

# Calculation of rovibrational spectra of water by means of particles-on-concentric-spheres models. I. Ground stretching vibrational state

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A new method is presented to compute bending frequencies and rotational structure in the ground and excited bending states of water-like molecules. As a zeroth-order approximation the water molecule is simulated by the two hydrogens confined to move on a sphere around the oxygen. Even the simplest approximation, choosing the radius of the sphere equal to the equilibrium bond length, gives better results for rotational levels than the rigid bender model does. A further improvement for both bending frequencies and rotational energy levels, especially in excited bending states, has been achieved by introducing an effective radius and an effective mass. These are calculated by averaging over stretching motions to reduce the Schrödinger equation to only the rotational and bending degrees of freedom.

## I. INTRODUCTION

This work is the latest in a series<sup>1-8</sup> trying to explore the provocative question<sup>6</sup>: "Are atoms and small molecules the same?" Less jocosely put, the question is one of whether or how much electrons in molecules share independent-particle or collective behavior with atoms in small molecules.

Recently two of us used a model of two particles confined to a sphere<sup>4</sup> or to two concentric spheres<sup>5</sup> to get some insight into angular correlations in two-electron atomic systems. In Ref. 5, the close relationship of this model to the so-called "rigid bender"<sup>9,10</sup> was pointed out. However, while the two models use the same bending potentials, the operators representing the kinetic energy are not identical. We shall show here that the model,<sup>4</sup> simulating the water molecule by the two hydrogens moving on a sphere around the oxygen, gives somewhat better results for rotational levels than does the rigid bender model. These differences might be more significant for nonrigid XY<sub>3</sub>-like molecules if one compares the levels predicted by a C<sub>3v</sub> semirigid molecular model with X-Y bonds of fixed length<sup>11</sup> and by three particles on a sphere, respectively. The model developed here should therefore be viewed as an independent approach naturally adapted to the description of angular motion whether correlated or independent-particle-like, which can thereby capture essential characteristics of excited states of rotation and bending vibrations of XY<sub>n</sub> molecules and, depending on the particular kind of interactions between Y particles, show how bending and collective rotation can transform to independent-particle rotation.

## II. THE DYNAMICAL MODEL

We start with the relative kinetic energy operator for a three-particle system, representing it in the form

$$\hat{T} = -\frac{1}{2\mu_1} \nabla_1^2 - \frac{1}{2\mu_2} \nabla_2^2 - \frac{1}{M} \nabla_1 \cdot \nabla_2, \quad (1)$$

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where

$$\frac{1}{\mu_i} = \frac{1}{m_i} + \frac{1}{M}; \quad (2)$$

here  $m_1$  and  $m_2$  are masses of the light particles,  $M$  is the mass of the heavy particle, particle 3; and  $\nabla_i$  ( $i = 1, 2$ ) is the derivative with respect to the vector

$$\mathbf{R}_i \equiv \mathbf{r}_i - \mathbf{r}_3, \quad (3)$$

where  $r_1, r_2$ , and  $r_3$  are radius vectors of the particles in laboratory coordinates. Note that, in contrast to the standard transformation of variables originally introduced by Curtiss, Hirschfelder, and Adler<sup>12</sup> for separation of the translational variable

$$\mathbf{z} = \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2 + M \mathbf{r}_3}{m_1 + m_2 + M} \quad (4)$$

(and used, e.g., by Holmgren, Waldman, and Klemperer<sup>13</sup> or by Tennyson and Sutcliffe<sup>14</sup> in variational calculations of triatomic molecules), our transformation of variables (3) and (4) is nonorthogonal in the space of mass-weighted Cartesian coordinates. The coupling term  $-(1/M)\nabla_1 \cdot \nabla_2$  therefore appears. It is small in the case of a heavy central and two light particles. The complication of the extra term is compensated by the fact that the lengths  $R_i$  of the vectors  $\mathbf{R}_i$  as well as the angle  $\gamma$  between them have a very clear physical significance.

We now seek an approximate solution of the Schrödinger equation

$$[\hat{T} + V(R_1, R_2, \gamma) - E] \Psi(\mathbf{R}_1, \mathbf{R}_2) = 0 \quad (5)$$

in the separable form

$$\Psi(\mathbf{R}_1, \mathbf{R}_2) = \frac{1}{R_1 R_2} \Phi(R_1, R_2) \chi(\varphi_1, \theta_1, \varphi_2, \theta_2), \quad (6)$$

which emphasizes the expectation that stretching motions are likely to be separable from bending/rotation motions. Note that the interbond angle  $\gamma$  is connected with the single-particle spherical coordinates  $\varphi_i, \theta_i$  by the relation

$$\cos \gamma = \cos \theta_1 \cos \theta_2 \cos(\varphi_2 - \varphi_1) + \sin \theta_1 \sin \theta_2. \quad (7)$$

A more detailed discussion of the separability implied here will be given in part II.<sup>15</sup>

Substituting the function (6) into Eq. (5), multiplying the resulting equation by  $\Phi(R_1, R_2)$ , and integrating over  $R_1$  and  $R_2$ , we find

$$[\hat{t}_0 + \Delta\hat{t} + \Delta\hat{t}' + W(\gamma) - E]\chi = 0, \quad (8)$$

where

$$\hat{t}_0 \equiv -\frac{1}{2\mu_1} \frac{\Delta_{\theta_1\varphi_1}}{\bar{R}_1^2} - \frac{1}{2\mu_2} \frac{\Delta_{\theta_2\varphi_2}}{\bar{R}_2^2}, \quad (9a)$$

$$\Delta\hat{t} \equiv -\frac{1}{\bar{M}\bar{R}_1\bar{R}_2} \nabla_{\theta_1\varphi_1} \cdot \nabla_{\theta_2\varphi_2}, \quad (9b)$$

$$\Delta\hat{t}' \equiv -\frac{1}{M} \left[ \Phi \frac{R_1}{R_2} \frac{\partial}{\partial R_1} \left( \frac{\Phi}{R_1} \right) dR_1 dR_2 \mathbf{n}_1 \cdot \nabla_{\theta_2\varphi_2} + 1 \leftrightarrow 2 \right], \quad (9c)$$

$$W(\gamma) \equiv \int \Phi \left[ -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} + V(R_1, R_2, \gamma) - \frac{\cos \gamma}{M} R_1 R_2 \frac{\partial^2}{\partial R_1 \partial R_2} \right] \frac{\Phi}{R_1 R_2} dR_1 dR_2, \quad (9d)$$

$$\bar{R}_i^{-2} \equiv \int R_i^{-2} \Phi^2 dR_1 dR_2, \quad (10a)$$

$$\bar{M}^{-1} \equiv M^{-1} \int \frac{\bar{R}_1 \bar{R}_2}{R_1 R_2} \Phi^2 dR_1 dR_2. \quad (10b)$$

Let us now specialize to the ground stretching vibrational state of an  $XY_2$  triatomic molecule ( $m_1 = m_2 = m$ ) and make use of a local-mode representation of the wave function  $\Phi(R_1, R_2)$  as a product<sup>15</sup>

$$\Phi(R_1, R_2) \simeq f(R_1) f(R_2), \quad (11)$$

where the function  $f(R)$  is chosen to satisfy an analog of the Born-Oppenheimer electronic equation for bond motion

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + W(R, R_e, \gamma_e) - \epsilon_0 \right] f(R) = 0. \quad (12)$$

In Eq. (12)  $R_e$  and  $\gamma_e$  are equilibrium values of the bond length  $R$  and the bond angle  $\gamma$ , respectively;  $\mu = \mu_1 = \mu_2$ . The assumption (11) results in a simplification of terms (9c) and (9d). Thus

$$\Delta\hat{t}' = \frac{2}{\bar{M}\bar{R}^2} (\mathbf{n}_1 \cdot \nabla_{\theta_2\varphi_2} + \mathbf{n}_2 \cdot \nabla_{\theta_1\varphi_1}), \quad (13)$$

$$W(\gamma) = W_0 + \int f^2(R_1) f^2(R_2) V(R_1, R_2, \gamma) dR_1 dR_2 - \frac{1}{\bar{M}\bar{R}^2} \cos \gamma, \quad (14)$$

where the constant  $W_0$  is determined by the relation

$$W_0 = 2 \left[ \epsilon_0 - \int f^2(R) V(R, R_e, \gamma_e) dR \right]. \quad (15)$$

The radius  $\bar{R}$  and the effective mass  $\bar{M}$  are defined by the expressions

$$\bar{R}^{-2} \equiv \int R^{-2} f^2(R) dR, \quad (16)$$

$$\bar{M}^{-1} \equiv M^{-1} \left[ \int \frac{\bar{R}}{R} f^2(R) dR \right]^2. \quad (17)$$

Omitting the term  $\Delta\hat{t}'$  in Eq. (8) we obtain an equation for two particles rotating on a sphere of radius  $\bar{R}$ :

$$\left[ -\frac{1}{2\mu} \frac{\Delta_{\theta_1\varphi_1}}{\bar{R}^2} - \frac{1}{2\mu} \frac{\Delta_{\theta_2\varphi_2}}{\bar{R}^2} + \Delta\hat{t} + W(\gamma) - E \right] \chi = 0 \quad (18)$$

which differs from Eq. (2) of Ref. 4 simply by the addition of a center-of-mass correction  $\Delta\hat{t}$  determined by Eq. (9b) with  $\bar{R}_1 = \bar{R}_2 = \bar{R}$ , i.e., the center of the sphere in the present model is not fixed in space, but is located at the heavy particle (effective mass  $\bar{M}$ ) and can move together with it. The effective mass  $\bar{m}$  of the light particles is determined by

$$\frac{1}{\bar{m}} = \frac{1}{\mu} - \frac{1}{\bar{M}}. \quad (19)$$

From now on we shall consider only the approximate equation (18). A role of the omitted term  $\Delta\hat{t}'$  will be studied in a separate publication.<sup>15</sup>

Following Ref. 4 we represent the desired solution in the form

$$\chi_0^J(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2) = \sum_{j_1 j_2} |j_1 j_2 J\rangle C_{j_1 j_2 J}, \quad (20)$$

where the vector-coupled function is

$$|j_1 j_2 J\rangle = \sum_{m_1} Y_{m_1}^{j_1}(\hat{\mathbf{R}}_1) Y_{-m_1}^{j_2}(\hat{\mathbf{R}}_2) \langle j_1 m_1 j_2 - m_1 | J 0 \rangle, \quad (21)$$

with  $\hat{\mathbf{R}}_k = \mathbf{R}_k/R$  ( $k = 1, 2$ ). The potential  $W(\gamma)$  is expanded in terms of the Legendre polynomials  $P_l(\cos \gamma)$  and then reexpressed in terms of the spherical harmonics [see relations (2.9) and (2.25) of Brink and Satchler<sup>16</sup>]. The center-of-mass correction  $\Delta\hat{t}$  in the basis set in question takes the form

$$\langle j_1 j_2 J | \Delta\hat{t} | j_1' j_2' J \rangle = -\frac{\alpha_1 \alpha_2}{\bar{M}\bar{R}^2} \langle j_1 j_2 J | \mathbf{C}_1(\hat{\mathbf{R}}_1) \cdot \mathbf{C}_2(\hat{\mathbf{R}}_2) | j_1' j_2' J \rangle, \quad (22)$$

where  $\mathbf{C}_k(\hat{\mathbf{R}}_k)$  is the vector with components  $\sqrt{4\pi/3} Y_{1m}(\hat{\mathbf{R}}_k)$  and

$$\alpha_k = \begin{cases} -j_k', & j_k = j_k' + 1 \\ j_k' + 1, & j_k = j_k' - 1 \end{cases} \quad (23)$$

(see Appendix 6 of Brink and Satchler<sup>16</sup>).

It is worthwhile discussing more carefully the symmetry properties of the Hamiltonian (18). In addition to overall rotations the latter is also invariant under three operations<sup>17,18</sup>: (i) inversion  $\hat{i}$  of space-fixed Cartesian coordinates ( $\hat{\mathbf{R}}_k \rightarrow -\hat{\mathbf{R}}_k$ ); (ii) the permutation  $\hat{P}$  of the hydrogens ( $\hat{\mathbf{R}}_1 \leftrightarrow \hat{\mathbf{R}}_2$ ); (iii) the product of (i) and (ii), the permutation inversion  $\hat{P}^*$ . Since the inversion operation multiplies the spherical harmonic  $Y_0^{j_k}(\hat{\mathbf{R}}_k)$  by a factor  $(-1)^{j_k}$  any function  $|j_1 j_2 J\rangle$  has definite parity  $(-1)^{j_1 + j_2}$ . We can now introduce new functions

$$|j_1 > j_2, J; s, \pm\rangle = (1/\sqrt{2}) [ |j_1 j_2 J\rangle \pm (-1)^J |j_2 j_1 J\rangle ] \quad (24a)$$

and

$$|j_1 > j_2, J; a, \pm\rangle = (1/\sqrt{2}) [ |j_1 j_2 J\rangle \mp (-1)^J |j_2 j_1 J\rangle ] \quad (24b)$$

which are, respectively, symmetric and antisymmetric with respect to  $\hat{P}_{12}$ . The indices (+) and (-) on the left-hand kets

of Eq. (24) denote the parity. The functions  $|\hat{j}jJ\rangle$  also have a definite symmetry with respect to  $\hat{P}_{12}$ , namely,  $\hat{P}|\hat{j}jJ\rangle = (-1)^j|\hat{j}jJ\rangle$ . The Hamiltonian in the new basis set therefore factors into four blocks, corresponding to different irreducible representations of the group  $\{\hat{E}, \hat{i}, \hat{P}_{12}, \hat{P}_{12}^*\}$ .

The standard labeling of the eigenstates of those blocks by means of the two limits: oblate ( $I_a = I_b < I_c$ ) and prolate ( $I_a < I_b = I_c$ ) symmetric tops (see Figure 4-1 of Townes and Schawlow<sup>19</sup>) is now briefly discussed. For any planar molecule the  $c$  axis is perpendicular to the plane of the molecule and the parity of rotational levels is determined by the factor<sup>20</sup>  $(-1)^{K_c}$ . This result immediately follows from the fact that symmetry properties of rotational wave functions do not change as  $I_b \rightarrow I_c$ . This is also true for the limit  $I_b \rightarrow I_a$  but in the latter case there are two possibilities for a  $C_{2v}$  triatomic. These depend on whether the  $a$  axis coincides with the symmetry axis of the equilibrium configuration or is perpendicular to it. Equilibrium moments of inertia of any  $C_{2v}$  triatomic with respect to the symmetry axis and that perpendicular to it are<sup>21</sup>  $2mR_e^2 \sin^2(\gamma_e/2)$  and  $2\mu R_e^2 \cos^2(\gamma_e/2)$ , respectively. Hence the latter is the  $a$  axis if

$$tg^2 \frac{\gamma_e}{2} > \mu/m, \quad (25)$$

which it must be for any molecule with the equilibrium angle larger than  $90^\circ$ . Therefore for the water molecule and any of its isotopic  $C_{2v}$  modification, the  $a$  axis is perpendicular to the symmetry axis. The limit of the prolate symmetric top is a linear triatomic (the opposite case corresponds to  $\gamma_e = 0^\circ$ ). Because the rotation through  $180^\circ$  around the  $a$  axis is generated by the permutation-inversion  $\hat{P}^*$ , this operation must multiply rotational wave functions by the factor  $(-1)^{K_a}$  (in correspondence with Tables 10.10 and A4 of Bunker.<sup>18(b)</sup>) Multiplying  $\hat{P}^*$  and  $\hat{i}$  one finds that rotational wave functions of the water molecule are symmetric or antisymmetric if  $K_a + K_b$  is even or odd,<sup>18,19</sup> respectively.

Let us now return to Eq. (18). If we note that the ground-state solution of the radial equation (12) is strongly localized near the equilibrium configuration, we can approximate  $f(R)$  by the  $\delta$  function  $\delta(R - R_e)$ . We then find  $\bar{R} = R_e$ ,  $\bar{M} = M$ , as expected. The potential (14) takes the form

$$W(\gamma) = W_0 + V(R_e, R_e, \gamma) - \frac{1}{MR_e^2} \cos \gamma. \quad (26)$$

The last term in Eq. (26) has a purely quantum-mechanical origin. Such extra potentials  $-\tilde{g}^{-1/4} \Delta (\tilde{g}^{1/4})$  usually appear<sup>22,23</sup> when the Podolsky transformation<sup>24</sup>  $\Psi \rightarrow \tilde{g}^{-1/4} \Psi$  (which changes the metric) is applied to the Laplacian  $\Delta$ .

The potential energy  $V(R_e, R_e, \gamma)$  in Eq. (26) is exactly the same as in the rigid bender model.<sup>9,10</sup> It is not simple to make a term-by-term comparison of the kinetic energy operator discussed here with that used in the rigid bender treatment.<sup>9,10</sup> However, in the present work we are certainly able to demonstrate that those two operators are different. In order to do so, we can with no loss of generality consider only states with zero total angular momentum, i.e., we study the projection of the kinetic energy operator into the subspace of internal coordinates. An essential characteristic of the rigid

bender model is its use of the so-called "least-squares"<sup>23</sup> large-amplitude internal variable  $\rho$ , which can be found as a function of Cartesian coordinates  $\mathbf{r}_A$  by minimizing the quadratic form<sup>25,26</sup>

$$L = \sum_A m_A |\mathbf{r}_A - \mathbf{S}(\varphi', \theta', \chi') \mathbf{a}_A(\rho') - \mathbf{z}|^2 \quad (27)$$

with respect to  $\varphi'$ ,  $\theta'$ ,  $\chi'$ , and  $\rho'$ . Here  $\mathbf{S}$  is a  $3 \times 3$  proper orthogonal matrix determining the orientation of the body-fixed axes,  $\mathbf{a}_A$  and  $\mathbf{z}$  are radius vectors of the  $A$ th nucleus of the semirigid model and of the center of mass, respectively. For triatomic molecules one can easily dispense with the rotational coordinates and search for the absolute minimum of a new form only with respect to the internal variable  $\rho'$ . This simplification is possible because for each value of  $\rho'$  just a single angle determines the orientation of the Eckart frame<sup>27,28</sup> in the plane of the running nuclear configuration  $\bar{\mathbf{r}}$ . Considering only the configurations lying in the plane of the model and representing two-dimensional vectors  $\mathbf{r}_A$ ,  $\mathbf{z}$ , and  $\mathbf{a}_A$  by complex numbers<sup>29</sup> we are led to the requirement that the form

$$L = \sum_A m_A |e^{-i\chi(\rho')} (\mathbf{r}_A - \mathbf{z}) - \mathbf{a}_A(\rho')|^2 \quad (28)$$

have its absolute minimum at  $\rho' = \rho$ . The third Euler angle  $\chi$  as a function of  $\rho'$  is determined by the equation<sup>29</sup>

$$\chi(\rho') = \arg \sum_A m_A r_A a_A^*(\rho'), \quad (29)$$

where the asterisk means complex conjugation and  $\sum_A m_A a_A = 0$ .

Let us now come back to the rigid bender. If  $R_1 = R_2 = R_e$  the least-squares angle  $\rho$  by definition coincides with the angle  $\bar{\rho} \equiv \pi - \gamma$ .<sup>9,10</sup> However, the two internal variables  $\rho$  and  $\bar{\rho}$  differ for arbitrary nuclear configurations and moreover  $\nabla_A \rho \neq \nabla_A \bar{\rho}$  even at  $R_1 = R_2 = R_e$ . To verify this statement one should merely compare the expression<sup>9</sup> for the inverse effective mass of the rigid-bender model based on its internal variable  $\rho$ :

$$\frac{1}{\mu_{RB}} \equiv \sum_{A=1}^3 \frac{1}{m_A} \left| \frac{\partial \rho}{\partial \mathbf{r}_A} \right|^2 = \frac{2(2m + M)}{m(m + M - m \cos \rho) R_e^2} \quad (30)$$

with the similar one based on our variable  $\bar{\rho}$ , appearing in the particles-on-concentric-spheres model:

$$\begin{aligned} \frac{1}{\mu_{POCS}} &\equiv \sum_{A=1}^3 \frac{1}{m_A} \left| \frac{\partial \bar{\rho}}{\partial \mathbf{r}_A} \right|^2 = \frac{1}{m} \left( \left| \frac{\partial \gamma}{\partial \mathbf{r}_1} \right|^2 + \left| \frac{\partial \gamma}{\partial \mathbf{r}_2} \right|^2 \right) \\ &+ \frac{1}{M} \left| \frac{\partial \gamma}{\partial \mathbf{r}_1} + \frac{\partial \gamma}{\partial \mathbf{r}_2} \right|^2 = \frac{2}{R_e^2} \left( \frac{1}{\mu} + \frac{1}{M} \cos \bar{\rho} \right). \end{aligned} \quad (31)$$

To verify Eq. (31) one should differentiate the identity  $\mathbf{R}_1 \cdot \mathbf{R}_2 = R_1 R_2 \cos \gamma$  with respect to  $\mathbf{r}_i$  ( $i = 1, 2$ ) and take into account the fact that

$$\frac{\partial R_i}{\partial \mathbf{r}_i} = \frac{\mathbf{R}_i}{R_i}, \quad i = 1, 2. \quad (32)$$

Expressions (30) and (31) coincide with each other only for linear configurations  $\rho = \bar{\rho} = 0, \pi$ .

TABLE I. Accuracy of calculations of bending frequencies by different methods for the Carney-Curtiss-Langhoff potential. The notation  $\Delta\nu$  is used for the difference  $\nu_{\text{app}} - \nu_{\text{accurate}}$ . Superscripts 0, 1, and 2 label different approximations corresponding to the particles-on-spheres model (see the text), RB = "rigid bender" and SRB = "semirigid bender."

| Quantum state    |           | $\Delta\nu^{(0)}$ | $\Delta\nu^{(1)}$ | $\Delta\nu_{\text{RB}}$ | $\Delta\nu_{\text{SRB}}$ | $\Delta\nu^{(2)}$ |
|------------------|-----------|-------------------|-------------------|-------------------------|--------------------------|-------------------|
| H <sub>2</sub> O | 1 $\nu_2$ | 17                | 26                | 29                      | 23                       | 8                 |
|                  | 2 $\nu_2$ | 40                | 59                | 64                      | 51                       | 23                |
|                  | 3 $\nu_2$ | 76                | 96                | 102                     | 84                       | 43                |
|                  | 4 $\nu_2$ | 89                | 127               | 136                     | 112                      | 58                |
| D <sub>2</sub> O | 1 $\nu_2$ | 1                 | 15                | 15                      | 13                       | 5                 |
|                  | 2 $\nu_2$ | 10                | 37                | 36                      | 31                       | 17                |
|                  | 3 $\nu_2$ | 7                 | 61                | 59                      | 52                       | 31                |
|                  | 4 $\nu_2$ | 28                | 87                | 87                      | 77                       | 47                |
| T <sub>2</sub> O | 1 $\nu_2$ | -3                | 15                | 11                      | 11                       | 8                 |
|                  | 2 $\nu_2$ | 7                 | 35                | 27                      | 26                       | 21                |
|                  | 3 $\nu_2$ | -4                | 58                | 45                      | 43                       | 36                |

If a semirigid molecular model is chosen *a priori* as in the rigid bender approach the potential energy has a term linear with respect to vibrational coordinates. This implies that nuclei will perform small-amplitude vibrations about equilibrium geometries other than those specified by the rigid bender model. The equation uniquely determining these equilibrium geometries for molecules with a single large-amplitude internal degree of freedom was derived in Ref. 25(a) at the same time as it was suggested on an intuitive basis by Fukui<sup>30</sup> for the reaction path. To stress the relationship between two approaches we, following Refs. 23 and 31, call the appropriate semirigid molecular model the "intrinsic" model.

Calculations of intrinsic models of the water molecule with different potentials have shown<sup>31</sup> that these models are very close to the appropriate semirigid bender models<sup>32</sup> ob-

TABLE III. Radii and masses used for calculations presented in Tables I and II.

|                  | $\bar{R}$ (Å)    |        |        | $\bar{M}_0$ (a.u.)  |        |        |
|------------------|------------------|--------|--------|---------------------|--------|--------|
|                  | CCL              | $B(A)$ | $B(B)$ | CCL                 | $B(A)$ | $B(B)$ |
| H <sub>2</sub> O | 0.9661           | 0.9669 | 0.9651 | 16.377              | 16.403 | 16.342 |
| D <sub>2</sub> O | 0.9637           | 0.9643 | 0.9632 | 16.272              | 16.291 | 16.253 |
| T <sub>2</sub> O | 0.9626           | 0.9631 | 0.9623 | 16.227              | 16.243 | 16.214 |
|                  | $R_e = 0.9572$ Å |        |        | $M_0 = 15.995$ a.u. |        |        |

tained by minimizing the potential energy with respect to stretching coordinates for each value of the bending angle. The fact that the semirigid bender model is close to the intrinsic model implies that the linear term in the potential energy is negligible. It can be shown<sup>33</sup> that this is true for any  $C_{2v}$  triatomic with a heavy particle in the center. The semirigid bender model therefore gives a nearly optimal separation of large- and small-amplitude nuclear motions in the water molecule.

In order to estimate the accuracy of our model and compare it with that of the rigid and semirigid bender models we carried out calculations with all three models for several potential surfaces for which very accurate calculations were made, and compared them with the results of those calculations reported in the literature. Details of the comparisons are available upon request. For those potentials we constructed and solved the Schrödinger equation describing large-amplitude bending motion of the semirigid molecular models in question ( $J = 0$ ) or its interactions with overall rotations ( $J > 0$ ). We diagonalized the Hamiltonian in a basis set constructed from rotational wavefunctions and Hermite polynomials. The method results are not in precise agreement with the calculations made in Refs. 9 and 10 using the Numerov-Cooley method. The nature of these discrepancies is unclear but possible errors are in any case at least an order of magnitude less than the accuracy of the approximations in question.

TABLE II. Accuracy of calculations of bending frequencies by different methods for Botschwina's potential energy functions (PEF). The notation is the same as in Table I.

| Quantum state    | PEF A             |                   |                         |                          |                   | PEF B             |                   |                         |                          |                   |    |
|------------------|-------------------|-------------------|-------------------------|--------------------------|-------------------|-------------------|-------------------|-------------------------|--------------------------|-------------------|----|
|                  | $\Delta\nu^{(0)}$ | $\Delta\nu^{(1)}$ | $\Delta\nu_{\text{RB}}$ | $\Delta\nu_{\text{SRB}}$ | $\Delta\nu^{(2)}$ | $\Delta\nu^{(0)}$ | $\Delta\nu^{(1)}$ | $\Delta\nu_{\text{RB}}$ | $\Delta\nu_{\text{SRB}}$ | $\Delta\nu^{(2)}$ |    |
| H <sub>2</sub> O | 1 $\nu_2$         | 29                | 38                      | 35                       | 22                | 21                | 20                | 29                      | 30                       | 23                | 14 |
|                  | 2 $\nu_2$         | 64                | 84                      | 76                       | 53                | 51                | 45                | 62                      | 66                       | 51                | 35 |
|                  | 3 $\nu_2$         | 102               | 133                     | 118                      | 80                | 87                | 67                | 98                      | 104                      | 81                | 62 |
|                  | 4 $\nu_2$         | 139               | 180                     | 158                      | 107               | 126               | 98                | 140                     | 142                      | 113               | 90 |
| D <sub>2</sub> O | 1 $\nu_2$         | 10                | 23                      | 19                       | 12                | 13                | 4                 | 17                      | 16                       | 13                | 8  |
|                  | 2 $\nu_2$         | 24                | 53                      | 43                       | 29                | 34                | 11                | 40                      | 37                       | 29                | 23 |
|                  | 3 $\nu_2$         | 43                | 87                      | 71                       | 50                | 59                | 22                | 62                      | 60                       | 48                | 41 |
|                  | 4 $\nu_2$         | 61                | 120                     | 101                      | 72                | 85                | 34                | 87                      | 85                       | 70                | 61 |
| T <sub>2</sub> O | 1 $\nu_2$         | 4                 | 20                      | 14                       | 10                | 13                | -0.3              | 6                       | 11                       | 10                | 9  |
|                  | 2 $\nu_2$         | 11                | 46                      | 32                       | 23                | 31                | 1.3               | 36                      | 26                       | 23                | 24 |
|                  | 3 $\nu_2$         | 24                | 77                      | 53                       | 40                | 57                | 8                 | 60                      | 44                       | 39                | 41 |
|                  | 4 $\nu_2$         | 33                | 103                     | 77                       | 59                | 77                | 14                | 84                      | 64                       | 56                | 60 |

TABLE IV. (A) Accuracy of the calculations of bending frequencies compared with variational calculations made by Bucknell and Handy. The notation is the same as in Table I. Calculations were made with the empirical potential of Smith and Overend (Ref. 38) and the *ab initio* potential of Ermler and Kern (Ref. 39). Accuracy of the calculations of rotational energy levels compared with variational calculations made by Bucknell and Handy. See Table IV(A) for details.

| (A)                       | $\Delta\nu^{(0)}$ | $\Delta\nu^{(1)}$ | $\Delta\nu_{RB}$          | $\Delta\nu_{SRB}$ | $\Delta\nu^{(2)}$ |                           |                  |                   |
|---------------------------|-------------------|-------------------|---------------------------|-------------------|-------------------|---------------------------|------------------|-------------------|
| SO potential <sup>a</sup> |                   |                   |                           |                   |                   |                           |                  |                   |
| $1\nu_2$                  | 73                | 83                | 70                        | 56                | 6                 |                           |                  |                   |
| $2\nu_2$                  | 109               | 129               | 109                       | 72                | -55               |                           |                  |                   |
| EK potential <sup>b</sup> |                   |                   |                           |                   |                   |                           |                  |                   |
| $1\nu_2$                  | 7                 | 18                | 21                        | 14                | 4                 |                           |                  |                   |
| $1\nu_2$                  | -2                | 22                | 25                        | 10                | -5                |                           |                  |                   |
| (B)                       |                   |                   |                           |                   |                   |                           |                  |                   |
|                           |                   |                   | SO potential <sup>a</sup> |                   |                   |                           |                  |                   |
|                           |                   |                   | $v=0$                     |                   |                   | $v=1$                     |                  |                   |
| $T$                       | $K_a$             | $K_c$             | $\Delta\nu^{(1)}$         | $\Delta\nu_{RB}$  | $\Delta\nu^{(2)}$ | $\Delta\nu^{(1)}$         | $\Delta\nu_{RB}$ | $\Delta\nu^{(2)}$ |
| 1                         | 0                 | 1                 | 0.8                       | 0.3               | 0.5               | 0.2                       | 0.2              | -0.3              |
|                           | 1                 | 1                 | -0.2                      | 1.2               | -0.8              | -0.2                      | 1.6              | 0.7               |
|                           | 1                 | 0                 | 0.3                       | 1.2               | -0.4              | 0.9                       | 0.5              | 0.7               |
| 2                         | 0                 | 2                 | 1.3                       | 1.2               | 0.3               | 0.4                       | 0.6              | -0.8              |
|                           | 1                 | 2                 | 0.8                       | 1.9               | -0.5              | 1.0                       | 1.9              | 0.2               |
|                           | 1                 | 1                 | 1.7                       | 2.0               | 0.2               | 1.5                       | 2.1              | 0.3               |
|                           | 2                 | 1                 | 3.5                       | 4.4               | -1.4              | 3.5                       | 6.0              | 3.1               |
|                           | 2                 | 0                 | 3.5                       | 4.4               | -1.2              | 3.5                       | 5.9              | 3.1               |
|                           |                   |                   |                           |                   |                   | EK potential <sup>b</sup> |                  |                   |
| 1                         | 0                 | 1                 | 1.2                       | 0.3               | 0.9               | 1.1                       | 0.2              | 0.8               |
|                           | 1                 | 1                 | -0.5                      | 1.3               | -1.4              | -0.1                      | 2.1              | -1.2              |
|                           | 1                 | 0                 | 0.0                       | 1.0               | -0.9              | 0.6                       | 2.2              | -0.5              |
| 2                         | 0                 | 2                 | 3.2                       | 1.0               | 2.3               | 3.0                       | 0.8              | 2.2               |
|                           | 1                 | 2                 | 1.3                       | 2.0               | -0.3              | 1.5                       | 2.6              | -0.1              |
|                           | 1                 | 1                 | 3.0                       | 1.9               | 1.6               | 3.5                       | 2.6              | 1.9               |
|                           | 2                 | 1                 | -2.2                      | 5.0               | -5.5              | -0.1                      | 8.2              | -4.3              |
|                           | 2                 | 0                 | -1.8                      | 4.9               | -5.1              | 0.3                       | 8.1              | -3.9              |

<sup>a</sup> Reference 36.

<sup>b</sup> Reference 37.

The radial equation (12) was also solved by the matrix diagonalization in a basis set constructed from Hermite polynomials.

### III. RESULTS

Now we are ready to discuss the results of our calculations presented in Tables I–VII. Tables I, II, and IV A present differences  $\Delta\nu$  between approximate and accurate (variational) values of bending frequencies calculated for different potentials. The accurate values were taken from the appropriate literature.<sup>34–36</sup> Superscripts 0, 1, and 2 label different approximations used to calculate energy levels in the particles-on-spheres model as follows: (0) two particles rotating on a sphere of radius  $R_c$  around a space-fixed center<sup>4</sup>; (1) like the zeroth, but with the center of that sphere allowed to move about due to the center-of-mass correction  $\Delta\hat{t}$ , (2) the same model as in (1) but with the radius of the sphere and the effective mass of the heavy particle calculated according to Eqs. (16) and (17). Table III gives values of these parameters for the Carney–Curtiss–Langhoff<sup>34</sup> and the two potentials of Botschwina.<sup>35</sup>

An unexpected result common to all potentials under consideration is that introduction of the center-of-mass cor-

rection  $\Delta\hat{t}$  for particles rotating on a sphere of radius  $R_c$  gives rise to *larger* errors; for D<sub>2</sub>O and T<sub>2</sub>O even averaging over stretching coordinates does not help. Another anomaly is that our model usually works better for the heavier isotopes.

For both D<sub>2</sub>O and T<sub>2</sub>O the rigid bender model ( $\Delta\nu_{RB}$ ) always gives more or less better results than Eq. (18) with

TABLE V. Mean absolute errors  $\overline{\Delta\nu} \equiv |\nu_{app} - \nu_{accurate}|$  and their standard deviations  $\overline{\delta\nu}$  obtained for the first 15 excited rotational energies ( $J = 1, 2, 3$  and all  $K_a, K_c$  values) with the Hoy–Bunker potential. Numbers 1 and 2 in the second column label our first- and second-order approximations; RB = “rigid bender.”

| $\nu$ | Model | H <sub>2</sub> O       |                        | D <sub>2</sub> O       |                        |
|-------|-------|------------------------|------------------------|------------------------|------------------------|
|       |       | $\overline{\Delta\nu}$ | $\overline{\delta\nu}$ | $\overline{\Delta\nu}$ | $\overline{\delta\nu}$ |
| 0     | 1     | 2.2                    | 1.5                    | 0.8                    | 0.5                    |
|       | RB    | 4.2                    | 3.4                    | 1.7                    | 1.3                    |
|       | 2     | 1.4                    | 1.3                    | 1.4                    | 1.3                    |
| 1     | 1     | 4.4                    | 3.4                    | 1.3                    | 0.7                    |
|       | RB    | 6.4                    | 5.4                    | 2.4                    | 2.0                    |
|       | 2     | 0.6                    | 0.5                    | 0.6                    | 0.5                    |

TABLE VI. Mean absolute errors  $\overline{\Delta v}$  and their standard deviations  $\overline{\delta v}$  obtained for the first 15 excited rotational levels ( $J = 1, 2, 3$ , and all  $K_a, K_c$  values) of  $H_2O$  in different bending states. Calculations were made with the two *ab initio* potentials (Refs. 45 and 46) and compared with the accurate calculations presented by Rao (Ref. 44).

| $v$ | Model | I                     |                       | II                    |                       |
|-----|-------|-----------------------|-----------------------|-----------------------|-----------------------|
|     |       | $\overline{\Delta v}$ | $\overline{\delta v}$ | $\overline{\Delta v}$ | $\overline{\delta v}$ |
| 0   | 1     | 1.8                   | 1.1                   | 2.4                   | 1.6                   |
|     | RB    | 3.9                   | 3.0                   | 4.3                   | 3.6                   |
|     | 2     | 1.5                   | 1.4                   | 1.5                   | 1.4                   |
| 1   | 1     | 3.6                   | 2.3                   | 4.2                   | 3.2                   |
|     | RB    | 5.6                   | 4.1                   | 6.7                   | 5.2                   |
|     | 2     | 0.9                   | 0.6                   | 1.0                   | 0.7                   |
| 2   | 1     | 5.5                   | 3.9                   | 7.0                   | 5.3                   |
|     | RB    | 8.0                   | 6.1                   | 9.6                   | 7.7                   |
|     | 2     | 1.3                   | 1.0                   | 1.1                   | 0.9                   |
| 3   | 1     | 8.8                   | 6.9                   | 11.0                  | 9.4                   |
|     | RB    | 11.8                  | 9.6                   | 14.4                  | 12.2                  |
|     | 2     | 3.1                   | 1.9                   | 2.1                   | 1.4                   |

$R = R_c$  and center-of-mass correction included ( $\Delta v^{(1)}$ ). For  $H_2O$ , the relative accuracies of the results obtained depend on the potential. The semirigid bender model ( $\Delta v_{SRB}$ ) works better than our model as long as averaging over stretching coordinates is not included. It turns out to be especially effective for Botschwina's first potential. However analysis of Tables I, II, and IV(A) allows us to conclude that our simplest dynamical model gives unexpectedly good results compared with typical more complicated molecular models in-

TABLE VII. Rotational structure of high excited bending states. Table represents rotational energies obtained by means of a fit (Ref. 47) to the experimental data in the fourth excited bending state as well as the energies predicted by our model for this state and the upper one.

| $J$ | $K_a$ | $K_b$ | (0,4,0) |           | (0,5,0)   |           |
|-----|-------|-------|---------|-----------|-----------|-----------|
|     |       |       | [45]    | $v^{(1)}$ | $v^{(2)}$ | $v^{(2)}$ |
| 1   | 0     | 1     | 23.7*   | 24.7      | 24.4      | 24.4      |
|     | 1     | 1     | 60.8    | 65.9      | 62.6      | 81.8      |
|     | 1     | 0     | 67.0*   | 71.8      | 68.6      | 87.8      |
| 2   | 0     | 2     | 70.4*   | 73.0      | 72.2      | 72.4      |
|     | 1     | 2     | 102.0*  | 109.4     | 105.6     | 124.7     |
|     | 1     | 1     | 120.9   | 126.8     | 123.1     | 142.6     |
|     | 2     | 1     | 224.9   | 244.7     | 233.1     | 296.5     |
|     | 2     | 0     | 225.7   | 245.3     | 233.7     | 296.9     |
| 3   | 0     | 3     | 138.6*  | 144.3     | 142.6     | 143.4     |
|     | 1     | 3     | 163.5*  | 174.0     | 169.4     | 188.7     |
|     | 1     | 2     | 200.9*  | 208.6     | 204.7     | 224.1     |
|     | 2     | 2     | 296.6   | 319.0     | 309.7     | 372.6     |
|     | 2     | 1     | 300.2*  | 321.8     | 306.7     | 370.5     |
|     | 3     | 1     | 467.9   | 513.6     | 490.3     | 607.7     |
|     | 3     | 0     | 467.9   | 513.7     | 490.4     | 607.8     |

volving vibrational coordinates etc. We shall see below that rotational structure is determined by our simple model even more accurately.

The data presented by Bucknell and Handy<sup>36</sup> for bending frequencies give much less information than do later calculations made in Refs. 34, 35, and 38. However, we have included their work in our comparison because it is the only comparable treatment that uses direct matrix diagonalization to calculate rotational structure. The calculations of Bucknell and Handy were carried out for two potential functions: an empirical potential suggested by Smith and Overend<sup>38</sup> and an *ab initio* potential calculated by Ermler and Kern.<sup>39</sup> (Note that the names of the potentials in Table I of Bucknell and Handy<sup>36</sup> must be interchanged.) Our calculations based on these potentials as well as on some others discussed below showed that introducing the center-of-mass correction  $\Delta \hat{t}$  does improve agreement between our calculations of rotational structure and accurate ones. This finding makes the results obtained for bending frequencies even more obscure. Below we present here only data taking into account this correction. Another surprise was that rotational levels predicted by the rigid and semirigid bender models are practically the same. Therefore we present only the results obtained by means of the former.

As seen from Table IV(B) the model simulating the  $H_2O$  molecule by two particles rotating on a sphere of radius  $R_c$  around a mobile center gives systematically better results than the rigid (and semirigid) bender model. This conclusion is supported by calculations of rotational structure for all other potentials used. The increased errors in the  $2_{21}$  and  $2_{20}$  rotational states for the Ermler-Kern potential when an average over stretching wave functions is performed is apparently accidental. The result is especially surprising for the first excited bending state and may be connected with some errors in variational calculations of Bucknell and Handy.<sup>36</sup> For all other potentials used this averaging does improve the accuracy of calculations in excited bending states but in those cases (as explained below) the accurate values used for the comparison here were obtained by means of a different method.

In Tables V and VI we compare results obtained for our model and the rigid bender with accurate nonrigid bender model calculations developed by Hoy and Bunker<sup>17,40</sup> (see also Refs. 41 and 42). In Table V we present mean absolute errors and standard deviations obtained for rotational levels ( $J = 1-3$ ) with the slight modification of the Hoy-Mills-Strey potential<sup>43</sup> suggested by Hoy and Bunker.<sup>40</sup> The rotational spacings corresponding to this potential almost coincide with those of observed levels, at least in the ground and first excited bending states of  $H_2O$  and  $D_2O$ .

In Tables V and VI we present the means of the deviations (and their standard deviations) of our results with those presented by Hoy and Bunker<sup>40</sup> and Rao<sup>44</sup> for the Rosenberg-Ermler-Shavitt *ab initio* potential<sup>45</sup> (Table VI) and by Rao<sup>44</sup> for the *ab initio* potential calculated by Hennig *et al.*<sup>46</sup> (Table VII). (It should be mentioned that the force constant  $f_{ra}$  is given in Table X of Rao<sup>44</sup> with the sign opposite to that of the original.<sup>46</sup> Since we do not know whether this is a misprint or an error in the program we have included calcu-

lations for both values. For the discussion here the difference is negligible. The comparison in Table VI makes use of the value given by Hennig *et al.*<sup>46</sup>)

Note that Rao's calculations allow us to estimate the accuracy of our model in highly excited bending states. It can be seen that error only increases slightly with increasing bending excitation when averaging over stretching modes is applied. This clearly contrasts with the behavior of the models which have the bond lengths fixed at the equilibrium value.

In Table VII we compare the predictions of our model for the rotational levels of the fourth excited bending state with those calculated using the empirical rotational constants in Ref. 47. Levels which were observed by Camy-Peyret *et al.*<sup>47</sup> are marked by asterisks. The last column gives the rotational energies predicted by our model for the fifth excited bending state. The calculations were carried out for the Hoy-Bunker potential.<sup>40</sup>

In conclusion, we have established that a simple dynamical model, previously used to study angular correlations in two-electron atoms, can provide quantitative descriptions of large-amplitude bending vibrations and bending-rotation interactions in the molecule H<sub>2</sub>O and its isotopes.

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