Accurate non-Born–Oppenheimer calculations of the lowest vibrational energies of D₂ and T₂ with including relativistic corrections

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A B S T R A C T

In this work we report very accurate variational calculations of the two lowest vibrational states of the D₂ and T₂ molecules within the framework that does not assume the Born–Oppenheimer approximation. The non-relativistic energies of the states obtained in the non-BO calculations are corrected for the relativistic effects of the order of α² calculated as expectation values of the operators representing these effects. The ν = 0 → 1 transition energy of D₂ obtained in the calculations is compared with the transition frequency obtained from the experimental spectra. The comparison shows the need to include corrections higher than second-order in α to further improve the agreement between the theory and the experiment.

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1. Introduction

The general theoretical framework for calculating energies of stationary bound states of atoms and molecules with a very high accuracy is provided by the quantum electrodynamics (QED) [1,2]. Within this framework an effective approach was developed to account for the relativistic effects in light molecular systems based on the perturbation theory with the zeroth-order level being the non-relativistic Schrödinger equation. The approach is called non-relativistic QED theory (NRQED). A description of the NRQED and of the way the effective operators representing the relativistic effects are derived can be found in [2], as well as other sources. In the NRQED theory the corrections are quantities proportional to different powers of the fine structure parameter α (where α = 1/c). Also, as shown by Bethe and Salpeter [3], an effective approach to account for the relativistic effects can be independently developed without using NRQED.

In the approach used in this work for the calculations at the non-relativistic level, the Born–Oppenheimer (BO) approximation concerning the separability of the motions of the electrons and the motions of the nuclei is not assumed. In non-BO calculations for molecules there are three types of inter-particle correlation effects that need to be described. These are the electron–electron, nucleus–nucleus, and nucleus–electron correlation effects. To achieve high accuracy in such calculations all three effects have to be adequately represented in the wave function. While the electron–electron correlation has been extensively studied and it is fairly well understood, the nucleus–nucleus correlation in calculations that treat both electrons and the nuclei on equal footing has not received much attention even though it is much stronger than the former. This is due to the nuclei being considerably heavier than electrons resulting in a much lower probability of finding them is the same point in space than for much lighter electrons. One can say that the nuclei avoid each other more (or correlate more) in their relative motion in the molecule than the electrons. As a result of this, while the independent particles model (i.e. the orbital model) works well for electrons, it is inadequate for nuclei.

To accurately describe the strong nuclear–nuclear correlation in a non-BO molecular calculation one needs to use basis functions that virtually vanish when two nuclei approach each other. In our diatomic non-BO calculations this is accomplished by using one-center explicitly correlated Gaussian functions (ECGF) multiplied by powers of the internuclear distance [4–6]. These types of functions can very effectively describe all three correlation effects mentioned above. In recent years we have reported several non-BO calculations on small molecules including D₂ and T₂ [7]. The calculations on those two systems were performed with 512 ECGFs. In the D₂ and T₂ calculations presented in this work the ECGF basis sets were extended to 10 000 functions leading to much more accurate results. Furthermore, besides the ground states, we also consider in this work the first excited states of the two molecules.

The feature that makes the correlated Gaussians suitable for quantum mechanical molecular all-particle calculations is the relative simplicity of the algorithms for calculating the Hamiltonian matrix elements with these functions. Since these functions were

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introduced to quantum chemistry by Boys [8] and Longstaff and Singer [9], they have been applied by several groups including Adamowicz and Sadlej [10] and Rychlewski and coworkers [11,12] in electronic calculations of small atomic and molecular system. In recent years we have extended their use to the non-BO atomic and molecular calculations. In those calculations we have used the non-relativistic Hamiltonian obtained by rigorously separating out the motion of the center-of-mass from the laboratory-frame Hamiltonian. The ‘internal’ Hamiltonian obtained this way is rotationally invariant and its eigenfunctions transform according to the irreducible representations of the SO(3) group of rotations. In particular the ground state (or any rotationless $| \mathbf{0} \rangle$) of a system with positive (natural) parity is represented by a spherically symmetric $s$-type wave function, which can be expanded in terms of spherically symmetric ECGFs. By including in these functions powers of the internuclear distances as preexponential multipliers the nuclear–nuclear correlation can be very effectively described as we showed in several calculations concerning ground and excited vibrational states of some small diatomic molecules [13,14].

In this work we also calculated the leading relativistic corrections of the order of $\alpha^2$ to the energies of the considered states. The algorithms for calculating these corrections for rotationless states of diatomic systems using the non-BO wave functions expanded in terms of ECGFs and the first-order perturbation theory were presented in our previous works [15,17]. There have been some works performed on D$_2$ and T$_2$ before. Wolniewicz calculated vibrational energies of these systems using the conventional approach involving determining the BO potential energy curve first, correcting it for adiabatic, non-adiabatic, relativistic and radiative corrections, and using it to calculate the vibrational energy levels [18]. A similar approach was also recently applied by Piszczatowski et al. [19] to calculate the dissociation energy of D$_2$ and H$_2$ with very high accuracy, which was achieved by including not only $\alpha^2$ relativistic corrections but also the quantum electrodynamics corrections of the order $\alpha^2$ and $\alpha^4$ (only the one-loop term). Their dissociation energy value of 36748.3633 cm$^{-1}$ with the assigned uncertainty of only 0.0009 cm$^{-1}$ is still off by about 0.02 cm$^{-1}$ from the most recent experimental value of 36748.343(10) cm$^{-1}$ [20].

We start this work with a brief description of the method used in the calculations (a more complete description of the method can be found in our recent reviews [4,5]). Next we describe the approach used to obtain a better estimate of the lowest experimental pure vibrational transition frequency of D$_2$. The results obtained in the calculations and their comparison with the experimental results are presented in the last section.

2. The method used in the calculations

In this work we consider the lowest two rotationless states of D$_2$ and T$_2$. In the non-relativistic calculations, which are done first and independently for each state, we use the conventional Rayleigh–Ritz variational method. The internal non-relativistic Hamiltonian used in the energy functional, which we minimize in the calculations, contains the internal non-relativistic Hamiltonian, $\hat{H}_{\text{nonrel}}$, obtained from the ‘laboratory-frame’ Hamiltonian by rigorously separating out the center-of-mass motion. The internal Hamiltonian for D$_2$ and T$_2$ has the following form:

$$\hat{H}_{\text{nonrel}} = -\frac{1}{2} \sum_{i=1}^{3} \sum_{l=1}^{3} \frac{1}{\mu_i} \mathbf{V}_i \cdot \mathbf{V}_i + \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{1}{m_0} \mathbf{V}_i \cdot \mathbf{V}_j + \sum_{i=1}^{3} q_i q_l \frac{1}{r_i} \sum_{j=1}^{3} q_j q_l \frac{1}{r_j}.$$  

(1)

In (1), $q_i = q_l = 1$ are the charges of the nuclei and $q_i$ = $q_l$ = $-1$ are the electron charges, $r_i$, $i$ = 1, 2, 3, are the position vectors of the second nucleus and the two electrons with respect to the first nucleus (placed in the center of the internal coordinate system; we call this nucleus the ‘reference particle’), $r_i$ are their lengths, $r_i = |r_i - \mathbf{r}_0|$, $m_0 = m_1 = 3670.4829654 m_0$, for D and $m_0 = m_1 = 5496.92158 m_0$ for T, $m_3 = m_3 = 1$ are the electron masses [21], and $\mu_i = m_i m_j / (m_0 + m_i)$ is the reduced mass of particle $i$. As one can notice, the internal Hamiltonian (1) describes three ‘pseudoparticles’ with charges equal to the charges of the original particles, but with masses changed to the reduce masses, moving in the central potential of the charge of the reference particle. The motions of the three pseudoparticles are coupled through the Coulomb interactions and through the so-called mass-polarization term, $-\frac{3}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} q_i q_j \mathbf{V}_i \cdot \mathbf{V}_j$.

To calculate the relativistic corrections of the order of $\alpha^2$ we use the Breit–Pauli Hamiltonian and the first-order perturbation theory. This approach has been used by others in very accurate calculations of light atoms and molecules [22–24]. The Breit–Pauli relativistic operators representing the mass–velocity (MV), Darwin (D), spin–spin (SS), and orbit–orbit (OO) interactions used in the present work were derived starting from their representations in the laboratory coordinate frame and transforming them to the internal coordinate system described above. More details concerning this transformation can be found in [15,16]. For D$_2$ and T$_2$ the transformed MV, D, SS, and OO Hamiltonians have the following form (in the Darwin term, the nuclear contributions proportional to the reciprocals of the squares of the nuclear masses are not included):

$$\hat{H}_{\text{MV}} = -\frac{1}{8} \left[ \frac{1}{m_0} \left( \sum_{i=1}^{3} \nabla r_i \right)^4 + \frac{1}{2} \sum_{i=1}^{3} \frac{1}{m_0} \nabla r_i \nabla r_i \right],$$

(2)

$$\hat{H}_{\text{D}} = -\frac{\pi}{2} \sum_{i=1}^{3} \frac{q_i}{m_i} \left[ q_0 \delta^3(r_i) + q_i \delta^3(r_i) \right]$$

(3)

$$\hat{H}_{\text{SS}} = 2\pi \sum_{i=1}^{3} \frac{q_i q_l}{m_i m_l} \delta^3(r_{i l}),$$

(4)

$$\hat{H}_{\text{OO}} = -\frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{q_i q_j}{m_i m_j} \left[ \frac{1}{r_i} \nabla \cdot \nabla \nabla r_i \cdot \nabla \nabla r_i + \frac{1}{r_j} \nabla \cdot \nabla \nabla r_j \cdot \nabla \nabla r_j \right] + \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{q_i q_j}{m_i m_j} \left[ \frac{1}{r_i} \nabla \cdot \nabla \nabla r_i + \frac{1}{r_j} \nabla \cdot \nabla \nabla r_j \right].$$

(5)

As the spin–orbit interactions are zero for D$_2$ and T$_2$ due to the singlet multiplicity of the electronic wave function, this effects do not contribute to the relativistic correction. Also, the spin–spin interaction between the nuclei and the electrons is zero because of the electrons’ singlet multiplicity. The total first-order relativistic correction in this work was calculated for each state as the expectation value of $\hat{H}_{\text{rel}}$ being:

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{MV}} + \hat{H}_{\text{D}} + \hat{H}_{\text{SS}} + \hat{H}_{\text{OO}}$$

(6)

with the non-BO wave function. Thus, as such, the relativistic correction depends on the nuclear masses through the dependency of the relativistic operators on these quantities and through the mass dependency of the non-BO wave function used in the calculation of the correction.

In expanding the spatial parts of the D$_2$ and T$_2$ non-BO wave functions we used one-center, spherically symmetric ECGFs that include even powers of the internuclear distance, $r_1$, as preexponential multipliers: [6]:

$$\phi_s = r_1^{m_0} \exp[-r(A_1 \cdot I_1) r_1].$$

(7)
where \( \mathbf{r} = \{ \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \} \) and \( ^t \) denotes the vector (matrix) transposition. The powers of \( \mathbf{r}_i \) ranged from 0 to 250 in the present calculations. Before the functions (7) are used in expanding the \( D_2 \) and \( T_2 \) wave functions they are symmetrized with respect to the permutations of the electron labels and the nuclear labels. Since the transformation between the laboratory and the internal coordinates is linear, the symmetrization operators, which originally are defined with respect to the laboratory coordinates, can be expressed in terms of the internal coordinates and directly applied to functions (7) [6].

In the present calculations we used 10000 basis functions for each considered state. These functions have been extensively optimized using the variational energy minimization applied independently to each state, i.e. the lowest (ground) state and the second lowest (first vibrationally excited) state. Both the linear expansion coefficients and the Gaussian exponential parameters, \( \{ A_i \} \), have been subject to the optimization. The calculations for the two \( D_2 \) states were initiated with the 10000 ECGFs taken from our previous calculations of the corresponding states of \( H_2 \) [25]. The \( m_i \) powers of \( \mathbf{r}_i \) were not reoptimized. The calculations for \( T_2 \) were initiated with the basis sets obtained for \( D_2 \).

The ECGFs used in the calculations have to be square integrable. This automatically happens if \( A_i \)'s are represented in Cholesky-factored form, \( A_i = L_i L_i^t \), with \( L_i \) being a lower triangular real matrix. Thus, in the calculations the elements of the \( L_i \) matrices replace the elements of the \( A_i \) matrices as the optimization variables. The optimization of \( L_i \)'s through the energy minimization for each state has been the most time consuming step of the calculations. To expedite the optimization we used the analytical gradient of the energy functional determined with respect to the \( L_i \) matrix elements. The optimization of each basis set was carried out by cycling over all functions in the set several times and reoptimizing the parameters of only one function at a time. We found such an approach most optimal for large basis sets.

After the basis set and the corresponding non-BO wave function and the non-relativistic energy were generated for each of the considered states, the calculations of the relativistic corrections were carried out. The non-relativistic and relativistic total energies were subsequently used to calculate the \( \nu = 0 \rightarrow \nu = 1 \) transition frequencies.

3. Estimation of pure vibrational \( = 0 \rightarrow 1 \) transition of \( D_2 \) from the available experimental rotation–vibrational spectra

The frequency of the pure vibrational transition \( j = 0, \nu = 0 \rightarrow 1 \) of the deuterium molecule, \( D_2 \), was estimated by fitting the positions of 57 lines (including duplicated lines) taken from the rotation–vibrational \( \nu = 0 \rightarrow 1 \) spectral data published in several sources [26–32], to the Dunham’s energy formula [33,34]:

\[
E_{ij} = \sum_{ij} Y_{ij} \left( \nu + \frac{1}{2} \right)^{J(J+1)}/C_j.
\]  

(8)

From the available spectral data we eliminated five lines obtained by Looi et al. [26], as they are not accurately reproduced by Dunham’s formula (8). This inaccuracy can be seen in the quantity \((E_{\text{Exp}} - E_{\text{Dunham}})/E_{\text{Exp}}\) whose value for each of the five lines is approximately equal to eight, while for the other lines used in the fit its value is about one.

The fitting produced the \( Y_{ij} \) parameters. As the higher order vibrational parameters, \( Y_{20}, Y_{30}, \) etc. cannot be determined from the available rotation–vibrational \( \nu = 0 \rightarrow 1 \) spectral data, we only use the \( Y_{10} \) parameter to determine the frequency of the pure ground vibrational transition, \( 0 \rightarrow 1 \), of \( D_2 \). The value of this transition is:

\[
Y_{0-1} = Y_{10} = 2993.6108(30) \text{ cm}^{-1}.
\]  

(9)

We are confident that this value is much more accurate then the value of 2993.56 cm\(^{-1}\) reported by Stoicheff [32].

The fitting calculations were performed by using a weighted non-linear least-square routine with the weights taken as the inverse squares of the corresponding uncertainties, \( u_i = 0.10–0.004 \text{ cm}^{-1} \), of the experimental data. The mean accuracy of the experimental data used in the calculations was 0.0429 cm\(^{-1}\). To obtain high quality Dunham’s parameters, \( Y_{\nu} \), we used the following in the fitting calculations: the minimum number of fitted parameters was set consistent with the minimum value of normalized standard deviation, \( \sigma \), and in determining the standard deviation, \( \sigma \), very carefully chosen values of the estimated standard errors, \( \sigma_r \), of the fitted parameters, \( i \) and of the coefficients, \( \alpha(i,j) \), correlating these parameters were employed. The results of the calculation are presented in Table 1. The uncertainty shown in the parentheses for each Dunham’s parameter was estimated from the standard deviation and it is given in units of the last two quoted digits of the value of the parameter.

Alternatively, the \( v_0 \rightarrow 1 \) transition can be estimated by using in the fitting 92 rotation–vibrational lines taken from Refs. [31,32,35,36]. These lines include the 57 \( \nu = 0 \rightarrow 0 \) transitions and 5 lines due to the \( \nu = 0 \rightarrow 2 \) transitions. The fitting of the 92 lines, where we used the mean experimental accuracy of 0.0433 cm\(^{-1}\), produced the following values of the vibrational parameters: \( Y_{10} = 3112.632(51) \) and \( Y_{20} = -59.511(25) \). These two parameters allows calculation of the fundamental vibrational transition using the formula:

\[
Y_{0-1} = Y_{10} + 2Y_{20} = 2993.6108(713) \text{ cm}^{-1}.
\]  

(10)

The larger standard error in (10) than in (9) results from the accumulation of errors due to \( Y_{10} \) and \( Y_{20} \).

To addition to the above two calculations another test calculation was performed where the ground \( v_0 \rightarrow 1 \) vibrational transition of \( D_2 \) was determined based on the nine high-accuracy experimental data measured by McKellar and Oka [27] with the mean experimental error of 0.0042 cm\(^{-1}\). The vibrational transition of \( v_0 \rightarrow 1 = 2993.6130(19) \) determined based on these nine lines is in a satisfactory agreement with the values of \( v_0 \rightarrow 1 \) obtained from the 57 and 92 line data sets. The test indicates that the transition frequency evaluated from the experimental data using (9) is reliable and can be used for comparison with the results of high-accuracy quantum–mechanical calculations. It should be pointed out that a similar data set of the \( D_2 \) rotation–vibrational transitions as used in this work was also employed by Bak et al. [37] for comparison of the results of spectral and \( ab \) initio calculations of the vibrational g-factors of the hydrogen molecule and its isotopomers.

Table 1

<table>
<thead>
<tr>
<th>( Y_{\nu} )</th>
<th>2993.6108(30)</th>
<th>2993.6130(19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_{10} )</td>
<td>( -1.0545(48) )</td>
<td>( -1.05450(54) )</td>
</tr>
<tr>
<td>( Y_{10} \times 10^{-4} )</td>
<td>2.27(15)</td>
<td>2.13(28)</td>
</tr>
<tr>
<td>( Y_{01} )</td>
<td>30.43956(60)</td>
<td>30.44047(53)</td>
</tr>
<tr>
<td>( Y_{00} \times 10^{-2} )</td>
<td>-1.1558(24)</td>
<td>-1.162(27)</td>
</tr>
<tr>
<td>( Y_{00} \times 10^{-6} )</td>
<td>5.61(30)</td>
<td>7.56(90)</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>1.2049</td>
<td>0.3852</td>
</tr>
<tr>
<td>( \sigma_r )</td>
<td>0.0109</td>
<td>0.0016</td>
</tr>
<tr>
<td>( J_{\text{max}} - J_{\text{min}} )</td>
<td>0–9</td>
<td>0–4</td>
</tr>
<tr>
<td>( v_0 \rightarrow 1 )</td>
<td>2993.6108(30)</td>
<td>2993.6130(19)</td>
</tr>
<tr>
<td>Data points</td>
<td>57</td>
<td>9</td>
</tr>
</tbody>
</table>
4. The results

In Table 2 we present the total non-relativistic energies for the two lowest vibrational states obtained in the calculations for D2 and T2. Based on the previous calculations for H2 [25] we believe that the tenth significant digit in each energy value is essentially converged. It is likely that for each system the ground \( \nu = 0 \) state converges slightly better than the first excited \( \nu = 1 \) state because the \( \nu = 1 \) state wave function is more complicated and more difficult to describe than the \( \nu = 0 \) state wave function. In Table 2 we also present the \((\text{H}_\text{rel}), (\text{H}_\text{nonrel}), (\text{H}_\text{SS}), (\text{H}_\text{OO})\) contributions to the \(\nu^2\) relativistic correction, as well as their sum added to the non-relativistic energies for each of the two systems. The relativistic corrections and the total non-relativistic and relativistic energies are also shown for two isolated D and T atoms. These values enable determination of the dissociation energies (DE) for the two systems. DE for D2 \((\nu = 0)\) is 36748.5620(10) cm\(^{-1}\) and for T2 \((\nu = 0)\) it is 37028.6975(10) cm\(^{-1}\). Our D2 DE can be compared with a recent experiment of Liu et al. [19]. In that work the \(\nu = 0 \rightarrow 1\) transition was calculated with inclusion of the leading relativistic \((\nu^2)\) and QED (the \(\nu^2\) correction and the one-loop term of the \(\nu^4\) correction). Their value for the \(\nu^2\) of 0.0235(3) cm\(^{-1}\) is almost cancelled by the \(\nu^4\) correction of \(-0.0215(2)\) cm\(^{-1}\). Without the QED correction their result would be by about 0.02 cm\(^{-1}\) higher than the experimental value. As the relativistic correction for D2 of 0.0176 cm\(^{-1}\) is by 0.0059 cm\(^{-1}\) smaller that for H2, it is reasonable to expect that the QED correction is also less negative for this system than for H2. Thus, the D2 \(\nu = 0 \rightarrow 1\) transition energy calculated without the QED correction, as it is done in this work, likely overestimates the experimental value by 0.01–0.02 cm\(^{-1}\). This is what happens with our result. Applying a similar argument to T2 suggests that the \(\nu = 0 \rightarrow 1\) transition energy of 2464.5171 cm\(^{-1}\) obtained for this system in this work should also be considered as an upper bound to the true value overestimating it by about 0.01 cm\(^{-1}\).

In Table 3 we also show the D2 \(\nu = 0 \rightarrow 1\) transition energy obtained by Wolniewicz [18]. His result of 2993.609 cm\(^{-1}\) is remarkably accurate suggesting that the procedure he used to calculate the QED (radiative) corrections was reliable.

Table 3

<table>
<thead>
<tr>
<th>System (state)</th>
<th>E_{\text{rel}} (10^{-1})</th>
<th>(\text{H}_\text{rel})</th>
<th>(\text{H}_\text{nonrel})</th>
<th>(\text{H}_\text{SS})</th>
<th>(\text{H}_\text{OO})</th>
<th>E_{\text{rel}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2 ((\nu = 0))</td>
<td>-1.63718808921</td>
<td>1.374586</td>
<td>0.102591</td>
<td>-0.047357</td>
<td>-1.1671797190</td>
<td></td>
</tr>
<tr>
<td>D2 ((\nu = 1))</td>
<td>-1.63532885896</td>
<td>1.364122</td>
<td>0.097798</td>
<td>-0.045667</td>
<td>-1.1535397180</td>
<td></td>
</tr>
<tr>
<td>D2 + D</td>
<td>-0.9972736049</td>
<td>1.368526</td>
<td>0.091183</td>
<td>-0.005445</td>
<td>-0.9974069433</td>
<td></td>
</tr>
<tr>
<td>T2 ((\nu = 0))</td>
<td>-1.6853367686</td>
<td>1.377117</td>
<td>0.103055</td>
<td>-0.047321</td>
<td>-1.1685456855</td>
<td></td>
</tr>
<tr>
<td>T2 ((\nu = 1))</td>
<td>-1.15703657764</td>
<td>1.354126</td>
<td>0.099125</td>
<td>-0.045925</td>
<td>-1.15731471942</td>
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</tr>
<tr>
<td>T + T</td>
<td>-0.99891811308</td>
<td>1.249091</td>
<td>0.099454</td>
<td>-0.000367</td>
<td>-0.9993142592</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) The relativistic corrections for the hydrogen-like atoms are calculated analytically using the exact non-relativistic ground state wave function, \(\psi_{\nu m}(r) = \mu^{1/2}r^{1/2}e^{\mu r}\), where \(\mu = m_n m_1/(m_n + m_1)\) is the reduced mass of the system (\(m_n\) is the nuclear mass and \(m_1\) is the electron mass). The corresponding expressions are: \(\langle H_{\nu}\rangle = -\frac{1}{2} \left( m_n^{1/2} + m_1^{1/2} \right)^2 \), \(\langle H_{\nu}\rangle = -\frac{1}{2} \frac{m_n m_1}{m_n + m_1} \), and \(\langle H_{\nu,\ell}\rangle = -\frac{1}{2} \frac{m_n m_1}{m_n + m_1}\).

Table 4

<table>
<thead>
<tr>
<th>System (state)</th>
<th>E_{\text{rel}} (10^{-1})</th>
<th>(\text{H}_\text{rel})</th>
<th>(\text{H}_\text{nonrel})</th>
<th>(\text{H}_\text{SS})</th>
<th>(\text{H}_\text{OO})</th>
<th>E_{\text{rel}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2 ((\nu = 0))</td>
<td>0.703846</td>
<td>0.648680</td>
<td>0.705667</td>
<td>0.689942</td>
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<tr>
<td>D2 ((\nu = 1))</td>
<td>0.904959</td>
<td>0.890653</td>
<td>0.906353</td>
<td>0.894605</td>
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<tr>
<td>T2 ((\nu = 0))</td>
<td>0.581653</td>
<td>0.570874</td>
<td>0.582673</td>
<td>0.573867</td>
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</tr>
<tr>
<td>T2 ((\nu = 1))</td>
<td>1.443562</td>
<td>1.502127</td>
<td>1.428359</td>
<td>1.483304</td>
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<tr>
<td>Wolniewicz [18]</td>
<td>1.567223</td>
<td>1.602852</td>
<td>1.563908</td>
<td>1.592899</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment (see Table 1)</td>
<td>2.191855</td>
<td>2.236727</td>
<td>2.187300</td>
<td>2.224135</td>
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<td>(\text{H}_\text{rel})</td>
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<td>2.136156</td>
<td>2.056241</td>
<td>2.246899</td>
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<td></td>
</tr>
<tr>
<td>(\text{H}_\text{nonrel})</td>
<td>3.113364</td>
<td>3.265511</td>
<td>3.099443</td>
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<td>(\text{H}_\text{SS})</td>
<td>5.745546</td>
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<tr>
<td>(\text{H}_\text{OO})</td>
<td>0.016328</td>
<td>0.015565</td>
<td>0.016402</td>
<td>0.015776</td>
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</table>
In the last step the non-relativistic wave functions obtained for the $\nu = 0$ and $\nu = 1$ states were used to determine some commonly calculated expectation values. The values are shown in Table 4. As expected $D_2$ has a slightly longer bond in both $\nu = 0$ and $\nu = 1$ states than $T_2$. Also the electrons are on average closer together in $T_2$ than in $D_2$ in both states. As the reduced masses of the electrons increase in going from $D_2$ to $T_2$, they approach on average slightly closer the T nucleus than the D nucleus. This effect is seen in a slightly smaller $\langle r_{T-e} \rangle$ distance than the $\langle r_{D-e} \rangle$ distance.

5. Summary

In this work we present very accurate non-BO calculations of the two lowest pure vibrational states of the $D_2$ and $T_2$ molecules employing the explicitly correlated Gaussian functions. The non-BO wave functions were used to evaluate the $\alpha^2$ relativistic corrections, which were added to the non-relativistic energies. These energies were then used to calculate the $\nu = 0 \rightarrow 1$ transition energies for the two systems. The comparison of the calculated result with the experimental value for the transition energy of $D_2$ shows an overestimation by about 0.01–0.02 cm$^{-1}$. This is explained based on the recent very accurate calculations of $H_2$ by Piszczatowski et al.\[19\] as resulting from neglecting the leading QED corrections of the order of $\alpha^2$.

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References