A model potential $V(r, R)$ is proposed for the proton of a hydrogen bond $R_A-H...B_R$, a model that is consistent with modern views of the hydrogen bond and is operative over a broad interval of variation of the distance $R$ between atoms $A$ and $B$. A procedure has been developed for reconstructing the dependence of the potential $V(r, R)$ on $r$ (the distance from $A$ to $H$) on the basis of available information on the dependence of the energy of the hydrogen bond $E_b(R)$. For weak bonds, a simple method is proposed for finding the wave functions and the lowest excited energy levels of the proton. Calculations have been performed for water dimer and motion of the proton in a single measurement.

**INTRODUCTION**

All properties of the hydrogen bond $A-H...B$ can be obtained if the adiabatic potential for the proton $V(r, R)$ is known, i.e., the energy of the electrons of the system, where $r$ is the coordinate of the proton relative to atom $A$; $R$ is the distance $AB$. We will subsequently assume that the bond is linear. The magnitude of $V(r, R)$ is determined not only by the properties of the atoms $A$ and $B$, but also the properties of the molecules to which these atoms belong, and which we will designate as $R_A$ and $B_R$. In [1, 2], a two-well potential was obtained. In a later study [3], only a certain asymmetry of the curve was found (Fig. 1). Finally, in [4, 5], for the dimer of water, the energy of the hydrogen bond $E_b(R)$ was obtained on the assumption that the proton is located at the minimum of the potential $V(r, R)$ with various values of $R$. The popular model potential of Lippincott and Schröder [6] has the shortcoming that the shape of the potential depends solely on the nature of atoms $A$ and $B$; both wells are similar in depth, but the model cannot be used if $R$ deviates significantly from the equilibrium $R_o$ (Fig. 1). These shortcomings remain, in part, in the modified potential proposed by Reid [7].

We are proposing a form of the model potential that is better justified physically, a form that is suitable in principle for any $R$ and is capable of describing a nonlinear bond as well; we will show how its parameters can be determined on the basis of certain experimental and theoretical data. We are also proposing a simplified form of the potential that is suitable for the vicinity of the minimum in $V(r, R)$ with respect to $r$, but with any value of $R$. With this form, analytical expressions can be obtained for the wave functions of several of the lowest states of the proton. Such a determination of parameters has been performed for water dimer in various approximations, in particular with an accounting for anharmonicity and the quantum character of the proton vibrations, as well as the circumstances that the vibrations of all three atoms of the $H_2O$ molecule are coupled.

**SELECTION OF MODEL POTENTIAL**

Examining first the molecule $R_A-H$, we must conclude that the $A-H$ bond is a valence bond. It is characterized by a rupture energy of 3-5 eV, and the nature of this bond is little changed when a second molecule $B_R$ is added (excluding the case of very strong hydrogen bonds). Therefore, it is convenient to approximate the corresponding potential by the Morse function

$$
V_A(r) = V_A^0(e^{-2\alpha(r-r_o)} - 2e^{-\alpha(r-r_o)}),
$$

where \( r_0 \) is the equilibrium position of the proton. In the first approximation, \( V_A^0 \) is equal to the energy of the A-H bond, and \( 2\alpha^2 V_A^0 = \frac{\partial^2 V}{\partial r^2} \bigg|_{r=r_0} \) is the square of the vibration frequency of the hydrogen atom \( \omega_0 \), multiplied by its mass \( m_H \). Thus, all three parameters \( V_A^0, r_0, \) and \( \alpha \) can be found from experiment. As regard the weaker bond H...B, we note that B is usually an electronegative atom, and hence we can consider that the molecule \( BR_a \) represents a certain dipole \( \mathbf{P} \) and that the energy of a hydrogen atom with charge \( e_H \) in its field will be equal to \( e_H^2 \mathbf{P} \cdot (R - r) \) (for a linear bond). If the direction of \( \mathbf{P} \) does not coincide with \( R - r \), we obtain

\[
e_H \mathbf{P} \cdot (R - r)
\]

and this creates a tendency to form a certain angle \( \angle ABH \). If rotations of the molecules or their fragments are in some way hindered, such electrostatic forces will determine a nonlinear bond. Strictly speaking, it is necessary to introduce a certain electrostatic energy that also includes the interaction of the electronegative atoms A and B with each other and with the radicals \( R_1 \) and \( R_2 \); we will designate this energy as \( V_{AB}(r, R) \). At large distances \( R \gg r_0 \), it dominates over all other types of interaction; and according to [8], it makes the principal contribution to the bond energy at the equilibrium distance \( R_0 \) as well. With decreasing distance \( R \), the approximation of charge-dipole interaction becomes inadequate, and we should expect stronger attraction between the H atom and the \( BR_a \) molecule. Also, van der Waals forces appear, proportional to \( 1/R^6 \), as well as partial charge transfer effects, mutual polarization, and, finally, exchange repulsion. All of these can be described by a certain short-range effect that depends on \( R - r \) and \( R_0 \), and which also can be approximated by the Morse potential \( V_B(R - r) \) plus an exponentially increasing repulsion \( V_{rep} \):

\[
V_B(R - r) = V_B^0 \left( e^{-2\omega(n-r_0')} - 2e^{-\alpha(n-r_0')} \right)
\]

\[
V_{rep} = Ae^{-\alpha(n-R_0)}
\]

where \( r_0' \) is the effective equilibrium distance between the atoms H and B, at which attraction is replaced by repulsion; \( r_0' \) is close to \( r_0 \). In subsequent calculations for water dimer, we will consider that \( r_0' = r_0 \). Thus, in addition to the previously discussed parameters \( V_A^0, \alpha, \) and \( r_0 \), we have five more parameters: \( C = e_H \mathbf{P}, V_B^0, \alpha', A, \) and \( \alpha \). For the evaluation of these parameters, we can use such accessible data as: 1) the increase in the AH distance \( r_0 + r_0 + \Delta r_0 \) due to the formation of a hydrogen bond; 2) the corresponding decrease in frequency of OH bond vibrations \( \omega_0 - \omega \); 3) the absolute magnitude of the energy of the hydrogen bond \( E_B(R_0) \);