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Variational calculation of the rovibrational spectrum of H₂O using the coupled-rotor basis

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We present rovibrational energies and transition intensities for H₂O calculated at several levels of approximation, beginning with the adiabatic approximation (separating slow bending and rotation from fast stretching modes), then coupling the slow modes with the symmetric stretch, and culminating with the inclusion of all the couplings in the Hamiltonian. Evaluation of each approximation is made by comparing the results of the *ab initio* spectra to experiment. A space-fixed rovibrational basis set is used for the variational calculations.

INTRODUCTION

Calculation of the rotational–vibrational spectrum of polyatomics has proven to be one of the most challenging tasks for the molecular theorist. In many cases, even triatomics have not yet been modeled sufficiently well to describe many states located experimentally. For example, although high resolution experiments for H₂O abound (Refs. 1–21 in Jensen's article¹), no theoretical method yet available has been adequate to assign and describe many of the highly excited rovibrational levels seen experimentally. Only recently, with the advent of very fast computers and efficient algorithms, has it become possible to perform accurate calculations of a large number of rovibrational energy levels.

The first essential progress since the pioneering work of Whitehead and Handy² was made by Chen, Maessen, and Wolfsberg,³ who calculated the rotational structure of the three fundamental bands and the $2\nu_2$ band with a reported accuracy of about 0.01 cm^{-1} using the method of Whitehead and Handy.² The rotational structure of some other low-lying overtones was calculated by Carter and Handy,⁴ using the bisector-frame Hamiltonians of Carter, Handy, and Sutcliffe.⁵

Another important development is Jensen's optimization¹ of the parameters of a potential function using the so-called "Morse-oscillator rigid bender internal dynamics (MORBID)" basis set.⁶ The fitting was performed for 550 observed rotation–vibration levels of six isotopic modifications of water. The high level of accuracy of Jensen's work provided both a standard for variational calculations and a spectroscopically accurate potential surface for energies up to $19\,000\text{ cm}^{-1}$ above the zero point.

High-lying vibrational energy levels were attacked from a completely different approach by Bačić, Watt, and Light (BWL).⁷ They made significant progress in this direction for $J = 0$ vibrational states of H₂O by calculating almost 200 vibrational states with impressive accuracy combining a discrete variable representation (DVR) method with a distributed Gaussian basis (DGB). Choi and Light⁸ have recently adapted a three-dimensional DVR to compute many $J \neq 0$ states.

Our own approach, stemming historically (but no longer logically or computationally) from the particles-on-spheres (POS) model of Natanson *et al.*^{9–11} has now converged very closely to the DVR approach and includes $J \neq 0$ states. Moreover, we compute transition intensities using the wave functions directly to generate an *ab initio* spectrum for low-lying rovibrational levels of water in addition to the highly excited vibrational energy levels of the water molecule. Since the experimental spectrum of water is well understood and extensive within the limits of this study, we use water as a test for our method before proceeding to other triatomics.

Standard basis sets of closed functional form utilized so far for the water molecule^{1,3,4} have a common shortcoming—they span Hilbert spaces which differ from that spanned by exact eigenfunctions. This complication comes from nonphysical singularities which are an integral part of any approach separating overall rotations by means of a body-fixed frame.¹² These singularities are probably irrelevant for low-lying levels, but could become crucial when a large part of the nuclear configuration space is accessible, as we can expect for highly excited vibrational states.

For the Wilson–Howard–Watson Hamiltonian¹³ exploited in the Whitehead–Handy variational method,² complications arise when the vibrations carry the system out of the region where vibrational coordinates are in one-to-one correspondence with nuclear geometries.¹⁴ The singularity of the Hamiltonian at the boundaries of such regions was

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realized by Adamov and Natanson.¹⁵ The direct consequence of their analysis is that an exact vibrational wave function cannot be rigorously represented as a converged series in the harmonic oscillator basis. Failure of vibrational calculations to converge due to the boundary singularities was indeed observed by Bartholomae, Martin, and Sutcliffe¹⁶ for the CH₂⁺ molecular ion (see Ref. 17 for comments). For triatomic molecules, linear configurations are the only source of the boundary singularities,¹⁷ but in general the boundaries of the one-to-one regions include nonlinear geometries making it extremely difficult to satisfy the correct boundary conditions with a separable basis set. Though the variational calculations of Chen, Maessen, and Wolfsberg³ do converge, the effects of singularities could be significant for highly excited vibrational states.

As follows Natanson and Adamov's analysis,¹⁸ similar boundary singularities exist for the Hougen–Bunker–Johns (HBJ) Hamiltonian.¹⁹ Without pursuing here the complicated analysis of the boundary conditions, let us simply note that the singularities exist in both HOH and OHH linear configurations in the HBJ representation. The MORBID basis set^{1,6} satisfies the correct boundary condition only in HOH linear configurations, though these configurations are far more crucial for calculating highly excited states of H₂O than HHO.

The representation of choice for describing the full range of states including high-energy, large-amplitude vibrations is the bisector frame representation.⁵ However, this representation generates divergences, particularly for linear configurations of triatomics, as already noted. This problem was addressed by Sutcliffe and Tennyson,²⁰ who examined basis sets both in the bisector-frame coordinates and in a finite-central-mass modification of Breit's coordinates.²¹ They showed that the singularities cancel in the latter system, but were unable to show this for the former system.

As OHH configurations were our special interest,²² we were looking for a basis set that is free from outlined defects everywhere in the physically accessible region of the nuclear configurational space. This leads us^{9–11} to the coupled rotor basis set

$$|j_1 j_2 J\rangle = \sum_{m_1} Y_{m_1}^{j_1}(\hat{\mathbf{R}}_1) Y_{-m_1}^{j_2}(\hat{\mathbf{R}}_2) \langle j_1, m_1; j_2, -m_1 | J 0 \rangle, \quad (1)$$

where $\hat{\mathbf{R}}_1$, $\hat{\mathbf{R}}_2$ are the unit vectors drawn from the oxygen toward the hydrogens. Use of the space-fixed basis set provides a convenient way to construct wave functions that satisfy the correct boundary conditions, including linear configurations. Moreover, while it is difficult to construct a separable body-fixed representation that satisfies the correct boundary conditions, constructing such a space-fixed basis requires less effort. In Appendix A, we show how a separable space-fixed basis set can be constructed for some four-atom molecules such as H₂O₂, HCCH, and H₂CO.

After it has been established that the space-fixed basis functions span the Hilbert space of interest, they can be converted to the body-fixed representation. For a variety of body-fixed frames, these wave functions can be written in the following general form

$$|j_1 j_2 J\rangle = \sum_K \mathcal{D}_{0-K}^{J*}(\Omega) F_{j_1 j_2}^{JK}(\theta_{12}), \quad (2)$$

where the functions $F_{j_1 j_2}^{JK}(\theta_{12})$ are determined by the particular choice of the frame. Incorporation of the permutational symmetry for *ABA* molecules can be most conveniently done in the bisector frame. The explicit expressions for the functions $F_{j_1 j_2}^{JK}(\theta_{12})$ in Eq. (2) were given by Nikitin and Ostrovsky²³ and exploited in detail by Hunter and Berry.²⁴ The computational technique developed in the latter work was used by us¹¹ to calculate transition matrix elements with the dipole moment function expressed in the bisector frame and is used here for the same purpose.

The basis set in the Breit-style body-fixed frame suggested by Sutcliffe and Tennyson²⁰ is connected with the basis set (1) via the linear transformation given by Eq. (A14) of Schatz and Kuppermann.²⁵ This implies that we deal with wave functions that satisfy the correct boundary conditions and thus the singularities in linear configurations compensate each other. The same is true for the bisector frame if basis set (2) is chosen by the functions described in Refs. 23 and 24. A certain advantage of the space-fixed representation (1) is that the kinetic energy operator has a much simpler form than its complementary body-fixed representation.

In this article, building on the POS model, we develop an accurate method for calculating rovibrational energy levels and intensities of H₂O and, more generally, a method that may be used to compute *spectra* of floppy three- and four-atom molecules. We thereby develop and discuss a hierarchy of methods, from the POS model and its neglect of couplings, through higher refinements to the most accurate method with all couplings as fully included as a finite-basis method permits. [No variational calculations of microwave transition intensities have been reported so far although significant progress has been made recently in this direction with applications to CH₂,²⁶ to H₂O⁺,²⁷ and to HLiH[−] and HCS[−] (Ref. 28)].

We examine four levels of approximation in this article. The first is the POS method, already introduced and discussed in Refs. 9–11, which serves as the primitive starting point for all the others. The next level is the adiabatic approach previously investigated for *J* = 0 states by Johnson and Reinhardt²⁹ and Bačić, Watt, and Light (BWL),⁷ and applied here to states with nonzero angular momentum. In the next level of refinement, we couple stretches of only one symmetry at a time, using the basis of symmetric and antisymmetric stretching states. Finally, we include all the stretch–bend couplings simultaneously. Here we refer to the latter two approaches as the supradiabatic method and the accurate method, respectively.

The differences between the adiabatic and accurate methods for *J* = 0 states are discussed at length by BWL. They find, not surprisingly, that the adiabatic approximation breaks down as more than one quantum is fed into the bending mode. The neglect of stretch–bend couplings in the adiabatic model ignores the nearly 2:1 stretch-to-bend frequency ratio and hence the well-known Fermi resonances. Here, we emphasize the effects of the various levels of approximation on the *J* ≠ 0 levels. For *J* = 0, there is no cou-

pling between the symmetric and antisymmetric stretching states, so in this case the supradiabatic and accurate methods are the same. However, this is no longer the case when $J \neq 0$, and we must consider both methods.

The article is organized as follows: Below, we present our method for calculating the adiabatic and nonadiabatic rovibrational spectrum of H₂O. We then discuss results of the calculations and compare each level of approximation, i.e., the POS and adiabatic approximations, the supradiabatic method, and the accurate method.

ROVIBRATIONAL MODEL FOR WATER

As suggested in Refs. 9(b) and 29, we write the space-fixed Hamiltonian in Radau coordinates

$$\hat{H} = -\frac{1}{2m} \left[\left(\frac{\partial}{\partial \mathbf{R}_1} \right)^2 + \left(\frac{\partial}{\partial \mathbf{R}_2} \right)^2 \right] + V(\mathbf{R}_1, \mathbf{R}_2), \quad (3)$$

where m is the mass of the light atoms. We use Radau coordinates, rather than local coordinates used previously,^{9,10} because there are fewer coupling terms in the Hamiltonian and they appear in the potential rather than in the kinetic energy.

The Radau coordinates, specific for XY_n systems, have the properties that the kinetic energy and the angular momentum are diagonal and all the identical Y particles are treated symmetrically. They were first introduced by Radau³⁰ and reintroduced independently by Möbius,³¹ Adamov and Natanson,³² and Smith.³³ For H₂O, they are defined as

$$\mathbf{R}_1 = \mathbf{r}_1 - \mathbf{r}_B, \quad \mathbf{R}_2 = \mathbf{r}_2 - \mathbf{r}_B,$$

$$\mathbf{r}_B = \alpha \mathbf{r}_O + \frac{(1-\alpha)}{2} \sum_{i=1}^2 \mathbf{r}_i,$$

$$\alpha = \sqrt{m_O/M_{O_2}}, \quad M_{O_2} = m_O + 2m.$$

In H₂O, the mass of the oxygen atom is so much greater than that of a hydrogen, that the origin, point B , is very near the oxygen atom. The physical interpretation gained in the local coordinate picture is largely preserved, but the off-diagonal contributions to the kinetic energy in the local coordinate Hamiltonian are avoided.

The wavefunction is expanded in a basis of stretching and bend-rotation functions

$$\Psi_{v,\tau}(\mathbf{R}_1, \mathbf{R}_2) = \frac{1}{R_1 R_2} \sum_{\nu} \Phi_{\nu}(R_1, R_2; \gamma) \chi_{v,\tau}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2). \quad (4)$$

The quantum number ν represents the stretching state described by $nm\kappa$, where n and m are the number of stretching quanta in each bond and κ is the permutational symmetry of $\Phi(R_1, R_2; \gamma)$. Using the notation of Child and Lawton,³⁴ κ is $+$ ($-$) for symmetric (antisymmetric) states. The index τ includes the number of bending quanta, the total angular momentum and the rotational quantum numbers K_a and K_c . The internal bond angle in Radau coordinates γ is defined by

$$\cos \gamma = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1), \quad (5)$$

where θ_i, ϕ_i are spherical coordinates of the Radau vectors in the space-fixed frame.

The function $\Phi_{\nu}(R_1, R_2; \gamma)$ is a solution to the fixed-angle Schrödinger equation with the radial Hamiltonian h_r ,

$$[h_r - \epsilon_{\nu}(\gamma)] \Phi_{\nu}(R_1, R_2; \gamma) = 0, \quad (6)$$

where

$$h_r = -\frac{1}{2m} \left[\left(\frac{\partial}{\partial R_1} \right)^2 + \left(\frac{\partial}{\partial R_2} \right)^2 \right] + V(R_1, R_2, \gamma). \quad (7)$$

The basis for expanding the solutions of Eq. (7) is comprised of symmetric and antisymmetric combinations of harmonic oscillator functions $f(R)$,

$$\Phi_{\nu}(R_1, R_2; \gamma) = \sum_{nm} c_{nm\kappa}(\gamma) N_{nm} [f_n(R_1) f_m(R_2) + \kappa f_m(R_1) f_n(R_2)], \quad (8)$$

where

$$N_{nm} = 1/\sqrt{2}, \quad \text{for } n \neq m,$$

$$N_{nm} = 1/2, \quad \text{for } n = m.$$

The two-dimensional Schrödinger equation (6) is integrated at the Gauss-Legendre quadrature points. The function $\epsilon_{\nu}(\gamma)$, instead of the potential $W_{\nu}(\gamma)$,^{9(b)} is the effective potential for the bend-rotation problem. It is essential that all potential couplings [the functions $W_{\nu\nu'}(\gamma)$ in Ref. 9(b)] vanish in the new basis set

$$\Psi_{nm\kappa, j_1 j_2 J; t, \pm}^{\pm, t}(\mathbf{R}_1, \mathbf{R}_2) = \frac{1}{R_1 R_2} \Phi_{nm\kappa}(R_1, R_2; \gamma) |j_1 j_2 J; t, \pm\rangle, \quad (9)$$

$$t_{\kappa} = t, \quad \text{for } \kappa = +, \quad t_{\kappa} \neq t, \quad \text{for } \kappa = -,$$

with the functions $|j_1 > j_2, J; t\rangle$ given by Eqs. (24a) and (24b) in Ref. 9(a). The label \pm stands for the parity associated with the sign of the factor $(-1)^{j_1+j_2}$; the label t stands for permutational symmetry. Evaluation of the kinetic energy operator in the basis set (9) is a more complicated problem because the functions Φ_{ν} now depend on γ . To take into account this dependence, the γ -dependent coefficients $c_{nm\kappa}(\gamma)$ on the right-hand side of Eq. (8) are expanded in Legendre polynomials

$$c_{nm\kappa}(\gamma) = \sum_{\beta} c_{nm\kappa}^{\beta} P_{\beta}(\cos \gamma) \quad (10)$$

and the basis functions (9) are represented as

$$\begin{aligned} \Psi_{nm\kappa, j_1 j_2 J; t, \pm}^{\pm, t}(\mathbf{R}_1, \mathbf{R}_2) &= \frac{1}{R_1 R_2} \sum_{j_1' j_2'} F_{nm}^{t, j_1' j_2'}(R_1, R_2) \\ &\times |j_1' > j_2', J; t, \pm\rangle \\ &+ \frac{1}{R_1 R_2} \sum_{j_1' j_2'} F_{nm}^{t', j_1' j_2'}(R_1, R_2) \\ &\times |j_1' > j_2', J; t', \pm\rangle, \end{aligned} \quad (11)$$

where $(-1)^{j_1'+j_2'} = (-1)^{j_1+j_2}$, the label $t' = s$, a in the second term differs from t ,

$$F'_{nm''j_1j_2j_1'j_2'}(R_1, R_2) = \sqrt{\frac{2 - \delta_{j_1'j_2'}}{2 - \delta_{j_1j_2}}} \sum_{n' < m', \beta} c_{nm'', n'm'}^\beta N_{n'm'} \\ \times [f_\beta(j_1j_2j_1'j_2'; J) + (t)(-1)^J \\ \times f_\beta(j_1j_2j_2'j_1'; J)] [f_{n'}(R_1)f_{m'}(R_2) \\ + \kappa f_{m'}(R_1)f_{n'}(R_2)] \quad (12)$$

with $(s) = +1$ and $(a) = -1$, and $f_\beta(j_1j_2j_1'j_2'; J)$ are the Percival–Seaton coefficients $\langle j_1j_2J | P_\beta(\cos \gamma) | j_1'j_2'J \rangle$.³⁵ When deriving Eq. (11), we also took into account that according to the definition of these coefficients

$$f_\beta(j_1j_2j_1'j_2'; J) = f_\beta(j_1'j_2'j_1j_2; J). \quad (13)$$

Evaluation of the angular part of the kinetic energy operator in the basis set (11) is a straightforward, though time-consuming, problem.

Diagonalizing the Hamiltonian in the basis set (9) provides us with the accurate rovibrational eigenvalues to an arbitrary convergence. There are several approximations that can be made to simplify this calculation. We will begin by describing them in order of increasing complexity. Our first approximation, a refinement of the POS method of Refs. 9–11, is the adiabatic approximation. The adiabatic approximation reduces the basis set (9) to a single stretching wave function for each bend–rotational level. The symmetry of the stretching wave function is determined by the value of κ in Eq. (8), and the level is determined by the nm pair. In the POS model, $\Phi_v(R_1, R_2; \gamma)$ is replaced by $\Phi_v(R_1, R_2; \gamma_e)$, where γ_e is the equilibrium bending angle in Radau coordinates, 107.76° for H₂O. As already mentioned, the adiabatic approximation accounts for angular variation in the stretching function. The adiabatic approximation and its effect on $J = 0$ states was studied extensively by Johnson and Reinhardt²⁹ and BWL.⁷

In the next level of approximation, the supradiabatic method, the basis set includes all the adiabatic states with the same value of κ . All the stretching states are thus coupled to each other as long as they belong to a Φ_v of the same symmetry κ and therefore all the bend–rotation states that are coupled to the stretching states of this symmetry are coupled together. The important 1:2 stretch–bend Fermi resonance neglected in the adiabatic approximation is taken into account here. For $J = 0$, this method is exact since the coupling terms between states of different κ are zero when there is no angular momentum. For small J , the coupling terms are very small and this approximation is very good.

The coupling terms neglected by the supradiabatic method mix the functions Φ_v and $\Phi_{v'}$ of different symmetry κ through moment-of-inertia terms. These are the coefficients for the couplings of angular momentum states of different symmetry. The nonadiabatic coupling is of the form

$$T_{v\tau, v'\tau'} = \sum_{j_1'j_2'} \int \left[\frac{j_1'(j_1' + 1)}{R_1^2} + \frac{j_2'(j_2' + 1)}{R_2^2} \right] \\ \times F'_{nm''j_1j_2j_1'j_2'}(R_1, R_2) F'^{\tau'}_{\tilde{n}\tilde{m}''\tilde{j}_1\tilde{j}_2\tilde{j}_1'\tilde{j}_2'}(R_1, R_2) \\ \times dR_1 dR_2, \quad (14)$$

where $t \neq t'$. Because we are mixing the symmetries, we introduce many more off-diagonal elements in the kinetic energy operator, forcing us to calculate many more terms, each small in practice, than we had computed previously. The Hamiltonian matrix we are left to diagonalize is correspondingly large, since we must now include angular momentum quantum numbers corresponding to different symmetries with the radial wave functions of different values of κ .

In practice, to solve the two-dimensional radial equation, we used 48 Gauss–Legendre points for the calculations of the levels listed here. Eighteen harmonic oscillator functions were symmetrized in the basis and 18 radial points were used for the radial integration, enough for convergence of the levels presented here, as numerical tests showed. The eigenvalues at all of the Gauss–Legendre points, taken together, define the bending potential used in the angular calculation. The eigenvector coefficients are also extracted so that their angular dependence can be included in the angular equation.

After diagonalizing the two-dimensional Hamiltonian, we followed the procedure of BWL by truncating the number of coefficients in the expansion of the radial wave function (really sets of Legendre polynomial expansions) to the number required to reach convergence. For n harmonic oscillator functions, the size of the expression for each radial wave function is $n[n + (-1)]/2$ for symmetric (antisymmetric) states. With the BWL procedure, we reduce n from 18 to about 8. Therefore, for symmetric states, the basis is reduced from 171 to 36. We couple this truncated set with the basis of coupled spherical harmonics, in practice, 40.

Calculation of transition intensities is a complement to our previous computations using POS wave functions. For those calculations, we used the Rosenberg–Ermiler–Shavitt (RES) electric dipole moment function³⁶ and separable POS wave functions

$$\Psi_{v,\tau}(\mathbf{R}_1, \mathbf{R}_2) = \frac{1}{R_1 R_2} \Phi_v(R_1, R_2) \chi_\tau(\theta_1 \phi_1 \theta_2 \phi_2) \quad (15)$$

to compute matrix elements of rovibrational transitions. The RES function is expressed in the internal bisector frame of the water molecule, while our wave functions are written in space-fixed coordinates. To perform the integration, the eigenfunctions are transformed to the bisector frame $x'y'z'$ using Eq. (2), in which the functions of the interbond angle were computed by means of the computational technique adopted from Ref. 24. Details of the bend–rotation intensity calculations are in Ref. 11.

To include stretches in the intensities calculations, we no longer perform the radial integration as $\delta(R - R_e)$, as done for bend–rotation calculations in the POS approximation, but now must integrate over the radial variables at each of the Gauss–Legendre points of the angular integration. As the space-fixed basis set is attached to Radau vectors, the appropriate body-fixed frame $x''y''z''$ should be chosen so that its x'' axis bisects the angle formed by these vectors. One thus needs to transform the RES dipole moment function given in the bisector frame $x'y'z'$ to the Radau vector bisector frame $x''y''z''$. The form of this transformation is given in Appendix B. If the dipole functions in the two frames are

represented by complex numbers $\mu' = \mu'_x + i\mu'_z$ and $\mu'' = \mu''_x + i\mu''_z$, respectively, then the transformation takes the form

$$\mu''(r_1, r_2, \theta_{12}) = e^{i\eta(r_1, r_2, \theta_{12})} \mu'(r_1, r_2, \theta_{12}), \quad (16)$$

where η is derived in Appendix B.

The transition matrix elements for the functions μ'_x and μ''_x are computed by expressing their arguments r_1, r_2, θ_{12} (bond coordinates) in terms of the magnitudes R_1, R_2 of the Radau vectors and the angle γ between them. The appropriate transformations were obtained using Eqs. (2.21) and (2.22) in Ref. 29. Due to the small H/O mass ratio, the differences between the variables r_1, r_2, θ_{12} and R_1, R_2, γ contribute only a relatively small change to the intensities. Because of the combination of the small mass ratio and the absence of large differences in the two bond lengths, the switching angle η is *very* small. We set it to zero in our calculations. To compute the intensities, we make use of representation (4) for the wave functions and compute first the transition integrals over R_1 and R_2 with $\Phi_v(R_1, R_2; \gamma)$ for γ at each quadrature point. The procedure then follows that of Ref. 11. We thereby compute the full three-dimensional transition amplitudes to an approximation as good as the wave functions and the dipole moment function permit. We present results from wave functions computed by the supradiabatic method. Although this method neglects symmetric-antisymmetric stretch couplings through rotation, we present intensities involving only the fundamental vibrational bands and the supradiabatic method is quite reliable in this regime.

RESULTS AND DISCUSSION

Energy levels

All calculations presented in these tables were done using the Carney-Curtiss-Langhoff potential,³⁷ mostly because this was the potential used for the accurate calculations of Chen, Maessen, and Wolfsberg (CMW),³ the only converged calculations of rovibrational levels available at the time this work was started. Vibrational levels are given the standard local mode assignments $\nu_2(nm)^*$.³⁴ In Table I, we present the discrepancies between our calculations and those of CMW for $J = 1$ levels. An analysis of these discrepancies shows that our calculations reported here have converged within 0.1 cm^{-1} . All our levels lie above those com-

puted by CMW, which confirms a very high quality of their calculations. To compare, we also report the discrepancies found by the latter authors for Hoy and Bunker's perturbation calculations.³⁸ The discrepancies found in Ref. 3 are generally significantly larger than those between the variational calculations. This is an indirect argument in support of the conclusion that the discrepancies are caused by severe perturbing effects mentioned in their summary by Beardsworth *et al.*³⁹ as a possible limitation in using the nonrigid bender Hamiltonian for H₂O.

Results of the accurate, supradiabatic, and adiabatic calculations for $J = 1$ and $J = 2$ are listed in Table II. We see immediately that the adiabatic approximation errs significantly even in the low bending states and gets worse with increasing excitation in the bending mode. This trend is consistent with that found by BWL for $J = 0$ states.

The supradiabatic method, which is exact for the $J = 0$ states, improves the results of the rovibrational energies over the adiabatic calculation. It appears that the most important couplings in the Hamiltonian required to compute reliable intermediate rovibrational energies and high-lying vibrational levels are the stretch-bend couplings ignored by the adiabatic approximation. The couplings neglected by the supradiabatic method are not very important for any of these low- J states. We see from Table II that nowhere is the difference between accurate and supradiabatic levels (ΔE_i) larger than 0.5 cm^{-1} . [For reasons that are not clear, nonadiabatic corrections to the 2_{02} and $0(10)^+$ rovibrational level are extremely sensitive to the error in the adiabatic vibrational basis, and we could not compute this energy accurately.] There are certain trends, however, that suggest the coupling does become more important with vibrational excitation. In particular, it appears that the coupling is most important to rotational structure with bending excitation. (We have too few accurate rotational energies to find any trends of how significant these couplings are with increasing J .) However, to the degree of the accuracy of existing potential surfaces for water, most of which differ from one another by such amounts, the supradiabatic method works very well.

Intensities

We now turn to the intensities. Here we present results using only supradiabatic wave functions in our calculations; we expect the wave functions to be more sensitive than the energies in the variational calculation, and we already determined the limitations of the adiabatic approach. Our values of transition intensities and experimental values of Flaud, Camy-Peyret, and Toth (FCT),⁴⁰ are listed in Table III. Using the supradiabatic wave functions, we have also computed transition intensities involving states with $J = 3$, not computed in our previous work with more approximate wave functions.¹¹ Table III (A) lists rotational transitions in the $2\nu_2$ band with an intensity greater than $1 \times 10^{-21} \text{ (cm}^{-1}/\text{molecule cm}^{-2})$. Previously,¹¹ we noted that we were unable to compute intensities in the $2\nu_2$ band accurately for any J using the POS wave functions because the method did not include the stretch-bend couplings that are particularly prominent due to the $2\nu_2-\nu_1$ interaction.

Before comparing our results with experimental results,

TABLE I. The discrepancies between our calculations and those of Chen, Maessen, and Wolfsberg (CMW) for $J = 1$ levels along with differences between Hoy and Bunker's calculations and CMW, reported by CMW (Ref. 3).

	0(00)		1(00)		0(10) ⁺ 0(10) ⁻ 2(00)		
	(CCL) ^a	(HB) ^b	(CCL) ^a	(HB) ^b	(CCL) ^a	(CCL) ^a	(CCL) ^a
1 ₀₁	0.02	-0.037	0.03	-0.047	0.09	0.06	0.01
1 ₁₁	0.03	-0.088	0.05	-0.127	0.08	0.03	0.08
1 ₁₀	0.03	-0.083	0.04	-0.132	0.03	0.03	0.05

^a Calculations based on the Carney-Curtiss-Langhoff potential.

^b Calculations based on the Hoy-Bunker potential, using Tables II and IV in Refs. 38 and 3, respectively.

TABLE II. (A) Listed are $J = 1$ energies and (B) listed are $J = 2$ energies above vibrational states indicated in the first column. Energies are listed for combinations of the rotational quantum numbers K_a and K_c , respectively. Vibrational states are listed using standard local coordinate notation. $\Delta E_1 = E_{\text{suprad}} - E_{\text{acc}}$, where approximate levels are solved with a Hamiltonian in which couplings of symmetric and antisymmetric radial states are neglected (for 1_{10} , these energies are identical). $\Delta E_2 = E_{\text{ad}} - E_{\text{acc}}$ is the difference between the adiabatic levels and the accurate ones. Experimental levels (Ref. 45) are listed for comparison. Energies are given in cm^{-1} .

(A)	1_{01}				1_{11}				1_{10}			
	Expt.	E_{acc}	ΔE_1	ΔE_2	Expt.	E_{acc}	ΔE_1	ΔE_2	Expt.	E_{acc}	ΔE_1	ΔE_2
0(00)	23.79	23.82	0.02	0.07	37.14	37.28	0.03	0.11	42.37	42.50	...	0.09
1(00)	23.81	23.77	0.11	0.26	40.22	40.72	0.12	0.38	45.76	46.17	...	0.30
2(00)	23.81	23.70	0.20	0.45	44.46	45.38	0.20	0.72	50.28	51.05	...	0.63
0(10) ⁺	23.40	23.46	0.03	0.08	36.24	36.32	0.03	0.06	41.44	41.53	...	0.04
0(10) ⁻	23.57	23.61	-0.02	0.02	35.57	35.84	-0.01	0.06	41.05	41.12	...	0.09
3(00)	23.80	23.63	0.29	0.62	50.68	52.05	0.29	1.35	56.75	57.93	...	1.13
1(10) ⁺	23.42	23.65	0.11	0.02	39.18	39.73	0.12	0.18	44.69	45.39	...	-0.12
1(10) ⁻	23.60	23.55	0.08	0.22	38.49	38.95	0.08	0.34	44.09	44.48	...	0.28
4(00)		23.56	0.37	0.78		62.38	0.38	2.31		68.48	...	1.00
2(10) ⁺		23.38	0.21	0.41		44.33	0.21	0.35		50.03	...	0.16
2(10) ^{-a}	23.63	23.49	0.17	0.42	42.15	43.12	0.17	0.71	48.05	48.87	...	0.60

(B)	2_{02}				2_{12}				2_{11}			
	Expt.	E_{acc}	ΔE_1	ΔE_2	Expt.	E_{acc}	ΔE_1	ΔE_2	Expt.	E_{acc}	ΔE_1	ΔE_2
0(00)	70.09	71.69	0.12	0.28	79.50	79.79	0.02	0.20	95.18	95.34	0.03	0.25
1(00)	70.22	70.39	0.23	0.66	82.32	82.22	0.05	0.61	98.90	99.13	0.12	0.78
2(00)	70.33	71.57	0.11	0.79	86.27	87.89	0.07	1.10	103.71	104.11	0.21	1.42
0(10) ⁺	68.89	b			77.84	78.14	0.01	0.14	93.41	93.63	-0.04	0.20
0(10)	69.29	70.90	0.48	0.62	77.64	77.67	0.04	0.21	93.46	93.63	-0.04	0.16
3(00)									110.40	111.06	0.31	2.23
1(10) ⁺									97.03	97.43	0.13	0.55

	2_{21}				2_{20}			
	Expt.	E_{acc}	ΔE_1	ΔE_2	Expt.	E_{acc}	ΔE_1	ΔE_2
0(00)	134.90	135.42	0.04	0.37	136.16	136.93	0.07	0.40
1(00)	147.56	149.39	0.13	1.18	148.74	150.53	0.13	1.21
2(00)	164.50	167.90	0.22	2.44	165.56	169.06	0.14	2.37
0(10) ⁺	131.65	131.94	0.05	0.16	132.92	134.55	0.05	0.28
0(10)	129.80	130.06	-0.02	0.29	131.28	131.59	0.20	0.52
3(00)	188.55	193.59	0.31	4.42				
1(10) ⁺	143.77	146.12	0.16	0.04				

^a Experimental values are from Ref. 46.

^b Refer to the text.

we must first determine how accurate the RES dipole moment function is for a particular band. Calculation of the integrated $2\nu_2$ band intensity using the accurate wave functions of Carney, Sprandel, and Kern (CSK)⁴¹ and the RES function gives a value of 7.9×10^{-20} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$), very close to the FCT result of 7.6×10^{-20} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$).⁴⁰ We have also computed the integrated $2\nu_2$ band intensity and obtained a result of 7.8×10^{-20} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$), quite close to CSK and FCT. We therefore expect that errors of transition intensities in the $2\nu_2$ band are largely due to our wave functions and not to the RES dipole moment function. Inspection of part A of Table III reveals that the *ab initio* intensities are consistently close to the experimental results, becoming slightly worse as the energy increases. In general, the wave functions in the $2\nu_2$ band are reliable in the supradiabatic approximation.

Part B of Table III lists rotational transitions in the ν_1

band involving states up to $J = 3$ for transitions with an intensity of more than 4×10^{-21} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$). Again, we first consider the accuracy of the RES dipole moment function in the ν_1 band. CSK found that using their accurate wave functions and the RES function, the integrated ν_1 band intensity is 1.9×10^{-18} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$) and is 3.8 times greater than the FCT result of 4.9×10^{-19} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$). We obtained the same result as CSK in our own calculations, 1.9×10^{-18} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$). We expect that our calculations of rotational transitions will deviate from the FCT values by about a 4:1 ratio, assuming a constant error in the RES function. We take this to mean that the RES dipole moment function does not accurately evaluate the ν_1 band, in contrast to the bending transitions. Hence we must ask how consistent our results remain over all the energies considered. The ratio of our results to the FCT results can be accounted for by assuming a discrepancy of a factor of 4 in the RES dipole function for ν_1 at the

TABLE III. (A) Intensities for rovibrational transitions in the $2\nu_2$ band of water. Energies, from Ref. 40, are given in cm^{-1} . Intensities are listed for a temperature of 296 K. The numbers in parentheses are powers of ten. (B) Intensities for rovibrational transitions in the ν_1 band of water. We estimate that *ab initio* results should be greater than the experimental results by a factor of 3.8 due to the RES dipole moment function (refer to the text). (C) Intensities for rovibrational transitions in the ν_3 band of water.

	ΔE	$J_{K_a K_c}^0 \leftarrow J_{K_a K_c}$	E_{lower}	Intensity ($\text{cm}^{-1}/\text{molecule cm}^2$)		
				Ref. 40, I_1	This work, I_2	I_2/I_1
(A)	3067.012	$1_{10} \leftarrow 2_{21}$	134.902	1.05(−19)	1.20(−19)	1.14
	3095.095	$1_{01} \leftarrow 2_{12}$	79.496	1.30(−19)	1.51(−19)	1.16
	3101.156	$2_{12} \leftarrow 3_{03}$	136.761	1.17(−19)	1.33(−19)	1.14
	3115.877	$3_{03} \leftarrow 3_{12}$	173.365	1.29(−19)	1.51(−19)	1.17
	3122.470	$3_{12} \leftarrow 3_{21}$	212.156	1.16(−19)	1.22(−19)	1.05
	3133.070	$1_{01} \leftarrow 1_{10}$	42.372	1.46(−19)	1.74(−19)	1.19
	3178.119	$1_{10} \leftarrow 1_{01}$	23.794	1.53(−19)	1.88(−19)	1.23
	3197.865	$3_{12} \leftarrow 3_{03}$	136.761	1.25(−19)	1.40(−19)	1.12
	3209.476	$3_{03} \leftarrow 2_{12}$	79.496	1.17(−19)	1.43(−19)	1.22
	3219.384	$3_{21} \leftarrow 3_{12}$	173.365	1.09(−19)	1.48(−19)	1.36
	3273.774	$2_{21} \leftarrow 1_{10}$	42.372	1.27(−19)	1.66(−19)	1.31
	3365.737	$3_{30} \leftarrow 2_{21}$	134.902	1.21(−19)	1.51(−19)	1.25
(B)	3503.276	$2_{21} \leftarrow 3_{30}$	285.419	1.61(−19)	6.17(−19)	3.83
	3522.741	$2_{12} \leftarrow 3_{21}$	212.156	5.41(−20)	2.09(−19)	3.86
	3563.590	$1_{10} \leftarrow 2_{21}$	134.902	8.18(−20)	3.61(−19)	4.41
	3598.136	$2_{12} \leftarrow 3_{03}$	136.761	4.61(−20)	2.22(−19)	4.82
	3600.958	$1_{01} \leftarrow 2_{12}$	79.496	6.69(−20)	3.13(−19)	4.68
	3615.237	$3_{12} \leftarrow 3_{21}$	212.156	2.37(−20)	1.39(−19)	5.86
	3618.007	$3_{03} \leftarrow 3_{12}$	173.365	4.05(−20)	2.19(−19)	5.40
	3638.082	$1_{01} \leftarrow 1_{10}$	42.372	7.38(−20)	4.20(−19)	5.69
	3674.697	$1_{10} \leftarrow 1_{01}$	23.794	1.56(−19)	9.67(−19)	6.20
	3690.632	$3_{12} \leftarrow 3_{03}$	136.761	2.20(−19)	1.43(−18)	6.50
	3711.103	$2_{12} \leftarrow 1_{01}$	23.794	2.07(−19)	1.48(−18)	7.14
	3711.876	$3_{03} \leftarrow 2_{12}$	79.496	2.06(−20)	1.73(−19)	8.42
	3746.323	$2_{21} \leftarrow 1_{10}$	42.372	1.72(−19)	1.27(−18)	7.38
	3800.443	$3_{30} \leftarrow 2_{21}$	134.902	3.23(−20)	8.56(−19)	4.53
(C)	3676.020	$2_{11} \leftarrow 3_{12}$	173.365	1.67(−19)	1.62(−19)	0.97
	3688.453	$2_{02} \leftarrow 3_{03}$	136.761	2.12(−19)	2.12(−19)	1.00
	3732.135	$0_{00} \leftarrow 1_{01}$	23.794	1.21(−19)	1.28(−20)	1.06
	3744.510	$3_{22} \leftarrow 3_{21}$	212.156	1.03(−19)	1.10(−20)	1.07
	3744.651	$3_{31} \leftarrow 3_{30}$	285.419	1.67(−19)	1.82(−19)	1.09
	3749.331	$1_{11} \leftarrow 1_{10}$	42.372	1.62(−19)	1.77(−19)	1.09
	3752.213	$2_{20} \leftarrow 2_{21}$	134.902	2.19(−19)	2.41(−19)	1.10
	3801.420	$2_{02} \leftarrow 1_{01}$	23.794	2.15(−19)	2.58(−19)	1.20
	3807.014	$2_{11} \leftarrow 1_{10}$	42.372	1.48(−19)	1.79(−19)	1.21
	3816.093	$3_{13} \leftarrow 2_{12}$	79.496	2.16(−19)	2.66(−19)	1.23

low energies, but the discrepancy gets systematically greater with increasing energy. If the error in the RES function is constant, an error may arise because the supradiabatic calculation does not fully account for stretch–rotation symmetry, since in this method the levels involving the symmetric stretch are not coupled to those involving the antisymmetric stretch, and this coupling becomes more important at higher energies. If the error in the RES dipole moment function is not constant, a greater part of the error may be in the dipole moment function itself.

Part (C) of Table III lists transitions in the ν_3 band with an intensity greater than 1×10^{-19} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$). The RES dipole moment function should give accurate results in the ν_3 band since the integrated band intensities of both CSK [7.9×10^{-18} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$)] and this work [8.5×10^{-18} ($\text{cm}^{-1}/\text{molecule$

cm^{-2})] based on the RES function give results close to the FCT value of 7.6×10^{-20} ($\text{cm}^{-1}/\text{molecule cm}^{-2}$). We find from Part (C) of Table III that the *ab initio* results using our wave functions are consistently accurate, though they do get slightly worse with higher energy. In fact, the errors in the *ab initio* intensities in each of the vibrational bands systematically increase with energy. This suggests that the errors in the RES dipole moment function are nonconstant and in part responsible for the discrepancies. If the errors were in the wave functions alone, we would not expect that the errors in the intensities would always increase with increasing energy, but rather that increases in one band would correlate with decreases in another band to which it is coupled. For a more complete analysis, it will be necessary to compute these intensities using wave functions from the fully coupled Hamiltonian to determine if this trend is due to

any approximations in the Hamiltonian.

The significance of the couplings at each level of approximation can now be summarized. In Refs. 9–11, we found that stretch–stretch and bend–rotation couplings in the POS model allow modest calculations of low-lying energy levels and intensities. Errors in the wave functions are reflected in the calculations of the transition intensities. The POS and adiabatic calculations are severely limited due to the neglect of stretch–bend couplings; with these methods, one can only calculate reasonable values for rotational transitions in the ground vibrational, pure ν_2 , and ν_3 vibrational bands, which are unaffected by Fermi resonances. The rovibrational energy levels themselves are not very accurate. Despite their inaccuracy, we demonstrated that the structure of the rotational levels due to vibrational excitation is predicted quite accurately by the POS model, better than many other approximate models now available.

In the adiabatic model, the complete angular dependence of the wave function is considered, as opposed to the POS method in which the angular dependence in the stretching functions is ignored. Nevertheless, bending excitations are only calculated for individual stretching levels. This is not a good approximation for highly excited states and we see significant deviations for accurate values of even low-lying rovibrational levels. For example, with only two quanta of bend, four of the five $J = 2$ states differ in energy by more than 1.0 cm^{-1} from the accurate results, and two of these differ by more than 2.0 cm^{-1} .

The supradiabatic method dramatically improves the results by including all the nonadiabatic couplings for $J = 0$ and neglecting only some very small terms for states of low J . The cost is the diagonalization of a larger matrix; computing the terms themselves does not consume much more time than for the adiabatic calculation. On the Cray X-MP/48, less than 2 h was needed to compute the levels listed here and some additional ones in the supradiabatic approximation, compared with about 15 h for the accurate calculation of the same levels. The off-diagonal nonadiabatic couplings required for the accurate calculation are relatively small, and are very costly to compute, since the kinetic energy term in the Hamiltonian is no longer diagonal. The result is that for rotational levels beyond $J = 2$, the calculation becomes very time intensive. An alternative in going from the supradiabatic to accurate calculation is to use a perturbation expansion, which should be both accurate and fast.

CONCLUSIONS

Starting with the particles-on-spheres model,^{9–11} we have extended our calculations of the spectrum of the water molecule by including all the couplings required to compute a high resolution spectrum. In doing so, we have examined various levels of approximation to determine the importance of each coupling with the goal of computing accurate energy levels, wave functions, and intensities. The very simple POS approximation is reliable for only the lowest rovibrational energy levels and intensities, and is unable to represent all the fundamental vibrational levels correctly because it does not account for the $2\nu_2-\nu_1$ Fermi resonance. However, for low-lying states that are unaffected by this coupling, the POS

method works very well. The more sophisticated adiabatic approach does a little better because the angular dependence of each stretching state is incorporated, but important stretch–bend couplings are still neglected, and for H₂O these couplings are the major obstacle for representing the intermediate and high-lying states. The supradiabatic method is the lowest-level calculation to include the stretch–bend couplings that are important for states of low J , and neglects only couplings of the symmetric and antisymmetric stretching states; it is exact for $J = 0$. This approximation preserves the diagonal kinetic energy terms when computed in the Radau coordinate scheme and gives very accurate energy levels for high vibrational and low rotational states, as well as reasonable intensities for many low-lying transitions. The accurate method as presented here needs to be made more efficient if it is to be applied to states highly excited in both vibrations and rotations; perturbation theory may be the answer here.

We anticipate that computing a larger rovibrational spectrum will permit the calculation and evaluation of the spectral statistics, a method that has been applied to vibrationally coupled and highly excited vibrational systems.⁴² However, we must compute an accurate spectrum for large J for any such analysis to be meaningful, since the dynamical interpretations of spectral statistics, such as the nearest-neighbor level spacings, are semiclassical. We must, therefore, compute many more rovibrational states using the accurate method before attempting to analyze the spectral statistics.

Some improvements of the current method would be useful before proceeding to further computations. The radial basis now consists of symmetrized coupled harmonic oscillators. We have found that the DGB offers a slight improvement in the convergence of the radial solution, but a far more dramatic improvement in efficiency is achieved by employing the numerical Numerov–Cooley basis.⁴³ Implementation of this basis is likely to facilitate the computation of higher states.

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APPENDIX A

Let us now show how the technique developed here can be extended to four-atom molecules. In this case, we have three coupled rotors ($\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2$). For $XYXX$ molecules with heavy Y and light X atoms (like HCCH or HOOH), the

vectors \mathbf{R}_1 and \mathbf{R}_2 are drawn from the centers of mass of the YX diatoms to the appropriate X atoms, whereas the vector \mathbf{R}_0 connects those two centers of mass. For H₂CO, \mathbf{R}_1 and \mathbf{R}_2 are the Radau vectors of the hydrogens in the CH₂ group, whereas the vector \mathbf{R}_0 is drawn from the center of mass of this atomic group to the oxygen. The coupled-rotor basis set is written as

$$|j_0, (j_1 j_2) j, J\rangle = \sum_m Y_{-m}^{j_0}(\hat{\mathbf{R}}_0) \mathcal{Y}_{j_1 j_2}^{jm}(\theta_1, \phi_1; \theta_2, \phi_2) \times \langle j_0, -m; j, m | J, 0 \rangle, \quad (\text{A1})$$

where θ_k, ϕ_k are spherical angles of the vector $\hat{\mathbf{R}}_k$ and $\mathcal{Y}_{j_1 j_2}^{jm}(\theta_1, \phi_1; \theta_2, \phi_2) = \mathcal{Y}_{j_1 j_2}^{jm}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2)$. Symmetrization of the wave functions (A1) with respect to permutation of identical particles and the inversion for molecules of both types is straightforward. [Symmetrization of the wave functions (A1) for the ammonia molecule would present a more challenging problem, but Radau coordinates are still the natural choice.]

By analogy with Eq. (A14) of Schatz and Kuppermann,²⁵ the basis functions (A1) can be represented as⁴⁴

$$|j_0, (j_1 j_2) j, J\rangle = \sum_m \mathcal{D}_{0m}^J(\Omega) \mathcal{Y}_{j_1 j_2}^{jm}(\theta_1, 0; \theta_2, \phi) \times \langle J, -m; j_0, m | J, 0 \rangle, \quad (\text{A2})$$

where $\phi = \phi_2 - \phi_1$ and Ω are Euler angles in the body-fixed frame attached to the vectors \mathbf{R}_0 and \mathbf{R}_1 according to Sutcliffe and Tennyson's recipe²⁰ (the vectors \mathbf{t}_1 and \mathbf{t}_2 in their notation). We can thus have three internal angles θ_1, θ_2 , and ϕ instead of the angle γ above, and the potential is now expanded as a series in the functions $\mathcal{Y}_{j_1 j_2}^{jm}(\theta_1, 0; \theta_2, \phi)$, instead of the Legendre polynomials in $\cos \gamma$.

APPENDIX B

The switching angle η between the bisector and Radau-vector-bisector body-fixed frames is most conveniently found by using the complex-number representation for two-dimensional vectors lying in the plane of the molecule.¹⁷ We choose the x and z projections of any such vector on the axes of the bisector frame to be the real and imaginary parts of the appropriate complex number. Let c_1 and c_2 be the complex-number representations of the vectors drawn from the oxygen to each of the hydrogens

$$c_1 = r_1 e^{i\theta_{12}/2}, \quad c_2 = r_2 e^{-i\theta_{12}/2}. \quad (\text{B1})$$

By analogy, we represent the Radau vectors as

$$\begin{aligned} \rho_1 &= R_1 e^{i\beta} = \alpha_+ c_1 + \alpha_- c_2, \\ \rho_2 &= R_2 e^{i(\beta - \gamma)} = \alpha_- c_1 + \alpha_+ c_2, \end{aligned} \quad (\text{B2})$$

where

$$\alpha_{\pm} = \frac{1}{2} \left(\sqrt{m_O / M_{O_{12}}} \pm 1 \right) = \frac{1}{2} (\alpha \pm 1). \quad (\text{B3})$$

By definition,

$$\rho_1^* \rho_2 = R_1 R_2 e^{-i\gamma} \quad (\text{B4})$$

and

$$\eta = \beta - \gamma/2, \quad (\text{B5})$$

so that

$$R_1 R_2 e^{2i\eta} = \rho_1^* \rho_2 \rho_1^2 / R_1^2 = \rho_1 \rho_2 = c_1 c_2 (\alpha_+^2 + \alpha_-^2) + \alpha_+ \alpha_- (c_1^2 + c_2^2). \quad (\text{B6})$$

Therefore,

$$R_1 R_2 e^{2i\eta} = \frac{m_O + m}{M_{O_{12}}} r_1 r_2 - \frac{m}{2M_{O_{12}}} (r_1^2 e^{i\theta_{12}} + r_2^2 e^{-i\theta_{12}}). \quad (\text{B7})$$

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