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Renner-Teller nonadiabatic coupling terms: An *ab-initio* study of the HNH molecule

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In this Communication we present the first theoretical/numerical treatment of nonadiabatic coupling terms (NACT) that originate from the Renner-Teller (RT) model, namely, those that follow from the splitting of an electronic level of a linear molecule when it becomes bent. These two newly formed states are characterized by different symmetries and are designated as *A* and *B*. Our main findings: (1) The RT NACTs are quantized as long as they are calculated close enough to collinear configuration of the molecule (in this case HNH). Their value is $\tau=1$ (the Jahn-Teller values in similar situations, are $\tau=1/2$). (2) Calculation of RT NACTs at bent configurations (i.e., at a distance from the linear axis) yield decreased values, sometimes by more than 50%. This last finding implies that in strongly bent configurations the two-state Hilbert subspace (formed by the above mentioned *A* and *B* states) is affected by upper states, most likely via Jahn-Teller *conical intersections*. (3) This study has also important practical implications. The fact that the RT NACTs decrease in (strongly) bent situations implies that analyzing spectroscopic data employing only the two Π -states may not be sufficient in order to achieve the required accuracy. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178789]

In 1934 Renner published a detailed study of a linear poly-atomic molecule, originally characterized by an electronic orbital angular momentum component $\Lambda\hbar$ (where $\Lambda \neq 0$) and by an angular momentum component, $\ell\hbar$, associated with the bending vibrations of the molecule, both defined with respect to the molecule axis. In this study Renner showed that by assuming the interaction between these two modes of motions to be strong enough, ℓ and Λ lose their relevance as quantum numbers and K , defined as $K=\Lambda\pm\ell$, becomes the *good* quantum number.¹⁻⁷ In what follows, this interaction is termed as the electronic-vibration coupling (EVC). In his study, Renner assumed the EVC, $\sigma(q)$, to be of the form¹

$$\sigma(q) = \sigma_0 q^2, \quad (1)$$

where q measures the deviation from linearity (see Fig. 1). In this way the spectrum of a decoupled vibrational bending state which is characterized for a given electronic state (e.g., a Π -state^{3,4}) by the quantum numbers (v, ℓ) , changes into a new spectrum of states characterized by the quantum numbers $(v^{(\pm)}, K)$ where $v^{(+)}$ and $v^{(-)}$ stand for the bending states related to an *A*-state and to *B*-state, respectively. In other

words, the EVC splits the original electronic state (if it is not a Σ -state) into two electronic states and numerates the finer structure in a different way.⁴

In fact, the above presentation is not of much concern for the issues to be discussed next. We are not interested in the spectrum of Renner-type molecules but in the fact that due to the EVC, a given electronic state splits into two electronic states, and that this splitting disappears once $q=0$, or, in other words, when the molecule becomes linear. This situation is termed, in what follows, as the Renner-Teller (RT) model. It is important to realize that the RT model,¹⁻⁷ just like the Jahn-Teller (JT) model,^{3,8-15} has its origin in points where two electronic states become degenerate.

The RT effect, again like the JT effect, can be traced down to the Born-Oppenheimer (BO) treatment¹⁶ and, therefore, expected to be associated with non-adiabatic coupling terms (NACT). However, the numerical/theoretical treatments concentrated on the potential energy surfaces and the corresponding potential coupling terms but not on the NACTs (reminiscent of what happened in case of JT studies). It is true that in recent years more and more attention is given to the NACTs themselves and their spatial structure.^{8,13-15,17-20} This statement applies well to the JT NACTs whereas the RT NACTs, to our knowledge, were never studied before.

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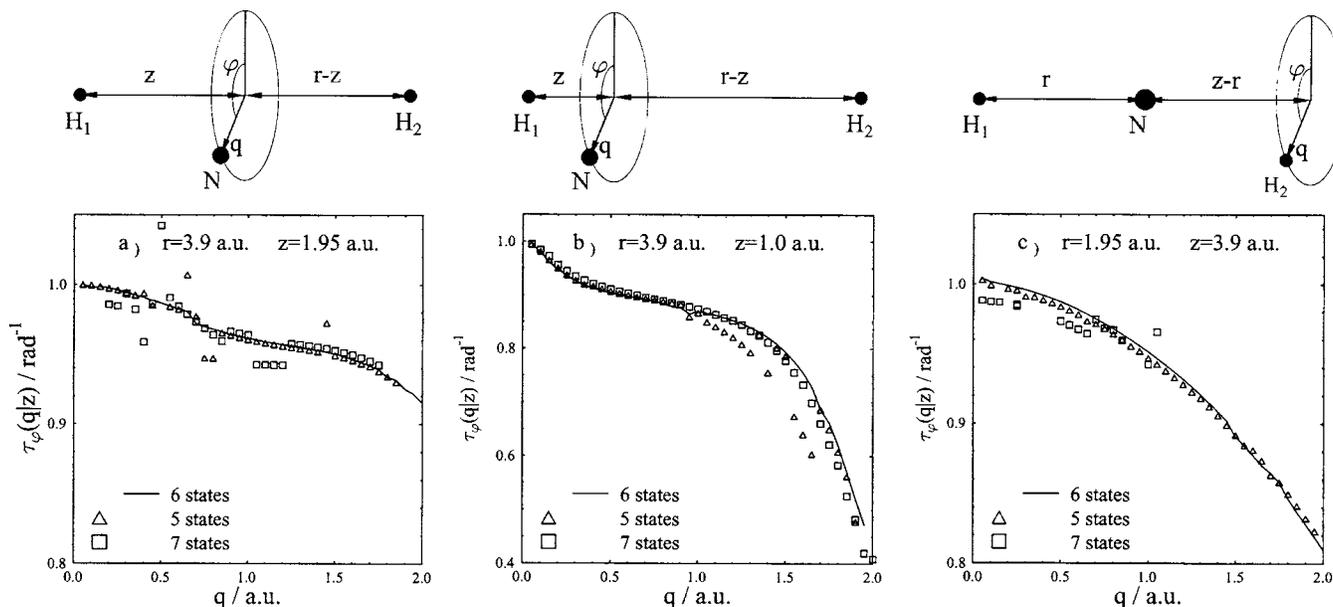


FIG. 1. *Ab-initio* Renner-Teller nonadiabatic coupling terms, $\tau_\varphi(q|z)$ as calculated for the collinear HNH molecule. The results are presented as a function of q —the vertical distance of the rotating atom from the fixed (collinear) axis—for different configurations: (a) The rotating atom is nitrogen and the calculations are done for $z=1.95$ a.u.; (b) The rotating atom is nitrogen and the calculations are done for $z=1.0$ a.u.; (c) The rotating atom is hydrogen and the calculations are done for $z=3.9$ a.u.

The main difference between the JT and the RT models is related to the positions of the points of degeneracy (PD) in configuration space. Whereas, in the case of JT PDs, each of them has to be searched, the situation in the case of the RT model is much “friendlier” as the PDs arrange themselves along *seams* known to coincide with the axis of the linear molecule (given by the equation $q=0$). In other words, while studying the RT effect we do not have to search for the PDs.

The current Communication presents the first study of RT NACTs. To carry out this study we first have to derive the corresponding NACTs. These are usually calculated between two adiabatic states:¹⁶

$$\tau_{12}(\mathbf{S}) = \langle \zeta_1(\mathbf{S}_e|\mathbf{S}) | \nabla \zeta_2(\mathbf{S}_e|\mathbf{S}) \rangle, \quad (2)$$

where \mathbf{s} and \mathbf{s}_e are nuclear and electronic coordinates, respectively. The states to be selected for this purpose are 2A_1 and 2B_1 which are degenerate along HNH axis, but then split once one of the atoms deviates from this line.¹⁻⁴ Thus, while moving away from collinearity the resulting nuclear configuration forms a plane of reflection symmetry so that the electronic eigenstates become either symmetric or antisymmetric with respect to the reflection. In what follows we consider the two lowest adiabatic decoupled degenerate-bending states, 2A_1 and 2B_1 related to the Π -state of the HNH system. For this molecule 2B_1 is the ground state and 2A_1 is the excited state.²¹

Like in the case of the JT studies we freeze the position of two atoms and follow the motion of the third atom.¹³⁻¹⁵ In the case of the JT model we calculate the NACTs along contours located in the plane of the three atoms.^{13-15,19} In the case of the RT model we encounter a different situation: Here, to surround the *seam* which implies surrounding the (straight) line that connects the two *frozen* atoms we have to calculate the NACTs along contours that are located on the planes that do not contain this axis. In the present study the

contour to be considered is located in a plane *perpendicular* to the collinear configuration of the HNH molecule (see Fig. 1, the upper schematic drawings). To carry out the calculation we attach to the moving atom three cylindrical coordinates (φ, q, z) . Locating the origin at the left-hand side of the hydrogen and assuming the z -axis to be along the molecular axis we get that: (1) the coordinate z measures the distance of the moving atom from the origin; (2) the radius q measures its vertical distance from the (molecule) axis; (3) the angle φ is the corresponding cylindrical angular coordinate [see Fig. 1]. The NACT to be considered in the present study is only the *angular* NACT $\tau_{\varphi 2}(\varphi|q, z)/q$ where $\tau_{\varphi 12}(\varphi|q, z)$ is defined as¹³⁻¹⁵

$$\tau_{\varphi 12}(\varphi|q, z) = \left\langle \zeta_1(\varphi|q, z) \left| \frac{\partial}{\partial \varphi} \zeta_2(\varphi|q, z) \right. \right\rangle. \quad (3)$$

Before we analyze the results we discuss the purpose of the calculations. In general, as in JT studies^{13-15,17-20} the angular NACT of the type given in Eq. (3) is used to calculate the topological (Berry) phase $\alpha(q, z)$, defined as²²

$$\alpha(q, z) = \int_0^{2\pi} \tau_{\varphi 12}(\varphi'|q, z) d\varphi'. \quad (4)$$

It is important to emphasize that, although the RT surfaces are not conical but parabolic,¹⁻⁴ we expect the corresponding topological phases [as given in Eq. (4)] to be integer multiples of π , essentially for the same reason they are integer multiples of π in the case of conical intersections.²²⁻²⁶ Thus

$$\alpha(q, z) = n\pi. \quad (5)$$

In our system, due to the cylindrical symmetry, $\tau_{\varphi 12}(\varphi|q, z)$ does not depend on φ and consequently

$$\alpha(q, z) = 2\pi\tau_\varphi(q, z), \quad (6)$$

where we dropped the indices (1,2). Next, due to Eq. (5) we find that $\tau_\varphi(q, z)$ is expected to be

$$\tau_\varphi(q, z) = \begin{cases} n \\ (2n+1)/2, \end{cases} \quad (7)$$

where n , as before, is an integer (and \hbar is assumed to be 1). It has to be emphasized that Eq. (7), just like Eq. (5), is expected to be valid in a given region in configuration space, if and only if the two states, 2A_1 and 2B_1 , form a Hilbert subspace in that region. Therefore, repeating the calculations for a given grid of (q, z) points yields an estimate for the size and the borders of such a region.

The calculation of the RT NACTs were carried out at the state-average CASSCF level employing the following basis functions: For the nitrogen we applied s , p , d , and f functions, and for the hydrogens we employed s , p , and d functions, all from the aug-cc-p VTZ set. We used the active space including all seven valence electrons distributed on ten orbitals. Five to seven different electronic states, including the two states specifically studied, were computed by the state-average CASSCF method with equal weights. The relevant NACTs, namely $\tau_\varphi(\varphi|q, z)$, were calculated employing the MOLPRO program.²⁷

We mentioned already the fact that $\tau_\varphi(\varphi|q, z)$ is cylindrical symmetric and therefore it is enough to calculate it at one point, i.e., $\varphi = \varphi_0$ on the required circle. In this sense the amount of computing time, as compared to the computing time required in the JT case, is reduced by more than two orders of magnitude.

In Fig. 1 are presented RT angular NACTs as calculated for different configurations. Two configurations refer to the case that *nitrogen* is rotating around the HH axis [see panels (a) and (b)] and one configuration refers to the case that *hydrogen* is rotating around the HN axis [see panel (c)]. The first two calculations are done for the case that the distance is $R_{\text{HH}} = 3.9$ a.u. In panel (a) are presented results for which the nitrogen is located at equal distance from the two hydrogens (and, therefore, $z = 1.95$ a.u.): In panel (b) the calculations are done for the case that $z = 1.0$ a.u. (thus, the nitrogen is much closer to one of the hydrogens). In both cases (as well as in the third case) the values of $\tau_\varphi(q, z)$ are presented as a function of q , the distance between the rotating atom (in this case the nitrogen) and the linear fixed axis.

The two main features to be noted are: (1) The value $\tau_\varphi(q \sim 0.0, z) \sim 1.0$ for all three cases which implies (in “our” language) that the RT NACTs, in the *slightly* bent HNH system, are quantized and their value is 1 (and not, e.g., $\frac{1}{2}$). This result is expected, as elaborated in the literature^{1,3} (see also a short discussion below); (2) however, it is also noted that $\tau_\varphi(q, z)$ decreases monotonically as q increases (i.e., as the molecule becomes more and more bent); but the rate of decrease is z -dependent. Thus, in panel (a) we get, for the largest studied bent configuration, the result

$$\tau_\varphi^{(N)}(q = 2 \text{ a.u.}, z = 1.95 \text{ a.u.}) \sim 0.92$$

here the upper subscript relates to the free atom — in this

case the *nitrogen*, whereas in panel (b), for a smaller z -value, we get a far more reduced value:

$$\tau_\varphi^{(N)}(q = 2 \text{ a.u.}, z = 1.0 \text{ a.u.}) \sim 0.40.$$

These values are to be compared with the expected value of 1.0.

In panel (c) are the results for the case that the right-hand side hydrogen is the free *rotating* atom whereas the left-hand side hydrogen and the nitrogen are *fixed*. Here, too, we get in the vicinity of the (collinear) axis, the quantized value, namely, $\tau_\varphi^{(H)}(q \sim 0.0, z = 3.9 \text{ a.u.}) \sim 1.0$, but then as q becomes larger, this function decreases so that at the largest (studied) bent configuration we have

$$\tau_\varphi^{(H)}(q = 2 \text{ a.u.}, z = 3.9 \text{ a.u.}) \sim 0.81.$$

It is important to realize that the calculations were done for a different number of electronic states to establish convergence. The strange finding to be observed is that, out of the three studied configurations, it is the first case (which fits best the natural structure of the HNH molecule) that yields the less stable outcomes.

In what follows we briefly explain why a small distortion from linearity causes $\tau_\varphi^{(N)}(q \sim 0.0, z)$ to be necessarily an integer as discussed earlier (and not a half integer, as in the case of the JT model). The angular NACT $\tau_\varphi^{(X)}(\varphi|q, z)$; $X = \text{N, H}$ corresponds to a rigid rotation of the NH_2 molecule around the HH axis, thus it equals to the matrix element of the electronic angular momentum component

$$[\tau_\varphi^{(N)}(\varphi|q, z)]_{nm} = -i \langle \zeta_m | \hat{\mathbf{L}}_z | \zeta_n \rangle. \quad (8)$$

When the molecule is almost linear the electronic eigenstates split from the $|\Lambda| = 1$ degeneracy to form two coupled adiabatic states with and the matrix elements of the almost linear molecule, are equal to the ± 1 . This shows that the two coupled adiabatic states are characterized by the quantum numbers: $K = 0, 2$, resulting in the conclusion that, the value of n in Eq. (5) is 2 and not 1. It is important to note, that from the general theory, the line-integral value is independent of the *shape* of the loop, as long as it encircles the same seam (and no other seams). Thus we conclude that the line-integral is expected to yield 2π for *any* loop that encircles the H-H axis, whether it corresponds to rigid motion or not. More about this issue will be discussed elsewhere.

To summarize this study we say the following: (1) The RT NACTs are quantized as long as they are located close enough to the linear axis. Their values in these configurations are $\tau_\varphi(q \sim 0, z) \sim 1$. This value has to be compared with JT values which, in similar situations, are half (odd) integers.^{22(a)} Once the calculation of the NACTs are done at strongly bent configurations (namely, when q becomes large), their values decrease by a significant amount, sometimes by more than 50%. This last finding implies that the two-state Hilbert subspace (formed by the above-mentioned 2A_1 and 2B_1 states) is, in such configurations, affected by upper states, most likely via nearby JT *conical intersection*. This conclusion will become the starting point for intensive studies related to this kind of interactions. (3) The present study has also important practical implications. The fact that

the RT NACTs show significant deviations from 1 in (strongly) bent configurations implies that analyzing spectroscopic data employing only the two Π -states may not be sufficient in order to achieve the required spectroscopic accuracy.

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