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# Proton position near $Q_B$ and coupling of electron and proton transfer in photosynthesis

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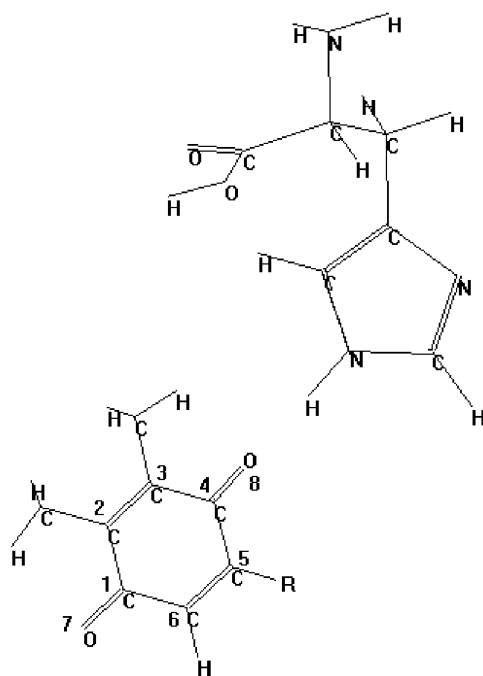
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## Abstract

We have calculated the energy levels and wavefunctions of a proton in a histidine (His)–plastoquinone (PQ) system in the reaction centre (RC) of photosystem 2 of higher plants and the RC of purple bacteria for different redox states of PQ  $Q_B$ . For oxidized  $Q_B$ , the proton is located near His. For once-reduced PQ, it is positioned in the middle between the nitrogen of His and the oxygen of PQ. For twofold-reduced PQ, the proton is localized near the oxygen of PQ. Using the values of total energy of the system in these states, we have also estimated the frequency of proton oscillations. On the basis of these results we propose a hypothesis about the coupling of electron–proton transfer.

## 1. Introduction

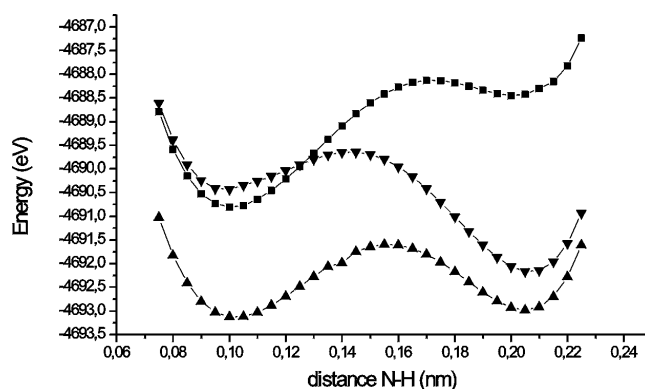
Although the discussions of the theoretical aspects of the relationship between atomic physics and biology were started in the 1930s [1, 2], intensive work by theoretical physicists in biology was initiated by the discovery of the important biological structures: the  $\alpha$ -helix in protein [3] and DNA structure [4]. At first these works were linked to quantitative descriptions of optical and radiospectroscopic properties of biologically important molecules [5] and also to the choice of approach to the description of biological processes [6]. After that the experimental and theoretical methods of quantum physics began to be widely applied to the study of elementary reactions in biological systems. After the 1960s, the number of works concerning photosynthetic systems began to increase. This situation was determined by the fact that the quantum phenomena in these systems are especially clearly manifested. The point is that the energy of the quantum taking part in the primary processes of photosynthesis is about one order larger than that of one in dark biochemical processes. Moreover, at this time tunnelling phenomena in photosynthetic electron transport were also being discovered [7–9]. Theories satisfactorily describing the experimental data for phenomena in photosynthesis such as energy migration in light-harvesting antenna complexes [10] and charge separation (generation of reduced acceptor and oxidized donor) after excitation of special pairs of reaction centres (RCs) [11, 12] were developed. The formulae for the rates of corresponding processes contain the characteristics of molecules taking part in them.



**Figure 1.** The schematic atom arrangement and numeration in PQ–His.

Now the coupling of electron and proton transport in RCs near  $Q_B$  is of great interest for scientists. The crux of the problem is the following. Coupling of electron and proton transfer occurs in the photosynthetic RC, the pigment–protein membrane complex with strictly determined chemical composition. The structure of the photosystem (PS) 2 RC of higher plants is thought to be very similar to the RC of purple bacteria. Later on, for distinctness, we will talk about the RC of higher plants, the structure of which was discussed in a review paper [13]. After the absorption of a light quantum by light-harvesting antenna pigments, energy migration to the RC, charge separation in the PS 2 RC, reduction of the primary electron acceptor, pheophytin, and of the secondary electron acceptor, bound PQ  $Q_A$ , the electron from the latter is transferred to  $PQ_B$ , reducing it to a semiquinone ion. After the second excitation of the RC, the process is repeated and  $Q_B$  is reduced by a second electron. It is well known that  $Q_A$  can accept only one electron, while  $Q_B$  works as a ‘two-electron’ gate [13]. After a second reduction and uptake of two protons from the outward side of the membrane, plastoquinol  $PQH_2$  leaves its binding site to be reoxidized by a cytochrome  $b_6f$  complex. This process results in the release of two protons on the inner side of the membrane. Two problems arise in connection with the PQ  $Q_B$  function. The first is: which electron characteristics of PQ in the different redox states are essential for its binding and detachment from its binding place, and also for the proton transfer across the membrane?

The second problem is: what is the mechanism of synchronization between  $Q_B$  reduction and proton transfer? Let us try to consider experimental and theoretical works related to the above-mentioned problems. Firstly, the structure of RC from bacteria *Rh. viridis* was determined by x-ray analysis [14]. A few groups of scientists studied the electronic properties of PQ and ubiquinones. So in the paper of Rinyi *et al* [15] electronic properties of quinones were studied in connection with charge stabilization in photosynthetic RC. In [16] the characteristics



**Figure 2.** Total electronic energy (in adiabatic approximation) of the PQ–His system for different states of PQ and different N–H distances. The N–H–O distance is equal to 0.3 nm. Symbol ■ denotes energy curves with charge 0; ▲-charge-1; ▼-charge-2.

of the quinones were estimated to study the influence of surroundings on the rate of the electron transport between  $Q_A$  and  $Q_B$ . Ericsson *et al* [17] investigated electrical and magnetic characteristics of neutral and charged quinone and plastoquinone radicals in relation to the build-up of H-bonds with the surrounding molecules. O'Malley [18] studied spin density and hyperfine couplings for H-bonded 1, 4-naphthoquinone and phylloquinone anion radicals to clarify the influence of the H-bond on the above-mentioned characteristics. Peluzo *et al* [19] investigated the electronic structure of  $Q_A$  in the context of the role of H-bonds in the electron transport from  $Q_A$  to  $Q_B$ . Moreover, Aderoth *et al* [20] ascertained that the aminoacids take part in proton transfer from outside the membrane to PQ  $Q_B$  in the RC of bacteria *Rh. sphaeroides*. In paper [21] the quantum-mechanical description of the proton transfer in biosystems, containing H-bonded chains, was presented. The authors applied the model of the small polaron for the definition of kinetic characteristics of proton transfer. However, this study was carried out only in a general manner, without a concrete definition of the system under consideration. One shortcoming is common for all the previous works dealing with the mechanism of coupling between electron and proton transfers. Although the electronic structure of single  $Q_B$  in different states has been considered [15–17], the influence of PQ reduction on proton transfer still remains to be solved.

In our previous works [22, 23] we have studied the electronic and energetic characteristics of the system PQ–His at the different redox states of PQ. The scheme of this system is presented in figure 1. The position of PQ and His was chosen on the basis of the known structure of purple bacteria RCs [24] and was corrected by the HyperChem program with the help of data about bond lengths and valence angles [23]. Such a system was chosen because the His residue is the nearest to PQ $_B$ , from which the electron transfer is supposed to occur [14]. Moreover, Stowell *et al* [25] have shown that His L190 in *Rh. sphaeroides* RCs and one of the two oxygen atoms of quinone (N8 in figure 1) is within an H-bond distance from the ring of His L190. For this system we determined the total electronic energy of the system as a function of the proton position on the straight line connecting the nitrogen of His and the oxygen of PQ. Such a proton position was chosen because the straight H-bond has minimal total energy [26]. These calculations were repeated for different distances between PQ and His. In doing so, the distance between the oxygen of PQ and the nitrogen of His varied from 0.2 to 0.5 nm. Figure 2 shows the dependence of the above-mentioned energy on the distance between the proton and the nitrogen atom of His. From figure 2 it can be seen that for the fixed position of PQ and

**Table 1.** Total minimal energy of system PQ–His for different states of PQ and different N–H···O distances.

N–O distance (nm)	Charge	N–H distance (nm)	Total energy (eV)	N–H distance (nm)	Total energy (eV)
0.2	0	0.095	–4686.8852	—	—
	–1	0.095	–4689.9113	—	—
	–2	0.095	–4687.8607	—	—
0.25	0	0.1	–4689.9807	—	—
	–1	0.105	–4692.5961	—	—
	–2	0.1	–4689.9939	—	—
0.3	0	0.1	–4690.8042	0.2	–4688.45
	–1	0.1	–4693.1255	0.205	–4692.98
	–2	0.1	–4690.4293	0.205	–4692.17
0.35	0	0.1	–4691.0595	0.265 01	–4688.75
	–1	0.1	–4693.2666	0.265 01	–4693.06
	–2	0.1	–4691.0902	0.265 01	–4692.50
0.4	0	0.1	–4691.0968	0.320 1	–4688.83
	–1	0.1	–4693.2449	0.310 1	–4692.99
	–2	0.1	–4691.3512	0.310 1	–4692.55
0.45	0	0.1	–4691.0944	0.360 1	–4688.89
	–1	0.1	–4693.1987	0.360 1	–4692.93
	–2	0.1	–4691.5203	0.360 1	–4692.62
0.5	0	0.1	–4691.0863	0.405	–4688.99
	–1	0.1	–4693.1612	0.405	–4692.92
	–2	0.1	–4691.631	0.405	–4692.71

His the dependence of energy resembles a curve with two potential wells (N–H–O distance is equal to 0.3 nm). For other N–H–O distances, these curves have either one (for N–H–O distances 0.2 and 0.5 nm) or two minima of energy for different distances. These minimal energies and corresponding distances are presented in table 1. As a result of this work, it has become qualitatively clear that at the PQ reduction a change in proton position occurs and the distance between PQ and His changes too.

The purpose of the present paper is to calculate wavefunctions and energetic levels, corresponding to the steady state of a proton with potential energy similar to that presented in figure 2. The results of this work permit us to make quantitative conclusions about the proton localization for different redox states of PQ.

## 2. Methods

Recall that the aim of the work is to calculate energy levels and wavefunctions of a proton in each of the previously obtained potential curves. Knowing the distance between energy levels, we try to evaluate the frequency of vibration of a proton in the His–PQ system. In a quantum-mechanical sense the proton is oscillating in the potential field created by all the atoms of histidine and plastoquinone. Such an oscillation of a proton can be investigated in terms of the one-dimensional Schrödinger equation:

$$-\frac{\hbar^2}{2m}\Psi'' + U(x)\Psi - E\Psi = 0. \quad (1a)$$

In (1a)  $U(x)$  is the given potential energy curve,  $E$ —energy of the proton in the system,  $\Psi$ —wavefunction of the proton.

The calculations have been performed using the system MATLAB, a special program for numerical calculations of Schrödinger equations. Since the potential energy curve was obtained numerically as separate points only [1], a spline interpolation (third-order spline interpolation) of the input data has been performed.

As treated mathematically, the Schrödinger equation is simply the eigenvalue and eigenfunction problem—the Sturm–Liouville problem. The universal difference method of numerical analysis of the Schrödinger equation can be used.

A mathematical statement of the problem is as follows. To solve our problem, the following Schrödinger problem in one dimension is considered:

$$\begin{aligned} -A\Psi'' + U(x)\Psi - E\Psi &= 0, \\ \Psi(-\infty) = \Psi(+\infty) &= 0, \quad A = \frac{\hbar^2}{2m} = \text{constant} > 0, \\ \int_{-\infty}^{+\infty} \Psi^*(x)\Psi(x) dx &= 1. \end{aligned} \quad (1b)$$

We extract in the indefinite region (1) some finite segment of the real axes, where the Sturm–Liouville problem will be formulated. This segment  $[a, b]$  must take into account the structure of the potential  $U(x)$ ; in doing so,  $U(a)$  and  $U(b)$  must be large enough to diminish the wavefunction to zero beyond the extracted segment. Now we can formulate the mathematical problem.

Let us calculate the eigenfunctions and eigenvalues of the following Sturm–Liouville problem:

$$\begin{aligned} -A\Psi'' + U(x)\Psi - E\Psi &= 0, \\ \Psi(a) = \Psi(b) &= 0. \end{aligned} \quad (1c)$$

Introduce on real axes the following grid:

$$\varpi_h = \{x_i\}, \quad i = 1, \dots, N \quad (2)$$

and approximate [27] the differential operator  $L = -A\frac{d^2}{dx^2} + U(x)$  with the difference operator

$$L_h y = -A \frac{y(x+h) - 2y(x) + y(x-h)}{h^2} + U(x) \quad (3)$$

where  $h$  is the grid step and  $x$  is defined in mesh points  $\{x_i\}$ .

Such a difference operator is known to have a second order approximation, i.e.  $\psi = L_h y - Ly = \frac{y^{(4)}(x)h^2}{12} + O(h^4)$ . Moreover, this difference operator can be shown to converge [27].

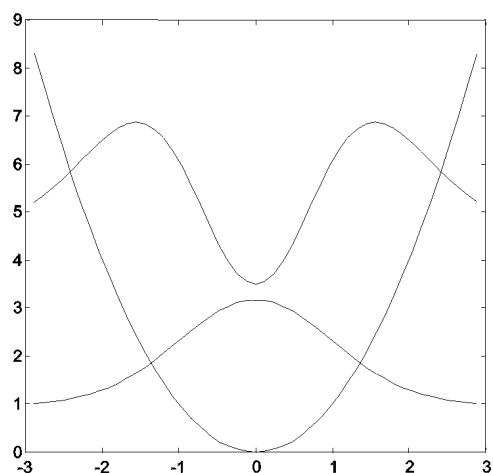
Now we can formulate the difference equations for problem (1). Divide the segment  $[a, b]$  into  $N$  subsegments, hence we have the difference scheme with  $N + 1$  mesh points with difference interval  $h = \frac{b-a}{N}$ ,  $x_i = a + ih$ ,  $i = 0, \dots, N$ . Assigning  $u_i = u(x_i)$  we have the following system of linear differential equations for  $y_i$ :

$$\begin{aligned} -\frac{A}{h^2}y_{n+1} + \left(u_n - \frac{2A}{h^2} - E\right)y_n - \frac{A}{h^2}y_{n-1} &= 0, \quad n = 1, \dots, N-1 \\ y_0 = y_N &= 0. \end{aligned} \quad (4)$$

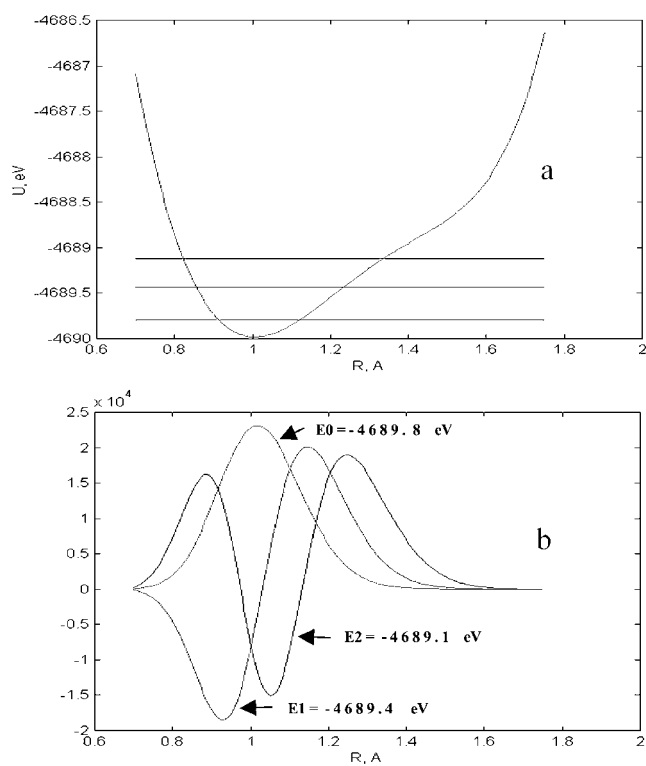
This is a typical problem of eigenvalues and eigenfunctions of a matrix. The solution can be obtained by the QR method of numerical calculations [27].

In order to verify the efficiency of the given approximation, we can use our method to calculate the energy levels and wavefunctions of the harmonic oscillator:

$$\begin{aligned} -\Psi'' + x^2\Psi - E\Psi &= 0, \\ \Psi(-\infty) = \Psi(+\infty) &= 0. \end{aligned} \quad (5)$$

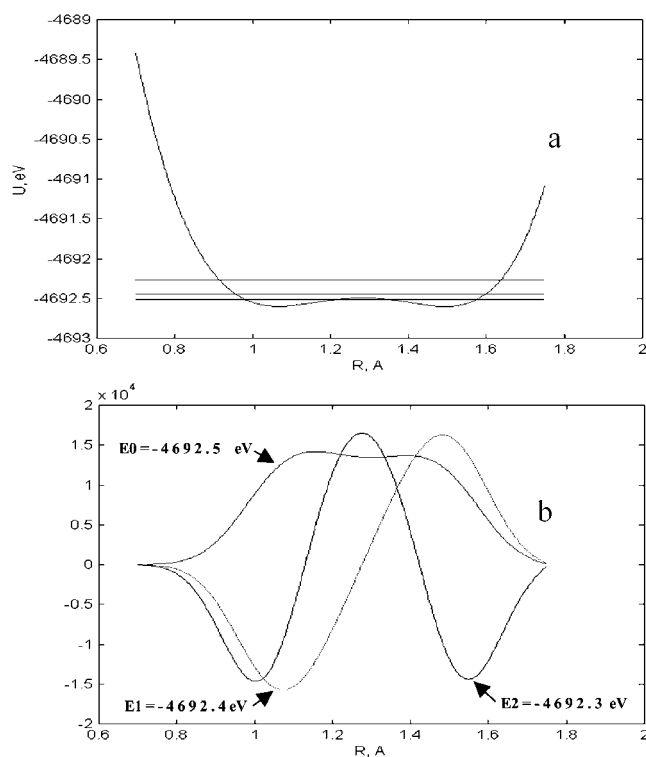


**Figure 3.** The four lowest wavefunctions of harmonic oscillator (5) numerically calculated with difference scheme (4) as the illustration of the possibilities of the method.



**Figure 4.** The total electronic energy of oxidized PQ and His (in the adiabatic approximation) for the different distance  $R$  between a proton and a nitrogen atom and energy levels for proton movement (a) and the corresponding wavefunction (b). The N–H–O distance is equal to 2.5 Å.

The analytical methods give for energy levels  $E_i = 1, 3, 5, \dots$ , and the wavefunctions can be expressed in terms of Hermite polynomials.



**Figure 5.** The total electronic energy of once-reduced PQ and His (in the adiabatic approximation) for different distances  $R$  between a proton and a nitrogen atom and energy levels for proton movement (a) and the corresponding wavefunction (b). The N–H–O distance is equal to 2.5 Å.

Taking segment  $[-5; 5]$ ,  $N_1 = 100$  at first and then  $N_2 = 200$ , we obtain with scheme (4) the following results:

$$\begin{array}{llll} \text{For } N_1 & E_1 = 0.9994; & E_2 = 2.9969; & E_3 = 4.9919. \\ \text{For } N_2 & E_1 = 0.9998; & E_2 = 2.9992; & E_3 = 4.9980. \end{array}$$

By Runge's formula [27] for refinement of the solution, we can obtain more precise results, namely:

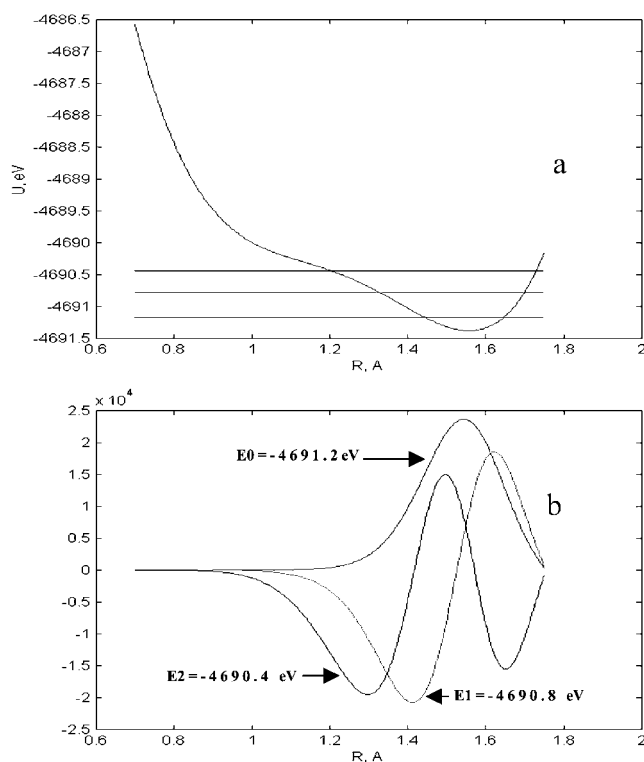
$$\begin{array}{ll} E_1 = 1.000\,000\,098\,039\,06; & E_2 = 3.000\,000\,889\,695\,07; \\ E_3 = 5.000\,003\,605\,109\,76. & \end{array}$$

Wavefunctions corresponding to these eigenvalues are shown in figure 3. They are totally consistent with well known table functions.

As we can see in figure 3 and from calculated energy levels, the results converge to the theoretically obtained values, and the accuracy of calculations is high enough and can be increased by contracting the difference interval.

With the aid of the developed program, the energy levels and wavefunctions of a proton in three states of the plastoquinone–histidine system have been determined for neutral, singly and doubly reduced states of plastoquinone. The results of calculations are presented in figures 4–6.





**Figure 6.** The total electronic energy of twofold-reduced PQ and His (in the adiabatic approximation) for the different distance  $R$  between a proton and a nitrogen atom and energy levels for proton movement (a) and the corresponding wavefunction (b). The N–H–O distance is equal to 2.5 Å.

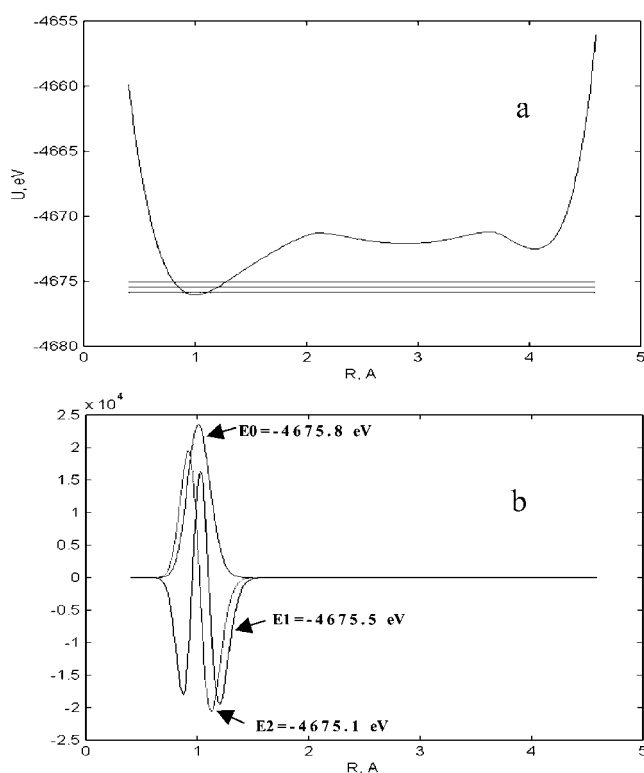
### 3. Results of calculation and discussion

For different states of PQ (oxidized, once-reduced, and twofold-reduced) and different N–H–O distances we estimated the energy levels and wavefunctions of a proton as a function of the distance between the nitrogen of His and a proton. As noted above, all energy dependence curves, similar to figure 2, can be divided into two parts: with one and two potential wells.

The results for the first type of curve are presented in figures 4–6 for N–H–O distance equal to 2.5 Å and different states of PQ. Now we discuss the peculiarities of the dependences under consideration. For the potential curve with one well (figures 4 and 6) the wavefunctions of the proton are localized either near the nitrogen atom of His (oxidized PQ) or near the oxygen atom of PQ (in the case of twofold-reduced PQ). This is apparent from the view of the corresponding wavefunctions.

It should be noted also that in both cases all three wavefunctions relevant to the lowest energy levels are located near one proper atom. It is interesting to point out that the energy difference between the first and second levels is greater than the energy of translational movement at room temperature ( $kT = 0.02$  eV). This means that it is impossible to excite the system on the second excited level at room temperature.

In the case of the two-well potential energy curve (figure 5) we see that the wavefunction of a proton for the lowest energy level is localized in the middle between the nitrogen of His



**Figure 7.** The total electronic energy of oxidized PQ and His (in the adiabatic approximation) for the different distances  $R$  between a proton and a nitrogen atom and energy levels for proton movement (a) and the corresponding wavefunction (b). The N–H–O distance is equal to 5 Å.

and the oxygen of PQ. The second level is more energetic ( $\Delta E = 0.1$  eV) than the first one. This means that at room temperature the wavefunction of the proton, corresponding to the second energetic level, is more delocalized. Such proton localization is indicative of H-bond formation in the once-reduced state of PQ. At the same time, the H atom of His forms a covalent chemical bond with twofold-reduced PQ.

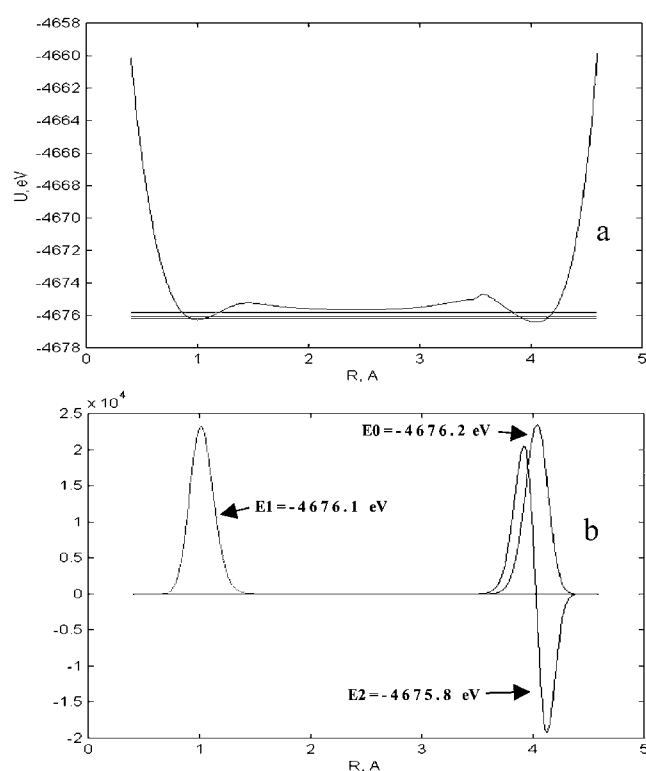
Consider now the proton delocalization in the case of the two-well potential (N–H–O distance is equal to 5 Å). In this case (figures 7, 8) the proton localization is the same as in the first case. The only dissimilarity is the following. The wavefunction corresponding to the second excited energetic level for twofold-reduced PQ has its maximal value near His (figure 8(b)).

Using the distance between the energetic levels, it is possible to estimate the frequency of proton vibration in the system under consideration. This value is equal to about  $3000 \text{ cm}^{-1}$  which, to an order of magnitude, corresponds to the experimental data [28].

#### 4. Conclusion

We have reduced the complex quantum-chemical problem of coupling electron and proton transfer to the simple problem of solving the one-dimensional Schrödinger equation.

Our estimates show that the reason for the proton movement to PQ is the increase of electron density on PQ. However, the questions remain: how is the missing proton on the His



**Figure 8.** The total electronic energy of twofold-reduced PQ and His (in the adiabatic approximation) for the different distances  $R$  between a proton and a nitrogen atom and energy levels for proton movement (a) and the corresponding wavefunction (b). The N–H–O distance is equal to 5 Å.

replaced and how are the electron transfer to PQ and the proton transport from the outer space of the thylakoid across the membrane coupled? We propose that this happens through the step-by-step transfer along the chain of H-bonds, the so-called proton channel, leading to the outside membrane.

In bacterial RCs the supposition concerning the existence of proton channels was discussed in [25]; such a channel containing eight water molecules is known in bacteriorhodopsin [29]. The appearance of proton transfer in photosynthetic RC and bacteriorhodopsin is favoured by the coincidence of the proton transport rates across the thylakoid membrane and the plasma membrane of *Halobacterium salinarium* [30]. We guess that the same scheme of coupling of electron transport may well take place in the *cyt*  $b_6f$  complex and oxygen-evolving systems.

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