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A new method for calculating the vibration-rotation-tunneling spectra of molecular clusters and its application to the water dimer

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Abstract: A new method is developed for calculating the vibration-rotation-tunneling spectra of molecular clusters consisting of rigid monomers. The method is based on generation of optimized bases for each monomer. First, a sequential symmetry adaptation procedure is developed for relating the symmetries of monomer basis functions with the symmetries of the eigenstates of the cluster. Then this symmetry adaptation procedure is used in the generation of optimized bases and combining them for finding the eigenstates. Symmetry adaptation problems related to the generation of optimized bases are identified and solutions are suggested. The method is applied to the water dimer by using the SAPT-5st potential surface. The results are encouraging for application to bigger clusters.

Key words: Molecular clusters, theoretical spectroscopy, sequential symmetry adaptation

1. Introduction

Molecular clusters are highly nonrigid systems.^{1,2} Their potential surfaces contain more than one global minimum separated by low energy barriers such that the molecule can tunnel through them. These tunnelings cause splittings in the vibration-rotation spectra. Prediction of these splittings with theoretical methods requires accurate quantum mechanical calculations. On the other hand, theoretical studies of clusters become prohibitive as the size of the cluster gets bigger because of the exponential scaling of basis sizes with the dimensionality of the system in quantum mechanics. As a result, it is necessary to figure out ways of reducing the sizes of bases.

One way of reducing the sizes of bases is by symmetry adaptation of basis functions and solving for each symmetry separately. However, the well-known method of symmetry adaptation is not very helpful. Although the sizes of bases grow exponentially, orders of molecular symmetry groups³ grow linearly. For example, the order of the molecular symmetry group of the water dimer⁴ is 16 and the order of the molecular symmetry group of the water trimer⁵ is 48.

A much more efficient way of reducing the computational cost is to use bases that are optimized for the particular problem at hand instead of primitive bases. The inefficiency of primitive bases results from the fact that they do not know anything about the potential surface of the system. The optimized bases that know about the underlying potential surface can be generated as linear combinations of some primitive basis functions by taking a model potential surface that resembles the actual potential surface as much as possible and solving for its eigenstates. This obviously makes it necessary to divide the problem into smaller parts since trying to find an optimized basis for the full problem is as difficult as solving it. In the case of molecular clusters, an obvious way of dividing the problem into smaller parts is to consider each monomer separately. In the rest of

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the paper, the main discussion will be about how optimized bases for each monomer can be generated and how they can be combined for the solution of the full problem.

In section 2, a sequential symmetry adaptation procedure will be derived. By finding the relations between the projection operators of the irreducible representations of the molecular symmetry group of the cluster and the projection operators of the irreducible representations of its subgroups, symmetries of monomer basis functions will be related to the symmetries of eigenstates of the cluster. This symmetry adaptation procedure will be used in section 3, in which generation of optimized monomer bases is discussed. It will be seen that generation of optimized bases creates its own problems related to symmetry adaptation. In order to guarantee generation of an efficient orthonormal basis, it will be necessary to modify the sequential symmetry adaptation procedure developed in section 2. In section 4, the method will be applied to the water dimer in order to illustrate its application. The paper will end with a discussion and conclusions.

2. Sequential symmetry adaptation

An analysis of the structure of the molecular symmetry groups shows that the molecular symmetry group of a molecular cluster consisting of n nonreacting monomers can be written in terms of its subgroups as⁶

$$G(MS) = ((G_{k_1} \otimes G_{k_2} \otimes \dots \otimes G_{k_n}) \textcircled{S} G_l) \otimes \varepsilon. \quad (1)$$

In the equation above, the groups G_{k_i} with $i = 1, \dots, n$ are the pure permutation subgroups of the monomers that have orders k_i ; the group G_l , which is of the order of l , is the subgroup containing the operations permuting the identical monomers, and the group ε is the inversion subgroup that contains the identity element E and the inversion element E^* .

In equation (1), \otimes denotes a direct product multiplication and \textcircled{S} denotes a semidirect product multiplication. The difference between a direct product and a semidirect product multiplication is that in a direct product multiplication both of the subgroups are invariant subgroups of the product group, while in a semidirect product multiplication only one of them is an invariant subgroup of the product group. Since the operations permuting the identical monomers bring in noncommutation, presence of a semidirect product multiplication is inevitable.

Symmetry adaptation of basis functions to an irreducible representation Γ of a group G can be done by application of the projection operator of that irreducible representation, which is given by^{7,8}

$$\hat{P}_G^\Gamma = \frac{d_\Gamma}{|G|} \sum_{g \in G} \chi^\Gamma[g]^* \hat{O}_g, \quad (2)$$

where g are the elements of the group G , d_Γ is the dimension of the irreducible representation Γ , $|G|$ is the order of the group G , \hat{O}_g is the operator representing g , and $\chi^\Gamma[g]$ is the character of g in the irreducible representation Γ . As shown in the appendix, for a group G that can be written as a semidirect product of 2 of its subgroups H and K , and satisfying the condition given in equation (36), the projection operator of an irreducible representation can be decomposed into the product of 2 terms such that

$$\hat{P}_G^\Gamma = \left(\frac{1}{|H|} \sum_{h \in H} \chi^\Gamma[h]^* \hat{O}_h \right) \left(\frac{1}{|K|} \sum_{k \in K} \chi^\Gamma[k]^* \hat{O}_k \right), \quad (3)$$

where the definitions of the terms are similar to those of equation (2). Please note that the condition given in equation (36) is always satisfied for any direct product group. Therefore, equation (3) applies to all of the group

multiplications in equation (1). Consequently, it follows that the symmetry adaptation of basis functions can be done in $n + 2$ steps sequentially. Furthermore, the characters in equation (3) can be decomposed to their irreducible components in groups H and K . Thus, if the character in the first parentheses in equation (3) can be expressed as $a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus \dots$ where a_i are nonnegative integers and Γ_i are the irreducible representations of the group H , then from the definition of projection operators it follows that this parentheses can be expressed in terms of the projection operators of the irreducible representations of the group H as

$$\frac{1}{|H|} \sum_{h \in H} \chi^\Gamma[h]^* \hat{O}_h = \frac{a_1}{d_1} \hat{P}_H^{\Gamma_1} + \frac{a_2}{d_2} \hat{P}_H^{\Gamma_2} + \dots, \quad (4)$$

where $\hat{P}_H^{\Gamma_i}$ is the projection operator and d_i are the dimension of the irreducible representation Γ_i . A similar expression can also be written for the second parentheses in equation (3) in terms of the projection operators of the irreducible representations of the group K . Obviously only the terms for which a_i is nonzero will contribute to the sum. Consequently, equation (4) or equally finding the coefficients a_i is useful for determining which symmetries of the monomer basis functions can be symmetry adapted to an irreducible representation of the product group.

3. Monomer basis representation method

If the symmetry adaptation procedure given in previous section is used with primitive bases, it cannot provide any optimization more than what one can achieve with the direct symmetry adaptation by using equation (2). On the other hand, a sequential symmetry adaptation procedure combined with the physically meaningful partitioning of the molecular symmetry groups given in equation (1) makes it possible to devise algorithms for obtaining symmetry adapted optimized bases.

On the other hand, generation of optimized bases creates its own problems related to symmetry adaptation. Primitive basis functions (plane waves, spherical harmonics, Wigner rotation functions ...) are the solutions of Hamiltonians corresponding to motions of free particles or free bodies. Since the kinetic energy is always absolutely symmetric, a free particle Hamiltonian has absolute symmetry too. Consequently, the basis functions that are obtained as solutions of that Hamiltonian also have absolute symmetry. As a result, application of a symmetry operation to a primitive basis function always results in another function in the same basis other than a possible phase factor. Thus the symmetry adapted basis functions can be obtained as linear combinations of primitive basis functions.

The case of optimized basis functions is different. An optimized basis function should know about the particular problem at hand so that the Hamiltonian of which the optimized basis functions are solutions should include a potential energy function. Since the potential surfaces do not have absolute symmetry, a Hamiltonian including a potential energy function cannot be absolutely symmetric either. This will restrict the symmetries of optimized basis functions that are obtained as solutions of the Hamiltonian. This means that application of a symmetry operation to an optimized basis function will not necessarily result in another basis function in the same optimized basis. As a result, solving a problem might be impossible when optimized basis functions are used unless special care is taken to ensure that the physically meaningful solutions of the Hamiltonian can be obtained as linear combinations of the optimized basis functions.

A discussion of how such optimized monomer bases can be found and how they can be combined for the solution of the full problem will be given in the following subsections.

Before starting to talk about the method, it should be noted that a basis function related with a monomer is a function that describes the orientation of the monomer in the cluster and a function related to inter-

monomer coordinates is a function that describes the orientation of the monomers with respect to each other. The monomers are assumed to be rigid bodies so that intra-monomer degrees of freedom are not considered. In the discussion, the language of Permutation Inversion (PI) group theory^{3,7,9} will be used since it provides the most natural way of handling the symmetries in molecular systems.

3.1. Generation of a monomer basis

An optimized basis for a monomer can be generated by taking a model Hamiltonian for that monomer and then solving for the eigenstates of the model Hamiltonian with a basis that has the required symmetry properties. Then a subset of the eigenstates of the model Hamiltonian can be taken as an optimized basis for that monomer. The model Hamiltonian should include the kinetic energy operator related to the monomer in the Hamiltonian of the cluster and a model potential surface for the monomer.

When the optimized basis functions are obtained as solutions of a model Hamiltonian they will have the symmetries of the pure permutation group of the monomer, G_{k_i} , since this is the group describing the symmetries of the model Hamiltonian. According to equation (3), this is certainly sufficient for performing sequential symmetry adaptation properly. However, as explained below, in order to guarantee invariance of the cluster basis while combining the monomer bases, it is better to follow a more complex path.

If the sequential symmetry adaptation procedure is used as it is, then there will be a problem related to the inversion symmetry of the cluster while combining the bases. The inversion operation certainly affects monomer coordinates. Therefore, when the inversion operation is applied to an optimized monomer function, the result will be another basis function for the same monomer. However, the resulting function will not be in the same basis since the model Hamiltonian of the monomer calculations cannot have the inversion symmetry of the *cluster*. Consequently, if the sequential symmetry adaptation procedure is used as it is, it will be necessary to deal with a generalized eigenvalue problem instead of a standard eigenvalue problem since the inversion operation creates new basis functions that are not orthogonal to the optimized monomer basis functions.

This problem can be overcome by using the properties of direct product groups. Since both the identity operation and the inversion operation are always in their own classes, the inversion subgroup can always be multiplied by another subgroup of the molecular symmetry group with direct product multiplication. If the basis functions that are used to generate optimized monomer bases are symmetry adapted to irreducible representations of the direct product group obtained from the pure permutation group of the monomer and the inversion subgroup of the cluster, then they will be symmetry adapted to the irreducible representations of both the pure permutation group of the monomer and the inversion subgroup of the cluster. In this case, the application of the inversion operation to optimized basis functions will not create new functions. In fact, they will be the eigenstates of the inversion operation with the eigenvalues ± 1 . If the same thing is true for all of the monomer bases, then a tensor product of the monomer bases will also be eigenstates of the inversion operation with the eigenvalues ± 1 . Consequently, the product basis of the monomer bases will be invariant under the effect of the inversion operation so that the symmetry adaptation of basis functions will not lead to a generalized eigenvalue problem, but to a standard eigenvalue problem.

To sum up, in order to generate an optimized basis for a monomer, the permutation group of that monomer, G_{k_i} , and the inversion subgroup, ε , of the molecular symmetry group of the *cluster* are taken and the direct product group of these 2 subgroups is formed. Then the eigenstates of the model Hamiltonian are solved for each symmetry separately after the basis functions are symmetry adapted. A subset of these eigenstates becomes the optimized basis for that monomer.

3.2. Generation of bases for other monomers

The procedure given in section 3.1 can be used for generating a contracted basis for each of the monomers. However, this will not be the optimal choice. Because, the molecular symmetry group of the cluster includes the subgroup G_l , which includes the symmetry operations permuting the identical monomers. Therefore, according to equations (1) and (3), full symmetry adaptation of basis functions requires the application of symmetry operations contained in this group. These symmetry operations will mix the monomer bases such that when they are applied to the basis functions of a monomer, the resulting function will be a basis function for another monomer. If this resulting basis function is not already available in the contracted basis of the monomer, it will not necessarily be orthogonal to the basis functions of the monomer. Therefore, unless there is a relation between the bases of different monomers, there will be problems with the full symmetry adaptation of basis functions because of the symmetry operations permuting identical monomers. As a result, a better way of constructing bases for all of the monomers is to find a basis for one of them, and then to generate bases for other monomers from the basis of this monomer.

The obvious choice for generating the bases for other monomers could be just to relabel the basis functions of a single monomer for other monomers. However, this will not help to solve of the symmetry adaptation problem posed above, unless the results of the symmetry operations permuting identical monomers are just to relabel the coordinates.

The general solution to that symmetry adaptation problem can be found as follows. Firstly, let us consider the case of a dimer. If the monomers are labeled as 1 and 2, then the group that contains the permutations of identical monomers will be $G_2 = \{E, P_{12}\}$, where the operation P_{12} is the permutation operation that permutes the monomers 1 and 2. Let us define $\phi_k^{(1)}$ as the k^{th} basis function in the optimized basis of the monomer 1 and $\phi_l^{(2)}$ as the l^{th} function in the optimized basis of the monomer 2, which is to be determined. Since what we are looking for is a relation between the 2 functions, and since it is the operation P_{12} that relates the 2 bases, a way of relating the 2 functions is with the following definition:

$$\phi_k^{(2)} = P_{12}\phi_k^{(1)}. \quad (5)$$

If the equation above is used for creating the basis functions of monomer 2, the application of the operation P_{12} (please note that $P_{12}P_{12} = E$) to product basis functions will not create new basis functions:

$$\begin{aligned} P_{12}\phi_k^{(1)}\phi_l^{(2)} &= P_{12}(\phi_k^{(1)}(P_{12}\phi_l^{(1)})) \\ &= \phi_k^{(2)}\phi_l^{(1)}. \end{aligned} \quad (6)$$

Instead, it will just carry a basis function in the basis of a monomer to another basis function in the basis of the other monomer. Consequently, the tensor product of the optimized bases becomes invariant under the effect of operations permuting identical monomers.

Although the discussion above is based on just 2 monomers, the idea can be extended to any bigger cluster. In the case of a trimer, for example, if the monomers are labeled as 1, 2, and 3, the cyclic group containing the permutations of identical monomers will be the group $G_3 = \{E, P_{123}, P_{132}\}$. In this case the basis of the monomer 2 can be generated by $\phi_k^{(2)} = P_{123}\phi_k^{(1)}$, and the basis of the monomer 3 can be generated from the basis of monomer 2 by $\phi_k^{(3)} = P_{123}\phi_k^{(2)}$. Thus, by repeated application of the generator of the group G_3 , it is possible to generate bases for all of the 3 monomers from the basis of a single monomer. This method can be extended to any bigger cluster provided that the group G_l is a cyclic group with order n (if there are

different types of monomers, the group G_l should have cyclic subgroups for every type of monomer). However, the procedure becomes ambiguous if the group G_l is not cyclic. For example, in the case of a trimer, if the group containing the permutations of the identical monomers were the group $G_6 = \{E, P_{123}, P_{132}, P_{12}, P_{13}, P_{23}\}$, there would be more than one way of generating bases for other monomers. For example, both of the operations P_{123} and P_{12} can be used to generate a basis for the monomer 2 from the basis of the monomer 1. If the operation P_{123} (P_{12}) is used, then the application of the operation P_{12} (P_{123}) may still create new basis functions. In such a situation, it is impossible to guarantee the invariance of the basis.

Before concluding this section, it should also be noted that a basis that is generated by using the generator of the group including the operations that permute identical monomers will have the same orthogonality relations as the original basis. For example, if one has an orthonormal basis for the monomer 1, i.e. $\langle \phi_k^{(1)} | \phi_l^{(1)} \rangle = \delta_{kl}$; then using the fact that $P_{12}^\dagger = P_{12}$, it can be shown easily that the basis of the monomer 2 generated by using equation (5) will have $\langle \phi_k^{(2)} | \phi_l^{(2)} \rangle = \delta_{kl}$ too.

Moreover, the basis functions of the monomer 2 will be eigenstates of the model Hamiltonian of the monomer 2, which is generated in the way that the eigenstates of the monomer 2 is generated. Thus, if \hat{H}_1^0 is the model Hamiltonian of the monomer 1, and $\phi_k^{(1)}$ is the k^{th} eigenstate of this model Hamiltonian with the eigenvalue ϵ_k such that $\hat{H}_1^0 \phi_k^{(1)} = \epsilon_k \phi_k^{(1)}$, then by defining the model Hamiltonian of the second monomer as

$$\hat{H}_2^0 = P_{12} \hat{H}_1^0 P_{12}^\dagger, \quad (7)$$

it can be shown that $\phi_k^{(2)}$ is an eigenstate of the model Hamiltonian \hat{H}_2^0 with the same eigenvalue such that $\hat{H}_2^0 \phi_k^{(2)} = \epsilon_k \phi_k^{(2)}$.

3.3. Combining monomer bases

After optimized bases for each monomer are generated, they can be combined with a primitive basis for the inter-monomer coordinates. Thus, the basis functions of the full problem before symmetry adaptation will be:

$$\psi_{i_1, i_2, \dots, i_n, l} = \chi_l \prod_{k=1}^n \phi_{i_k}^{(k)}. \quad (8)$$

In the equation above, χ_l is the l^{th} basis function for the inter-monomer coordinates, and $\phi_{i_k}^{(k)}$ is the i_k^{th} basis function of the monomer k .

As discussed in previous sections, these basis functions will be invariant under the effect of any permutation inversion operation. Therefore, even if the symmetry adaptation to the full symmetry of the cluster is not pursued, calculations will result in eigenstates having the correct symmetry properties. Nevertheless, symmetry adaptation is always useful for reducing the computational cost. Moreover, when the functions are symmetry adapted, no further effort is necessary for identifying the symmetries of eigenstates after the calculations.

Since the monomer basis functions are symmetry adapted to the irreducible representations of the group formed by taking the direct product of the pure permutation group of the monomers and the inversion group of the cluster, properties of the direct product multiplication ensure that these basis functions will also be symmetry adapted to the irreducible representations of the pure permutation groups of the monomers. Consequently, the properties of direct product also ensure that the basis functions of the cluster calculations will be symmetry

adapted to the irreducible representations of the group $G_{k_1} \otimes G_{k_2} \otimes \dots \otimes G_{k_n}$. At this point, the application of the sequential symmetry adaptation procedure requires finding the correlations between the irreducible representations of the groups G_{k_i} and the irreducible representations of the molecular symmetry group of the cluster. The procedure for finding correlations is well known.⁷ After that, correct combinations of basis functions can be symmetry adapted to the irreducible representations of the molecular symmetry group of the cluster in 2 steps by using equation (3). One of the steps will be related to the subgroup containing the operations permuting the identical monomers and the other step will be related to the inversion subgroup of the cluster.

The step related to the inversion subgroup will already be trivial. Since monomer basis functions are symmetry adapted to the group $G_{k_i} \otimes \varepsilon$, there will be 2 bases that are symmetry adapted to 2 different irreducible representations of the group $G_{k_i} \otimes \varepsilon$ and at the same time that are symmetry adapted to the irreducible representation Γ of the group G_{k_i} . One of these bases will be symmetry adapted to the irreducible representation $\Gamma \otimes G = \Gamma_g$, which will have even parity, and one of them will be symmetry adapted to the irreducible representation $\Gamma \otimes U = \Gamma_u$, which will have odd parity. Thus, if it is necessary to have a basis for the monomer 1 that is symmetry adapted to the irreducible representation Γ , then the basis that should be used for the monomer 1 will be $\Gamma_g \oplus \Gamma_u$, where the labels of the irreducible representations are used to mean any basis function belonging to that symmetry. The bases of all of the monomers can be found similarly. Thus, when the correlations are found and the product basis is formed there will be 2^n different product bases that differ from each other by the symmetries of monomer functions. Since inter-monomer coordinates are usually invariant under the effect of the inversion operation, half of these terms will have even parity and half of them will have odd parity. According to equation (3), symmetry adaptation to inversion symmetry requires the application of the operator $(E \pm E^*)/2$. Therefore, since the basis functions already have either even or odd symmetry, they will either be annihilated or left invariant by the application of this functional. Consequently, after finding the correlations, fully symmetry adapted basis functions can be generated in one step by application of the operations permuting identical monomers as follows:

$$\Psi^{(\Gamma_\alpha)} = \frac{1}{|G_t|} \sum_{g \in G_t} \chi^{\Gamma_\alpha}[g]^* \hat{O}_g \chi_l \prod_{k=1}^n \phi_{i_k}^{(k)}. \quad (9)$$

In the equation above, Γ_α is an irreducible representation of the molecular symmetry group, and $\chi^{\Gamma_\alpha}[g]$ is the character of the operation g represented by the operation \hat{O}_g in the irreducible representation Γ_α .

3.4. Solution of the full problem

In order to find the eigenvalues of the Hamiltonian, the elements of the matrix representing the Hamiltonian should be calculated. They can be evaluated easily if the Hamiltonian is partitioned as $\hat{H} = \sum_{k=1}^n \hat{H}_k^0 + \hat{\Delta}T + \hat{\Delta}V$, where \hat{H}_k^0 's are the model Hamiltonians for the monomers, $\hat{\Delta}T$ is the kinetic energy terms that are not included in the model Hamiltonians, and $\hat{\Delta}V = \hat{V} - \sum_{k=1}^n \hat{V}_k^0$ is the difference between the potential surface of the full problem and the sum of the model potential surfaces of the model Hamiltonians.

The basis functions of the full problem become eigenstates of the zeroth order Hamiltonian for the full problem such that by defining $\hat{H}^0 = \sum_{k=1}^n \hat{H}_k^0$, and expanding the wave function in the product basis given in

equation (8), the following eigenvalue relation is obtained

$$\hat{H}^0 \psi_{i_1, i_2, \dots, i_n, l} = \left(\sum_{k=1}^n \epsilon_{i_k} \right) \psi_{i_1, i_2, \dots, i_n, l}. \quad (10)$$

Therefore, the matrix elements of the Hamiltonian in the basis of the full problem will be given by

$$\begin{aligned} \langle \psi_{i'_1, i'_2, \dots, i'_n, l'} | \hat{H} | \psi_{i_1, i_2, \dots, i_n, l} \rangle &= \sum_{k=1}^n \epsilon_{i_k} \delta_{ll'} \prod_{r=1}^n \delta_{i_r, i'_r} \\ &+ \langle \psi_{i'_1, i'_2, \dots, i'_n, l'} | \hat{\Delta T} + \hat{\Delta V} | \psi_{i_1, i_2, \dots, i_n, l} \rangle. \end{aligned} \quad (11)$$

Thus, in order to calculate the matrix elements of the Hamiltonian, it is necessary to evaluate matrix elements of the $\hat{\Delta T}$ and $\hat{\Delta V}$ terms, in the basis of the full problem. These terms can be evaluated in the primitive bases of monomers and in the primitive basis of inter-monomer coordinates; then they can be transformed to the contracted basis of the cluster. If the terms $\hat{\Delta T}$ and $\hat{\Delta V}$ are small, then these terms can be considered as a small perturbation and the basis functions will resemble the eigenstates of the actual problem. In such a case, convergence of the results can be obtained by using a small number of contracted basis functions. However, this may not be the case for many problems.

4. Application to the water dimer

The water dimer has been studied extensively both experimentally^{10–23} and theoretically.^{24–31} In this work, some of the earlier works on the water dimer will be utilized.

Among the theoretical studies of the water dimer, Althorpe and Clary were the first to perform 6-dimensional calculations. Firstly, Althorpe and Clary studied the water dimer by separating the stretching coordinate from the angular coordinates adiabatically.²⁴ This adiabatic approximation was justified later with a more exact treatment.²⁹ Leforestier and co-workers were the first to do fully coupled 6-dimensional calculations with basis sets. They published 2 papers.^{27,28} The calculations were done with a coupled product basis of Wigner rotation functions by using the pseudo-spectral split Hamiltonian (PSSH) formalism in which the kinetic energy terms are evaluated in the coupled product basis of Wigner rotation functions and the potential energy is evaluated in the grid basis. Finally, van der Avoird and co-workers developed a new potential surface called SAPT-5s³⁰ by using the Symmetry Adapted Perturbation Theory (SAPT).^{32–34} This potential surface was tuned for predicting the vibration-rotation-tunneling levels of the water dimer, which led to the development of a new potential surface called SAPT-5st.³¹ The tuned potential surface describes the experimental data with near spectroscopic accuracy.^{30,31,35}

In the following section, the MBR method developed in section 3 will be used for calculating the vibration-rotation-tunneling (VRT) spectra of the water dimer. In calculations, adiabatic approximation of Althorpe and Clary, PSSH formalism of Leforestier and co-workers, and the potential surface of Groenenboom et al. will be used. The main difference in the calculations here from the previous calculations is the generation of optimized bases for each monomer in the cluster by using the MBR method. It will be seen that the method leads to successful results with a basis that has a much smaller size than any of the bases used in previous studies of the water dimer.

4.1. Structure of the water dimer

The structure of the water dimer was first determined by Dyke and co-workers via rotation spectra.^{10,11} By examining the experimental data, Dyke realized the presence of tunneling splittings and made a group theoretical classification of the ro-vibrational levels⁴ by using Permutation Inversion (PI) group theory.^{7,9} It was shown that the equilibrium structure of the water dimer has a plane of symmetry and a nonlinear hydrogen bond. The equilibrium structure of the water dimer is roughly depicted in Figure 1.

By including all feasible permutation inversion operations it is possible to generate 16 different configurations. Due to the presence of a plane of symmetry in the equilibrium structure, there is 2-fold structural degeneracy and only 8 of these structures are nonsuperimposable. There exist 3 distinct tunneling motions that connect 8 degenerate minima on the intermolecular potential surface (IPS). These tunneling motions are: acceptor switching, in which the protons of acceptor monomer exchange their positions; interchange tunneling, in which the roles of acceptor and donor monomers are interchanged; and bifurcation tunneling, in which the protons of the donor monomer exchange their positions.

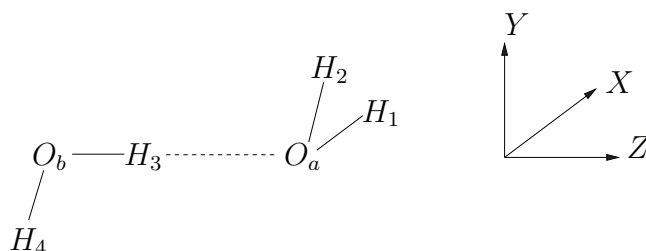


Figure 1. Equilibrium structure and the definition of the body fixed frame of the water dimer.

The splittings for $J = 0$ rotational level of the water dimer are shown in Figure 2. Each energy level is labeled with the irreducible representations of the G_{16} PI group, which is the molecular symmetry group of the water dimer. The group G_{16} is isomorphic to the D_{4h} point group and its character table is given in Table 1. If the oxygen atoms in the molecule are labeled as a and b , the hydrogen atoms bonded to oxygen a are labeled as 1 and 2, and the hydrogen atoms bonded to oxygen b are labeled as 3 and 4; then this group can be written as⁶

$$G_{16} = \left((G_2^{(1)} \otimes G_2^{(2)}) \otimes G_2^{(12)} \right) \otimes \varepsilon, \quad (12)$$

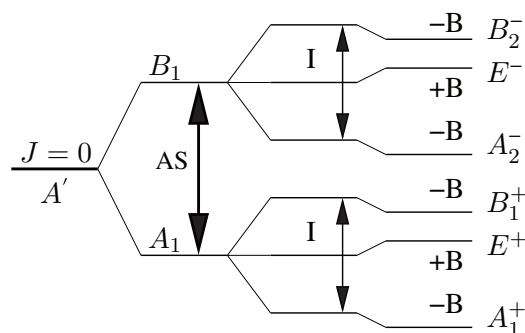


Figure 2. Correlation diagram for the rotation-tunneling states of $(H_2O)_2$ for $J = 0$. In the figure AS, I and B refers to acceptor switching, interchange tunneling, and bifurcation tunneling, respectively. Levels are labeled with the irreducible representations of the G_{16} PI group.

where the monomer permutation groups are $G_2^{(1)} = \{E, (12)\}$, $G_2^{(2)} = \{E, (34)\}$, the group containing the operations that permute the identical monomers is $G_2^{(12)} = \{E, (ab)(13)(24)\}$, and the inversion group is $\varepsilon = \{E, E^*\}$.

4.2. Hamiltonian and the outline of calculation strategy

The Hamiltonian for the inter-molecular motion of a nonrigid system consisting of 2 rigid polyatomic fragments can be written as³⁶

$$\hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \hat{K}_1 + \hat{K}_2 + \hat{K}_{12} + \hat{V}. \quad (13)$$

In the equation above, R is the distance between the centers of mass of the monomers. μ is the reduced mass of the dimer given by $\mu = (M_1 M_2)/(M_1 + M_2)$, where M_i is the total mass of the monomer i .

In the Hamiltonian \hat{K}_i is the kinetic energy operator of the monomer i , which can be expressed in the body fixed frame of the monomer as $\hat{K}_i = A\hat{j}_{ix}^2 + B\hat{j}_{iy}^2 + C\hat{j}_{iz}^2$, in terms of the angular momentum operators around the body fixed axes of the monomer, which are the molecular symmetry axes in this case. For calculations, the z axis is defined as the bisector of the HOH angle. The plane of the molecule is defined to be the xz plane. Since the monomers are considered to be rigid A, B and C are constants.

In equation (13), \hat{K}_{12} defines the kinetic energy operator corresponding to the end-over-end rotation of the dimer. It is given by

$$\hat{K}_{12} = \frac{1}{2\mu R^2} (\hat{J}^2 + \hat{j}^2 - 2\hat{J} \cdot \hat{j}). \quad (14)$$

In the equation above \hat{J} is the total angular momentum of the system given by $\hat{J} = \hat{j}_1 + \hat{j}_2 + \hat{L}$, where \hat{j}_i 's are the monomer angular momentum operators, and \hat{L} is the angular momentum operator for the end-over-end rotation of the dimer. \hat{j} is defined as $\hat{j} = \hat{j}_1 + \hat{j}_2$.

In order to evaluate the \hat{K}_{12} term, it is necessary to express all the angular momentum operators in a common reference system. This reference system is the body fixed frame of the dimer, of course. The z axis of the body fixed frame of the dimer is defined along the line joining the center of mass of the monomers and the y axis of the body fixed frame of the dimer is defined to be along the bisector of the HOH angle of the acceptor monomer in the equilibrium configuration. In this reference frame, \hat{K}_{12} is expressed as

$$\hat{K}_{12} = \frac{1}{2\mu R^2} (\hat{j}_1^2 + \hat{j}_2^2 + 2\hat{j}'_{1z}\hat{j}'_{2z} + \hat{j}'_{1+}\hat{j}'_{2-} + \hat{j}'_{2+}\hat{j}'_{1-} - 2\hat{J}'_z\hat{j}'_z - \hat{J}'_+\hat{j}'_- - \hat{J}'_-\hat{j}'_+). \quad (15)$$

For $J = 0$, this equation reduces to

$$K_{12} = \frac{1}{2\mu R^2} (\hat{j}_1^2 + \hat{j}_2^2 + 2\hat{j}'_{1z}\hat{j}'_{2z} + \hat{j}'_{1+}\hat{j}'_{2-} + \hat{j}'_{2+}\hat{j}'_{1-}). \quad (16)$$

In the equations above ' denotes that the operator refers to the body fixed frame of the dimer, not to the body fixed frame of the monomers.

In order to solve the eigenvalue problem, first the stretching coordinate will be separated from the angular coordinates adiabatically. This was first done by Althorpe and Clary²⁴, and led to successful results.

Table 1. Character table of the G_{16} PI group, which is the molecular symmetry group of the water dimer. This group is isomorphic to the D_{4h} point group. This character table is taken from a paper by Dyke.⁴

G_{16}	E	(12) (34)	(ab)(13)(24) (ab)(14)(23)	(ab)(1324) (ab)(1423)	(12)(34)	E^*	(12)* (34)*	(ab)(13)(24)* (ab)(14)(23)*	(ab)(1324)* (ab)(1423)*	(12)(34)*
A_1^+	1	1	1	1	1	1	1	1	1	1
A_2^+	1	-1	-1	1	1	1	-1	-1	1	1
B_1^+	1	1	-1	-1	1	1	1	-1	-1	1
B_2^+	1	-1	1	-1	1	1	-1	1	-1	1
E^+	2	0	0	0	-2	2	0	0	0	-2
A_1^-	1	1	1	1	1	-1	-1	-1	-1	-1
A_2^-	1	-1	-1	1	1	-1	1	1	-1	-1
B_1^-	1	1	-1	-1	1	-1	-1	1	1	-1
B_2^-	1	-1	1	-1	1	-1	1	-1	1	-1
E^-	2	0	0	0	-2	-2	0	0	0	2

First, the angular Hamiltonian is written in the form

$$\hat{H}_{ang} = \hat{h}_1^0 + \hat{h}_2^0 + \Delta\hat{K} + \Delta\hat{V}, \quad (17)$$

where the model Hamiltonians, \hat{h}_i^0 , for the 3-dimensional monomer problems are given by $\hat{h}_i^0 = \hat{K}_i + \hat{V}_i^0$, where \hat{K}_i is the monomer's kinetic energy operator in equation (13), and \hat{V}_i^0 is the model potential energy surface for the 3-dimensional problem, which is the rotation of the monomers.

By comparing equation (17) with the Hamiltonian given in equation (13), it is easily seen that $\Delta\hat{K} = \hat{K}_{12}$ and $\Delta\hat{V}$ terms can be identified as $\Delta\hat{V} = \hat{V} - \hat{V}_1^0 - \hat{V}_2^0$.

The results of the angular calculations will be used to find an effective potential surface for the radial coordinate so that the total Hamiltonian can be written as

$$\hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + V_{eff}(R). \quad (18)$$

The details of monomer calculations will be given in section 4.3, and the details of 5-dimensional angular calculations and radial calculations will be given in section 4.4.

4.3. Generation of monomer bases

In order to generate an optimized basis for one of the monomers, it is necessary to define a model potential surface for the model Hamiltonian of the monomer calculations. Since the 2 monomers in the water dimer are in different conditions (one of them is a hydrogen donor and the other is a hydrogen acceptor), the model potential surface should sample both of these properties in an average manner. The Energy Selected Basis (ESB) method^{37,38} fits this purpose very well. In the ESB method, a model potential surface is generated as a marginal potential in which the potential at a point is the minimum value of the potential energy with respect to all other coordinates.

For solving the water dimer problem with ESB method, it is necessary to generate a 3-dimensional marginal potential. Labeling the monomers as 1 and 2, the model potential for monomer 1 in the field of monomer 2 will be

Table 2. Character table of the G_4 permutation inversion group.

G_4	E	(12)	E^*	$(12)^*$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

$$\hat{V}_1^0(\zeta_1) = \hat{V}(\zeta_1, \zeta_2^{min}; R), \quad (19)$$

where $\zeta_1 = (\alpha_1, \beta_1, \gamma_1)$ and $\zeta_2 = (\alpha_2, \beta_2, \gamma_2)$ refer to the Euler angles of monomers, which describe the orientation of the body fixed frame of the monomers with respect to the body fixed frame of the dimer.

In calculations, a pseudo-spectral approach will be adopted. The spectral basis functions will be the symmetric top basis functions, which are given by

$$|jkm\rangle = \frac{1}{2\pi} \sqrt{\frac{2j+1}{2}} D_{mk}^{j*}(\alpha, \beta, \gamma), \quad (20)$$

where $D_{mk}^j(\alpha, \beta, \gamma)$ is a Wigner rotation function, expressed in terms of Euler angles α , β , and γ . The exact functional form and the symmetry properties of Wigner rotation functions can be found elsewhere.³⁹

Construction of a grid basis for nonproduct bases is discussed by Corey et al.^{40,41} for the case of spherical harmonics, and later it is applied to the Wigner rotation functions by Leforestier.²⁸ According to his prescription, the grid basis consists of a uniform grid for the angles α and γ whose range is $(0, 2\pi)$, and Gauss-Legendre quadrature points for $\cos\beta$ whose range is $(-1, 1)$. The grid points in β are distributed symmetrically with respect to $\beta = \pi/2$. In the case of the angles α and γ , grid points are evenly and periodically distributed between 0 and 2π and they are given by

$$\phi_j = j \left(\frac{2\pi}{N} \right) \quad (21)$$

where ϕ is either α or γ , N is the number of DVR points and $j = 0, 1, \dots, N-1$. Defining $|\alpha_i\rangle$, $|\beta_j\rangle$, $|\gamma_k\rangle$, as the basis functions localized around the points α_i , β_j and γ_k for the angles α , β , and γ , respectively, $|\alpha_i\beta_j\gamma_k\rangle = |\alpha_i\rangle|\beta_j\rangle|\gamma_k\rangle$ represents a direct product basis function in the grid basis.

Symmetry adaptation of primitive basis functions should be done for each irreducible representation of the group formed by direct product multiplication of the pure permutation group of the monomer and the inversion subgroup of the *cluster*. For the water dimer problem this is the group G_4 , whose character table is given in Table 2. Please note that the inversion operation in this group refers to the inversion of the whole dimer, not just a single monomer.

In order to find the symmetry adapted functions, it is necessary to find the effects of the symmetry operations on the primitive basis functions. For this purpose, first the effects of symmetry operations on the Euler angles should be found. In the case of molecular clusters, finding the results might be tricky since the symmetry operations affect not only the body fixed frames of the monomers but also the body fixed frame of the cluster. An easy way has been suggested.⁶ The results are summarized in Table 3.

In the case of symmetric top basis functions, functions that are symmetry adapted to the irreducible representations of the group G_4 will be in the form of

Table 3. Transformation properties of Euler angles under the effect of the symmetry operations of the G_4 molecular symmetry group and the effect of the permutation inversion operations on symmetric top basis functions.

E	α	β	γ	$ jkm\rangle$
(12)	α	β	$\pi + \gamma$	$(-1)^k jkm\rangle$
E^*	$\pi - \alpha$	β	$-\gamma$	$(-1)^k j\bar{k}\bar{m}\rangle$
(12)*	$\pi - \alpha$	β	$\pi - \gamma$	$ j\bar{k}\bar{m}\rangle$

Table 4. Parameters for symmetry adapting the basis functions in monomer calculations. Forms of the basis functions are given in equations (22) and (23).

Representation	p	k	s	l
A_1	0	even	0	0
A_2	1	even	0	1
B_1	0	odd	1	1
B_2	1	odd	1	0

$$|jkm; p\rangle = N_p (|jkm\rangle + (-1)^p |j\bar{k}\bar{m}\rangle), \quad (22)$$

where over-bars denote negation and the normalization constant is given by $N_p = 1/(2 + 2\delta_{k0}\delta_{m0})$. In equation (22), p is either 0 or 1, and k is either even or odd depending on the symmetry. Table 4 gives the values of the parameter p for each symmetry level. Symmetry adaptation reduces the range of m . For functions $|jkm; p\rangle$, reduced range of m becomes $0 \leq m \leq j$.

Symmetry adaptation of the grid basis can also be done. The transformation properties of the Euler angles given in Table 3 require that if α_i and γ_k are grid points, then $\pi - \alpha_i = \bar{\alpha}_i$, $\pi + \gamma_k = \gamma_k^*$, $-\gamma_k = \bar{\gamma}_k$, and $\pi - \gamma_k = \bar{\gamma}_k^*$ should also be grid points. The symmetry adapted basis functions will be in the form of

$$|\alpha_i \beta_j \gamma_k; sl\rangle = N_l (|\alpha_i \beta_j \gamma_k; s\rangle + (-1)^l |\bar{\alpha}_i \beta_j \bar{\gamma}_k; s\rangle), \quad (23)$$

where

$$|\alpha_i \beta_j \gamma_k; s\rangle = \frac{1}{\sqrt{2}} (|\alpha_i \beta_j \gamma_k\rangle + (-1)^s |\alpha_i \beta_j \gamma_k^*\rangle), \quad (24)$$

and the normalization constant is given by $N_l = 1/\sqrt{2(1 + \delta_{\alpha_i \bar{\alpha}_i} \delta_{\gamma_k \bar{\gamma}_k})}$. Symmetry adaptation of the grid basis reduces the ranges of the angles α and γ . The reduced range of the angle α becomes $\frac{\pi}{2} \leq \alpha_i \leq \frac{3\pi}{2}$ and the reduced range of the angle γ becomes $0 \leq \gamma_k < \pi$. According to equation (21), 0 is always a grid point. As a result of that, the transformation properties of Euler angles given in Table 3, require that π always be a grid point too. According to equation (21), this requires that N be an even number in calculations.

In the calculations, it will be necessary to make transformations between the 2 bases. The transformation matrix elements were given by Leforestier:⁴²

$$T_{\alpha_i \beta_j \gamma_k}^{jkm} = \sqrt{\frac{2j+1}{2}} \frac{e^{im\alpha_i}}{\sqrt{N_\alpha}} \frac{e^{ik\gamma_k}}{\sqrt{N_\gamma}} \sqrt{w_{\beta_j}} a_{mk}^j(\cos \beta_j). \quad (25)$$

Table 5. Transformation properties of Euler angles under the effect of the symmetry operations of the G_{16} permutation inversion group.

E	$\alpha_1, \beta_1, \gamma_1$	$\alpha_2, \beta_2, \gamma_2$	$ j_1 k_1 m_1 j_2 k_2 m_2\rangle$
E^*	$\pi - \alpha_1, \beta_1, -\gamma_1$	$\pi - \alpha_2, \beta_2, -\gamma_2$	$(-)^{k_1+k_2} j_1 \bar{k}_1 \bar{m}_1 j_2 \bar{k}_2 \bar{m}_2\rangle$
(12)	$\alpha_1, \beta_1, \pi + \gamma_1$	$\alpha_2, \beta_2, \gamma_2$	$(-)^{k_1} j_1 k_1 m_1 j_2 k_2 m_2\rangle$
(34)	$\alpha_1, \beta_1, \gamma_1$	$\alpha_2, \beta_2, \pi + \gamma_2$	$(-)^{k_2} j_1 k_1 m_1 j_2 k_2 m_2\rangle$
$(ab)(13)(24)$	$-\alpha_2, \pi - \beta_2, \pi + \gamma_2$	$-\alpha_1, \pi - \beta_1, \pi + \gamma_1$	$(-)^{j_1+j_2} j_2 k_2 \bar{m}_2 j_1 k_1 \bar{m}_1\rangle$

In the equation above, N_α and N_γ are the number of grid points for the angles α and γ , and w_{β_j} is the weight of the grid point β_j of the Gauss-Legendre quadrature for $\cos\beta$. The exact functional form of the $d_{mk}^j(\cos\beta)$ functions can be found elsewhere.³⁹ Transformations between bases can be done in 3 steps. This idea is suggested and used by Leforestier and co-workers, and the details can be found in their water dimer paper.²⁷

After the monomer calculations are done and a subset of the resulting eigenstates is taken as an optimized basis, it is necessary to find an optimized basis for the second monomer. According to the prescription given in section 3.2, this should be done by using the generator of the group that contains the operations permuting the identical monomers. For the water dimer the generator of the group that contains the permutations of the monomers is the operation $(ab)(13)(24)$. The effects of this operation on the Euler angles and on the primitive bases are given in Table 5.

If the i^{th} optimized basis function belonging to an irreducible representation of the group G_4 of the monomer 1 has the form

$$\psi_i^{(1)} = \sum_l c_{il} |j_l k_l m_l; p\rangle, \quad (26)$$

where c_{il} is the expansion coefficient, then the corresponding basis function belonging to the same irreducible representation of monomer 2 will have the form

$$\psi_i^{(2)} = (ab)(13)(24)\psi_i^{(1)} = \sum_l (-1)^{j_l} c_{il} |j_l k_l \bar{m}_l; p\rangle. \quad (27)$$

It is also necessary to generate a grid basis for the monomer 2, from the grid basis of monomer 1. This will be done in the same way that the spectral basis of monomer 2 is generated from the spectral basis of monomer 1. Thus, in order to generate a grid basis for the monomer 2 the operation $(ab)(13)(24)$ should be applied to the grid basis functions of the monomer 1. If $|\alpha_{1i}, \beta_{1j}, \gamma_{1k}; sl\rangle$ is a symmetry adapted grid basis function of monomer 1, then the corresponding symmetry adapted grid basis function, $|\alpha_{2i}, \beta_{2j}, \gamma_{2k}; sl\rangle$, of the monomer 2 will be

$$|\alpha_{2i}, \beta_{2j}, \gamma_{2k}; sl\rangle = (ab)(13)(24)|\alpha_{1i}, \beta_{1j}, \gamma_{1k}; sl\rangle. \quad (28)$$

According to the transformation properties given in Table 5, if a grid basis function of the monomer 1 is localized around the point $(\alpha_{1i}, \beta_{1j}, \gamma_{1k})$, then the corresponding grid basis function for the monomer 2 will be localized around the point $(-\alpha_{1i}, \pi - \beta_{1j}, \pi + \gamma_{1k})$. The effect of the permutation operation $(ab)(13)(24)$ on the Euler angles of the monomers is to relabel the angles so that they belong to monomer 2, and to change the point the basis function is localized. Thus, this operation also mixes the order of the basis functions.

Table 6. This table shows which monomer bases should be combined for obtaining bases for water dimer calculations with the group G_{16} . In the table, labels of the irreducible representations are used to imply basis functions belonging to that symmetry. For an explanation of how to obtain mutually orthogonal bases for the doubly degenerate levels (i.e. E_x^+ , E_y^+) see Ocak.⁶

G_{16}	Bases	G_{16}	Bases
A_1^+	$(A_1 \otimes A_1) \oplus (A_2 \otimes A_2)$	A_1^-	$(A_1 \otimes A_2) \oplus (A_2 \otimes A_1)$
A_2^+	$(B_1 \otimes B_1) \oplus (B_2 \otimes B_2)$	A_2^-	$(B_1 \otimes B_2) \oplus (B_2 \otimes B_1)$
B_1^+	$(A_1 \otimes A_1) \oplus (A_2 \otimes A_2)$	B_1^-	$(A_1 \otimes A_2) \oplus (A_2 \otimes A_1)$
B_2^+	$(B_1 \otimes B_1) \oplus (B_2 \otimes B_2)$	B_2^-	$(B_1 \otimes B_2) \oplus (B_2 \otimes B_1)$
E_x^+	$(A_1 \otimes B_2) \oplus (A_2 \otimes B_1)$	E_x^-	$(A_1 \otimes B_1) \oplus (A_2 \otimes B_2)$
E_y^+	$(B_2 \otimes A_1) \oplus (B_1 \otimes A_2)$	E_y^-	$(B_1 \otimes A_1) \oplus (B_2 \otimes A_2)$

After optimized bases for both of the monomers are generated, they can be combined for the solution of the angular problem. Since the monomer basis functions are symmetry adapted to the irreducible representations of the groups $G_2^{(1)} \otimes \varepsilon$ and $G_2^{(2)} \otimes \varepsilon$, dimer basis functions will be symmetry adapted to the irreducible representations of the group $G_2^{(1)} \otimes G_2^{(2)}$. At this point, in order to obtain symmetry adapted functions it is necessary to find the correlations between the irreducible representations of the group G_{16} and the groups $G_2^{(1)}$ and $G_2^{(2)}$. Then the correlations between the group G_4 and the pure permutation groups of the monomers can also be found, and it can be determined which basis functions of specific symmetry should be combined for each irreducible representation of the group G_{16} . The operations are cumbersome but how to do them is well known⁷ and the details can be found elsewhere.⁶ The results are summarized in Table 6. Please note that the basis functions indicated in this table are those having the correct inversion symmetry; see section 3.3.

According to equation (3), the final step of symmetry adaptation to an irreducible representation Γ involves the application of the operator

$$\frac{1}{2}(E + \chi^\Gamma[(ab)(13)(24)]^*(ab)(13)(24)), \quad (29)$$

where $\chi^\Gamma[(ab)(13)(24)]$ is the character of the symmetry operation $(ab)(13)(24)$ in the irreducible representation Γ .

4.4. Angular and radial calculations

In order to solve the eigenvalue problem for the 5-dimensional angular problem, it is necessary to evaluate the matrix elements of the angular Hamiltonian given in equation (17). Since the contracted basis functions of the monomers are already the eigenstates of the model Hamiltonians, their evaluation is easy. The term $\hat{\Delta}K$ in that equation can be evaluated in the primitive basis of the monomers easily, and then can be transformed to the contracted bases of the monomers by using the transformation matrix obtained by solving the eigenstates of the model Hamiltonians of the monomers. The term $\hat{\Delta}V$ can be evaluated easily in the grid basis that is a tensor product of the monomer grid bases, and then can be transformed to the contracted bases of monomers in 2 steps first by transforming from grid basis to the primitive functional basis and then transforming from the primitive functional basis to the optimized angular basis of the dimer.

Once the angular problem is solved at several fixed R values, the eigenvalues for the full problem can be found by fitting the results of the angular calculations to a Morse function and solving for the eigenvalues. The

Hamiltonian for this 1-dimensional problem is given in equation (18). Since the Morse potential, given in the form

$$V(r) = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}), \quad (30)$$

includes 3 parameters, D , α , and r_0 , it is sufficient to solve the angular problem at 3 different R values.

When the Morse fit is done, the eigenvalues of the Hamiltonian, given in equation (18), can be found easily, since, for $J = 0$, the eigenvalues are analytic. According to Landau and Lifschitz, the eigenvalue of the n^{th} level is given by⁴³

$$E_n = -D \left(1 - \frac{\alpha}{\sqrt{2\mu D}} \left(n + \frac{1}{2} \right) \right)^2, \quad (31)$$

where n is an integer ranging from zero to the greatest value for which the expression in the parentheses is positive.

4.5. Details of calculations

The calculations are done by using the SAPT-5st potential surface developed by Groenenboom et al.^{30,31} The source code of this potential surface was made available to the scientific community by Groenenboom et al.³⁵ and can be obtained via ftp from the site ftp.aip.org under the directory /epaps/. The mass of H_2O is taken as 18.010560 and the moments of inertia of water monomers are taken as $A = 27.8806 \text{ cm}^{-1}$, $B = 14.5216 \text{ cm}^{-1}$ and $C = 9.2778 \text{ cm}^{-1}$. These values are the same as the values that are used in the original calculations by Groenenboom et al.

While doing the calculations the primitive functional bases of the monomers are taken as symmetric top bases with $j \leq 10$ and $m \leq 8$. Before the symmetry adaptation this corresponds to a basis size of ≈ 1650 . The numbers of grid points in α and γ are set to 26 and the number of grid points in β is set to 15 before symmetry adaptation. All of the calculations are done for $J = 0$.

In monomer calculations, the spectral basis is fully symmetry adapted and the grid basis is symmetry adapted to the permutations of the protons but not to the inversion symmetry. This provides a better way of sampling the potential surface, since the marginal potential obtained by ESB method do not have inversion symmetry. The matrix representing the Hamiltonian operator in the symmetry adapted symmetric top basis is stored in memory, and the diagonalization is done directly.

Angular calculations are done by using the Symmetry Adapted Lanczos (SAL) algorithm.⁴⁴ The use of the SAL algorithm allows one to diagonalize more than one symmetry at once. In the case of the water dimer problem considered here, the SAL method made it possible to solve for the eigenvalues of the A_1^+ and B_1^+ levels together, and also A_2^- and B_2^- levels together. This results from the fact that the angular bases of the A_1^+ and B_1^+ levels and similarly the angular bases of the A_2^- and B_2^- levels are the same before symmetry adaptation (see Table 6). In the case of doubly degenerate levels calculations should be done separately for each level since the bases of double degenerate levels are unique to themselves. However, use of the SAL algorithm still makes the calculations faster since in the SAL algorithm projection operators are used to obtain the symmetry adapted eigenfunctions.

Angular calculations are done at 3 different fixed R values, which are 5.38 a.u., 5.53 a.u., and 5.68 a.u. The ground states eigenvalues are used to define a potential surface for the stretching motion. The potential surface of the stretching motion is found by making a nonlinear data fit to the Morse function by using Newton's

Table 7. A comparison of the results of MBR calculations with the results of Groenenboom et al. The results of Groenenboom et al. are taken from table III of their paper.³¹ The results in the table are given in units of cm^{-1} . MBR results are obtained by using 100 angular basis functions per monomer. In the table a is the splitting due to acceptor tunneling; i_1 and i_2 are the splittings between A_1^+/B_1^+ and A_2^-/B_2^- levels due to interchange tunneling.

Symmetry	Groenenboom et al.	MBR
A_1^+	-1076.8643	-1075.2116
E^+	-1076.4312	-1074.8698
B_1^+	-1076.1419	-1074.4688
A_2^-	-1065.6333	-1063.0106
E^-	-1065.2540	-1062.6818
B_2^-	-1064.9825	-1062.3926
a	11.19	12.14
i_1	0.722	0.743
i_2	0.651	0.618

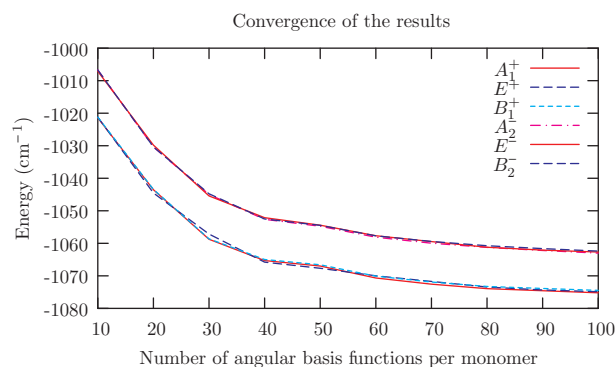


Figure 3. Convergence of the results of the MBR calculations with the number of angular basis functions per monomer.

algorithm.⁴⁵ In order to converge the results it was necessary to use 100 basis functions per monomer for the angular calculations.

4.6. Results

A comparison of the MBR results with the original calculations of Groenenboom et al. is given in Table 7 and also shown graphically in Figure 4. In the table, i_1 is the tunneling splitting due to interchange tunneling between the A_1^+ and B_1^+ levels, which is calculated as $i_1 = E(B_1^+) - E(A_1^+)$, where $E(x)$ denotes the energy of the level x ; i_2 is the interchange tunneling between the A_2^- and B_2^- levels, which is calculated as $i_2 = E(B_2^-) - E(A_2^-)$; and a is the tunneling splitting due to acceptor switching, which is calculated as $a = ((E(A_1^+) + E(B_1^+)) - (E(A_2^-) + E(B_2^-)))/2$. As can be seen from the table, the results are in good agreement with each other. In particular, the tunneling splittings are in very good agreement. From the table, it can be seen that the MBR calculation leads to eigenvalues that are higher than the results of Groenenboom et al. This can be attributed to the fact that the stretching coordinate is treated in different ways in the 2 calculations. In the calculations of Groenenboom et al. the stretching coordinate is handled with a DVR grid of 49 equally spaced points.³¹ On the other hand, in the MBR calculations the stretching coordinate is separated from the

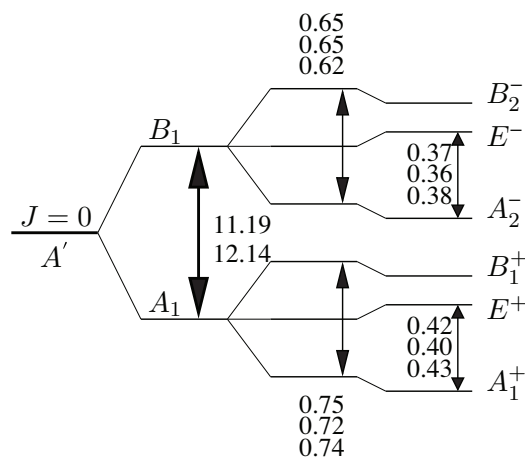


Figure 4. A comparison of the results of mbr calculations (lower numbers) with the original calculations of Groenenboom et al. (middle numbers) and the experimental data (upper numbers). Experimental data are not available for the acceptor switching.

angular coordinates adiabatically. Therefore, because of this difference the calculations of Groenenboom et al. are less approximate than the MBR calculations.

From the comparison of the MBR results with the original results, it can be said that the MBR method gives good results. Since the number of optimized basis functions that are used for each monomer (100) is much smaller than the number of primitive basis functions (≈ 1650), it can also be said that the method is efficient.

If the calculations were done with the same primitive bases but without generation of any optimized bases, it would be possible to decrease the size of the basis by a factor of 16 with the help of standard symmetry adaptation procedures since the order of the molecular symmetry group of the water dimer is 16. On the other hand, the use of the MBR method decreases the size of the basis of a single monomer by almost the same factor. Consequently, the size of the cluster basis becomes about 16 times smaller than what one would be able to achieve with standard symmetry adaptation procedures.

The calculations given here can be improved in several ways. Firstly, the stretching coordinate can be treated more accurately. This can be achieved either by using more points to find the Morse potential or by using more exact ways to handle it as Groenenboom et al. have done or by using sequential diagonalization truncation schemes. However, this does not really seem to be necessary since the results are quite successful. Secondly, from Figure 3, it can be seen that the convergence of the results is not uniform. The changes in the results when the number of angular basis functions per monomer is increased from 50 to 60 are greater than the changes in the results when the number of angular basis functions per monomer is increased from 40 to 50. This shows that simply taking the states with the lowest energies as an optimized basis is not the best way of choosing a subset of monomer eigenstates. It might be possible to devise better strategies while forming the contracted bases in order to obtain the best possible contracted basis. Although this does not seem to be a big problem for a 6-dimensional system, it might be important while studying higher dimensional systems.

The method developed in this paper can also be tested with other potential surfaces. There exist accurate full-dimensional (12-dimensional) potential surfaces for the water dimer that were developed recently.^{46,47} These potential surfaces, being full-dimensional, include both the intermolecular and the intramolecular degrees of freedom. However, since a 12-dimensional problem is too big to handle quantum mechanically, researchers that are studying these potential surfaces do not make fully coupled calculations. There exist 2 approaches

in the studies of full-dimensional potential surfaces. The first approach is to consider only the intermolecular degrees of freedom. Huang et al. used this rigid monomer approach for calculating the VRT levels of $(H_2O)_2$ and $(D_2O)_2$ ¹⁸ in which the calculations were done with the code developed by Groenenboom et al. for the SAPT-5st potential surface.³¹ The second approach is to separate intermolecular and intramolecular degrees of freedom adiabatically.^{48,49} In this 6+6 dimensional approach, first an adiabatic intermolecular potential surfaces is found by calculating intramolecular vibrational energy levels. Then this adiabatic potential surface is used in the calculations of intermolecular VRT levels. The MBR method can be combined with either approach used in studies of the water dimer with full-dimensional potential surfaces. A comparison of the results of MBR calculations with the previous studies might be a further test for the MBR method.

5. Discussion and conclusions

Given a Hamiltonian describing the motion of a system, eigenstates of this Hamiltonian will inevitably have the same symmetry properties as the Hamiltonian. In calculations, symmetry adaptation of basis functions can be done and each symmetry can be solved separately. This will help with reducing the computational cost of calculations. Symmetry adaptation of basis functions will guarantee that the resulting eigenstates will have a correct symmetry since any linear combination of basis functions will have the same symmetry as the basis functions. On the other hand, if the basis functions are not symmetry adapted, it is necessary to ensure that the eigenstates having correct symmetries can be obtained as linear combinations of basis functions. Consider the primitive spectral basis functions that are used in these calculations. As can be seen from Tables 3 and 5, application of any symmetry operation within the molecular symmetry group of the water dimer (please note that the symmetry operations that are not given in these tables can be expressed as products of the ones that are given) to symmetric top basis functions always results in a function within the same basis other than a possible phase factor. Consequently, even if the basis functions are not symmetry adapted, eigenstates having the correct symmetries can be obtained as linear combinations of the basis functions by calculations. The reason why the symmetric top basis works well in this calculation is related to the fact that these functions correspond to solution of a Hamiltonian describing the motion of a symmetric top rotating freely. The Hamiltonian describing the motion of a free body has only a kinetic energy term, and the kinetic energy operators have absolute symmetry. A free body may move anywhere in the space; since the space is isotropic it will have the same spectrum and the same eigenstates. As a result of that, application of any symmetry operation to these eigenstates always results in a function that can be expressed in terms of the eigenstates. Similarly, plane waves would work well for any problem describing the motion of a particle moving on a line regardless of the potential surface of the motion because the plane waves are the eigenstates of a Hamiltonian describing the motion of a free particle on a line. Another example is spherical harmonics that describe the motion of a free particle on a 2-sphere. These functions will work well with any Hamiltonian describing the motion of a particle on a 2-sphere regardless of what the potential surface is.

The problem with such primitive bases is that they are inefficient. In order to converge the calculations it is necessary to use a large number of primitive basis functions. As is well known, the efficiency of basis functions can be improved by letting them know about the underlying potential surface. This can be achieved by taking a model Hamiltonian that includes a potential energy function resembling the actual potential energy surface as much as possible, and then taking its eigenstates as an optimized basis for the actual problem. The Hamiltonian to be used for finding the optimized basis of a monomer should include the kinetic energy term of the monomer and a model potential surface. When the eigenstates of the model Hamiltonian are obtained they will have the symmetries of the model Hamiltonian, and these symmetries will not be the same as the Hamiltonian of the

full problem. The model Hamiltonian of a monomer cannot have any symmetries related to the inversion of the cluster or permutations of identical monomers, since it does not contain any information about them. What remain are symmetries related to the permutations of identical nuclei within the monomer. Therefore, when optimized basis functions of a monomer are obtained as a subset of the eigenstates of a model Hamiltonian, symmetries of these optimized basis functions will belong to irreducible representations of the group describing the permutational symmetries of identical nuclei within the monomer (the groups that are labeled as G_{k_i} in equation (1)). Provided that there exist optimized bases for each monomer, then the question becomes whether these basis functions can yield eigenstates of the full problem having proper symmetries or not. If the optimized basis of the cluster that is formed by using the optimized bases of monomers is not symmetry adapted for the full calculations, the answer is certainly no. In order to illustrate the point consider the water dimer problem considered here. A group theoretical analysis shows that the optimized basis functions of a monomer will be in the form of

$$\phi_i = \sum_l c_{il} |j_l k_l m_l\rangle \quad (32)$$

where k_l is either odd or even. When the permutation operation (12) is applied to the functions given above, by using the transformation properties given in Table 3 the result is obtained as

$$(12)\phi_i = \sum_l (-1)^{k_l} c_{il} |j_l k_l m_l\rangle. \quad (33)$$

Since k_l is either odd or even, the value of $(-1)^{k_l}$ is the same for all of the terms. Consequently, the result is really the original function times a phase factor. This is a result of the fact that the group $G_2^{(1)}$ includes the operation (12). However, consider what will happen when the symmetry operation E^* is applied to the optimized basis functions of the monomers. The effect of this operation on primitive basis functions can be seen in Table 3. Thus, when the inversion operation is applied to the optimized basis function given in equation (32), the result will be

$$E^* \phi_i = \sum_l (-1)^{k_l} c_{il} |j_l \bar{k}_l \bar{m}_l\rangle \quad (34)$$

Although the application of this operation introduces an overall phase factor again, this time m 's and k 's are changed. Therefore, the result is a new function, and it cannot be another optimized basis function since the model Hamiltonians of monomers do not include any information about the inversion symmetry of the cluster. A similar problem also occurs when the symmetry operation $(ab)(13)(24)$ is applied to the optimized basis functions. Consequently, from the illustration above it follows that the eigenstates of the full problem cannot be obtained as linear combinations of the optimized basis functions. In order to guarantee obtaining eigenstates having correct symmetries, optimized basis functions of monomers can be symmetry adapted. However, this will lead to a generalized eigenvalue problem instead of a standard eigenvalue problem since the new functions are not orthogonal to the optimized basis functions, i.e. the function in equation (34) is not orthogonal to the function in equation (32). Although there exist well-known methods of basis set orthogonalization, their application is not desirable in this case since they will destroy the optimized nature of the basis set. Since handling a generalized eigenvalue problem numerically is much harder than a standard eigenvalue problem, trying to avoid it is better. Consequently, in this paper while trying to develop an efficient method for calculating the spectra of molecular clusters, it was necessary to devote most of the discussion to the symmetries of molecular clusters.

The fact that the idea of obtaining optimized bases makes it necessary to divide the problem into smaller parts, it also makes it necessary to analyze how the symmetries of these parts are related to the symmetries of the full problem. This is what equations (1) and (3) achieve. The importance of equation (1) is that the partitioning of the molecular symmetry group of a cluster in that way is physically meaningful. Each of the groups G_{k_i} describes the symmetries of the model Hamiltonians of monomer calculations, and the group G_l describes the symmetries related to the permutations of identical monomers. The presence of a semidirect product in this equation complicates the analysis, but since the permutation of identical monomers brings in noncommutation of symmetry operations, its presence is inevitable. An analysis of the projection operators of semidirect product groups leads to equation (3). Thus equations (1) and (3) show that, for a cluster consisting of n monomers, symmetry adaptation of basis functions can be done in $n + 2$ steps sequentially. As long as primitive bases are used for calculations there is no difference between doing symmetry adaptations sequentially or in a single step. In this paper, sequential symmetry adaptation is combined with the idea of finding optimized basis functions and a new method for calculating the VRT spectra of molecular clusters named Monomer Basis Representation (MBR) is developed in section 3. The method suggests solutions to the symmetry adaptation problems related to the generation of optimized bases. The problem related to inversion symmetry is solved by using the technique of sequential symmetry adaptation again. It has been suggested that the invariance of the basis functions under the effect of the inversion operation can be achieved by symmetry adapting primitive monomer basis functions to the inversion subgroup while generating the optimized basis for the monomers. This will force them to be eigenstates of the inversion operator with the eigenvalues ± 1 . Consequently, the basis functions that are obtained as a tensor product of the monomer basis functions will be the eigenstates of the inversion operator with the eigenvalues ± 1 . Thus, the basis that is obtained as a direct product of the optimized monomer bases becomes invariant under the effect of the inversion operation. Symmetry adaptation of monomer basis functions to the inversion symmetry of the cluster makes them physically meaningless. However, they are just basis functions and as it can be seen from the results of computations they can be used to solve the full problem quite efficiently.

It has also been shown that the product basis of the optimized monomer bases can be made invariant under the effect of the operations permuting identical monomers by finding an optimized basis for a single monomer and then generating bases for other monomers from the basis of that monomer by repeated application of the generator of the group containing the symmetry operations permuting identical monomers. This way of generating bases for all of the monomers made it necessary to assume that the order of the group G_l is equal to the number of monomers: $l = n$.

While developing the method, the primitive bases of the monomers were never referenced. Thus, the nature of the primitive monomer bases does not matter. They can be product bases of 1-dimensional bases, or they can be multidimensional coupled bases. The symmetry adaptation procedure given here will work regardless of the nature of the primitive bases used in the monomer calculations.

Application of the MBR method has been illustrated by calculating the VRT spectra of the water dimer by using the SAPT-5st potential surface of Groenenboom et al.³¹ The calculations are done by using Wigner rotation functions as primitive bases. The use of the MBR method made it possible to decrease the size of monomer bases by a factor of ≈ 16 . The results of the calculations are in good agreement with both the original calculations of Groenenboom et al. and also with the experimental results. A detailed discussion of the results can be found in section 4.6.

Because of its efficiency, the MBR method can be used for studies of clusters bigger than dimers. In particular, since some experimental data about the water trimer are available,^{50–56} many researchers started to

work on it.^{5,57–65} However, since the size of the water trimer problem is too big to handle quantum mechanically, all the theoretical studies performed to date are based on very reduced dimensionality models, even for rigid monomers. The method developed in this paper may make it possible to study clusters as big as the water trimer with more realistic models. For example, consider the 9-dimensional Hamiltonian derived by van der Avoird et al.⁵ In that model, all of the monomers are allowed to rotate around their centers of mass but the centers of mass of monomers are fixed in space. If the trimer calculation required about the same number of optimized angular basis functions for a monomer, then a study of the 9-dimensional angular problem of the water trimer would require 10^6 basis functions. Although a problem of that size can be handled with iterative methods, it is still quite big. Nevertheless, it is reasonable to expect that the trimer problem can be solved with fewer optimized basis functions per monomer. Firstly, the water trimer is much more symmetric than the water dimer. Secondly, a study of the water trimer with a pairwise potential surface will have much deeper potential wells. A qualitative model for a possible application of the MBR method to the water trimer has already been reported.⁶ Its implementation remains a task for future work.

6. Decomposition of projection operators

In order to find a relation between the projection operators of a product group and the projection operators of its subgroups, it is necessary to find a relation between the characters of the elements of the product group and the characters of the elements of the subgroups. Such a relation can be derived from the following character equation, which holds in any irreducible representation of any group:⁶⁶

$$N_i\chi(C_i)N_j\chi(C_j) = d \sum_k c_{ijk} N_k\chi(C_k). \quad (35)$$

In the equation above, C_i , C_j , and C_k are classes of the group; N_i , N_j , and N_k are the number of elements in these classes; and the coefficients c_{ijk} are defined by the class multiplication equation $C_i C_j = \sum_k c_{ijk} C_k$; and d is the dimension of the irreducible representation.

Consider a group G that can be written as a semidirect product of 2 of its subgroups H and K such that $G = H \circledast K$. If h is an element of group H that is in class C_i of the group G and k is an element of the group K that is in class C_j of the group G , and $g = hk$ is an element of the group G that is in class C_m , then provided that the class multiplication constants satisfy the equation

$$c_{ijk} = r\delta_{km}, \quad (36)$$

where r is an integer, equation (35) reduces to

$$\chi(h)\chi(k) = d\chi(g), \quad (37)$$

and equation (3) follows. Consequently, equation (36) is the sufficient condition for which the sequential symmetry adaptation will work for any irreducible representation of the product group. This equation seems to be satisfied in many cases for the physically meaningful partitioning of the molecular symmetry group of molecular clusters given in equation (1). The examples include molecular symmetry groups of the clusters $(H_2O)_2$, $(CO_2)_2$, $(H_2O)_3$, $(H_2O)_2D_2O$. However, although it has been argued before⁶ that the equation (36) holds for any irreducible representation of any semidirect product group, this is not the case. For example, if pairwise permutations of monomers were a feasible symmetry operation for the water trimer so that the

molecular symmetry group were G_{96} instead of G_{48} , then equation (36) would not hold for the semidirect product multiplication defined by equation (1).

It should also be noted that equation (37) holds for any 1-dimensional representation. This follows from the fact that 1-dimensional representations are representations by nonzero complex numbers and a representation should satisfy equation (37) by definition of representation since the characters of the elements are just the complex numbers representing them. Consequently, even if the condition given in equation (36) does not hold, sequential symmetry adaptation can still be used for 1-dimensional representations.

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