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# A Simple Method for Estimating Activation Energies of Proton-Transfer Reactions†

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A simple analytical procedure for estimating activation energies of elementary proton-transfer reactions is proposed and successfully applied to a variety of cases. The procedure is based on a particular partition of the electronic Hamiltonian, which allows the identification of the most important contributions to the activation energy for proton hopping, and yields reliable potential energy profiles, comparable with those obtained at the ab initio HF/MP2 level of computation.

## Introduction

Research in bioenergetics is increasingly focusing attention on the role played by H-bond chains in many processes, such as proton transport across membranes[1] and long-range electron transfer (ET).[2,3]

It is an old concept,[4−6] now widely accepted, that H-bond chains constitute efficient pathways for proton transport, as confirmed by kinetic measurements of proton transport in gramicidin A.[7] Indeed, that is not the only role that such chains can play: it was also suggested that suitable combinations of proton and hydrogen atom hoppings, along a H-bond chain connecting two redox sites of a protein, can be a low energy pathway for long-range electron transfer (ET).[8] Such a hypothesis goes beyond the known concept of ET coupled to proton transfer (PT),[9,10] inasmuch it assigns to hydrogen atoms the role of electron carriers in long-range ET, thus allowing for an alternative simple mechanism of long-range ET in proteins, in which the indirect coupling provided by the high energy states of the interposed species are no longer needed.[11−13]

That mechanism, called proton assisted electron transfer (PAET), was successfully applied to ET between primary and secondary quinone of photosynthetic reaction centers.[14,15] Apart from this particular but important case, PAET is also in line with the finding that hydrogen atom transfer can be a suitable pathway for ET in systems consisting of amino acid residues with an unpaired electron, in cases where the two redox partners are connected by one or more H-bonds;[16] moreover, both experimental and theoretical evidence has been recently provided in support of PAET in a DNA−acrylamide complex.[17]

The analysis of the kinetics of proton and hydrogen motions in such H-bond chains is thus important for a better assessment of their role in biosystems, but computations of reliable potential energy surfaces are often ruled out by the size of the systems. It is then necessary to find out a method which allows for estimating potential energy profiles and surfaces from a few experimental and/or theoretical data pertaining to equilibrium points both of the separated moieties and of the H-bonded complex, such as the strengths and the vibrational frequencies of the X−H bonds in the isolated moieties, the energy differences between the two possible equilibrium configurations of the H-bond complex and their nuclear geometries and vibrational frequencies. In this paper we give a contribution along this direction by considering the simplest case of proton transfer in linear H-bond complexes.

## The Two Morse Model

Let us start by assuming that for proton-transfer reactions the Born Oppenheimer approximation holds so that the usual separation of nuclear and electronic motions can be invoked. The electronic Hamiltonian operator for a generic

$$\mathrm{A{-}H\cdots B^-}$$

system, where A is a polyatomic molecule with $N$ nuclei and $n - 1$ electrons and $\mathrm{B^-}$ is a polyatomic anion with $M$ nuclei and $m$ electrons, can be partitioned as follows:

$$\mathscr{H}^{\mathrm{el}}_{\mathrm{tot}} = \mathscr{H}_{\mathrm{AH}} + \mathscr{H}_{\mathrm{BH}} + \mathscr{V} = \mathscr{H}^{\circ} + \mathscr{V} \qquad (1)$$

where $\mathscr{H}_{\mathrm{AH}}$ and $\mathscr{H}_{\mathrm{BH}}$ are the electronic Hamiltonian operators of the isolated A−H and B−H molecules, and

$$\mathscr{V} = \sum_{i}^{n}\sum_{\mu}^{m}\frac{e^2}{r_{i\mu}} - \sum_{i}^{n}\sum_{\xi}^{M}\frac{Z_\xi e^2}{r_{i\xi}} - \sum_{\mu}^{m}\sum_{a}^{N}\frac{Z_a e^2}{r_{\mu a}} + \sum_{\xi}^{M}\sum_{a}^{N}\frac{Z_\xi Z_a e^2}{r_{\xi \mathrm{a}}} \qquad (2)$$

where Latin (Greek) indexes refer to electrons and nuclei of A and B.

The partition of the total electronic Hamiltonian has been done in such a way that $\mathscr{V}$ does not involve the coordinates of the H-bonded proton; the same partition, with $\mathscr{V}$ independent of the proton coordinates, also holds for $\mathrm{(A{-}H\cdots B)^+}$ complexes, with $\mathscr{H}^{\circ} = \mathscr{H}_{\mathrm{AH^+}} + \mathscr{H}_{\mathrm{BH^+}}$, and in all other cases where the two equilibrium configurations differ for the position of a proton, not of a whole hydrogen atom.

Let $\psi_{\mathrm{r}}^{\mathrm{A}}$ and $\psi_{\mathrm{s}}^{\mathrm{B}}$ be the eigenfunctions of $\mathscr{H}_{\mathrm{AH}}$ and $\mathscr{H}_{\mathrm{BH}}$, with eigenvalues $E_{\mathrm{r}}^{\mathrm{A}}$ and $E_{\mathrm{s}}^{\mathrm{B}}$:

$$\mathscr{H}_{\mathrm{AH}}\psi_{\mathrm{r}}^{\mathrm{A}} = E_{\mathrm{r}}^{\mathrm{A}}\,\psi_{\mathrm{r}}^{\mathrm{A}} \qquad (3)$$

$$\mathscr{H}_{\mathrm{BH}}\psi_{\mathrm{s}}^{\mathrm{B}} = E_{\mathrm{s}}^{\mathrm{B}}\,\psi_{\mathrm{s}}^{\mathrm{B}} \qquad (4)$$

If the overlap between $\psi_{\mathrm{A}}$ and $\psi_{\mathrm{B}}$ were zero, there would not be any difficulty in assigning a set of $n$ electrons $\{i\}$ to

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† This paper is dedicated to the memory of professor Guido Sodano.

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A−H and a set of $m$ electrons $\{j\}$ to B−H, so that the wave functions of the total Hamiltonian can be expanded in terms of simple product functions:

$$\psi(r_i, r_j)_t = \psi_r^A(r_i)\psi_s^B(r_j) \tag{5}$$

where the index $t$ is a short notation for $rs$.

If overlap cannot be neglected, as in the case under consideration, where the distances between atoms of the two moieties can be less than 3 Å, the wave function must allow for exchange of electrons, so that the simple product function must be replaced by the antisymmetrized product of wave functions:

$$\Phi(r_i, r_j)_t = \mathcal{A}\,\psi_r^A(r_i)\psi_s^B(r_j) \tag{6}$$

where $\mathcal{A}$ is the antisymmetrizing operator.

The electronic energy of the H-bond complex can be obtained by starting from the Hamiltonian partition of eq 1, taking $\mathcal{H}_{AH} + \mathcal{H}_{BH}$ as the unperturbed Hamiltonian and using perturbation theory. However, in the case we are dealing with, the unperturbed wave function $\Phi_o$ is not an eigenfunction of $\mathcal{H}_0$; as shown by Yaris and Murrell and Shaw,[18,19] that situation can be handled by using Löwdin's reduced resolvent technique.[20]

The total wave function is written as the action of a wave operator $\mathcal{W}$ on $\Phi_o$:

$$\Phi = \mathcal{W}\Phi_o \tag{7}$$

By introducing the projection operator $\mathcal{O}$:

$$\mathcal{O} = \frac{|\Phi_o\rangle\langle\psi_o|}{\langle\Phi_o|\psi_o\rangle} \tag{8}$$

and its orthogonal complement, $\mathcal{P} = 1 - \mathcal{O}$, it can be shown[20] that

$$\mathcal{W} = 1 + \mathcal{T}\mathcal{H} \tag{9}$$

with

$$\mathcal{T} = \mathcal{P}[\alpha\mathcal{O} + \mathcal{P}(\mathcal{E} - \mathcal{H})\mathcal{P}]^{-1}\mathcal{P} \tag{10}$$

and $\alpha$ an arbitrary scalar chosen in such a way that $[\alpha\mathcal{O} + \mathcal{P}(\mathcal{E} - \mathcal{H})\mathcal{P}]^{-1}$ exists.

To obtain the energy expression, we multiply the Schrödinger equation $(\mathcal{H} - \mathcal{E})|\Phi\rangle = 0$ on the left by $\langle\psi_o|$ and integrate over all electron coordinates:

$$E = \frac{\langle\psi_o|\mathcal{H}|\Phi\rangle}{\langle\psi_o|\Phi_o\rangle} = E_o + \frac{\langle\psi_o|\mathcal{V}|\Phi\rangle}{\langle\psi_o|\Phi_o\rangle} \tag{11}$$

where, according to eqs 3 and 4, $E_o$ is the sum of the energies of the isolated, noninteracting A−H and B−H molecules:

$$E_o = E_o^A + E_o^B \tag{12}$$

Substituting expressions 7 and 9 in expression 11, the total energy of the H-bond complex takes the form:

$$E = E_o + \frac{\langle\psi_o|\mathcal{V}|\Phi_o\rangle}{\langle\psi_o|\Phi_o\rangle} + \frac{\langle\psi_o|\mathcal{V}\mathcal{T}\mathcal{H}|\Phi_o\rangle}{\langle\psi_o|\Phi_o\rangle} \tag{13}$$

The second term on the right-hand side of the above expression can be considered as the first order correction to the total energy.

The last term can be further written as the sum of different contributions by expanding the inverse operator $[\alpha\mathcal{O} + \mathcal{P}(\mathcal{E} - \mathcal{H})\mathcal{P}]^{-1}$ about the point $\epsilon - \mathcal{H}_o$, with $\epsilon$ being a complex quantity with the dimension of energy, $E_o + ix$, so that there will be no problem involving singularity of $\mathcal{T}$.[20]

By using only the first term of the expansion and taking the limit $\epsilon \to E_o$, the following contribution to the total energy is obtained:[19]

$$E^{(2)} = \sum_{t\neq 0} \frac{\langle\psi_o|\mathcal{V}|\psi_t\rangle}{(E_o - E_t)\,\langle\psi_o|\Phi_o\rangle^2} (\langle\psi_t|\mathcal{H}|\Phi_o\rangle\,\langle\psi_o|\Phi_o\rangle - \langle\psi_o|\mathcal{H}|\Phi_o\rangle\,\langle\psi_t|\Phi_o\rangle) \tag{14}$$

which can be considered as the equivalent of the second-order energy correction of the Rayleigh−Schrödinger perturbation theory.

Since the antisymmetrizing operator commutes with the Hamiltonian operator and $\psi_o$ is an eigenfunction of the unperturbed Hamiltonian, eq 14 can be rewritten in the form:

$$E^{(2)} = \sum_{t\neq 0} \frac{\langle\psi_o|\mathcal{V}|\psi_t\rangle}{(E_o - E_t)\,\langle\psi_o|\Phi_o\rangle^2} (\langle\Phi_t|\mathcal{V}|\psi_o\rangle\,\langle\psi_o|\Phi_o\rangle - \langle\Phi_o|\mathcal{V}|\psi_o\rangle\,\langle\psi_t|\Phi_o\rangle) \tag{15}$$

in which only the perturbation $\mathcal{V}$ is involved.

In conclusion, the energy expression up to the second order of perturbation theory is

$$E = E_o^A + E_o^B + \frac{\langle\psi_o|\mathcal{V}|\Phi_o\rangle}{\langle\psi_o|\Phi_o\rangle} + \sum_{t\neq 0} \frac{\langle\psi_o|\mathcal{V}|\psi_t\rangle}{(E_o - E_t)\,\langle\psi_o|\Phi_o\rangle^2} \times (\langle\Phi_t|\mathcal{V}|\psi_o\rangle\,\langle\psi_o|\Phi_o\rangle - \langle\Phi_o|\mathcal{V}|\psi_o\rangle\,\langle\psi_t|\Phi o\rangle) \tag{16}$$

Until now no approximations have been done, inasmuch no terms of the electronic Hamiltonian have been neglected; thus eq 16 is rigorous at the second order of the perturbation theory. Of course, eq 16 is valid only for nondegenerate case, as the ground state of a H-bond complex is expected to be.

Let us now turn to the physical problem we whish to tackle here, namely the modeling of the potential energy profiles for proton motion between the two equilibrium sites of a H-bond complex, by analyzing how the terms of eq 16 depend on the coordinates of the H-bonded proton. We will consider only the stretching coordinates $r$, the most important coordinates in the dynamics of proton transfer, even though generalization to a complete set of proton coordinates is in line of principle possible.

The unperturbed energy of eq 16 is simply given by the sum of the energy of the noninteracting A−H and B−H molecules and therefore its dependence on $r$ can be well represented by the sum of two Morse functions.

As concerns the first-order contribution to the total energy, we have already remarked that the perturbation operator $\mathcal{V}$ does not explicitly depend on the proton coordinates and therefore on $r$, since in its expression, cf. eq 2, only the nuclei of A and B but not H are involved. That is an important feature, because it means that the $r$ dependence of this term comes only from the wave function dependence on $r$. Therefore, in the crude adiabatic approximation, which certainly can be invoked for small amplitude of vibrations, that term is a constant and does not contribute at all to the potential energy for proton transfer.

The same also holds for the term at the numerator of the second order energy contribution. Here the situation is slightly more complicated for the presence of the factor $1/(E_o - E_t)$, which is itself, of course, a function of $r$. However, the majority of these terms will be small, because $E_o - E_t$ is large. Moreover, only those electronic excited states for which $E_t(r)$'s exhibit shapes different from that of $E_o(r)$ will significantly contribute, since in all other cases the $r$ dependence of $(E_o - E_t)$ tends to disappear on making the difference.

On the basis of the above considerations, we can tentatively neglect the first and second-order energy corrections, so that the potential energy for proton motion between the A and B equilibrium sites can be written:

$$E(r) = E_o^A(r) + E_o^B(r) \tag{17}$$

Thus we obtain the very simple result that the potential energy for the motion of the H-bonded proton is given by the sum of the A−H and B−H stretching potentials of the noninteracting partners. The latter ones can be well represented by two Morse functions:

$$E(r) = D_{AH}(1 - e^{-\alpha(r - r^\circ_A)})^2 + D_{BH}(1 - e^{\beta(r - R + r^\circ_B)})^2 \tag{18}$$

where $R$ denotes the A−B distance in the H-bond complex, a parameter, and $r^\circ_A$ and $r^\circ_B$ are the equilibrium bond distances of A−H and B−H, respectively.

According to the theoretical derivation above, the two Morse potential should be able to predict potential energy profiles for proton hopping in linear H-bond complexes, only from the knowledge of the potential energy of proton stretching of the two separated partners, on the condition that terms appearing in the expressions of the first and the second energy corrections give negligibly small contributions. To test if that condition is satisfied, we will compare the potential energy profiles obtained by eq 18 with those obtained by HF/MP2 computations. The results, discussed in the next section, show that the agreement is good, especially when the heavy atom distances are not too long, usually shorter than 3 Å, which represents the region of the potential energy surface of major interest for biochemical systems, where the heavy atoms are usually nitrogens and oxygens. Those results can be easily rationalized on the light of the energy expression given by the second-order perturbation theory: for longer heavy atom distances, the wave function dependence on the proton coordinates becomes significant, so that the first and the second-order energy corrections begin to contribute.

## Results

To test the potentialities and limitations of the proposed potential, we have compared potential energy profiles and vibrational states, a much stringent test, predicted by the two Morse potential with their counterparts obtained from potential energy profiles computed at the HF/MP2 level of the theory, for simple both symmetric and non symmetric A−H···B system, at different A−B distances (hereafter $R$).

All the ab initio computations have been performed by the Gaussian94 package,[21] using the standard 6-31g** basis set. Potential energy profiles have been computed optimizing all geometrical parameters, but $R$, at the MP2 level of the theory. For the computations of the vibrational frequencies, the HF/MP2 potential energy profiles have been fitted by fourth or eighth degree polynomials, for single or double minimum potentials. To our experience polynomial interpolation has revealed preferable to cubic spline, which requires very dense grids. Vibrational states have been computed by the variational method, using a basis of harmonic wave functions centered at the equilibrium points, in the case of single minimum potentials, and midway between the two heavy atoms for double well potentials. The completeness of the chosen basis has been verified in each case. Analytical solutions of the one-dimensional Schrödinger equation with the two Morse potential should also be possible by using the method recently developed by Skála et al.,[22] but for the lowest energy states the variational method yields results sufficiently accurate for our purposes.

**TABLE 1: Parameters for the X−H Bonds Considered in This Work, Determined from Dissociation Energies, Vibrational Frequencies, and Equilibrium Bond Lengths of Water, Ammonia, HF, and HI[44,45]**

| | $D$ (kcal/mol) | $\alpha$ (Å$^{-1}$) | $r^\circ$ (Å) |
|---|---|---|---|
| O−H | 119.0 | 2.26 | 0.96 |
| N−H | 110.0 | 2.23 | 1.01 |
| F−H | 146.7 | 2.18 | 0.92 |
| I−H | 70.6 | 1.76 | 1.61 |

**Symmetric Systems.** We have considered the following complexes: $H_5O_2^+$, $HF_2^-$, $H_3O_2^-$, and $N_2H_7^+$, which have been extensively studied in the past.[23−33] For the first three complexes, ab initio HF/MP2 computations predict single minimum nuclear configurations, with the proton lying midway between the two heavy atoms, whereas for $N_2H_7^+$ two shallow minima separated by a barrier of only 0.19 kcal/mol are predicted.

For symmetric H-bond complexes, the potential energy function of eq 18, hereafter $V(r)$, has three parameters, which have to be determined from properties of the separated moieties and of the H-bond complex. To keep things as simple as possible, we have started by fixing $D$'s, $\alpha$'s, and $r^\circ$'s from the dissociation energies, the stretching vibrational frequencies and the equilibrium bond distances of $H_2O$, HF, and $NH_3$. The adopted parameters are reported in Table 1.

We have used dissociation energies instead of protonation affinities, because the latter ones, when used in conjunction with vibrational frequencies to determine the $\alpha$'s, yield very low values, causing an unreasonable slow rise of the potential energy profiles in the region of short X−H distances, which significantly affect the energies of the vibrational states. Thus, considering that in symmetric systems the main role played by $D_{X-H}$ is that of determining the curvature of $V(r)$ around the equilibrium configuration, which indeed depends on the product $\alpha^2 D$, dissociation energies can be used if the $\alpha$ parameters are chosen consistently.

With the parameters of Table 1, we have obtained, at different $R$, the activation energies for proton hopping reported in Table 2 and summarized in Figures 1−4a as potential energy surfaces.[34]

The activation energies predicted by $V(r)$ are in good agreement with those predicted by HF/MP2 computations, especially at $R$ distances not too longer than those corresponding to the fully optimized HF/MP2 nuclear configurations. At $R$ values corresponding to the HF/MP2 minimun energy nuclear configurations, the two Morse potential predicts single minimum potential energy profiles for proton motion for all the four cases investigated, in agreement with HF/MP2, but for $N_2H_7^+$, for which the latter method predicts a double minimum potential but with a barrier of only 0.19 kcal/mol. At slightly longer $R$ distances, the agreement is still excellent, the activation energies predicted by the two methods differ for a few tenths of kcal/mol, the largest discrepancy being 1.0 kcal/mol for $N_2H_7^+$ at $R$ = 2.8 Å.

As the heavy atom distance increases, and with it the proton elongation for going from one equilibrium point to the other,

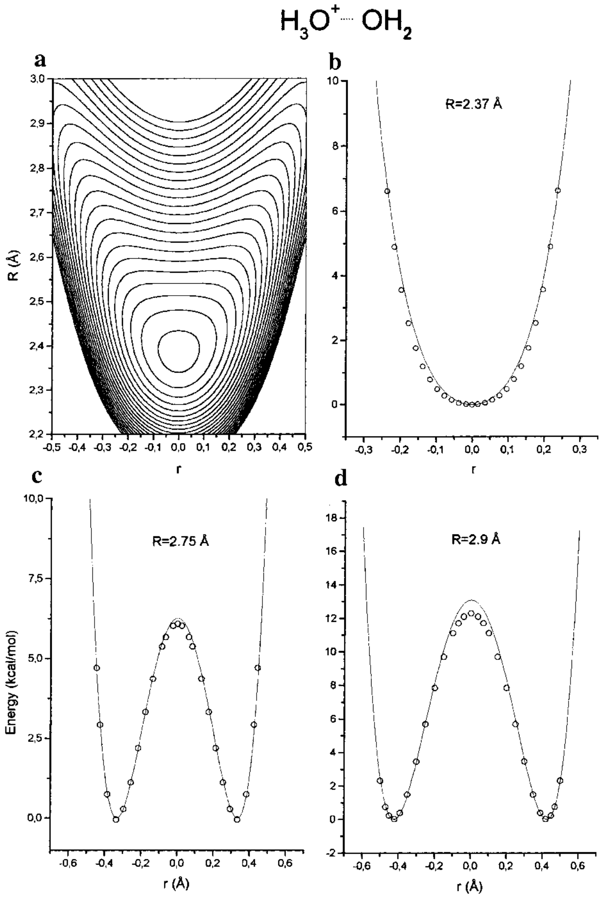

**Figure 1.** (a) Potential energy surface for $H_5O_2^+$ as a function of the H-bonded proton ($r$) and heavy atoms ($R$) stretching coordinates from parameters reported in Table 1. Contour line spacing is 2 kcal/mol. The energy dependence on R has been modeled by a $\sigma/R^{12}$ potential.[34] (b−d) Potential energy profiles for proton transfer at different heavy atom distances predicted by HF/MP2 computations, circles, and by $V(r,R)$, full lines, setting $r°$'s from the HF/MP2 optimized O−H bond lengths and using for the other parameters the values reported in Table 1.

**TABLE 2: Predicted Activation Energies (kcal/mol) for Proton Hopping at Different Values of the Heavy Atom Distance *R*, Using the Parameters of Table 1**

| | | $\Delta E^{\#}$ | |
|---|---|---|---|
| | $R$ (Å) | $V(r)$ | MP2 |
| $H_5O_2^+$ | 2.37 | | |
| | 2.60 | 1.5 | 1.7 |
| | 2.75 | 5.8 | 6.1 |
| | 2.90 | 13.91 | 12.3 |
| $H_3O_2^-$ | 2.45 | | |
| | 2.70 | 3.6 | 3.5 |
| | 2.90 | 13.91 | 10.7 |
| $HF_2^-$ | 2.28 | | |
| | 2.54 | 0.8 | 1.2 |
| | 2.75 | 10.2 | 7.9 |
| $N_2H_7^+$ | 2.59 | | 0.2 |
| | 2.80 | 2.9 | 3.9 |
| | 3.00 | 10.8 | 11.0 |

the wave function dependence on $r$ becomes appreciable and $V(r)$ moves away from its computed counterpart. The effects of the neglected terms begin to be significant for $R$ longer than 2.8 Å, but for our purposes this is not dramatic, because proton transfer usually occurs after $R$ as decreased to values at which tunneling becomes effective, so that only the region of the potential energy surface corresponding to relatively shorter $R$ is really important.

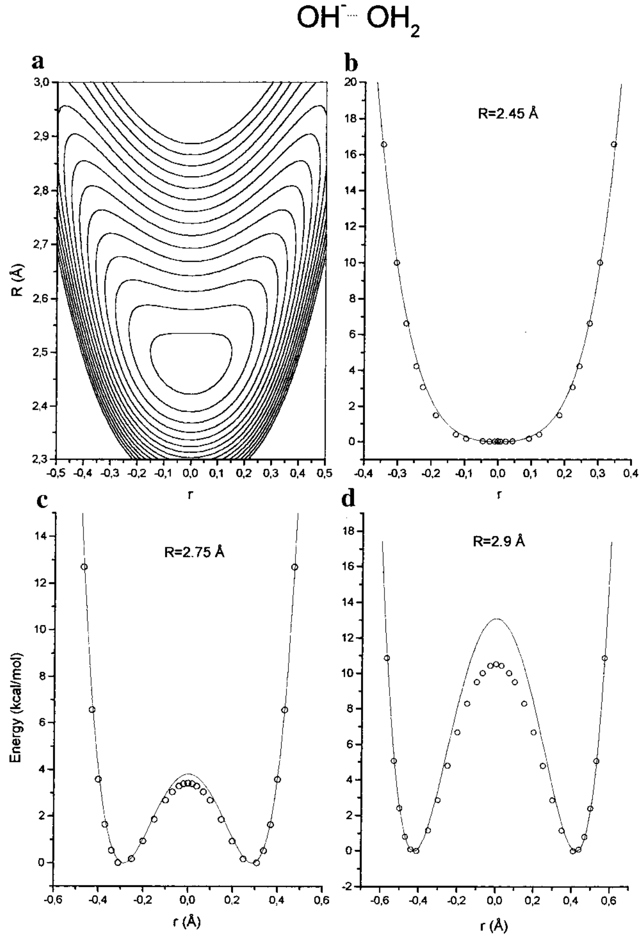

**Figure 2.** (a) Potential energy surface for $H_3O_2^-$ as a function of the H-bonded proton ($r$) and heavy atoms ($R$) stretching coordinates from parameters reported in Table 1. Contour line spacing is 2 kcal/mol. The energy dependence on R has been modeled by a $\sigma/R^{12}$ potential.[34] (b−d) Potential energy profiles for proton transfer at different heavy atom distances predicted by HF/MP2 computations, circles, and by $V(r,R)$, full lines, setting $r°$'s from the HF/MP2 optimized O−H bond lengths and using for the other parameters the values reported in Table 1.

On the contrary, with the parameters of Table 1, $V(r)$ yields vibrational states whose energies are significantly different from those obtained by using the potential energy profiles computed at HF/MP2 level of theory. For instance, for $H_5O_2^+$ the energy of the lowest three vibrational states are overestimated by ca. 300, 800, and 1100 $cm^{-1}$, a difference which can significantly affect the predicted rates for proton transfer. That discrepancy can be due to the fact that until now we have used a set of parameters which refer to a generic X−H bond and not to the specific one in the A−H molecule. For instance, for the cationic $H_5O_2^+$ and $N_2H_7^+$ complexes we have used parameters determined from properties of $H_2O$ and $NH_3$, rather than of $H_3O^+$ and $NH_4^+$, as the theoretical basis of the two Morse potential would suggest. Since the adoption of a different set of parameters for each molecule is not very convenient, a way out is that of fixing some of the parameters from properties of the H-bond complex, rather than of the isolated partners. Among the three parameters appearing in $V(r)$, the most suitable for being fixed from properties of the complex is certainly $r°$, because the equilibrium A−H and B−H bond distances in A−H···B are often experimentally known and, at any rate, the easiest to be computed.

In the cases of two minima separated by a potential energy barrier, $r°$'s can be easily set from the computed X−H

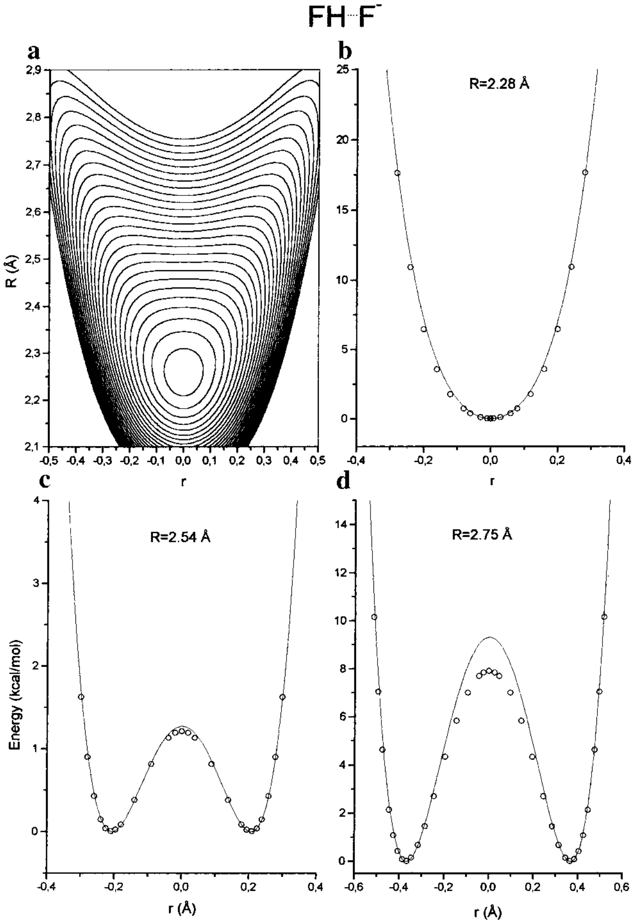

**Figure 3.** (a) Potential energy surface for $HF_2^-$ as a function of the H-bonded proton ($r$) and heavy atoms ($R$) stretching coordinates from parameters reported in Table 1. Contour line spacing is 2 kcal/mol. The energy dependence on R has been modeled by a $\sigma/R^{12}$ potential.[34] (b−d) Potential energy profiles for proton transfer at different heavy atom distances predicted by HF/MP2 computations, circles, and by $V(r,R)$, full lines, setting $r°$'s from the HF/MP2 optimized O−H bond lengths and using for the other parameters the values reported in Table 1.

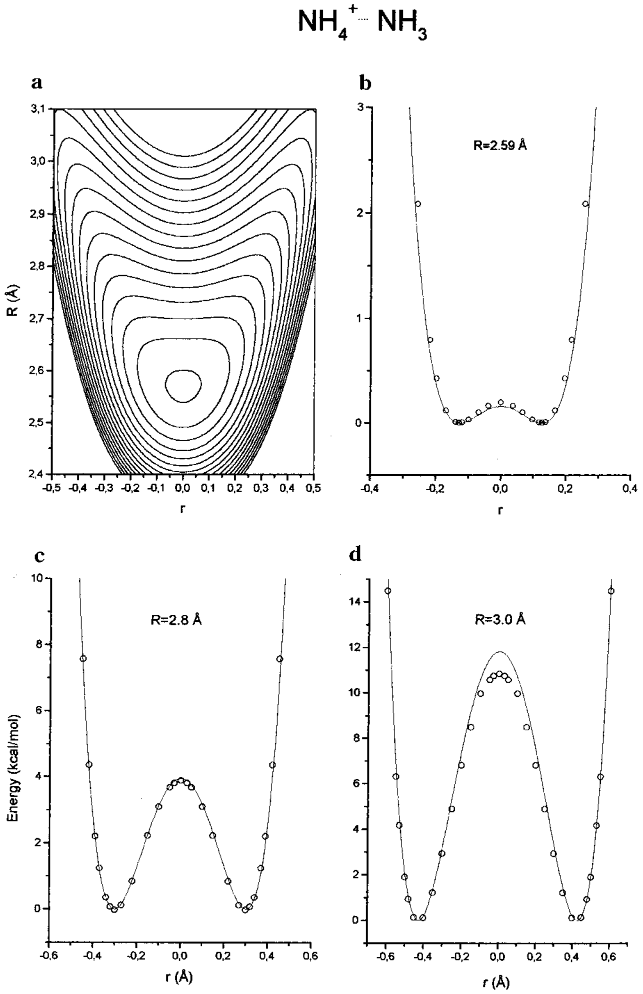

**Figure 4.** (a) Potential energy surface for $N_2H_7^+$ as a function of the H-bonded proton ($r$) and heavy atoms ($R$) stretching coordinates from parameters reported in Table 1. Contour line spacing is 2 kcal/mol. The energy dependence on R has been modeled by a $\sigma/R^{12}$ potential.[34] (b−d) Potential energy profiles for proton transfer at different heavy atom distances predicted by HF/MP2 computations, circles, and by $V(r,R)$, full lines, setting $r°$'s from the HF/MP2 optimized O−H bond lengths and using for the other parameters the values reported in Table 1.

equilibrium distances, whereas for single minimum potential we have resorted to the curvatures at the equilibrium points computed at HF/MP2 level of theory. The results obtained by fixing $r°$'s from the equilibrium position of the H-bonded protons, leaving the other two parameters unchanged, are reported in Table 3.

The agreement is more than satisfactory, even for the lowest lying vibrational states. The activation energies predicted by V($r$) are slightly better than those obtained by fixing all the parameters from properties of the isolated partners, whereas the shapes of the potential energy profiles predicted by the two methods are now very similar each other, as testified both by the data in Figures 1−4 (b−d) and by the energies of the vibrational states reported in Table 3. The largest difference between the vibrational energies predicted by $V(r)$ and by HF/MP2 computations is now *ca.* 150 $cm^{-1}$. Moreover, for $N_2H_7^+$ at $R = 2.595$ Å, that obtained by HF/MP2 full geometry optimization, we also obtain a double minimum potential for proton hopping with a barrier between the two minima of 0.15 kcal/mol, cf. Figure 4b.

The energy splitting between the symmetric and the antisymmetric combinations of the two localized vibrational states, which are physically the most interesting quantity, being related to transition times, are also well predicted. At $R = 2.75$ Å, V($r$) yields an energy difference of 72.6 $cm^{-1}$, versus 77.6 obtained by HF/MP2; at $R = 2.9$ Å, the computed energy differences are 1.8 and 2.3 $cm^{-1}$, respectively.

The same level of accuracy has been obtained also for the other complexes; all results are reported in table 3 and Figures 2−4.

**Asymmetric Systems.** In the case of asymmetric H-bond complexes, the choice of the parameters becomes more involved, because the $D_{X-H}$'s play now a role in determining the energy differences between the two possible equilibrium sites. Thus, whishing to set parameters from properties of the separated partners, the use of protonation affinities become necessary in order to obtain the right energy difference between the two possible equilibrium configurations A−H···B and A···H−B. The other possibility is that of fixing the parameters from properties of the H-bond complex. Usually, the data available from experiments or computations are, in the case of double well potentials, the two equilibrium distances, $r_{AH}$ and $r_{BH}$ and the energy difference between the two equilibrium proton sites. Thus, a practical choice is that of fixing $r°$'s from the known equilibrium distances and of changing the X−H dissociation energies of the separated partners by an equal but opposite

**TABLE 3: Adopted Parameters and Predicted Activation Energies (kcal/mol) and Vibrational Levels (cm$^{-1}$) for the Four Symmetrical Systems of Figures 1−4**

| | | | $\Delta E^{\#}$ | | $n = 0$ | | $n = 1$ | | $n = 2$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R$ (Å) | $r°$ | $V(r)$ | MP2 | $V(r)$ | MP2 | $V(r)$ | MP2 | $V(r)$ | MP2 |
| $H_5O_2^+$ | 2.37 | 0.920 | | | 740 | 689 | 2407 | 2331 | 4389 | 4386 |
| | 2.60 | 0.940 | 1.53 | 1.77 | 567 | 518 | 1112 | 1080 | 2372 | 2305 |
| | 2.75 | 0.950 | 6.26 | 6.13 | 1064 | 1073 | 1137 | 1150 | 2536 | 2530 |
| | 2.90 | 0.965 | 13.09 | 12.27 | 1341 | 1321 | 1343 | 1323 | 3610 | 3500 |
| $H_3O_2^-$ | 2.70 | 0.956 | 3.81 | 3.50 | 833 | 796 | 1062 | 1042 | 2257 | 2195 |
| | 2.90 | 0.965 | 13.09 | 10.65 | 1339 | 1239 | 1340 | 1243 | 3608 | 3196 |
| $HF_2^-$ | 2.28 | 0.890 | | | 964 | 903 | 3043 | 2908 | 5387 | 5254 |
| | 2.54 | 0.906 | 1.27 | 1.21 | 488 | 480 | 1127 | 1126 | 2407 | 2409 |
| | 2.75 | 0.923 | 9.32 | 7.91 | 1249 | 1176 | 1267 | 1203 | 3096 | 2804 |
| $N_2H_7^+$ | 2.59 | 0.969 | 0.15 | 0.19 | 366 | 371 | 1307 | 1392 | 2708 | 2917 |
| | 2.80 | 0.995 | 3.94 | 3.91 | 831 | 833 | 1022 | 1031 | 2177 | 2190 |
| | 3.00 | 1.011 | 11.83 | 10.96 | 1263 | 1224 | 1266 | 1228 | 3362 | 3213 |

**TABLE 4: Adopted Parameters and Predicted Energy Differences and Activation Energies for the Three Asymmetrical Systems Discussed in the Text[a]**

| | | | | | | | $\Delta E$ | | $\Delta E^{\#}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| A−H···B | R | Δ | $\alpha_{AH}$ | $\alpha_{BH}$ | $r°_{AH}$ | $r°_{BH}$ | $V(r)$ | MP2 | $V(r)$ | MP2 |
| $NH_4^+\cdots H_2O$ | 3.0 | 30.0 | 1.98 | 2.61 | 1.02 | 0.98 | *b* | 25.0 | 3.51 | 3.35 |
| | 3.2 | | | | | | 32.6 | 28.2 | 11.8 | 10.6 |
| | 2.9 | | | | | | 20.7 | 22.8 | 0.80 | 0.86 |
| | ≤2.8 | | | | | | *c* | *c* | *c* | *c* |
| | 3.2 | 27.0 | 2.00 | 2.57 | | | *b* | 28.2 | 13.0 | 10.6 |
| | 2.9 | 31.5 | 1.97 | 2.63 | | | *b* | 22.8 | 1.1 | 0.86 |
| | 3.2 | 21.3 | 2.23 | 2.26 | | | *b* | 28.2 | 13.4 | 10.6 |
| | 3.0 | | | | | | 24.7 | 25.0 | 3.61 | 3.35 |
| | 2.9 | | | | | | 21.8 | 22.8 | 0.35 | 0.86 |
| $NH_3\cdots HI$ | 3.57 | 28.0 | 2.23 | 1.76 | 0.99 | 1.60 | *b* | 3.0 | 4.2 | 3.5 |
| | 3.37 | | | | | | 0 | ∼0 | 0.6 | 1 |
| | 3.30 | | | | | | *c* | *c* | | |
| $F^-\cdots H_2O$ | 2.80 | 17.3 | 2.18 | 2.26 | 0.93 | 0.95 | *b* | 6.9 | 13.8 | 12.1 |
| | 2.38 | | | | | | *c* | *c* | | |
| | 3.0 | | | | | | 8.2 | 8.3 | 27.5 | 22.5 |
| | 3.0 | 17.8 | 2.18 | 2.26 | 0.94 | 0.97 | *b* | 8.3 | 26.2 | 22.5 |
| | 2.8 | 25.5 | 2.40 | 2.05 | 0.93 | 0.96 | *b* | 6.9 | 13.3 | 12.1 |
| | 3.0 | 23.6 | 2.38 | 2.07 | 0.94 | 0.97 | *b* | 8.3 | 26.4 | 22.5 |

[a] All energies are in kcal/mol, distances in Å, α in Å$^{-1}$. [b]Imposed from MP2 computations. [c] Single minimum potential.

amount Δ, to be determined from the energy difference between the two equilibrium site. The α values can be either kept frozen to the values reported in Table 1, since the curvatures around the minima can be adjusted by a suitable choice of the $r°$'s, or slightly changed consistently with the changes made on the dissociation energies.

We have considered the following three asymmetric systems: $NH_4^+\cdots H_2O$, $NH_3\cdots H{-}I$, and $F\cdots H_2O$, which have already been investigated at HF/MP2 level.[35−37]

For $NH_4^+\cdots H_2O$, MP2 computations predict a stable minimum for the proton bound to the nitrogen atom and a shallow one for $NH_3\cdots H_3O^+$, at $R = 2.9$ Å, which disappears at shorter $R$.[35] The energy difference between the two minima at $R = 3.0$ Å is 24.98 kcal/mol at MP2 level of the theory, with $r°_{N-H} = 1.05$ and $r°_{O-H} = 1.06$ Å. By fixing $r°$'s and Δ from the MP2 X−H distances and energy difference of the two equilibrium points and setting α's from the same force constants used for obtaining the values in Table 1, $V(r)$ yields a barrier to proton hopping of 3.5 kcal/mol, starting from the less stable minimum, to be compared with 3.35 obtained at HF/MP2 level.[21]

Keeping the same parameters, V($r$) yields (i) at $R \leq 2.8$ Å a single minimum profile, in accordance with HF/MP2; (ii) at $R = 2.9$ a barrier of 0.80 kcal/mol and an energy difference between the two minima of 20.7 kcal/mol, versus 0.86 and 22.8 predicted by HF/MP2; (iii) at $R = 3.2$ an energy difference of 32.6, (28.2 MP2) and a barrier of 11.8 (10.6) kcal/mol.

The changes of the equilibrium X−H bond lengths as $R$ changes are also well predicted. At $R = 2.9$, $V(r)$ predicts 1.11 and 1.07 Å for O−H and N−H, respectively, versus 1.095 and 1.05 predicted by HF/MP2, whereas at $R = 3.2$ the N−H bond distance is 1.04 for both methods and the O−H one is 1.04 from the analytical potential versus 1.034 predicted by HF/MP2 computations.

Very similar results are obtained both by leaving the α unchanged and by imposing for each value of $R$ the computed MP2 energy difference. All the results are summarized in Table 4, together with the parameters used in each case.

For $NH_3\cdots H{-}I$, we have used the α values reported in Table 1 and changed the dissociation energies of ±28 kcal/mol in order to have the same energy difference between minima as in MP2 computations, ca. 3 kcal/mol in favor of the neutral form.[36] At $R = 3.574$ Å, $V(r)$ yields a double well profile, with the two minima separated by a barrier of 4.2 kcal/mol, slightly higher than 3.5 predicted by MP2. Keeping fixed these parameters, $V(r)$ yields at $R = 3.37$ a double minimum potential with the two equilibrium nuclear configurations at about the same energy and at $R = 3.3$ Å a single minimum potential, in both cases in good agreement with MP2 computations.

Finally we have considered the $F^-\cdots H_2O$ complex, for which HF/MP2 full optimization yields a single minimum potential, with $R = 2.38$ Å and $r_{O-H} = 1.11$ Å. At $R = 2.8$ Å HF/MP2 computations predicts a double well potential with the two minima located at $r_{O-H} = 1.03$ Å and $r_{F-H} = 1.02$ Å and an energy difference of 6.9 kcal/mol in favor of the $F^-\cdots H_2O$ form.

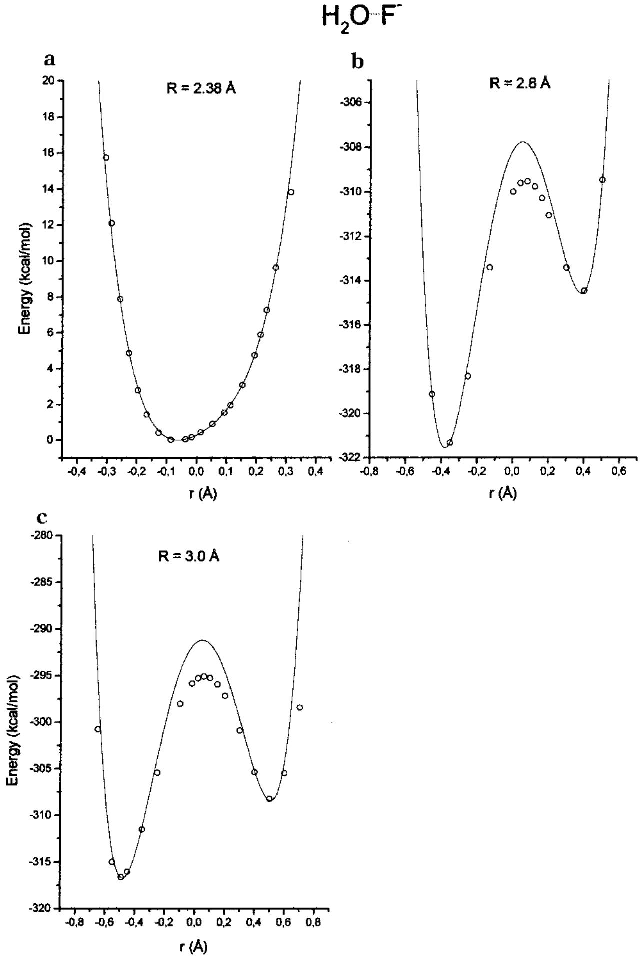

**Figure 5.** Potential energy profiles for proton motion in the $H_2O{\cdots}F^-$ complex predicted by HF/MP2 computations, circles, and $V(r,R)$, full lines.

From these values we have set the two $r^\circ$ and the $\Delta$ parameters, cf. Table 4, with which, keeping the $\alpha$ values of Table 1, $V(r)$ yields a barrier to proton hopping of ca. 13.8 kcal/mol, 1.7 kcal/mol higher than that predicted by HF/MP2 computations. Keeping fixed all parameters, $V(R)$ yields a single minimum potential energy profile at $R = 2.38$, in agreement with HF/MP2, and at $R = 3.0$ Å a double well potential characterized by an energy difference between the two minima of 8.2 kcal/mol, 8.3 from HF/MP2, and a barrier of 27.5 kcal/mol, 22.5 from HF/MP2, cf. Table 4.

A better agreement can be obtained if the $\Delta$ and the $r^\circ$'s parameters are allowed to change as R changes: the results for $H_2O{\cdots}F^-$ are shown in Figure 5, see also Table 4, which testifies that not only the energy of the stationary points but also the shape of the potential energy profiles for proton motion are well predicted by the two Morse potential.

## Discussion and Conclusions

The numerical tests discussed previously suggest that the approximations on which the two Morse potential holds are justified, at least in the region of the potential energy surfaces (PES) of relatively short heavy atom distances. Thus the first conclusion which can be drawn is that, among all terms which contribute to determine the potential energy profile for proton motion between the two equilibrium sites of a H-bond complex, the additive contribution of the A−H and B−H stretching potentials of the separated partners plays a prominent role. That result has important implications, not only for it offers a powerful interpretative key for understanding the properties of H-bond complexes, but also for it allows to build up potential energy profiles for proton hopping from the knowledge of a few properties of the complex and of the separated partners. Thus the two Morse potential must be considered as a well sound theoretical model for representing proton-transfer reactions between H-bonded molecules rather than a fitable potential for interpolating ab initio results.

Of course, as any theoretical model, it is based on approximations, which pose limits to its applicability. One of the major limitation of the two Morse potential is in treating H-bonds with relatively large heavy atom distances. The results reported in Tables 3 and 4 indicate that barriers to proton hopping are always overestimated with respects to HF/MP2 counterparts as R increases. This is very probably due to the fact that variations of the wave function become appreciable for proton displacement from the equilibrium position longer than 0.4 Å, so that if the activated state is located at longer distance, the contribution of the first- and second-order corrections can no longer be neglected. That effect is not dramatic, because it is known that proton transfer reactions usually take place after $R$ has decreased to values short enough for tunneling occurs. Thus, to study the dynamics of proton transfer it is sufficient to have an accurate representation of the potential energy surface (PES) in the region of relatively short $R$, in which the approximations done appear to be justified. In the previous section we have shown that accurate PES can be constructed at the cost of only two reliable ab initio computations, one for each proton position, for a few values of the $R$ around the region in which proton tunneling is possible.

Another limitation is in treating systems characterized by single minimum potentials with an accuracy high enough to obtain reliable energies for the low lying vibrational states. In that case problems are simply due to the fact that parametrization become more difficult, because of the limited number of information, so that one has to resort to properties, such as the curvature around the equilibrium point, which cannot be easily obtained from ab initio computations for large systems.

Finally, it must be remarked that the partition of the electronic Hamiltonian employed here does not hold for hydrogen atom transfer and therefore the two Morse potential is not applicable to these cases.

Among all other advantages which emerge by themselves, we remark the easiness of the parametrization, a very important point for our purposes, the estimate of potential energy barriers for proton transfer in complex systems, for which only a limited number of experimental or theoretical data are usually available, and the fact that the two Morse potential offers the possibility of having analytical expressions of the potential energy profiles for proton hoppings, which represents a great advantage for dynamical computations.

About 50 years ago, Lippincott and Schroeder have suggested, to our knowledge without any theoretical justification, a potential energy function for treating the vibrational spectra of linear H-bonds which was based on the sum of two Morse type functions, somewhat different from the usual ones, for the A−H and B−H stretching vibrations plus terms for modeling the interaction between the two heavy atoms.[38,39] Both the A−H equilibrium distances and the frequency shifts of several A−H···B complexes in crystals were well predicted. The theoretical treatment described above allows for understanding why Lippincott and Schroeder treatment of small proton oscillations in H-bonded systems worked so well: for small amplitude of vibration the wave function dependence on the proton coordinates can be safely neglected, so that the only term which contributes to the potential energy is the unperturbed one, which is well modeled by the function used by Lippincott and Schroeder. Of course, all the results of Lippincott and Schroeder are further evidence that for small oscillations around the equilibrium points the first and the second order corrections to the total energy, cf. eq 16, can be neglected.

The two Morse potential is fundamentally different from the empirical valence bond (EVB) model proposed by Warshel,[40,41] which has been used by Miller and co-workers[42] and by Sagnella et al.[43] for H-bonded systems. The EVB model is a general way of representing analytically the PES for a reactive system. It is based on the two state model, namely, on the assumption that the wave function of the system can be written in the whole region of nuclear coordinates as a linear combination of two valence bond wave functions, one for the reactants the other for the products. In the EVB model, the coupling between these two reference states, as well as its dependence on the reactive coordinates, plays a fundamental role, but its form is not known a priori and must be obtained by fitting the computed energies around the transition state. On the contrary, the two Morse potential is not so general, resulting from a partition of total Hamiltonian operator which applies only to proton transfer, but it allows the estimates of energy barriers for proton hopping without any information on the activated state. It is therefore particularly suitable for experimentalists and in all those cases where the size of the system under consideration makes the evaluation of the whole potential energy surfaces for proton hopping computationally too demanding. We have already used the two Morse potential for representing proton motions driven by electron transfer in photosynthetic reaction center,[14] so the interested reader can find there an example of application to large systems.

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