2\Omega_l}. \tag{21}$$

Now, one can easily verify that $\overline{n}_l$ and A_l given by Eqs. (19) and (21) satisfy Eq. (11). Therefore, they form, together with Eqs. (14) and (15), the selfconsistent solution of the problem. From Eqs. (12) and (16) results the following equation from which the quantities Δ_k should be determined:

$$\Delta_k = -\frac{1}{2}\sum_l \frac{V(k_1 l)\Delta_l}{(\overline{\mathscr{E}}_l^2 + \Delta_l^2)^{1/2}}. \tag{22}$$

This equation differs from the similar equation derived in the Witkowski paper (Eq. (49) in [1]) only by a factor 2. For the cut off Hamiltonian [1] a similar equation to Eq. (50) in [1] can be easily written. We note, that equation (22) is formally identical with the integral equation which appears in the BCS theory. In the cut-off Hamiltonian [1] the solutions $\Delta \neq 0$ exist only for $V < 0$, and from Eq. (2) one can see that $V(k, 0)$, which is present in equation determining the Δ_0 parameter for the ground state, is indeed usually negative.

3. Ground state energy

Now we are in position to calculate the expression for the ground state energy of our model hydrogen bond. From Eq. (1) we see, that

$$E_0 = \langle H \rangle = 2 \sum_k \overline{\mathscr{E}}_k \overline{n}_k + \sum_{k,l} V(k, l) B_{kl} \tag{23}$$

inserting Eqs. (10), (19), (21), and (22) into Eq. (23) we get

$$E_0 = \sum_k \overline{\mathscr{E}}_k \left(1 - \frac{\overline{\mathscr{E}}_k}{\Omega_k} \right) - \tfrac{1}{2} \sum_k \frac{\Delta_k^2}{\Omega_k}, \tag{24}$$

or

$$E_0 = \sum_k \overline{\mathscr{E}}_k - \sum_k \frac{\overline{\mathscr{E}}_k^2 + \Omega_k^2}{2\Omega_k}. \tag{25}$$

Let us put $\overline{\mathscr{E}}_0 = 0$, i.e. the ground state energy before the formation of hydrogen bond is taken as zero. In order to find $\overline{\mathscr{E}}_k$ we must first determine the chemical potential μ. Let us put $\mathscr{E}_{k \neq 0} \gg \Delta_k$. This is reasonable, as Δ_k should have the order of magnitude of the hydrogen bond energy, and $\overline{\mathscr{E}}_{k \neq 0}$ is one of the excitation energies of non-bonding electrons. Before the formation of hydrogen bond we have $\mu = 0$, and, as hydrogen bond is weak, we can expect that putting $\overline{\mathscr{E}}_{k \neq 0} \approx \mathscr{E}_{k \neq 0}$ does not introduce a great error. Taking this all into account we can write

$$E_0 = 2\overline{\mathscr{E}}_0 - \frac{\overline{\mathscr{E}}_0^2 + \Omega_0^2}{\Omega_0} + 0 \left(\frac{\Delta_{k \neq 0}^4}{\overline{\mathscr{E}}_{k \neq 0}^4} \right). \tag{26}$$

The factor 2 which multiplied the term with $k = 0$ in Eq. (25) comes from the fact that there are two spin-orbitals belonging to the state $k = 0$. Now according to Eqs. (4) and (19), the chemical potential is to be determined from the following relation

$$\sum_k \left\{ 1 - \frac{\overline{\mathscr{E}}_k - \mu}{[(\overline{\mathscr{E}}_k - \mu)^2 + \Delta_k^2]^{1/2}} \right\} = 2 \tag{27}$$

or, approximately:

$$\frac{\overline{\mathscr{E}}_0 - \mu}{[(\overline{\mathscr{E}}_0 - \mu)^2 + \Delta_0^2]^{1/2}} = \kappa, \tag{28}$$

where

$$\kappa = \sum_{k \neq 0} \frac{\Delta_k^2}{2\overline{\mathscr{E}}_k^2} - 1 + 0\left(\frac{\Delta_{k \neq 0}^4}{\overline{\mathscr{E}}_{k \neq 0}^4}\right) \tag{29}$$

Let us assume that $\kappa < 0$, then

$$\overline{\mathscr{E}}_0 - \mu = -\frac{\Delta_0|\kappa|}{(1 - \kappa^2)^{1/2}}, \qquad \Omega_0 = \frac{\Delta_0}{(1 - \kappa^2)^{1/2}}. \tag{30}$$

For $\Delta_0 = 0$ we have $\mathscr{E}_0 - \mu = 0$, $\overline{n}_0 = 1$, $\overline{n}_{k \neq 0} = 0$, as it should be. Inserting Eq. (30) into (26) one gets

$$E_0 = -\frac{\Delta_0(1 + |\kappa|)^2}{(1 - \kappa^2)^{1/2}}. \tag{31}$$

This equation seems to be more correct than that obtained in Witkowski's paper [1], as it takes into account the fact that the total number of non-bonding electrons is constant during the formation of hydrogen bond. Witkowski's expression for the ground state energy is correct only for $\kappa = 0$ and in this case agrees with our result. We see that the lowering of energy after formation of hydrogen bond satisfies the condition $|E_0| \geqslant \Delta_0$, as $|\kappa| < 1$ must hold. If this last inequality is not fulfilled, then the dynamical model cannot be applied to such hydrogen bond. Such situation can arise, of course, in the case of a very strong hydrogen bond, and as we noted at the very beginning of this paper such cases cannot be properly described by such model. The reason for this lies in the derivation of the Hamiltonian (1) (see [1, 2]). We note now that κ and Δ_0 are not independent, because of Eq. (22). For $\kappa < 0$, Δ_0 diminishes with the increase of $|\kappa|$. For $\kappa = -1$ we have $\Delta_0 = 0$ (as $\Delta_{n \neq 0}$, see Eq. (29)). In the case $\kappa > 0$ the expression for the ground state energy is the same as in Eq. (31), however, now Δ_0 increases with increase of κ. Therefore, for $\kappa \in (-1,0)$, the hydrogen bond energy diminishes slower than Δ_0 and is not a linear function of Δ_0. The opposite situation arises for $\kappa \in (0, 1)$, when the hydrogen bond energy increases faster than Δ_0.

We can conclude that the change in the chemical potential of non-bonding electrons during the formation of hydrogen bond gives the additional stabilization of this bond, which was not noticed in the previous papers [1, 2].

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