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5 **Ortho-para nuclear-spin isomerization energies for all bound vibrational states of**
6 **ditritium (T_2) from non-Born-Oppenheimer variational calculations performed with**
7 **explicitly correlated all-particle Gaussian functions**
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14 Direct variational calculations, where the Born-Oppenheimer (BO) approximation is not assumed,
15 are performed for all 26 bound rovibrational states corresponding to the lowest rotational excitation
16 (*i.e.* the $N = 1$ states) of the tritium molecule (T_2). The non-BO energies are used to determine
17 the ortho-para isomerization energies. All-particle explicitly correlated Gaussian basis functions are
18 employed in the calculations and over 11 000 Gaussians independently generated for each state are
19 used. The exponential parameters of the Gaussians are optimized with the aid of analytically calcu-
20 lated energy gradient determined with respect to these parameters. The non-BO wave functions are
21 used to calculate expectation values of the inter-particle distances and the triton-triton correlation
22 functions.
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I. INTRODUCTION

As triton has a spin of one half, the tritium molecule, like the hydrogen molecule, can appear in isomeric forms corresponding to the parallel (ortho) and antiparallel (para) orientations of the nuclear spins. The para tritium has the total nuclear spin of zero (singlet state) and it is the lower energy species of the two isomers. The ortho tritium has the total nuclear spin of one (triplet state), and in the room temperature, similarly to hydrogen, should constitute 75% of the tritium gas because of its three-fold degeneracy in opposite to the para tritium whose singlet nuclear state is not degenerate. The isotopologues of hydrogen involving tritium have been of interest for more than three decades mainly because of their importance in fusion research. There have been surprisingly few experimental studies of the rovibrational spectrum of T_2 . Souers and coworkers measured the infrared spectra of the tritium isotopologues of hydrogen in both liquid and solid states [1, 2]. Also, the Raman spectrum of T_2 was recorded by Edwards *et al.* [3].

The interest in high-accuracy calculations of the rovibrational spectra of small molecular systems has been present in the quantum chemistry research from the very beginning. In recent years such calculations have involved the artificial-channels method of Balint-Kurti *et al.* [4] and Moss [5], the Lagrange-mesh method of Pilon and Baye [6], and various other methods specifically designed to study three-particle systems [7–9]. In some of these methods the Born-Oppenheimer (BO) approximation was not assumed from the start. Other methods assumed the BO approximation and employed the electronic BO potential energy surface augmented with adiabatic, non-adiabatic, relativistic, and radiative corrections as the potential in the Schrödinger equation representing the motion of the nuclei, which is solved to determine the rovibrational energies [10, 11].

Direct variational calculations of bound states of atomic and molecular systems with an arbitrary number of nuclei and an arbitrary number of electrons without assuming the Born-Oppenheimer (BO) approximations have also been a focus of our works for over two decades [12–14]. Recently we have developed a method to perform non-BO calculations for rotationally excited diatomic molecules with an arbitrary number of σ electrons [15]. The method was applied to study charge asymmetry in all bound vibrational levels of the HD^+ ion and the HD molecule [16, 17]. In the present study the method is used to determine the ortho-para isomerization energies for all bound vibrational states of T_2 . The isomerization energies are calculated using the total non-BO energies of the vibrational states obtained for the ground and first-excited rotational states of the system. The total energies of the states are also used to calculate the energies of the corresponding rovibrational transitions. These transitions are compared with the experimental Q-branch lines in the Raman spectrum of T_2 recorded by Edwards *et al.* [3]. A comparison is also made with the results of the calculations performed by Hunt *et al.* [18] where the adiabatic approximation was used to determine the energies of the rovibrational levels.

In our non-BO calculations we employ explicitly correlated all-particle Gaussian functions (ECGs) for expanding the wave function of the system. The non-linear parameters of the Gaussians are extensively optimized using the variational method. In the variational energy minimization we employ the analytical energy gradient determined with respect to these parameters. The use of the gradient is key in obtaining very accurate results in the calculations. Also, the use of the gradient allows for extending the basis set of ECGs in the calculations to sizes exceeding 10 000 functions.

II. METHOD

Not assuming the BO approximation means treating all particles forming the system on equal footing with rigorous accounting for their given masses, M_i and the electrostatic interactions between their charges, Q_i . Without invoking any approximations, the total non-relativistic laboratory-frame Hamiltonian of the system can be separated into an operator representing the motion of the center of mass and an operator representing the internal energy of the system. This separation in our approach is performed by a coordinate transformation from the laboratory Cartesian coordinate system, to an internal Cartesian coordinate system. The center of the internal coordinate frame is placed at a selected reference particle. The transformation to the internal coordinates together with the conjugate momentum transformation yields the Hamiltonian representing the internal energy of the system (called the internal Hamiltonian) that is used in the present calculations. The Hamiltonian explicitly depends on the masses of the nuclei. The triton mass in the present calculations is: $M_t = 5496.92158m_e$, where m_e is the electron mass [19]. More information on the nonadiabatic Hamiltonian and the center-of-mass transformation can be found in Ref. [12].

As internal Hamiltonian is isotropic (spherically symmetric; atom-like), its eigenfunctions transform according to the irreducible representations of the $SO(3)$ rotation group. These eigenfunctions separate into subsets of states corresponding to different values of the total rotational quantum number, N . For the ground and first-excited rotational states they are $N = 0$ and $N = 1$, respectively. Within each subset of states corresponding to a particular N , the states represent different "vibrational" excitations. We put the term vibrational in quotes, because, strictly speaking, the vibrational quantum number (v) is not a good quantum number due to the coupling between the electronic and vibrational motions in the calculations where the BO approximation is not assumed. Thus, v should be regarded as a number that enumerates the consecutive states in a particular manifold corresponding to a certain value of the total rotational quantum number N .

The ECG basis set used in the calculations of the rotationless $N = 0$ states of T_2 was introduced in Ref. [12] and

has the following form:

$$\phi_k(\mathbf{r}) = r_1^{m_k} \exp[-\mathbf{r}'(L_k L'_k \otimes I_3)\mathbf{r}], \quad (1)$$

where $\mathbf{r}$ is a vector of the internal coordinates of the particles 2 to N forming the system with respect to the reference particle 1 (in the present calculations one of the two triton nuclei). L_k in (1) is an $n \times n$ rank n lower triangular matrix of nonlinear variational parameters, I_3 is the 3×3 identity matrix, and $\otimes$ denotes the Kronecker product. r_1 is the distance between particle 2 (the other triton nucleus) and particle 1 and m_k is an even non-negative integer, which in the present calculations varies in the 0-250 range.

In systems with two electrons and two identical fermionic nuclei (like T_2 ; the spin of triton is: $S_t = \frac{1}{2}$) the wave function representing the internal state of the system is a product of a spatial function representing the nuclei and the electrons, a spin function for the electrons, and a spin function for the nuclei. In the ground state of T_2 both electronic and nuclear spin functions are antisymmetric with respect to the permutation of the respective particles because they represent singlet states. The spatial function is symmetric with respect to the permutation of the nuclei and also symmetric with respect to the permutation of the electrons. A symmetric spatial wave function can be constructed using basis function (1). This is ditritium in the (nuclear) low-spin state called para- T_2 . The permutational symmetry of the electrons and the nuclei is implemented in basis functions (1) by projecting each basis function using the symmetry-projection operator $\mathcal{P}$:

$$\psi_k = \mathcal{P}\phi_k = \sum_P \chi_P r_1^{m_k} \exp[-\mathbf{r}'(\tau'_P L_k L'_k \tau_P \otimes I_3)\mathbf{r}], \quad (2)$$

where the sum runs over all permutations of the labels of identical particles and where τ_P are permutational matrices transforming the internal coordinates. There are four permutations in the sum over P on the right hand side of (2) and the corresponding τ_P matrices in the internal coordinates have the following form:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 \\ -1 & 0 & 1 \\ -1 & 1 & 0 \end{pmatrix}. \quad (3)$$

The coefficients χ_P are obtained from the matrix elements of the irreducible representation of the considered state, and for the ground state of T_2 they are all ones. Note that the $r_1^{m_k}$ factor is symmetric with respect to permuting the tritons. The states with the wave functions constructed this way are $N = 0$ states, *i.e.* the rotational ground states.

In the other form of ditritium, the ortho ditritium, the nuclear spin wave function (high-spin state) is symmetric with respect to the permutation of the tritons and the spatial wave function is symmetric. The spatial wave function is still symmetric with respect to the permutation of the electrons and the electronic spin function is antisymmetric. The antisymmetric nuclear component of the spatial wave function of ortho ditritium represents the first excited rotational state with $N = 1$, as the permutation of the nuclei is equivalent to rotating the molecule by 180° around its rotational axis. The ECG basis functions which can describe such a state are obtained by multiplying the $N = 0$ ECGs (1) by the z coordinate of the $\mathbf{r}_1$ vector, z_1 [20]:

$$\phi_k(\mathbf{r}) = z_1 r_1^{m_k} \exp[-\mathbf{r}'(L_k L'_k \otimes I_3)\mathbf{r}]. \quad (4)$$

These functions are $N = 1$ eigenfunctions of the square of the total angular momentum operator and also eigenfunctions of the operator representing the z -axis projection of the total angular momentum.

In ortho ditritium the spatial wave function is antisymmetric with respect to the permutation of the tritons. In Gaussians (4), the asymmetry automatically happens because the $z_1 = Z_2 - Z_1$ factor (Z_1 and Z_2 are the z coordinates of the nuclei in the laboratory coordinate frame) is antisymmetric with respect to the permutation of the tritons. Thus, if the remaining part of the basis function, *i.e.* the $r_1^{m_k} \exp[-\mathbf{r}'(L_k L'_k \otimes I_3)\mathbf{r}]$, is made symmetric with respect to this permutation, the whole basis function is antisymmetric. This symmetrization is achieved by operating on this part of the Gaussian with the same projection operator, $\mathcal{P}$, as applied to Gaussians (1) used for expanding the $N = 0$ wave functions. Thus, in the calculations of states of the para and ortho ditritium basis functions (1) and (4), respectively, are used.

The approach used in the present T_2 calculations is the same as used before in the H_2 [21] and D_2 [22] calculations. In the optimization of the linear expansions coefficients of the wave function in terms of ECGs and the ECG nonlinear parameters Gaussian basis functions the Rayleigh-Ritz variational scheme is employed. As mentioned, the variational energy minimization is performed with the aid of the energy gradient determined with respect to the L_k matrix elements. The gradient is obtained analytically by the direct differentiation of the non-BO energy of the particular state with respect to the matrix elements. The algorithms for calculating the overlap and Hamiltonian matrix elements and the matrix elements of the energy gradient for ECGs (1) and (4) were presented in Refs. [12] and [20], respectively. In Refs. [21] and [22] we also described how the ECG basis set is grown for each state and how the total non-BO energy is typically converging with the number of basis functions.

In the previous paper on T_2 [23] we reported very accurate direct non-BO calculations for the $v = 0, \dots, 26$, $N = 0$ states (*i.e.* pure vibrational states). Up to 16 000 of the $N = 0$ ECGs were used in the basis set for each state in the calculations. The results of that work are used in the present calculations of the ortho-para isomerization energies.

The ortho-para isomerization energies of H_2 calculated with the approach employed in the present work [21] agreed with the experimental results with the accuracy of the experimental data. A similar accuracy level one can expect to be achieved in the present calculations.

III. RESULTS

In this work the focus of the calculations are the 26 bound $N = 1$, $v = 0, \dots, 25$ rovibrational levels of T_2 (ortho ditritium). At the $N = 0$ level there are 27 bound states, but the top $v = 26$ one is only marginally bound [23]. An attempt to converge the $N = 1$, $v = 26$ state below the dissociation threshold made in this work failed. The present $N = 1$ calculations has yielded energies and the corresponding wave functions. The energies allow for determining the dissociation energy and the ortho-para isomerization energy for each vibrational level. The wave functions are used to calculate the expectation values of the inter-particle distances and the triton-triton correlation function (see below).

The total energies of the $N = 1$, $v = 0, \dots, 25$ states obtained in the calculations are presented in Table I. For each states three energy values are shown. The first is the energy obtained for the $N = 0$ state with K ECGs (note that K increases with the increase of the level of the vibrational excitation from $K = 11\,000$ for the $v = 0$ state to $K = 16\,000$ for the $v = 26$ state). The second is the energy obtained for the corresponding $N = 1$ state with the number of ECGs equal to $K - 1000$ (this is the number of functions in the $N = 0$ basis set used to generate the starting set in the $N = 1$ calculation). The third in the energy of the $N = 1$ state obtained after addition of 1000 ECGs to the $(K - 1000)$ basis set (after this addition the number of functions in the basis set becomes equal to K , which is the same number of functions as in the $N = 0$ basis set).

A comparison of the energies obtained for each $N = 1$ rovibrational state with $K - 1000$ and K basis functions allows for assessing the energy convergence. That convergence varies from state to state and, as one can see, is much better for the lower states than for top ones. So, while for the $v = 0$ state ten digits in the energy are practically converged, only eight digits are converged for the $v = 25$ state.

The total energies of the $N = 1$ states from Table I are used to calculate the corresponding dissociation energies shown in Table II. These energies are compared with the results of Hunt *et al.* [18] obtained within the adiabatic approximation. In Table II we also show the ortho-para isomerization energies obtained by subtracting the $N = 0$ energy from the $N = 1$ energy for each vibrational state. The energies of the $N = 0$ rovibrational states are taken from our previous work [23]. The present isomerization energies are compared in Table II with the adiabatic results of Hunt *et al.* [18] for the six lowest states they considered in their calculations. As one can see, while our dissociation energies differ from the results of Hunt *et al.* by about $1\text{--}2\text{ cm}^{-1}$, the isomerization energies are essentially identical.

There exists in the literature a set of Raman experimental transition energies [3] the present results can be compared to. The comparison is show in Table III and also includes a comparison with the results of Hunt *et al.* [18] obtained using the adiabatic approximation. As one can see, including adiabatic and non-adiabatic effects to infinite order, as it is done in the present non-BO calculations, reduces the discrepancies between the adiabatic results of Hunt *et al.* and the experimental results for the $(v = 0, N = 0) \rightarrow (v = 1, N = 0)$ and $(v = 0, N = 1) \rightarrow (v = 1, N = 1)$ transitions by approximately a factor of two. The remaining discrepancy is likely due to the relativistic and QED effects which are not included in the present calculations because the algorithms for calculating these effects with the non-BO wave functions have not been implemented yet (apart from the relativistic effects implemented for $N = 0$ states of diatomic systems [24, 25]).

Finally, in Table IV we show expectation values of the triton-triton (r_{tt}), triton-electron (r_{te}), and electron-electron (r_{ee}) distances calculated using the non-BO $N = 0$ and $N = 1$ wave functions expanded in terms of K ECGs. The results show the expected trends. All distances for both $N = 0$ and $N = 1$ groups of states increase with the vibrational excitation. Also, an increase occurs, as expected, in moving from the $N = 0$ state to the $N = 1$ state for each particular vibrational quantum number. This increase, which is due to the centrifuge force, is the smallest for the $v = 1$ state (0.0004 a.u.) and the largest for the $v = 25$ state (0.0160 a.u.). Apparently, the centrifuge force is too strong to allow the $(v = 26, N = 1)$ state to be bound. The results shown in Table IV can be used to benchmark calculations performed using the conventional approach bases in the lowest order on the BO approximation.

The complexity of the non-BO wave functions of the $N = 1$ states of T_2 can be, perhaps, best represented by plotting the triton-triton correlation functions for various rovibrational states. The T-T correlation function is the one-particle relative density of the two tritons associated with the internal coordinate $\mathbf{r}_1$. The correlation function is defined as [26]:

$$g_i(\boldsymbol{\xi}) = \langle \Psi_i(\mathbf{r}) | \delta(\mathbf{r}_1 - \boldsymbol{\xi}) | \Psi_i(\mathbf{r}) \rangle = \int_{-\infty}^{\infty} |\Psi_i(\boldsymbol{\xi}, \mathbf{r}_2, \mathbf{r}_3)|^2 d\mathbf{r}_2 d\mathbf{r}_3, \quad (5)$$

where $\delta(\mathbf{r}_1 - \boldsymbol{\xi})$ is the 3-dimensional Dirac delta function. In Fig. 1 the correlation functions calculated for the $v = 0, 12$, and 25 rovibrational states with $N = 1$ rotational quantum number are shown and compared with the correlation functions calculated for the corresponding $N = 0$ states. The oscillatory character of the density provide a clear justification for including the $r_1^{m_k}$ factors in basis functions (4). These factors allow for representing the radial

(vibrational) oscillation in the wave function associated with the vibrational excitation level of the state the wave function represents. The correlation functions plotted in Fig. 1 also show the angular behavior of the T-T relative density associated with the rotational $N = 0 \rightarrow N = 1$ excitation.

IV. SUMMARY

All bound vibrational states corresponding to the $N = 1$ rotational excitation of the T_2 molecule have been studied with direct variational non-BO calculations using large sets of explicitly correlated all-particle Gaussian functions. Each state has been calculated separately by generating a basis set of ECGs specifically for that state. The ECGs in the basis set have been extensively optimized in terms of the Gaussian non-linear parameters using an energy-minimization method. The optimization of the exponential Gaussian parameters has been aided by the analytical energy gradient determined with respect to these parameters. The sizes of the basis sets used in the calculations range from 11 000 for the lowest state to 16 000 for the two highest states. 26 bound $N = 1$ states have been obtained in the calculations. The calculated energies of the $N = 1$ states and the corresponding energies of the $N = 0$ states obtained in the earlier calculations [23] have been used to determine the ortho-para isomerization energy for each vibrational state. The isomerization energies show, as expected, a decreasing trend with increasing vibrational excitation. The results agree with the previous calculations performed for the lowest six vibrational states with the conventional approach based in the zeroth-order on the BO approximation [18]. Future work will involve implementation of the algorithm for calculating the leading relativistic corrections for the $N = 1$ rovibrational states of diatomic systems. Development of algorithms to calculate diatomic rovibrational states with N greater than one will also be carried out.

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TABLE I: The convergence of the total nonrelativistic non-BO energies of the $N = 1$, $v = 0, \dots, 25$ rovibrational states of T_2 with the number of basis functions. The energies of the $N = 0$, $v = 0, \dots, 26$ rovibrational states taken from Ref. [23] are also shown. All values are given in a.u. (hartrees).

	v	no.ECGs	Energy	v	no.ECGs	Energy	v	no.ECGs	Energy	v	no.ECGs	Energy
$N = 0$	0	11 000	-1.168 535 675 71	1	12 000	-1.157 306 577 87	2	12 000	-1.146 441 883 89	3	12 000	-1.135 936 002 23
$N = 1$	0	10 000	-1.168 353 133 91	1	11 000	-1.157 129 301 92	2	11 000	-1.146 269 794 93	3	11 000	-1.135 769 033 18
		11 000	-1.168 353 133 98		12 000	-1.157 129 302 16		12 000	-1.146 269 795 55		12 000	-1.135 769 034 05
$N = 0$	4	12 000	-1.125 784 216 46	5	12 000	-1.115 982 714 88	6	12 000	-1.106 528 629 62	7	12 000	-1.097 420 089 95
$N = 1$	4	11 000	-1.125 622 311 98	5	11 000	-1.115 825 832 16	6	11 000	-1.106 376 737 60	7	11 000	-1.097 273 176 58
		12 000	-1.125 622 313 15		12 000	-1.115 825 833 62		12 000	-1.106 376 740 96		12 000	-1.097 273 178 78
$N = 0$	8	12 000	-1.088 656 283 24	9	12 000	-1.080 237 540 97	10	13 000	-1.072 165 433 95	11	13 000	-1.064 442 896 27
$N = 1$	8	11 000	-1.088 514 347 15	9	11 000	-1.080 100 599 78	10	12 000	-1.072 033 523 45	11	12 000	-1.064 316 073 59
		12 000	-1.088 514 350 00		12 000	-1.080 100 603 21		13 000	-1.072 033 527 97		13 000	-1.064 316 079 57
$N = 0$	12	14 000	-1.057 074 373 28	13	15 000	-1.050 065 987 64	14	15 000	-1.043 425 812 66	15	15 000	-1.037 164 044 89
$N = 1$	12	13 000	-1.056 952 722 68	13	14 000	-1.049 949 610 08	14	14 000	-1.043 314 858 44	15	14 000	-1.037 058 691 53
		15 000	-1.056 952 729 39		15 000	-1.049 949 620 16		15 000	-1.043 314 869 46		15 000	-1.037 058 703 42
$N = 0$	16	15 000	-1.031 293 408 60	17	15 000	-1.025 829 523 61	18	15 000	-1.020 791 412 19	19	15 000	-1.016 202 103 84
$N = 1$	16	14 000	-1.031 193 876 42	17	14 000	-1.025 736 099 00	18	14 000	-1.020 704 424 05	19	14 000	-1.016 121 978 41
		15 000	-1.031 193 890 94		15 000	-1.025 736 107 76		15 000	-1.020 704 442 21		15 000	-1.016 121 997 98
$N = 0$	20	15 000	-1.012 089 379 99	21	15 000	-1.008 486 791 66	22	15 000	-1.005 434 807 53	23	15 000	-1.002 982 415 44
$N = 1$	20	14 000	-1.012 016 640 80	21	14 000	-1.008 422 115 41	22	14 000	-1.005 379 039 56	23	14 000	-1.002 936 675 72
		15 000	-1.012 016 670 98		15 000	-1.008 422 146 74		15 000	-1.005 379 058 48		15 000	-1.002 936 696 63
$N = 0$	24	16 000	-1.001 188 692 49	25	16 000	-1.000 122 488 00	26	16 000	-0.999 818 403 64	T+T		-0.999 818 113 08
$N = 1$	24	15 000	-1.001 154 527 86	25	15 000	-1.000 102 296 95						
		16 000	-1.001 154 544 35		16 000	-1.000 102 308 02						

TABLE II: Comparison of the dissociation energies for the $(v, 1)$ states of T_2 obtained in the present calculations ($E_{diss}(\text{present}) = E(v, 1) - 2 E_D$) and the dissociation energies calculated by Hunt *et al.* [18] using the adiabatic approximation (in parenthesis the difference between the two sets of results are shown). The para-ortho isomerization energies ($\Delta = E(v, 1) - E(v, 0)$) obtained in the present calculations are compared with the isomerization energies calculated using the results of Hunt *et al.* All values are in cm^{-1} .

v	$E_{diss}(\text{present})$	$E_{diss}[\text{18}]$	$\Delta(\text{present})$	$\Delta[\text{18}]$
0	36989.1616	36988.311 (0.851)	40.0633	40.064
1	34525.8152	34524.766 (1.049)	38.9075	38.908
2	32142.4290	32141.205 (1.224)	37.7690	37.769
3	29837.7783	29836.377 (1.401)	36.6453	36.646
4	27610.8304	27609.271 (1.559)	35.5337	35.534
5	25460.7517	25459.040 (1.712)	34.4315	34.432
6	23386.9156		33.3357	
7	21388.9146		32.2433	
8	19466.5739		31.1507	
9	17619.9699		30.0544	
10	15849.4516		28.9500	
11	14155.6674		27.8330	
12	12539.5989		26.6977	
13	11002.5940		25.5397	
14	9546.4346		24.3492	
15	8173.3648		23.1198	
16	6886.1873		21.8416	
17	5688.3423		20.5024	
18	4584.0194		19.0877	
19	3578.2891		17.5812	
20	2677.2740		15.9578	
21	1888.3671		14.1879	
22	1220.4865		12.2355	
23	684.4500		10.0341	
24	293.3127		7.4947	
25	62.3736		4.4290	

TABLE III: Comparison of the experimental Raman $(v = 0, N = 0) \rightarrow (v = 1, N = 0)$ and $(v = 0, N = 1) \rightarrow (v = 1, N = 1)$ transition energies of T_2 [3] with the present results and the results of Hunt *et al.* [18]. All values are in a.u.

Transition	Experiment Raman [3]	Present work	Hunt <i>et al.</i> [18]
$(v = 0, N = 0) \rightarrow (v = 1, N = 0)$	2464.320	2464.5021	2464.701
$(v = 0, N = 1) \rightarrow (v = 1, N = 1)$	2463.155	2463.3464	2463.545

TABLE IV: Expectation values of the triton-triton, triton-electron, and electron-electron distances calculated for the $(v, 0)$ and $(v, 1)$ states of T_2 . All values are in a.u.

v	$\langle r_{tt} \rangle$ N=0	$\langle r_{tt} \rangle$ N=1	$\langle r_{te} \rangle$ N=0	$\langle r_{te} \rangle$ N=1	$\langle r_{ee} \rangle$ N=0	$\langle r_{ee} \rangle$ N=1
0	1.4284	1.4291	1.5639	1.5643	2.1877	2.1882
1	1.4833	1.4840	1.5929	1.5933	2.2241	2.2246
2	1.5395	1.5402	1.6225	1.6229	2.2617	2.2622
3	1.5970	1.5978	1.6526	1.6530	2.3007	2.3012
4	1.6560	1.6568	1.6835	1.6839	2.3412	2.3417
5	1.7167	1.7175	1.7152	1.7156	2.3834	2.3840
6	1.7793	1.7802	1.7477	1.7481	2.4276	2.4282
7	1.8440	1.8449	1.7812	1.7817	2.4741	2.4747
8	1.9112	1.9121	1.8159	1.8164	2.5231	2.5238
9	1.9811	1.9821	1.8519	1.8524	2.5751	2.5758
10	2.0543	2.0553	1.8894	1.8899	2.6306	2.6313
11	2.1312	2.1323	1.9286	1.9292	2.6901	2.6909
12	2.2125	2.2137	1.9700	1.9706	2.7544	2.7553
13	2.2991	2.3003	2.0139	2.0145	2.8244	2.8254
14	2.3920	2.3933	2.0608	2.0615	2.9012	2.9022
15	2.4926	2.4940	2.1114	2.1121	2.9862	2.9874
16	2.6027	2.6043	2.1666	2.1674	3.0813	3.0827
17	2.7247	2.7265	2.2275	2.2284	3.1891	3.1906
18	2.8621	2.8642	2.2959	2.2969	3.3129	3.3147
19	3.0198	3.0222	2.3740	2.3752	3.4576	3.4598
20	3.2050	3.2078	2.4655	2.4669	3.6306	3.6333
21	3.4293	3.4329	2.5759	2.5777	3.8430	3.8464
22	3.7127	3.7175	2.7150	2.7174	4.1141	4.1187
23	4.0937	4.1007	2.9015	2.9050	4.4810	4.4878
24	4.6633	4.6754	3.1798	3.1857	5.0308	5.0425
25	5.7479	5.7807	3.7095	3.7255	6.0766	6.1082
26	20.6605		11.1115		20.7849

FIG. 1: Correlation functions for rovibrational states corresponding to the $\nu=1, 12$, and 25 vibrational quantum numbers and the $N=0$ (on the left) and $N=1$ (on the right) rotational quantum numbers. One quarter of the cross section along the xy plane for each correlation function is shown. To obtain the whole cross section, the presented density has to be reflected in the xz and xy planes. For the $N = 0$ states this reflection produces a spherically symmetric function. For the $N = 1$ states the reflection generates a function which is zero along the y axis, but non-zero along the x axis.