Relevance of hydrogen bond definitions in liquid water

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To evaluate the relevance of treating the hydrogen bonds in liquid water as a digital (discrete) network and applying topological analyses, a framework to optimize the fitting parameters in various hydrogen bond definitions of liquid water is proposed. Performance of the definitions is quantitatively evaluated according to the reproducibility of hydrogen bonding in the inherent structure. Parameters of five popular hydrogen bond definitions are optimized, for example. The optimal choice of parameters for the hydrogen bond definitions accentuates the binary nature of the hydrogen bonding and the intrinsic network topology of liquid water, especially at the low temperature region. The framework provides a solid basis for network analyses, which have been utilized for water, and is also useful for designing new hydrogen bond definitions. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2431168]

INTRODUCTION

Water has dozens of anomalous properties. In condensed phases, water molecules are bound to each other by hydrogen bonds to form a three-dimensional network structure. Many anomalous properties of water are explained by, or at least related to, this network-formative character of the water molecule.[1] Although hydrogen bonding is not amenable to direct experimental measurement, the hydrogen bond network is certainly the core property of water.

The most important aspect of the hydrogen bond network of water is the tetrahedral local order (TLO) and the ice rule. Both of these short-ranged orders are satisfied in all the crystal ice structures, and also held in part even in liquid water and amorphous ice. The structural difference between these phases resides not in the local order but in the network connectivity. Topological analysis is therefore a powerful tool to understand the structure and dynamics of aqueous systems.[2–4]

Many hydrogen bond definitions are proposed and utilized for network analysis in the previous simulation studies. In most cases, however, their criteria are chosen arbitrarily to reproduce some aspect of the network and their basis is not clear.[2–15]

Two criteria are often used for determining the hydrogen bonds, i.e., by energy and by geometry. With energetic criteria, a pair of water molecules is defined as hydrogen bonded when the interaction energy is less than the threshold value.[3–7] With geometric criteria, on the other hand, the hydrogen bond is determined by the relative configuration of two water molecules.[8–11] A pair of water molecules is defined as hydrogen bonded when the intermolecular oxygen-oxygen or oxygen-hydrogen distance is less than the threshold value, and limitation to the angle between intermolecular O–O vector and covalent O–H vector (H–O–O angle) is often used concomitantly.[12] Hybrid criteria by both energy and geometry are also utilized.[13–15]

Different criteria may give the different network topologies for the same structure. Nevertheless, network analysis should be robust for the choice of the criteria.[7] Meanwhile, immoderately biased criteria will certainly give a wrong perspective to the network connectivity.[3] There should be a solid basis in determining the hydrogen bonding and evaluating its relevance.

INHERENT STRUCTURE

The concept of hydrogen bonding regards the intermolecular electrostatic interaction between two water molecules as a discrete bond and treats the molecular configuration as a network (graph). Is it correct in reality? Or is it only an artificial operation to help understand the adjacency, such as setting a distance threshold to count the number of adjacent molecules in simple liquid? If the latter is correct, the network topology depends upon human decision and the network analysis becomes only an analogy. Many experimental results support, however, the former. Femtosecond two-dimensional IR spectroscopy shows that hydrogen bonds in liquid water are broken only fleetingly.[16] It means that the hydrogen bond rearrangement is performed quickly and the network connectivity is well defined for most of the time. Another example is in the polymorphism of ice. When a crystal is compressed with very high pressure, coordination number increases in general. In case of ice, on the other hand, all the structures of ice polymorphs obey the ice rule. Four-coordinated network is conserved in all ice phases. These findings indicate that the discrete nature of hydrogen bonds, i.e., network-formative nature, is intrinsic to water. Then there must be an adequate way to define the hydrogen bond uniquely so as to reproduce the intrinsic network topology.

In ice, hydrogen bonds flicker because of the thermal fluctuation, but the inherent crystalline order is still conserved. If thermal fluctuation is eliminated, flickering is sup-
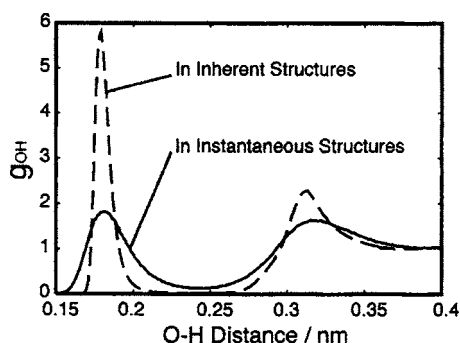
FIG. 1. Radial distribution functions. Radial distribution functions of inter-molecular oxygen-hydrogen pair are plotted. The solid and dashed lines represent the instantaneous and inherent structures, respectively. TIP4P water model is used and the temperature is 253 K (i.e., TMD). In the inherent structure, the distribution between first and second peaks almost touches the abscissa.
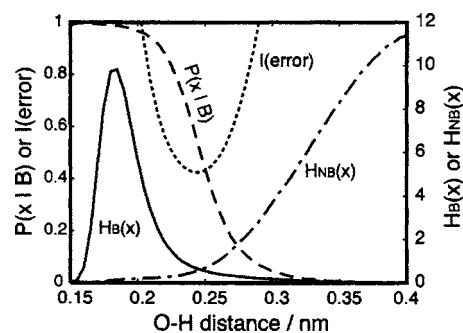

FIG. 2. Optimal decision boundary. Probabilities and error magnitude are plotted against intermolecular oxygen-hydrogen distance r_{OH}. The solid, dot-dashed, dashed, and dotted lines correspond to $H_B(x)$, $H_{NB}(x)$, hydrogen bond probability $P(B|x)$, and the error magnitude $I(error)$, respectively. $H_B(x)$ and $H_{NB}(x)$ use the right ordinate. TIP4P water model is used and the temperature is 253 K (i.e., TMD). The error magnitude becomes minimum at the optimal decision boundary, $r_{OH}=0.25$ nm, where $H_B(x)$ and $H_{NB}(x)$ cross and $P(B|x)=0.5$.

pressed and the inherent structure is recovered. Similarly, hydrogen bond rearrangement in liquid water is also regarded as a reflection of inherent structure on which thermal fluctuation is applied.[17,18] By eliminating the thermal fluctuation, the backbone network structure becomes apparent.[2,4]

We choose the network topology of the inherent structure, to eliminate the effect of the thermal fluctuation, as a reference, and apply the method of informatics. Network topology of an instantaneous structure can be regarded as that of the inherent structure on which thermal noise is added. In Fig. 1, intermolecular oxygen-hydrogen radial distribution functions (RDFs) of the instantaneous and inherent structures of liquid water at the temperature of maximum density (TMD) are plotted. It is evident from the figure that the first and second peaks of the RDF in the inherent structure are isolated by the deep well, where the first peak corresponds to hydrogen bonding. Hydrogen bond is thus well discretized, i.e., there is no ambiguity in deciding the hydrogen bonding, in the quenched structure. We therefore simply decide that a pair of water molecules is hydrogen bonded if the intermolecular oxygen-hydrogen distance is shorter than 0.25 nm in the inherent structure. A pair of water molecules in an instantaneous structure is defined to be in "B" state if one of the four intermolecular oxygen-hydrogen combinations resides in the first peak of the RDF when the structure is quenched. Otherwise, the pair is in "NB" state.

The problem now comes to the estimation of the connectivity of a hydrogen bond, which is discretized in the inherent structure, by means of the instantaneous relative configuration of a pair of water molecules. This is a typical decision problem in pattern classification. We introduce the Bayesian decision theory to determine the optimal estimates. Only the outline is shown here and the details are described in the Appendix.

Suppose a definition of hydrogen bonding is given. With the definition, a pair of water molecules is decided as hydrogen bonded if they satisfy the given criteria. Such a set of conditions for decision is called "classifier." This decision does not always coincide with the bond state in the inherent structure, which we choose as the reference. This disagreement is an error in estimation. The probability of errors, say $P(error)$, can be statistically determined by comparing the

bond state in the inherent structure and the bond state decided by the classifier. The latter depends upon the given criteria, therefore the error probability is a function of criteria. When a classifier is given, we can optimize the criteria for the classifier in order to minimize the error probability.

In actual calculation, when a pair of water molecules is chosen randomly from the system, they are not hydrogen bonded in both instantaneous and inherent structures in most cases unless they are close to each other. That is $P(error)$ is almost zero. We therefore introduce the error magnitude. $I(error)$, instead.

$$I(error) = (N-1)P(error). \tag{1}$$

$I(error)$ denotes the uncertainty of the number of hydrogen bonds per molecule.

Let us define the classifier to decide the hydrogen bond state, i.e., B or NB, by setting a threshold value for the intermolecular O–H distance. This classifier decides the hydrogen bond state to be B if the intermolecular O–H distance x between a pair of water molecules is shorter than a given criterion. Bayesian decision theory simply tells us that the optimal criterion to make the error probability (and error magnitude) minimum is positioned at x, where $H_B(x)$ is equal to $H_{NB}(x)$, where $H_B(x)$ and $H_{NB}(x)$ denote the number of pairs per molecule in B and NB states whose O–H distance is x, respectively.[19] It is called Bayesian optimal decision boundary. Error magnitude can also be used as a measure for evaluating different hydrogen bond (HB) definitions.

These functions for liquid water at TMD are plotted against intermolecular O–H distance r_{OH} in Fig. 2. The optimal decision boundary is 0.25 nm in this case, where $H_B(x)$ is equal to $H_{NB}(x)$ and $I(error)$ becomes minimum. The hydrogen bond probability, $P(B|x)$, has a sigmoidal shape; it changes rapidly around the optimal decision boundary. The binary nature of hydrogen bond in the inherent structure is thus well reflected in the instantaneous structure. Water is suitable for network analysis.[2,4]

One can design a new classifier to decide the hydrogen bonding. The optimal decision boundary (i.e., threshold

value) is automatically determined at the value where $H_B(x)$ and $H_{NB}(x)$ balance. The performance of the classifier is measured by the error magnitude $I(\text{error})$.

METHOD

SIMULATION METHOD

Let us apply this framework to find the optimal fitting parameters for various classifiers (i.e., hydrogen bond definitions) and compare their performances based on the error magnitude. Isobaric replica exchange molecular dynamics simulations are performed for four water models, TIP4P, TIP4P/2005, SPC/E, and NvdE,[6,20–22] at nine different temperatures between TMD and 40 K below TMD. In the present work, TMD is chosen as the standard in order to compare different water models at the same condition. TMD values for each water model are 253, 278, 241, and 287 K, respectively.[20,22,23] Replica exchange method is useful to avoid structural trapping at low temperature.[24] Pressure is set constant at 1 atm. 512 water molecules are put in a cubic simulation cell with periodic boundary condition. Temperature and pressure are kept constant with Nose-Poincare-Andersen thermobarostat.[25] Interaction is truncated smoothly between 0.95 and 1 nm with a switching function. All the simulations are executed in at least 1 ns. No crystallization is observed during our calculation even at the temperatures below the melting point. At the lowest temperature in the present simulations (i.e., 40 K below TMD), the system is in a low density amorphous structure where HBs and TLO are apparent.[26]

Note that evaluation of each water model itself is beyond the scope of the present work. A different water model may give a different network topology, but the validity of the model cannot be evaluated by the reproducibility of the network topology only.

CLASSIFIERS

Five typical classifiers are prepared. Each classifier decides the hydrogen bond by one or two criteria (geometric or energetic ones). Classifier 1 decides the hydrogen bond by energetic criteria, i.e., it decides as hydrogen bonded when the pair interaction between two water molecules is below the threshold value.[3–7] Classifiers 2 and 3 are hybrid ones; the former decides by the pair interaction and O–O distance[13] and the latter decides by both the pair interaction and H–O–O angle.[14] Classifiers 4 and 5 are geometric ones. Classifier 4 decides by intermolecular oxygen-hydrogen distance only.[11] Classifier 5 decides as hydrogen bonded when distance is shorter than threshold and cosine of H–O–O angle is larger than threshold.[12]

Another classifier, 6, is also prepared to evaluate the performance of five classifiers. This classifier determines the hydrogen bonding directly by Bayesian optimal decision boundary on the two-dimensional parametric space by hydrogen bond O–H distance and H–O–O angle instead of setting threshold values for each parameter. It is expected to give the best performance among the prepared classifiers.

RESULTS AND DISCUSSIONS

Performance of the six classifiers is listed in Table I. Only the results at the highest (TMD) and the lowest (40 K below TMD) temperatures are listed for each water model, which correspond to normal and supercooled liquid water, respectively. The optimal threshold values for each classifier, shown in the table, are close to those in the literature.[4,11–14] It is found that the values in the literature are not quite optimal but adequate, at least below TMD. The optimal threshold values are slightly different for different water models. On the other hand, the difference in performance between the classifiers is large. A bad classifier always gives a bad estimate for all temperatures and all water models. Geometric criteria (classifiers 4–6) are of better performance than the energetic criteria (classifiers 1–3). A difference of error magnitude between classifiers 4 and 5 is very small, though information by H–O–O angle is added to the latter. Difference of error between classifiers 5 and 6 is larger than that between classifiers 4 and 5. This tendency indicates that the additional criteria by H–O–O angle improves the performance only a little. The most affordable classifier is classifier 4, deciding the hydrogen bond by O–H distance only. It is not the best, but is one of the simplest criteria. The error by classifier 4 is increased by only 6% in average from the best estimate (classifier 6) for all the water models. Optimal threshold for classifier 4 is about 0.25 nm for all water models.

At much higher temperature than TMD, error magnitude will become unacceptably large. It then becomes difficult to estimate the HB state in the inherent structure from the instantaneous one. Even if another better decision rule is introduced, the performance will not be improved because the thermal fluctuation becomes very large and the trajectory does not go over the topography of the potential energy landscape faithfully. Network analysis is neither very appropriate nor reliable in such conditions.

Time series of a hydrogen bond along the molecular dynamics trajectory are exemplified in Fig. 3. The results decided by both classifier and result from the inherent structure are indicated. Fitting parameters used for each classifier are the optimal ones in Table I. Unrealistic oscillation emerges at classifiers 1 and 3, which is somewhat improved with classifier 2. On the other hand, classifiers 4–6 act similarly; they reproduce the behavior of the inherent structure very well. Such tendencies correspond to the error magnitudes in Table I.

To verify the network topology determined by the classifiers, the number of rings (i.e., cyclic paths along the network) in the network is counted and compared with that in the inherent structure. Ring size distribution is often utilized to characterize the network topology in various studies.[2–5] In Fig. 4, the averaged number of rings in the network is plotted against the ring size. There are two groups in the classifiers. Classifiers 2, 4, 5, and 6 reproduce the distribution of the inherent structure much better than classifiers 1 and 3 do. With classifiers 1 and 3, some backbone hydrogen bonds are misjudged, leading to the merging of small rings and

TABLE I. Evaluation of classifiers. The optimal fitting parameters and their error magnitudes at two temperatures, TMD and 40 K below TMD, are listed for six different classifiers. E, r_{OO}, r_{OH}, and $\cos\theta_{HOO}$ are the threshold values for pair interaction energy, intermolecular oxygen-oxygen and oxygen-hydrogen distances, and H–O–O angle, respectively. Lower temperature corresponds to the low density liquid water state. I(error) denotes the uncertainty of the number of hydrogen bonds per molecule, i.e., per about four hydrogen bonds of the molecule.

Classifier	Thresholds	TIP4P			TIP4P/2005		SPC/E		NvdE	
		253 K	213 K	253 K[a]	278 K	238 K	241 K	201 K	287 K	247 K
1	E (kJ/mol)	−9.0	−9.0	−10.0[b]	−10.0	−11.0	−10.0	−10.0	−8.5	−9.0
	I(error)	0.762	0.400	(0.778)	0.886	0.312	0.602	0.280	1.002	0.338
2	E (kJ/mol)	−1.0	−1.0	0.0[c]	−1.0	−1.0	−1.5	−1.5	−3.0	−2.0
	r_{OO} (nm)	0.325	0.325	0.35	0.325	0.325	0.325	0.325	0.325	0.325
	I(error)	0.552	0.234	(0.786)	0.682	0.310	0.418	0.148	0.920	0.270
3	E (kJ/mol)	−7.0	−7.0	−10.0[d]	−7.6	−7.7	−7.8	−7.6	−6.8	−6.7
	$\cos\theta_{HOO}$	0.834	0.842	0.866	0.843	0.843	0.830	0.846	0.818	0.831
	I(error)	0.618	0.284	(0.760)	0.740	0.360	0.482	0.190	0.920	0.288
4	r_{OH} (nm)	0.250	0.250	0.220[e]	0.250	0.250	0.245	0.245	0.245	0.245
	I(error)	0.422	0.156	(0.650)	0.550	0.222	0.314	0.096	0.786	0.202
5	r_{OH} (nm)	0.255	0.255	0.245[f]	0.255	0.255	0.250	0.245	0.25	0.255
	$\cos\theta_{HOO}$	0.718	0.758	0.866	0.740	0.753	0.764	0.759	0.744	0.741
	I(error)	0.416	0.152	(0.508)	0.540	0.218	0.310	0.094	0.778	0.198
6	I_0(error)	0.400	0.142		0.524	0.208	0.296	0.088	0.760	0.190

[a]Threshold values are taken from literature. The error magnitude (in parentheses) is calculated for reference by applying them to TIP4P at 253 K.
[b]Reference 4.
[c]Reference 13. Original paper uses ST2 water model.
[d]Reference 14. Original paper uses SPC/E water model.
[e]Reference 11.
[f]Reference 12. Original paper uses SPC water model.

increase of large rings. Any of them does not match exactly, however, the distribution of the inherent structure, that is, the network topology might be modified somewhat by quenching. At higher temperature, this disagreement will be emphasized. Results by classifiers 2, 4, 5, and 6 are all alike, suggesting that the network topology is robust against the hydrogen bond definitions; almost identical network topology is obtainable if hydrogen bond is defined reasonably.

Strong interaction and network formability are the dif-ferent aspects of hydrogen bond. The concept of hydrogen bonding is applicable to other systems than water. Actually, strong electrostatic interaction is commonly existent in various molecules. It should be noted, however, that not all of them are network formative. Network is elicited only when the hydrogen bonding has a discrete nature. Water is of the same case. For other systems, special care should be taken to
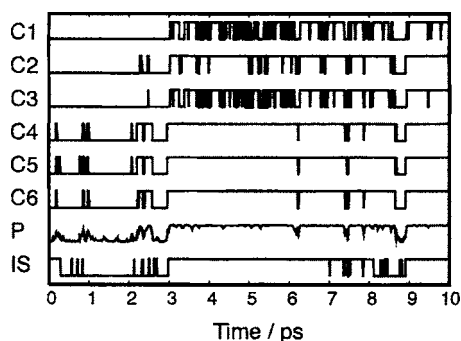

FIG. 3. Time series of hydrogen bond. Time series of decisions for a pair of water molecule by the classifiers are plotted against time. TIP4P water model is used and the temperature is 253 K (i.e., TMD). From top to bottom, lines indicate the decisions by classifiers 1–6 (C1–C6), hydrogen bond probability $P(B|x)$ on the basis of classifier 6 (P), and the hydrogen bond state in the inherent structure (IS), respectively. Optimal parameters listed in Table I are used for the classifiers. In each line, up and down correspond to B and NB states, respectively. According to the present framework, classifiers 4–6 are of good performance to reproduce the hydrogen bond state.
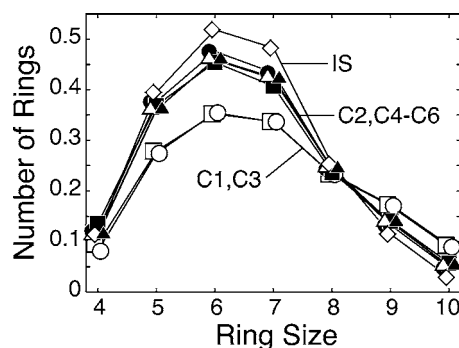

FIG. 4. Network topology. The network topology of liquid water is analyzed by means of the ring size distribution. Water model is TIP4P and temperature is 253 K (i.e., TMD). The averaged number of rings per water molecule is plotted against the ring size. The lines correspond to the result by different classifiers. Classifiers 1–6 are indicated by open square, filled square, open circle, filled circle, open triangle, and filled triangle, respectively. The diamond indicates the reference ring distribution in the inherent structure. Classifiers 1 and 3 miss some of the backbone hydrogen bonds, leading to a decrease of small rings and an increase of nine- and ten-membered rings. Other classifiers are of almost the same performance in reproducing the network topology.

define the network. The present framework will be helpful when one determines whether the bonding is discrete enough or not.

CONCLUSION

To evaluate the relevance of treating the hydrogen bonds in liquid water as a digital network and applying topological analyses, an unbiased decision framework for hydrogen bond of water is proposed. By using the inherent structure as a reference, the optimal decision boundary is decided uniquely for the given parameter space. Performance of the classifiers can also be evaluated by the error magnitude. Different classifiers can be compared directly by this error magnitude. According to this framework, a simple decision by intermolecular O–H distance is most affordable. This classifier actually reproduces the hydrogen bond rearrangements and network topology of the inherent structure very well. The present work corroborates the HB definitions in the previous studies. When the criteria are chosen optimally, hydrogen bonds in liquid water are well discretized and the HB network can be treated as a topological matter. One can also design new and better criteria with the present framework.

ACKNOWLEDGMENTS

APPENDIX: BAYESIAN DECISION THEORY

Suppose a relative configuration of a pair of water molecules is projected onto a parameter space, say x. x is a scalar or vector variable that consists of, for example, intermolecular O–H distance, pair interaction energy, etc. The probability that the pair at condition x is in B state is denoted by $P(B|x)$. We call it "hydrogen bond probability" at condition x. When the distance between the pair is very large, $P(B|x)$ becomes zero, i.e., there is no probability that the pair of water molecules is hydrogen bonded. Naturally $P(NB|x) = 1 - P(B|x)$. $P(B|x)$ can be directly calculated by using the molecular simulation as follows:

$$P(B|x) = H_B(x)/(H_B(x) + H_{NB}(x)), \tag{A1}$$

where $H_B(x)$ and $H_{NB}(x)$ are the number of pairs per molecule in B and NB states at condition x, respectively. $H_B(x)$ is also written as

$$H_B(x) = p(x)(N-1)P(B|x), \tag{A2}$$

where N is the number of molecules in the system and $p(x)$ is the probability of finding a pair of water molecules at condition x. The integral of $H_B(x)$ over the whole parametric space, $\int H_B(x)dx$, is about 4, meaning that a water molecule has about four hydrogen bonds in average.

When all the degrees of freedom are used as the parameter x, the state is explicitly decided by x, and $P(B|x)$ must be discrete. In general, one or two parameters are chosen as x and $P(B|x)$ changes continuously but sharply as a function of x. $P(B|x)$ is expected to be a natural definition of hydrogen bonding by a continuous function.

The problem now comes into the framework of Bayesian decision theory.[19] A set of conditions to decide the hydrogen bond state is called a classifier. Let us define the classifier to decide the hydrogen bond state, i.e., B or NB, by setting a threshold value for the intermolecular O–H distance. This classifier decides the hydrogen bond state to be B if the intermolecular O–H distance x between a pair of water molecules is in a value range, say $\mathbf{R}_B$. According to Bayesian decision theory, the probability of error is then defined as

$$P(\text{error}) = P(x \in \mathbf{R}_B, NB) + P(x \notin \mathbf{R}_B, B)$$

$$= \int_{x \in \mathbf{R}_B} P(NB|x)p(x)dx + \int_{x \notin \mathbf{R}_B} P(B|x)p(x)dx, \tag{A3}$$

where $P(x \in \mathbf{R}_B, NB)$ is the probability that the pair of water molecules is not hydrogen bonded in the inherent structure but decided as hydrogen bonded by the classifier. $P(\text{error})$ is not useful to treat hydrogen bonds because $P(\text{error})$ becomes very small when N is very large. We introduce here the error magnitude, $I(\text{error})$, instead,

$$I(\text{error}) = \int_{x \in \mathbf{R}_B} H_{NB}(x)dx + \int_{x \notin \mathbf{R}_B} H_B(x)dx$$

$$= (N-1)P(\text{error}). \tag{A4}$$

$I(\text{error})$ denotes the uncertainty of the number of hydrogen bonds per molecule. For example, $I(\text{error}) = 0.4$ indicates that the uncertainty in the number of hydrogen bonds is about 10% because one water molecule has four hydrogen bonds in average. An optimal choice of $\mathbf{R}_B$ minimizes $P(\text{error})$ and $I(\text{error})$. According to Bayesian decision rule, the optimal decision boundary for the classifier is given at x where $P(B|x) = P(NB|x) = 0.5$, that is, the boundary is located at x where $H_B(x) = H_{NB}(x)$. At this limit, $I(\text{error})$ becomes

$$I_0(\text{error}) = \int \min[H_{NB}(x), H_B(x)]dx, \tag{A5}$$

where the integral is performed over the parameter space.

The optimal decision boundary is a curved hypersurface when x is a vector. In the actual case, on the other hand, hydrogen bonding is usually defined by a couple of geometrical/energetic thresholds and the thresholds are given by a combination of plain boundaries. Such plain boundaries are not necessarily optimal.

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