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Cross-contamination of the fitting parameters in multidimensional tunneling treatments

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Abstract

In this paper we examine the two-dimensional tunneling formalism used previously to fit the hydrogen-transfer and internal-rotation splittings in the microwave spectrum of 2-methylmalonaldehyde in an effort to determine the origin of various counterintuitive results concerning the isotopic dependence of the internal-rotation splittings in that molecule. We find that the cause of the problem lies in a “parameter contamination” phenomenon, where some of the numerical magnitude of splitting parameters from modes with large tunneling splittings “leaks into” the parameters of modes with smaller tunneling splittings. We show that such parameter contamination, which greatly complicates the determination of barrier heights from the least-squares-fitted splitting parameters, will be a general problem in spectral fits using the multi-dimensional tunneling formalism, since it arises from subtle mathematical features of the non-orthogonal framework functions used to set up the tunneling Hamiltonian. Transforming to a physically less intuitive orthonormal set of basis functions allows us to give an approximate numerical estimate of the contamination of tunneling parameters for 2-methylmalonaldehyde by combining a dominant tunneling path hypothesis with results recently given for the hydrogen-transfer-internal-rotation potential function for this molecule.

Keywords

Large amplitude motion; Multidimensional tunneling formalism; Cross-contamination of parameters; Internal rotation; Inversion; 2-Methylmalonaldehyde

1. Introduction

Recent studies [1,2] using a group-theoretically derived multidimensional tunneling formalism to fit microwave spectra of the —OH and —OD isotopologs of 2-methylmalonaldehyde (2-MMA) encountered an unexpected problem with the CH₃ internal-rotation tunneling parameters in the two species O=C—C(CH₃)=C—OH and O=C—C(CH₃)=C—OD, namely: the tunneling parameter $3|\hbar_3|$ describing the A/E splitting arising from the pure methyl-top internal rotation motion was found to increase from 334.5 MHz to

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1044.6 MHz upon deuteration, suggesting a significant decrease in barrier height for the —OD isotopolog. This increase in A/E splitting upon deuteration seems counterintuitive on two levels: (i) One would expect almost no noticeable effect on the internal rotation barrier height from such a distant (see Fig. 1 of [2]) deuteration. (ii) If there were to be some mass effect on the splitting, then deuteration makes the molecule heavier, so that involvement of other atoms of the molecule in the methyl-top internal rotation motion should only increase the effective mass of this motion, and thus decrease the A/E splitting. At the time, no satisfactory explanation for this counterintuitive result could be found. Further empirical evidence could come from the closely related molecule 5-methyltropolone [3], but unfortunately no deuterated data exists for this molecule. An analogous large increase in A/E splitting was not found when the —NH₂ [4] and —ND₂ [5] isotopologs of methylamine (CH₃NH₂) were treated using the same tunneling formalism, but the large change in reduced moments of inertia for internal rotation motion in deuterated isotopologs of CH₃NH₂ means that V_3 barrier heights should be compared, rather than energy level splittings, and a final spectroscopic analysis for CH₃-ND₂ has not yet been published [5].

The tunneling formalism under discussion involves in fact two main splitting parameters h_2 and h_3 , which are associated with quite different tunneling motions (see Section 2). In 2-MMA, where the counterintuitive results are found, $|h_2| \gg |h_3|$. In CH₃NH₂, where no counterintuitive results are found, $|h_2| \approx |h_3|$. This led to speculation in [2] that the tunneling splitting parameters in the multidimensional tunneling formalism were not conceptually pure, i.e., that (by some unknown mathematical mechanism) a small amount of the large parameter h_2 in 2-MMA could “leak into” and contaminate the fitted value of the much smaller parameter h_3 . Since h_2 for the —OH isotopolog is nearly eight times larger than for —OD, the contamination of h_3 caused by leakage from h_2 could be much larger for —OH than for —OD. Furthermore, this “parameter leakage mechanism” might well give rise to no noticeable discrepancy in the h_3 values for CH₃NH₂ and CH₃ND₂, since h_2 and h_3 have comparable magnitudes for methylamine.

In this paper: (i) we supplement the tunneling matrix formalism for methylamine-like molecules [6] in a way that allows us to determine the origin of the counterintuitive results on the tunneling parameters in 2-MMA, and (ii) we give a numerical estimate of the contamination of tunneling parameters for the 2-MMA molecule by combining a dominant tunneling path hypothesis with results on potential parameters recently given by Gulaczyk and Kręglewski [7].

2. Brief review of the form of the Hamiltonian matrix in the tunneling formalism of [6]

In preparation for the detailed discussion to follow, we briefly review some aspects of the tunneling formalism in [6]. The physical model assumes that the molecule is confined for many vibrations to one of its n identical minima (frameworks), but that it occasionally tunnels from one of these minima to another. Tunneling between these frameworks gives rise to splittings in what would otherwise be an ordinary asymmetric-rotor microwave spectrum. To treat the tunneling problem we use vibrational functions localized on equivalent minima

as basis functions; their explicit form is assumed to be unknown because of difficulties in parametrizing these functions to the necessary level of accuracy. Although we are not able to calculate explicitly various integrals involving these “unknown” vibrational functions, we can treat these integrals as the fitting parameters of the phenomenological Hamiltonian. The problems which arise from non-orthogonality of these basis functions are the cause of the cross-contamination of the fitting parameters discussed in more detail later in the text.

We start our discussion from the Hamiltonian matrix of the tunneling formalism, which for given J has the form of a partitioned matrix, with rows and columns labeled by $|m; K\rangle$. The integer m , satisfying $1 - m \leq n$, labels the frameworks in the molecule among which tunneling occurs; the quantum number K , satisfying $-J \leq K \leq +J$, labels the projection along the molecule-fixed z axis of each of the $2J + 1$ rotational functions of given J and M . (The projection along the laboratory-fixed Z axis is given by M , but this quantum number can be ignored for energy level calculations in the absence of external electric or magnetic fields.) The large blocks in the partitioned Hamiltonian matrix are thus labeled by a pair of framework numbers (m', m'') . A given location within each $(2J + 1) \times (2J + 1)$ (m', m'') block is labeled by a pair of rotational projection quantum numbers (K', K'') .

The diagonal blocks with $m' = m'' \equiv m$ contain matrix elements of the form $\langle m; K' | H | m; K'' \rangle$. The K', K'' matrix elements are identical for each m , and contain a sum of terms arising from operators in the vibration-rotation Hamiltonian of a (hypothetical) non-tunneling molecule whose vibrational excursions are constrained to be small enough that the molecule remains confined to framework m , i.e., constrained to be small enough that the molecule cannot undergo any tunneling motions. These diagonal blocks are of no further interest for the present discussion.

The off-diagonal blocks with $m' = m'' + 1$ or $m' = m'' - 1$ contain matrix elements of the form $\langle m + 1; K' | H | m; K'' \rangle$ or $\langle m - 1; K' | H | m; K'' \rangle$. Each of these $m = \pm 1$ tunneling matrix elements consists of a sum of terms that resemble, but are not identical to, the terms found in the $m = 0$ diagonal blocks of the previous paragraph. They are often referred to as nearest-neighbor tunneling matrix elements, because they connect “adjacent” basis functions in some appropriately ordered basis set. Group-theory requires that various matrix elements in these blocks are related by symmetry considerations, i.e., they must have the same magnitude, but their phase factors may be different. We are interested here only in the rotationally-independent (i.e., constant) part of the diagonal elements within these off-diagonal blocks. These can all be represented by the $m = 1 \rightarrow 2$ matrix element $h_2 \equiv \langle 2; K = 0 | H | 1; K = 0 \rangle$, since the nearest-neighbor tunneling frequency h_2 (as defined in [6]) is the same for all m values and depends only on the difference $|m| = |m' - m''| = |(m \pm 1) - m| = 1$.

The off-diagonal blocks with $m' = m'' + 2$ or $m' = m'' - 2$ contain matrix elements of the form $\langle m + 2; K' | H | m; K'' \rangle$ or $\langle m - 2; K' | H | m; K'' \rangle$. Various matrix elements in these $m = \pm 2$ tunneling blocks are also related by symmetry considerations. We are again interested only in the rotationally-independent part of the diagonal elements within each of these blocks, which we represent by $h_3 \equiv \langle 3; K = 0 | H | 1; K = 0 \rangle$. Again, h_3 is the same for all m

values and depends only on the difference $|m| = 2$. The parameter h_3 is called the next-nearest-neighbor tunneling frequency here.

Next-next-nearest-neighbor, next-next-next-nearest-neighbor, etc. tunneling matrix elements are defined in an analogous way with $|m' - m''| = 3, 4$, etc., but they are not of interest for the present discussion.

A referee has correctly pointed out that the nearest-neighbor, next-nearest-neighbor, etc. nomenclature used in the previous two paragraphs is quite confusing because the $1 \rightarrow 2$ and $1 \rightarrow 3$ tunneling motions correspond to two completely different physical motions in this problem. We thus add as a clarification the fact that this nomenclature arose historically from a purely mathematical point of view, since the permutation-inversion operator $[(123)(45)(78)(9,10)]^{(n-1)}$ applied to a wavefunction localized in framework 1 generates an isoenergetic wavefunction localized in framework n , where $1 \leq n \leq 6$ (see Fig. 2 of [1]). This formal group-theoretical relation then suggests representing the six frameworks as six points on a circle, each separated by 60° from its two nearest neighbors. If only tunneling motions that occur as a sequence of $n \rightarrow n+1$ steps on the circumference of this circle are considered for labeling purposes, then the nearest-neighbor nomenclature makes sense. When, however, $n \rightarrow n+2$ tunneling motions are visualized as occurring in one step by having the system point move directly across the interior of the circle, then this labeling nomenclature becomes confusing.

3. Main cause of the problem

Physically speaking, the main cause of the inconsistent results in the least-squares fitted tunneling splitting parameters in [1,2] comes from the explicit assumption of a non-orthonormal basis set when setting up the Hamiltonian matrix followed by the implicit assumption of an orthonormal basis set when this matrix is diagonalized. The mathematical considerations below, which reformulate the tunneling formalism of [6] to take into account the fact that the framework basis functions are not mutually orthogonal, have been mentioned previously [8–10] by one of the authors, but that material is developed more fully here.

As is well known, when each eigenfunction Ψ_k of Schrödinger's equation is expanded in terms of a basis set ϕ_j as $\Psi_k = \sum_j \phi_j V_{jk}$, then Schrödinger's equation takes the form

$$H\Psi_k = H \left[\sum_j \phi_j V_{jk} \right] = \Psi_k W_k = \left[\sum_j \phi_j V_{jk} \right] W_k, \quad (1)$$

where W_k is the eigenvalue to which Ψ_k belongs. Multiplying by ϕ_i^* and integrating then yields the usual matrix equation (in an obvious mixture of subscripted and unsubscripted matrix notation)

$$\sum_j \langle \phi_i | H | \phi_j \rangle V_{jk} = \sum_j H_{ij} V_{jk} = HV = \sum_j \langle \phi_i | \phi_j \rangle V_{jk} W_k = \sum_j \Delta_{ij} V_{jk} W_k = \Delta VW. \quad (2)$$

If the basis set is orthonormal, the overlap-integral matrix $\Delta = E$ (the identity matrix), and we obtain the usual expression for diagonalizing a matrix H by using the matrix V containing its eigenvectors in columns,

$$V^{-1}HV = W. \quad (3)$$

In tunneling problems, however, basis functions having the form of near-harmonic-oscillator vibrational wavefunctions localized in only one framework are assumed to have a non-zero overlap integral with similar basis functions localized in another framework, so that $\Delta \neq E$. In connection with this assumption, it is interesting to note that if infinite walls are erected to separate the various framework positions in the potential function, then basis functions localized on a given framework will vanish at the walls around that framework. As a consequence, no mathematical communication whatever will occur between basis functions localized on different frameworks, i.e., all matrix elements $\langle p | H | q \rangle \equiv 0$ if framework p and framework q are different. Even if basis functions localized on a given framework are allowed to extend into regions containing other frameworks, but are constrained to be orthogonal to basis functions for these other frameworks, a problem still arises in the tunneling formalism since tunneling splittings caused by constant terms h in the Hamiltonian must all vanish, i.e., $\langle p | h | q \rangle \equiv 0$ if $p \neq q$. Thus, non-orthogonal basis sets, and overlap-integral matrices $\Delta \neq E$ in Eq. (2), are unavoidable features of traditional tunneling formalisms.

Making use of a common mathematical device we can diagonalize the Hermitian overlap-integral matrix Δ , using a diagonalization expression analogous to Eq. (3),

$$U^{-1}\Delta U = d, \quad (4)$$

and then formally define the $+1/2$ and $-1/2$ powers of Δ by the equation

$$\Delta^{\pm 1/2} \equiv U d^{\pm 1/2} U^{-1}. \quad (5)$$

The matrices $\Delta^{\pm 1/2}$ permit us to start from Eq. (2) and write

$$HV = \Delta VW \rightarrow \quad (6)$$

$$(\Delta^{-1/2} H \Delta^{-1/2})(\Delta^{+1/2} V) = H^{fit} V^{fit} = (\Delta^{+1/2} V) W = V^{fit} W, \quad (7)$$

so that the solution matrices V and W in Eq. (6) for given H and E (i.e., the eigenvectors and eigenvalues of H) can be obtained by solving an ordinary eigenvalue problem involving the modified matrices in Eq. (7), i.e., by solving $H^{fit} V^{fit} = V^{fit} W$.

As it happens, it was always assumed for least-squares fitting purposes in the spectral analyses carried out in [1–4] that $E = E$, so that in fact the matrix equation $H^{fit} V^{fit} = V^{fit} W$ was always solved, i.e., the diagonalization procedure in Eq. (3) was carried out. As a result, elements of the tunneling matrix H^{fit} were parameterized in terms of various molecular constants, and these constants were then adjusted until differences $W_a - W_b$ in the eigenvalues agreed in a least-squares sense with the corresponding experimentally observed transition frequencies $\nu_{ab} = W_a - W_b$. In reality, however, $E \neq E$, so that the matrix equation $HV = VW$ should have been solved. Eq. (7) indicates that this equation has the same eigenvalues as the modified equation $H^{fit} V^{fit} = V^{fit} W$, so that the calculated transition frequencies $W_a - W_b$ are the same in either treatment. We can use the concept of “contamination” to describe differences between the matrix elements of H and H^{fit} . The amount of contamination in the fitted matrix element $(H^{fit})_{ij}$, i.e., in the matrix element mistakenly thought in [1–4] to correspond only to the tunneling path $i \rightarrow j$, can be obtained from Eq. (8a). Conversely, the true tunneling matrix element $(H)_{ij}$ for the path $i \rightarrow j$ can be obtained from the fitted parameters $(H^{fit})_{pq}$ by using Eq. (8b).

$$(H^{fit})_{ij} = \sum_{pq} (\Delta^{-1/2})_{ip} (H)_{pq} (\Delta^{-1/2})_{qj} \quad (8a)$$

$$(H)_{ij} = \sum_{pq} (\Delta^{+1/2})_{ip} (H^{fit})_{pq} (\Delta^{+1/2})_{qj} \quad (8b)$$

Eq. (8) indicates that the fitted matrix elements in H^{fit} are relatively simple linear combinations of the physically meaningful tunneling matrix elements in H , and vice versa. If Eq. (8) is evaluated only for $J=0$, then we see that the fitted values of the tunneling frequencies $(H^{fit})_p$ are also linear combinations of the physically meaningful tunneling frequencies h_n occurring in the operator H of Eq. (31) of [6]. It is for this reason that we say that a part of the magnitude of all tunneling frequencies in the problem will “leak into” or “contaminate” the magnitude of any given fitted tunneling frequency. This type of leakage is a general phenomenon that will occur in any multidimensional tunneling problem treated using the formalism of [6] (or any similar formalism that assumes the overlap matrix $S = E$ during the least-squares fitting process).

Eq. (8b) can be used to determine the effect on the tunneling parameters in H of adding an arbitrary constant E_0 to all energies on the diagonal of H^{fit} , i.e., to determine the effect of using a fitting Hamiltonian $H^{fit} + E_0$ with an energy origin shifted by E_0 , instead of using H^{fit} with “its original” energy origin. (In the shorthand notation of this paragraph, E_0 represents a scalar constant when added to the Hamiltonian operator H^{fit} , but represents E_0 times the unit matrix when added to the Hamiltonian matrix H^{fit} .)

$$\begin{aligned}
 (H^{shifted})_{ij} &= \sum_{pq} (\Delta^{+1/2})_{ip} (H^{fit} + E_0)_{pq} (\Delta^{+1/2})_{qj} = \sum_{pq} (\Delta^{+1/2})_{ip} (H^{fit})_{pq} (\Delta^{+1/2})_{qj} + E_0 \Delta_{ij} \\
 &= (H)_{ij} + E_0 \Delta_{ij},
 \end{aligned}$$

(9)

Eq. (9) indicates (somewhat counterintuitively) that H does not just acquire the additive constant E_0 on its diagonal, but all tunneling parameters, which occur by definition in off-diagonal positions in the H matrix, are also affected by a change in the energy origin of H^{fit} when E . On the other hand (now as intuitively expected), the eigenvalues W in Eq. (6) do each acquire an additive constant E_0 , since from Eqs. (6) and (9):

$$W^{shifted} = V^{-1} \Delta^{-1} H^{shifted} V = V^{-1} \Delta^{-1} (H + E_0 \Delta) V = W + E_0. \quad (10)$$

4. Theoretical development based on the introduction of an orthonormal set of vibrational framework functions

In this section we focus on defining two sets of vibrational basis functions that are useful in discussing the origin of the problem, rather than focusing on the two sets of eigenvector coefficients V and V^{fit} multiplying the same basis set, that arose in the equations of Section 3. We follow essentially the procedures, notation, and explanations given in Ref. [6], but give more detail, since understanding well the nature of these basis functions is the easiest way to understand the origin of the present problem.

4.1. Two different sets of vibrational framework functions

We consider two kinds of large-amplitude vibrational framework-functions, namely the set $\{|\dot{i}\rangle\}$, which was discussed in detail in Section 4 of [6], and a set $\{|\dot{i}; new\rangle\}$. For the purposes of this section, all functions in both sets correspond to the same vibrational state in the molecule, i.e., they are characterized by the same vibrational quantum numbers. It is sufficient to consider only the vibrational part of the total basis functions because, as discussed in connection with Table 8 of [6], total basis functions in the tunneling formalism there are formed from products of a vibrational (torsional-wagging) factor and an independent rotational factor.

Each torsional-wagging function in the set $\{|\dot{i}\rangle\}$ is strictly localized around minimum i on the potential surface, i.e., it begins to die off exponentially long before it approaches other minima on the surface. The function $|\dot{i}\rangle$, for $i = 2, \dots, n$ (where n is the number of frameworks, with $n = 6m$ for the methylamine-like case), is constructed from the torsional-wagging function $|1\rangle$ localized around minimum 1 by the group theoretical operation

$$|i\rangle = a^{i-1}|1\rangle, \quad (11)$$

where a is an m -fold extended permutation-inversion group operation [6] corresponding to (123)(45) in the permutation-inversion group for methylamine and to (123)(45)(78)(9,10) for 2-MMA. The set of framework functions $\{|i\rangle\}$ representing the same torsional-wagging state localized on each of the frameworks i , for $i = 1, 2, \dots, 6m$, is not an orthonormal set since the overlap integrals $\langle i | j \rangle$ with $i \neq j$ are not zero.

On the other hand, an orthonormal basis set $\{|i: new\rangle\}$ can be constructed by taking linear combinations of the $\{|i\rangle\}$ according to the Löwdin transformation [11]:

$$|i: new\rangle = \sum_{k=1}^n (\Delta^{-1/2})_{ki} |k\rangle, \quad (12)$$

where the matrix $\Delta^{-1/2}$ is defined in Eq. (5). We show in the Appendix that

$$\langle i: new | j: new \rangle = \delta_{ij} \text{(orthonormality)} \quad (13)$$

$$|i: new\rangle = a^{i-1} |1: new\rangle, \quad (14)$$

where Eq. (14) is the analog of the procedure illustrated in Table IV of [6]. Note that because of the linear combinations in Eq. (12), $|i: new\rangle$ is no longer completely localized near minimum i . As a result, the orthogonal basis functions constructed above have lost their simple “tunneling” meaning, since each such basis function involves distributing differently weighted copies of a given harmonic-oscillator vibrational wavefunction over many equilibrium frameworks.

4.2. General expressions for contamination coefficients caused by the non-zero overlap integrals

We give in this section a relation between two types of tunneling matrix elements $\langle i | h_v | j \rangle$ and $\langle i: new | h_v | j: new \rangle$, where h_v represents an operator in the Hamiltonian that depends only on the large-amplitude and small-amplitude vibrational coordinates, i.e., an operator with no dependence on the total angular momentum operators J_x , J_y or J_z . The quantities $\langle i | h_v | j \rangle$ are the physically meaningful “true” tunneling matrix elements, since they are defined in terms of basis functions strictly localized near a given minimum, while $\langle i: new | h_v | j: new \rangle$ are the quantities determined in the least-squares fits of [1–5], since they are obtained from matrix diagonalizations of H^{fit} in Eq. (8a) that are carried out assuming an orthonormal basis set with all off-diagonal overlap integrals equal to zero.

Using the group theoretical manipulations described in connection with Eqs. (20) and (21) of Ref. [6], it is found that the matrix elements $\langle i|h_v|j\rangle$ and $\langle i:new|h_v|j:new\rangle$ (for given $i = 1, 2, \dots, n$ and given $j = 1, 2, \dots, n$) can be reduced to the forms $\langle 1|h_v|r\rangle$ and $\langle 1:new|h_v|r:new\rangle$, respectively, for some $r = 1, 2, \dots, N$, where $n = 6m$ and $N = 3m + 1$ for the methylamine-like case. From Eqs. (5) and (12), we have the following relation between $\langle 1:new|h_v|r:new\rangle$ and the $\langle j|h_v|k\rangle$ for $r = 1, 2, \dots, N$:

$$\langle 1:new|h_v|r:new\rangle = \sum_{j,k=1}^n (\Delta^{-1/2})_{1j} \langle j|h_v|k\rangle (\Delta^{-1/2})_{kr}. \quad (15)$$

This leads immediately (after setting $h_v = 1$) to

$$\langle 1:new|r:new\rangle = \sum_{j,k=1}^n (\Delta^{-1/2})_{1j} \Delta_{jk} (\Delta^{-1/2})_{kr} = \delta_{1r}, \quad (16)$$

which serves as a check on the formalism, since the functions $|i:new\rangle$ were constructed to be orthogonal. It is shown in the Appendix that we can use Eqs. (5) and (15) to express $\langle 1:new|h_v|r:new\rangle$ as a sum of the true tunneling matrix elements $\langle 1|h_v|1+j\rangle$.

$$\langle 1:new|h_v|r:new\rangle = \sum_{j=0}^{N-1} A(r,j) \langle 1|h_v|1+j\rangle \quad (17)$$

We refer to the coefficients $A(r,j)$ as “contamination coefficients.” They describe linear combinations of tunneling matrix elements, rather than linear combinations of basis functions, and are given (in the notation of [6] and for $0 \leq j \leq 3m$) by:

$$A(r, j=0) = \frac{1}{6m} \left(\frac{1}{d_1} + \frac{(-1)^{r-1}}{d_2} + \sum_{s=1}^{3m-1} \frac{2 \cos\{(r-1)s\varepsilon\}}{d_{2s+1}} \right),$$

$$A(r, j=3m) = \frac{1}{6m} \left[\frac{1}{d_1} + \frac{(-1)^{r-1}(-1)^{3m}}{d_2} + \sum_{s=1}^{3m-1} \left(\frac{2 \cos\{[3m-(r-1)]s\varepsilon\}}{d_{2s+1}} \right) \right],$$

$$\begin{aligned} A(r, j) = & \frac{1}{6m} \left[\frac{1}{d_1} + \frac{(-1)^{r-1}(-1)^j}{d_2} + \sum_{s=1}^{3m-1} \left(\frac{2 \cos\{[j-(r-1)]s\varepsilon\}}{d_{2s+1}} \right) \right] \\ & + \frac{1}{6m} \left[\frac{1}{d_1} + \frac{(-1)^{r-1}(-1)^j}{d_2} + \sum_{s=1}^{3m-1} \left(\frac{2 \cos\{[-j-(r-1)]s\varepsilon\}}{d_{2s+1}} \right) \right], \end{aligned} \quad (18)$$

where, with $i \equiv \langle 1|1+i\rangle$, $s = 1, 2, \dots, 3m-1$, and $\varepsilon \equiv 2\pi/6m$, we define

$$d_1 = 1 + \sum_{k=1}^{3m-1} 2\Delta_k + \Delta_{3m},$$

$$d_2 = 1 + \sum_{k=1}^{3m-1} (-1)^k 2\Delta_k + (-1)^m \Delta_{3m}, \quad (19)$$

$$d_{2s+1} = 1 + \sum_{k=1}^{3m-1} 2\Delta_k \cos(ks\epsilon) + (-1)^s \Delta_{3m}$$

4.3. Avoidance of an ambiguity involved in the tunneling matrix elements $\langle 1|h_v|r\rangle$

As pointed out following Eq. (9), the value of the true tunneling matrix element $\langle 1|h_v|r\rangle$ obtained from Eq. (8b) is dependent on the constant term in the fitting Hamiltonian H^{fit} , i.e., is dependent on the arbitrarily chosen origin of the energy scale in H^{fit} , even when $r = 1$. The matrix element $\langle 1 : new|h_v|r : new\rangle$ for $r = 1$, however, is independent of this constant term because of Eq. (13). It is therefore inconvenient to use Eq. (17) when $r = 1$, since the left side is independent of the arbitrarily chosen energy origin, while the right side is composed of terms whose values do depend on this choice.

To remove the ambiguities associated with Eq. (17), we define a modified tunneling matrix element $\langle 1||h_v||s\rangle$ ($s = 1, 2, \dots, N$) by

$$\langle 1||h_v||s\rangle \equiv \langle 1|h_v - h_0|s\rangle. \quad (20)$$

If we choose $h_0 \equiv \langle 1|h_v|1\rangle$, then $\langle 1||h_v||s\rangle$ is independent of any constant shift c in the energy origin, since the new operator $h_v' = h_v + c$ satisfies

$$\langle 1||h_v'||s\rangle = \langle 1|[(h_v + c) - \langle 1|h_v'|1\rangle]|s\rangle = \langle 1|h_v + c - h_0 - c|s\rangle = \langle 1||h_v||s\rangle. \quad (21)$$

We can use Eq. (17) and the new quantity in Eq. (20) to obtain an expression similar to Eq. (17)

$$\langle 1 : new|h_v|r : new\rangle = h_0 \delta_{r,1} + \sum_{j=1}^{N-1} A(r; j) \langle 1||h_v||1+j\rangle, \quad (r = 1, 2, \dots, N), \quad (22)$$

where all terms are independent of any constant shift in the Hamiltonian operator h_v , except when $r = 1$.

4.4. Contamination of tunneling matrix elements in the 2-MMA molecule

To focus on the essential features of the contamination problem in 2-MMA, we consider only the three lowest-order non-tunneling and tunneling overlap integrals $\langle 0 | \equiv 1$, $\langle 1 |$, and $\langle 2 |$, and only the three lowest-order non-tunneling and tunneling matrix elements $\langle 1 | h_v | 1 \rangle \equiv 0$, $\langle 1 | h_v | 2 \rangle$, and $\langle 1 | h_v | 3 \rangle$. We also approximate $(1 + a_1 + b_2)^{-1}$ as $(1 - a_1 - b_2)$, since the tunneling overlap integrals are assumed to obey $|a_1| \ll 1$ and $|b_2| \ll 1$. With these simplifications, and using summation procedures similar to those in Eqs. (A.13)–(A.15), we obtain from Eqs. (18), (19), and (22):

$$\langle 1 : new | h_v | 2 : new \rangle = (1 - \Delta_2) \langle 1 | h_v | 2 \rangle - \Delta_1 \langle 1 | h_v | 3 \rangle \quad (23)$$

$$\langle 1 : new | h_v | 3 : new \rangle = -\Delta_1 \langle 1 | h_v | 2 \rangle + \langle 1 | h_v | 3 \rangle \quad (24)$$

Since $|\langle 1 : new | h_v | 2 : new \rangle| \gg |\langle 1 : new | h_v | 3 : new \rangle|$ from the fit of the 2-MMA experimental data, we also have $|\langle 1 | h_v | 2 \rangle| \gg |\langle 1 | h_v | 3 \rangle|$ for physically meaningful tunneling matrix elements. Accordingly, $\langle 1 : new | h_v | 3 : new \rangle$ will be contaminated by $\langle 1 | h_v | 2 \rangle$ much more than $\langle 1 : new | h_v | 2 : new \rangle$ is contaminated by $\langle 1 | h_v | 3 \rangle$ in 2-MMA.

5. Numerical estimate of contamination in the tunneling parameter $\langle 1 : new | h_v | 3 : new \rangle$ of 2-MMA, using potential parameters and a dominant-path approximation

To begin the estimation, we assume that the hydrogen-transfer tunneling motion can be described phenomenologically by the following Hamiltonian

$$H = -F \frac{\partial^2}{\partial s^2} + V_6 \frac{1}{2} (1 - \cos 6s). \quad (25)$$

Eq. (25) can be considered to be a one-dimensional dominant-path approximation for the hydrogen-transfer tunneling motion (i.e., for the H-transfer plus corrective CH₃-internal-rotation motion).

To perform numerical calculations using Eq. (25), we need values for F and V_6 . For present purposes, we set V_6 equal to the ab initio value (1492.9 cm⁻¹) given by Gulaczyk and Kręglewski [7]. F is often determined from structural information, but the situation for 2-MMA is complicated, because we need an effective F value that properly averages two contributions to the total momentum at any given point along the H-transfer path, one contribution generated by the OH hydrogen atom moving at one velocity, and another contribution generated by the CH₃ hydrogen atoms moving at some different velocity. Rather than trying to calculate this effective F from structural information along some assumed tunneling path in this two-dimensional space, we instead adjust F to get agreement

with experimentally determined tunneling splittings. But even here a problem arises, because there are no allowed electric-dipole transitions between states of different A, B, E₁, and E₂ symmetries, so the required “experimental” energy differences must in fact be calculated from the same fitted tunneling parameters whose degree of contamination we are trying to determine.

Eq. (31) of the tunneling formalism of [6] indicates that energies $W(\Gamma)$ for states of 2-MMA belonging to symmetry species Γ can be expressed in terms of the three lowest-order tunneling parameters as

$$W(A_1) = 2h_{2v} + 2h_{3v} + 2h_{4v}$$

$$W(E_1) = h_{2v} - h_{3v} - 2h_{4v} \quad (26)$$

$$W(E_2) = -h_{2v} - h_{3v} + 2h_{4v}$$

$$W(B_1) = -2h_{2v} + 2h_{3v} - 2h_{4v},$$

By substituting the fitted values of $h_{2v} = -21013.006$ MHz and $h_{4v} = 9.306$ MHz for 2-MMA-d0, or $h_{2v} = -2695.574$ MHz and $h_{4v} = 1.766$ MHz for 2-MMA-d1, as determined by Ilyushin et al. [2], we obtain numerical values for the two energy splittings in Eq. (27), which do not depend on h_{3v} (the value of which, as mentioned earlier, is thought to be much more strongly contaminated than the value of h_{2v}).

$$W(B_1) - W(A_1) = -4h_{2v} - 4h_{4v} \quad (27)$$

$$W(E_2) - W(E_1) = -2h_{2v} + 4h_{4v}.$$

Adjusting the value of F in Eq. (25) to get agreement with Eq. (27) leads to a system of two equations in one unknown, and to a value of F for each isotopolog of

$$F(2 - \text{MMA} - \text{d0}) = 11.27 \text{ cm}^{-1}, \quad (28)$$

$$F(2 - \text{MMA} - \text{d1}) = 7.14 \text{ cm}^{-1}.$$

We can now use Eq. (25) together with the F and V_6 parameters chosen above to calculate the energy levels associated with a hypothetical pure hydrogen-tunneling motion. For this motion there is no direct $1 \rightarrow 3$ tunneling path, because the coordinate for this purely internal-rotation motion “does not exist” in the one-dimensional Hamiltonian of Eq. (25). We can again express the resultant energy levels in terms of the three lowest-order tunneling contributions [6]

$$W(A_1) = 2h_{2v} + 2h'_{3v} + 2h_{4v}$$

$$W(E_1) = h_{2v} - h'_{3v} - 2h_{4v} \quad (29)$$

$$W(E_2) = -h_{2v} - h'_{3v} + 2h_{4v}$$

$$W(B_1) = -2h_{2v} + 2h'_{3v} - 2h_{4v},$$

where the $1 \rightarrow 3$ tunneling parameter is now called h_{3v}' . Eq. (24) shows that for the two-dimensional tunneling problem in 2-MMA, the fitted matrix element $\langle 1: new | h_v | 3: new \rangle$ contains two contributions. Since the direct $1 \rightarrow 3$ large-amplitude torsional coordinate is missing in the one-dimensional Hamiltonian of Eq. (25), it seems reasonable to set $\langle 1 || h_v || 3 \rangle = 0$ when Eq. (29) is applied to eigenvalues from Eq. (25), and to thus equate h_{3v}' in Eq. (29) with the contamination contribution in Eq. (24):

$$h'_{3v} = -\Delta_1 \langle 1 || h_v || 2 \rangle. \quad (30)$$

A linear combination of the four energies in Eq. (29) then gives

$$h'_{3v} = [W(A_1) + W(B_1) - W(E_1) - W(E_2)]/6. \quad (31)$$

After substituting eigenvalues calculated from Eq. (25) into Eq. (31), we obtain

$$h'_{3v}(2 - \text{MMA} - \text{d0}) = 77.57 \text{ MHz} \quad (32)$$

$$h'_{3v}(2 - \text{MMA} - \text{d1}) = 1.69 \text{ MHz},$$

which are our estimated cross-contamination contributions to the values of $h_{3v}(2\text{-MMA-d0}) = -111.49 \text{ MHz}$ and $h_{3v}(2\text{-MMA-d1}) = -348.21 \text{ MHz}$ given in [2].

Although these h_{3v}' values are not quantitatively reliable (because of the simplifying assumptions mentioned at the beginning of this section), they clearly show that the contamination effect is much smaller in 2-MMA-d1 than in 2-MMA-d0. Accordingly, it is reasonable that the barrier height for the *pure* CH₃ internal rotation should be deduced from the value of $h_{3v} = \langle 1 : new | h_v | 3 : new \rangle$ for 2-MMA-d1. Combining the Hamiltonian operator for the *pure* CH₃ internal rotation

$$H = -G \frac{\partial^2}{\partial \alpha^2} + V_3 \frac{1}{2} (1 - \cos 3\alpha) \quad (33)$$

with $G(2\text{-MMA-d1}) = 5.6378 \text{ cm}^{-1}$, which was calculated from the structural parameters in Ref. [7], and $h_{3v} = \langle 1 : new | h_v | 3 : new \rangle = -348.2129 \text{ MHz}$ for 2-MMA-d1 [2], we find $V_3 = 327 \text{ cm}^{-1}$ for the barrier height of the CH₃ internal rotation.

6. Discussion

The numerical results in Eq. (32) for the corrections h_{3v}' are not fully satisfactory, because they do not fully remove the discrepancy in V_3 barrier heights for -OH and -OD isotopologs of 2-MMA, as can be seen from the following procedure. In principle, h_{3v}' can be used to correct the tunneling splitting $W(E) - W(A)$ for the pure CH₃ internal rotation problem according to the equation,

$$W(E) - W(A) = -3(\langle 1 : new | h_v | 3 : new \rangle - h_{3v}'). \quad (34)$$

This corrected E-A splitting can then be compared with energy differences calculated from the Hamiltonian for the pure CH₃ internal-rotation problem in Eq. (33), using a fixed value of G and various values of V_3 . If we take $G(2\text{-MMA-d0}) = 5.6380 \text{ cm}^{-1}$ and $G(2\text{-MMA-d1}) = 5.6378 \text{ cm}^{-1}$, as obtained from the structural parameters in [7], we find internal-rotation potential barriers for the two isotopologs of

$$V_3(2 - \text{MMA} - d0) = 375 \text{ cm}^{-1} \quad (35)$$

$$V_3(2 - \text{MMA} - d1) = 326 \text{ cm}^{-1}.$$

The difference of 50 cm^{-1} in Eq. (35) shows that only about half of the 90 cm^{-1} discrepancy noted in Eq. (3) of [2] has been accounted for. Two possible reasons come to mind. (i) F may not be nearly constant in Eq. (25), but may instead be a rather strongly varying function of the path variable s . (ii) A one-dimensional treatment like that in Eq. (25) may never be able to mimic the real two-dimensional hydrogen transfer motion.

There are, of course, other ways to try to remove this discrepancy. One method is presented in Ref. [7], where a two-dimensional potential energy function of the hydrogen transfer angle ρ and torsional angle τ of the following form

$$V(\rho, \tau) = V_t(\rho) - (1/2)V_3(\rho) \cos(3\tau) - (1/2)V_6(\rho) \cos(6\tau) \quad (36)$$

is considered. As shown in Table 2 of [7], four parameters in $V(\rho, \tau)$ were first calculated by quantum chemistry, and then two of these were adjusted somewhat by fitting them to $J=0$ experimental splittings [2] for both isotopologs of 2-MMA. Keeping these parameters fixed, the threefold barrier height contained in the function $V_3(\rho)$ was determined to be 332.7 cm^{-1} and 333.0 cm^{-1} , respectively, for the -OH and -OD isotopologs. The method of Ref. [7] thus completely removes the discrepancy between the two internal-rotation barrier heights.

Another method is presented in Ref. [12], where a hybrid formalism is described in which the internal rotation motion is treated using an explicit potential function, while the hypothetical pure hydrogen transfer motion is treated by a tunneling formalism. Fits to microwave transitions [2] using a computer program based on this formalism gave barrier heights of $V_3 = 302.4 \text{ cm}^{-1}$ and 315.4 cm^{-1} , respectively, for the -OH and -OD isotopologs. The method of Ref. [12] thus reduces the discrepancy from its pure tunneling value [2] of 90 cm^{-1} to the significantly smaller value of 13 cm^{-1} .

In conclusion, we reemphasize the main point of this paper, which is to draw attention to the phenomenon of “parameter contamination” that occurs in least-squares fits to experimental data using multidimensional pure-tunneling Hamiltonian formalisms whenever the tunneling splittings associated with the various large-amplitude motions have very different orders of magnitude. This contamination prevents an accurate determination of barrier heights along the hypothetical one-dimensional tunneling paths that are frequently constructed to gain qualitative understanding of the potential surface.

Appendix A

Proofs of Eqs. (13) and (14) are shown below. These proofs make use of the overlap-integral matrix $\mathbf{U}$, which is real and symmetric, because $\phi_{1t}(\beta)$ and $\psi_{1w}(\gamma)$ in the first row of Table IV of [6] are (by assumption) chosen to be real. The proofs also make use of $\mathbf{U}^{\pm 1/2}$, which are complex if the eigenvectors $\mathbf{U}$ from Table VI of [6] are used directly in their definitions in Eq. (5). The matrices $\mathbf{U}^{\pm 1/2}$ can also be made real, if the two eigenvectors belonging to a degenerate E_s representation in Table VI of [6] are replaced by their sum and difference, so that eigenvectors containing only real cosine functions or only real sine functions arise. In the equations below we assume that $\mathbf{U}$ is real, but allow $\mathbf{U}^{\pm 1/2}$ to be either real or complex. Note also that since $\mathbf{U}\mathbf{U}^\dagger = \mathbf{E}$ (the identity matrix), $\mathbf{U}^{-1} = \mathbf{U}^\dagger$, from which it also follows that $(\mathbf{U}^{\pm 1/2})^\dagger \equiv [(\mathbf{U}^{\pm 1/2})^*]^\dagger = \mathbf{U}^{\pm 1/2}$.

The proof of Eq. (13) is as follows.

$$\begin{aligned}
\langle i: new | j: new \rangle &= \sum_{k,m} (\Delta^{-1/2})_{ik} \langle k | m \rangle (\Delta^{-1/2})_{mj} = \sum_{k,m} (\Delta^{-1/2})_{ik} \Delta_{km} (\Delta^{-1/2})_{mj} \\
&= \sum_{k,m,s} (\Delta^{-1/2})_{ik} (\Delta^{1/2})_{ks} (\Delta^{1/2})_{sm} (\Delta^{-1/2})_{mj} = \sum_s (\Delta^{-1/2} \Delta^{1/2})_{is} (\Delta^{1/2} \Delta^{-1/2})_{sj} = \sum_s \delta_{is} \delta_{sj} \\
&= \delta_{ij}.
\end{aligned}$$

(A.1)

Next a more general theorem is proved, namely: Transformation properties of the torsional-wagging framework functions $|i: new\rangle$ ($i = 1, 2, 3, \dots$) under operations of the extended-permutation-inversion group G_{12}^m in [6] are the same as those for the framework functions $|i\rangle$ ($i = 1, 2, 3, \dots$). That is, if

$$T|i\rangle = \sum_m D(T)_{mi} |m\rangle, \quad (\text{A.2})$$

where T is any one of the extended-permutation-inversion group operations $a^r b^s$ in Eq. (16) of [6], then

$$T|i: new\rangle = \sum_m D(T)_{mi} |m: new\rangle. \quad (\text{A.3})$$

Proof

Because T is an extended-permutation-inversion group operation, and because of the real phase choice for $\phi_{1i}(\beta)$ and $\psi_{1w}(\gamma)$ in Table IV of [6], the matrix $D(T)_{mi}$ in Eq. (A.2) is real, and each column contains only one non-zero entry, leading to

$$\sum_m D(T)_{mi} |m\rangle = +|q\rangle \text{ or } -|q\rangle, \quad (\text{A.4})$$

where the integer q labels one of the framework functions in Table IV of [6], and depends on the operation T and on the initial function $|i\rangle$. The columns of $D(T)$ in Eq. (A.4) are orthonormal, so that

$$D(T)^{tr} D(T) = E. \quad (\text{A.5})$$

Furthermore, the analog of Eq. (A.2) for $|i: new\rangle$ takes the form

$$T|i:new\rangle = T \sum_k (\Delta^{-1/2})_{ki} |k\rangle = \sum_k (\Delta^{-1/2})_{ki} T|k\rangle = \sum_{k,t} (\Delta^{-1/2})_{ki} D(T)_{tk} |t\rangle. \quad (\text{A.6})$$

From group theoretical considerations we have

$$\begin{aligned} \Delta_{ij} &= \langle i|j\rangle = T\langle i|j\rangle = \sum_{km} D(T)_{ki} D(T)_{mj} \langle k|m\rangle \quad (\text{A.7}) \\ &= \sum_{km} D(T)_{ik}^{\text{tr}} \langle k|m\rangle D(T)_{mj} = [D(T)^{\text{tr}} \Delta D(T)]_{ij}, \end{aligned}$$

which, when rewritten in matrix notation, shows that $D(T)$ and Δ commute:

$$D(T)\Delta = \Delta D(T). \quad (\text{A.8})$$

We now use Eq. (4) to diagonalize Δ in Eq. (A.8), first in matrix notation, then with indices (with no summation convention):

$$\begin{aligned} U^{-1}D(T)UU^{-1}\Delta U &= U^{-1}\Delta UU^{-1}D(T)U = (U^{-1}D(T)U)d = d(U^{-1}D(T)U) \quad (\text{A.9}) \\ (U^{-1}D(T)U)_{ij}d_{jj} &= d_{ii}(U^{-1}D(T)U)_{ij} \end{aligned}$$

Eq. (A.9) shows that $(U^{-1}D(T)U)_{ij} = 0$ whenever $d_{jj} \neq d_{ii}$ and is unrestricted otherwise. Since Eq. (A.9) is satisfied, the following equation is also satisfied

$$(U^{-1}D(T)U)_{ij}(d^{-1/2})_{jj} = (d^{-1/2})_{ii}(U^{-1}D(T)U)_{ij}, \quad (\text{A.10})$$

provided that $(d^{-1/2})_{ii} > 0$ for all i , so that $d_{jj} = d_{ii}$ always leads to $(d^{-1/2})_{jj} = (d^{-1/2})_{ii}$. Eq. (A.10) can be rewritten in matrix notation and then manipulated, using Eq. (5), to obtain

$$D(T)U(d^{-1/2})U^{-1} = U(d^{-1/2})U^{-1}D(T) = D(T)\Delta^{-1/2} = \Delta^{-1/2}D(T), \quad (\text{A.11})$$

which shows that $D(T)$ and $\Delta^{-1/2}$ also commute. Eq. (A.6) then leads to Eq. (A.3):

$$\begin{aligned} T|i:new\rangle &= \sum_{k,t} (\Delta^{-1/2})_{ki} D(T)_{tk} |t\rangle = \sum_t [D(T)\Delta^{-1/2}]_{ti} |t\rangle \quad (\text{A.12}) \\ &= \sum_t [\Delta^{-1/2}D(T)]_{ti} |t\rangle = \sum_{m,t} D(T)_{mi} (\Delta^{-1/2})_{tm} |t\rangle = \sum_m D(T)_{mi} |m:new\rangle \end{aligned}$$

We now sketch the rather long derivation of Eqs. (17)–(19), which begins by making the series of substitutions shown in Eq. (A.13), where the origin of each equal sign is explained following the equation.

$$\begin{aligned}
 \langle 1:new|h_v|r:new\rangle &\rightarrow \langle 0:new|h|v=r-1:new\rangle = \sum_{t,u=0}^{n-1} (\Delta^{-1/2})_{0t} \langle t|h|u\rangle (\Delta^{-1/2})_{uv} \\
 &= \sum_{t,u,p,q=0}^{n-1} [U_{0p}(d^{-1/2})_{pp}(U^{-1})_{pt}] \langle t|h|u\rangle [U_{uq}(d^{-1/2})_{qq}(U^{-1})_{qv}] \\
 &= (n^{-2}) \sum_{t,u,p,q=0}^{n-1} [e^{+i\varepsilon 0p} e^{-i\varepsilon tp} e^{+i\varepsilon uq} e^{-i\varepsilon vq}] (d^{-1/2})_{pp} (d^{-1/2})_{qq} \langle t|h|u\rangle \\
 &= (n^{-2}) \sum_{p,q=0}^{n-1} (d^{-1/2})_{pp} (d^{-1/2})_{qq} [e^{-i\varepsilon vq}] \times \sum_{t,u=0}^{n-1} [e^{+(1/2)i\varepsilon(q-p)(u+t)} e^{+(1/2)i\varepsilon(q+p)(u-t)}] \langle t|h|u\rangle.
 \end{aligned}$$

(A.13)

The first arrow involves decreasing framework numbers by one unit, i.e., changing row and column labels from the range 1 to $n = 6m$ to the range 0 to $n - 1$, and also involves dropping the subscript v from h_v , to free this letter up for other uses. The first and second equalities are from Eqs. (15) and (5), respectively. The third equality uses the fact that the structure of the overlap matrix is the same as the structure of the Hamiltonian matrix, so eigenvalues and eigenvectors of have the form shown in Table 6 of [6] (where $\varepsilon \equiv 2\pi/6m$). Rows of the eigenvectors in that table are to be renumbered from 0 to $n - 1$. Eigenvector columns in that table are also renumbered from 0 to $n - 1$, in such a way that column 0 contains a normalized version of the A_1 eigenvector, columns $s = 1$ to $3m - 1$ contain normalized E_s eigenvectors, column $3m$ contains the normalized B_1 eigenvector, and columns $s = 3m + 1$ to $6m - 1$ contain the complex conjugate of the normalized E_{6m-s} eigenvectors. With these new labels, elements of the eigenvector matrix U take the simple form $U_{pq} = (6m)^{-1/2} e^{+i\varepsilon pq}$. The last equality in Eq. (A.13) regroups terms in preparation for carrying out two summations.

In Eq. (A.14) we change the summation over row and column labels t, u of the matrix $\langle t|h|u\rangle$ that occurs in the last line of Eq. (A.13) to a summation along each of the $2n - 1$ diagonals parallel to the principal diagonal, and then carry out the sum over $t + u$ to show that all non-zero contributions to Eq. (A.13) must have $q = p$.

$$\begin{aligned}
\langle 0: new | h | v: new \rangle &= (n^{-2}) \sum_{p,q=0}^{n-1} (d^{-1/2})_{pp} (d^{-1/2})_{qq} [e^{-i\epsilon v q}] \left\{ \sum_{j=0}^{n-1} e^{+(1/2)i\epsilon(q+p)j} \langle 0 | h | j \rangle \right. \\
&\times \sum_{k=j}^{2n-2-j'} e^{+(1/2)i\epsilon(q-p)k} + \sum_{f=1}^{n-1} e^{-(1/2)i\epsilon(q+p)f} \langle f | h | 0 \rangle \left. \sum_{g=f}^{2n-2-f'} e^{+(1/2)i\epsilon(q-p)g} \right\} \\
&= (n^{-2}) \sum_{p,q=0}^{n-1} (d^{-1/2})_{pp} (d^{-1/2})_{qq} [e^{-i\epsilon v q}] \left\{ \sum_{j=0}^{n-1} e^{+(1/2)i\epsilon(q+p)j} \langle 0 | h | j \rangle \right. \\
&\rangle \sum_{k=j}^{2n-2-j'} e^{+(1/2)i\epsilon(q-p)k} + \sum_{j=n-1}^1 e^{-(1/2)i\epsilon(q+p)(n-j)} \langle n-j | h | 0 \rangle \\
&\rangle \sum_{k=2n-j}^{2n-2+j'} e^{+(1/2)i\epsilon(q-p)(k-n)} \left. \right\} = (n^{-2}) \sum_{p,q=0}^{n-1} (d^{-1/2})_{pp} (d^{-1/2})_{qq} [e^{-i\epsilon v q}] \sum_{j=0}^{n-1} e^{+(1/2)i\epsilon(q+p)j} \\
&\langle 0 | h | j \rangle \sum_{k=j}^{2n-2+j'} e^{+(1/2)i\epsilon(q-p)k} = (n^{-2}) \sum_{p,q=0}^{n-1} (d^{-1/2})_{pp} (d^{-1/2})_{qq} [e^{-i\epsilon v q}] \\
&\left. \sum_{j=0}^{n-1} e^{+(1/2)i\epsilon(q+p)j} \langle 0 | h | j \rangle n \delta_{qp} \right]
\end{aligned}
\tag{A.14}$$

The first equality in Eq. (A.14) is obtained from the last equality in Eq. (A.13) by changing from a row (t) and column (u) summation over $\langle t | h | u \rangle$ to a summation over the $2n-1$ diagonals, which are labeled by $j = u - t$, when $j \geq 0$, and by $f = t - u$, when $f > 0$. Positions along the diagonals are given by the indices $k = g = t + u$. The index $t + u$ increases by two units as we move one step down along any given diagonal (since $t - u$ is fixed), and a $(')$ is added to the appropriate summation signs to indicate this. The second equality is obtained by first changing the summation variable g to $k = n + g$, and then changing the summation variable f to $j = n - f$, where we also make use of the various relations in Eqs. (20) and (21) of [6] to keep the matrix element $\langle t | h | u \rangle$ in a convenient form in each sum. The third equality is obtained by collecting terms in the two sums over j and k . The final equality arises when the geometric series represented by the sum over k is evaluated explicitly.

In Eq. (A.15) we give the final few steps required to arrive at Eqs. (17)–(19).

$$\begin{aligned}
\langle 0: new | h | v: new \rangle &= (n^{-1}) \sum_{p=0}^{n-1} (d^{-1})_{pp} [e^{-i\epsilon v p}] \sum_{j=0}^{n-1} e^{+i\epsilon p j} \langle 0 | h | j \rangle \\
&= \sum_{j=0}^{n-1} (n^{-1}) \left[\sum_{p=0}^{n-1} (d^{-1})_{pp} e^{+i\epsilon p(j-v)} \right] \langle 0 | h | j \rangle = \sum_{j=0}^{n-1} (n^{-1}) \left[(d^{-1})_{00} + \sum_{p=1}^{3m-1} (d^{-1})_{pp} 2 \cos \epsilon p \right. \\
&\quad \left. (j-v) + (-1)^{j-v} (d^{-1})_{3m,3m} \right] \langle 0 | h | j \rangle = (n^{-1}) \left[(d^{-1})_{00} + \sum_{p=1}^{3m-1} (d^{-1})_{pp} 2 \cos \epsilon p (v) \right. \\
&\quad \left. + (-1)^v (d^{-1})_{3m,3m} \right] \langle 0 | h | 0 \rangle + \sum_{j=1}^{3m-1} (n^{-1}) \left[(d^{-1})_{00} + \sum_{p=1}^{3m-1} (d^{-1})_{pp} 2 \cos \epsilon p (j-v) \right. \\
&\quad \left. + (-1)^{j-v} (d^{-1})_{3m,3m} \right] \langle 0 | h | j \rangle + \sum_{j=1}^{3m-1} (n^{-1}) \left[(d^{-1})_{00} + \sum_{p=1}^{3m-1} (d^{-1})_{pp} 2 \cos \epsilon p (-j-v) \right. \\
&\quad \left. + (-1)^{j-v} (d^{-1})_{3m,3m} \right] \langle 0 | h | j \rangle + (n^{-1}) \left[(d^{-1})_{00} + \sum_{p=1}^{3m-1} (d^{-1})_{pp} 2 \cos \epsilon p (3m-v) \right. \\
&\quad \left. + (-1)^{3m-v} (d^{-1})_{3m,3m} \right] \langle 0 | h | 3m \rangle
\end{aligned}
\tag{A.15}$$

The first equality in Eq. (A.15) is obtained from the last equality in Eq. (A.14) by summing over q . The second equality is a regrouping of terms, to bring the equation more into the form of Eq. (17). The third equality breaks the sum over $p = 0$ to $n - 1$ into three parts. The fourth equality breaks the sum over $j = 0$ to $n - 1$ into four parts.

To make the final comparison with Eqs. (17)–(19), we must add 1 to the framework numbers in the matrix elements of h , to obtain $\langle 1: new | h | 1 + v: new \rangle$, $\langle 1 | h | 1 + j \rangle$, etc. in Eq. (A.15), and set $v = r - 1$, $n = 6m$ everywhere, and must also note that the energy denominators are related by: $d_{00} = d_1$, $d_{3m,3m} = d_2$, and $d_{ss} = d_{2s+1}$.

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