Accurate non-Born–Oppenheimer calculations of the lowest vibrational energies of D_2 and T_2 with including relativistic corrections

Sergiy Bubin [a,*], Monika Stanke [b], Marcin Molski [c], Ludwik Adamowicz [d,e]

[a] Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA
[b] Department of Physics, Nicholas Copernicus University, ul. Grudziądzka 5, Toruń, PL 87-100, Poland
[c] Department of Theoretical Chemistry, Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, Poznań, PL 60-780, Poland
[d] Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA
[e] Department of Physics, University of Arizona, Tucson, AZ 85721, USA

ABSTRACT

In this work we report very accurate variational calculations of the two lowest vibrational states of the D_2 and T_2 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 α^2 calculated as expectation values of the operators representing these effects. The $v = 0 \rightarrow 1$ transition energy of D_2 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.

© 2010 Elsevier B.V. All rights reserved.

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 $\alpha = 1/c$). 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 elec-

tron–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 D_2 and T_2 [7]. The calculations on those two systems were performed with 512 ECGFs. In the D_2 and T_2 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

* Corresponding author.
  E-mail address: bubin@email.arizona.edu (S. Bubin).

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 $J = 0$ state) 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 α^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 α^2 relativistic corrections but also the quantum electrodynamics corrections of the order α^3 and α^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:

$$\hat{H}_{\text{nonrel}} = -\frac{1}{2}\left(\sum_{i=1}^{3}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^{3}\sum_{j\neq i}^{3}\frac{1}{m_0}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right)$$
$$+ \sum_{i=1}^{3}\frac{q_0 q_i}{r_i} + \sum_{i<j}^{3}\frac{q_i q_j}{r_{ij}}. \tag{1}$$

In (1), $q_0 = q_1 = 1$ are the charges of the nuclei and $q_2 = q_3 = -1$ are the electron charges, $\mathbf{r}_i, i = 1, 2, 3$, 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, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|, m_0 = m_1 = 3670.4829654 m_e$ for D and $m_0 = m_1 = 5496.92158 m_e$ for T, $m_2 = m_3 = m_e = 1$ are the electron masses [21], and $\mu_i = m_0 m_i/(m_0 + m_i)$ 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, $-\frac{1}{2}\sum_{i=1}^{3}\sum_{j\neq i}^{3}\frac{1}{m_0}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}$.

To calculate the relativistic corrections of the order of α^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):

$$\hat{H}_{\text{MV}} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{3}\nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{3}\frac{1}{m_i^3}\nabla_{\mathbf{r}_i}^4\right], \tag{2}$$

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

$$\hat{H}_{\text{SS}} = 2\pi\frac{q_2 q_3}{m_2 m_3}\delta^3(r_{23}) \tag{4}$$

$$\hat{H}_{\text{OO}} = -\frac{1}{2}\sum_{i=1}^{3}\sum_{j=1}^{3}\frac{q_0 q_j}{m_0 m_j}\left[\frac{1}{r_j}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j} + \frac{1}{r_j^3}\mathbf{r}_j\cdot(\mathbf{r}_j\cdot\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right]$$
$$+\frac{1}{2}\sum_{i=1}^{3}\sum_{j>i}^{3}\frac{q_i q_j}{m_i m_j}\left[\frac{1}{r_{ij}}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right]. \tag{5}$$

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:

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{MV}} + \hat{H}_{\text{D}} + \hat{H}_{\text{SS}} + \hat{H}_{\text{OO}} \tag{6}$$

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 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]:

$$\phi_k = r_1^{m_k}\exp\left[-\mathbf{r}'(A_k\otimes I_3)\mathbf{r}\right], \tag{7}$$

where $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3\}'$ and ′ denotes the vector (matrix) transposition. The powers of r_1 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, $\{A_k\}$, 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_k powers of r_1 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_k's are represented in Cholesky-factored form, $A_k \equiv L_k L'_k$, with L_k being a lower triangular real matrix. Thus, in the calculations the elements of the L_k matrices replace the elements of the A_k matrices as the optimization variables. The optimization of L_k'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_k 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 $v = 0 \rightarrow v = 1$ 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 $J = 0$, $v = 0 \rightarrow 1$ of the deuterium molecule, D_2, was estimated by fitting the positions of 57 lines (including duplicated lines) taken from the rotation–vibrational $v = 0 \rightarrow 1$ spectral data published in several sources [26–32], to the Dunham's energy formula [33,34]:

$$E_{vJ} = \sum_{i,j} Y_{ij} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j. \tag{8}$$

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 $(E_{exp} - E_{theor})/\delta_{exp}$ 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 $v = 0 \rightarrow 1$ 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:

$$v_{0\rightarrow 1} = Y_{10} = 2993.6108(30) \text{ cm}^{-1}. \tag{9}$$

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, $u_i = 0.10 - 0.004$ 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_{ij}, 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, $\hat{\sigma}$, and in determining the standard deviation, σ, very carefully chosen values of the estimated standard errors, σ_i, of the fitted parameters, i, and of the coefficients, $cc(i,j)$, 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 $v = 0 \rightarrow 1$ lines mentioned above, as well as 30 lines due to the $v = 0 \rightarrow 0$ transitions and 5 lines due to the $v = 0 \rightarrow 2$ 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:

$$v_{0\rightarrow 1} = Y_{10} + 2Y_{20} = 2993.6108(713) \text{ cm}^{-1}. \tag{10}$$

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 frequence 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
Dunham's spectral parameters (in cm^{-1}) fitted to the available D_2 spectral lines corresponding to the $0 \rightarrow 1$ rovibrational transitions of this molecule.

Y_{ij}		
Y_{10}	2993.6108(30)	2993.6130(19)
Y_{11}	−1.05454(48)	−1.05450(54)
$Y_{12} \times 10^{-4}$	2.27(15)	2.13(28)
Y_{01}	30.43956(60)	30.44047(53)
$Y_{02} \times 10^{-2}$	−1.1558(24)	−1.162(27)
$Y_{03} \times 10^{-6}$	5.61(30)	7.56(90)
$\hat{\sigma}$	1.2049	0.3852
σ	0.0109	0.0016
$J_{min} - J_{max}$	0–9	0–5
$v_{0\rightarrow 1}$	2993.6108(30)	2993.6130(19)
Data points	57	9

Table 2
Total non-relativistic non-BO energies (E_{nonrel}), mass–velocity (MV), Darwin (D), spin–spin (SS), and orbit–orbit (OO) relativistic corrections, and the total energies (non-relativistic + relativistic corrections; $E_{rel} = E_{nonrel} + \alpha^2(\langle H_{MV}\rangle + \langle H_D\rangle + \langle H_{SS}\rangle + \langle H_{OO}\rangle)$ of the two lowest pure vibrational states ($v = 0$ and 1) of D_2 and T_2. We also show the corresponding energies and the relativistic corrections[a] for pairs of the dissociated atoms. All values are in hartrees.

System (state)	E_{nonrel}	$\langle H_{MV}\rangle$	$\langle H_D\rangle$	$\langle H_{SS}\rangle$	$\langle H_{OO}\rangle$	E_{rel}
D_2 ($v = 0$)	−1.16716880921	−1.634543	1.374586	0.102591	−0.047375	−1.16717971190
D_2 ($v = 1$)	−1.15352889586	−1.601481	1.346122	0.097798	−0.045667	−1.15353971800
D + D	−0.99972923049	−1.248639	0.999183		−0.000544	−0.99974094333
T_2 ($v = 0$)	−1.16853567568	−1.638226	1.377617	0.103055	−0.047321	−1.16854658555
T_2 ($v = 1$)	−1.15730657764	−1.610923	1.354126	0.099125	−0.045925	−1.15731741942
T + T	−0.99981811308	−1.249091	0.999454		−0.000367	−0.99983142592

[a] The relativistic corrections for the hydrogen-like atoms are calculated analytically using the exact non-relativistic ground state wave function, $\psi(r_1) = \mu^{3/2}\pi^{1/2}e^{-\mu r_1}$, where $\mu = m_0 m_1/(m_0 + m_1)$ is the reduced mass of the system (m_0 is the nuclear mass and m_1 is the electron mass). The corresponding expressions are: $\langle \hat{H}_{MV}\rangle = -\frac{5}{8}\left(\frac{1}{m_0^3} + \frac{1}{m_1^3}\right)\mu^4$, $\langle \hat{H}_D\rangle = \frac{\mu^3}{2m_1^2}$, and $\langle \hat{H}_{OO}\rangle = -\frac{\mu^3}{m_0 m_1}$.

4. The results

In Table 2 we present the total non-relativistic energies for the two lowest vibrational states obtained in the calculations for D_2 and T_2. Based on the previous calculations for H_2 [25] we believe that the tenth significant digit in each energy value is essentially converged. It is likely that for each system the ground $v = 0$ state converges slightly better than the first excited $v = 1$ state because the $v = 1$ state wave function is more complicated and more difficult to describe than the $v = 0$ state wave function. In Table 2 we also present the $\langle \hat{H}_{MV}\rangle$, $\langle \hat{H}_D\rangle$, $\langle \hat{H}_{SS}\rangle$, and $\langle \hat{H}_{OO}\rangle$ contributions to the α^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 D_2 ($v = 0$) is 36748.5620(10) cm^{-1} and for T_2 ($v = 0$) it is 37028.6975(10) cm^{-1}. Our D_2 DE can be compared with a recent experiment of Liu et al. [38], where the value of 36748.36286(88) cm^{-1} was obtained. It can also be compared with theoretical work [19], where the values of 36748.5634(5) cm^{-1} (without the inclusion of QED corrections) and 36748.3633(9) cm^{-1} (with QED corrections) were obtained.

The D_2 and T_2 $v = 0 \rightarrow 1$ transition frequencies calculated as the differences of the corresponding total energies of the two states are presented in Table 3. We show the results obtained with and without the relativistic corrections. The frequencies are compared with the frequencies obtained by Wolniewicz [18]. In his calculations Wolniewicz used an approach based on the Born–Oppenheimer approximation with corrections for the finite masses of the nuclei (adiabatic and non-adiabatic) and for the leading relativistic and radiative corrections added to each point of the potential energy curve subsequently used in calculating the vibrational energies. Table 3 also includes a comparison with the experimental frequency.

Wolniewicz concluded his work by saying that the most important source of errors in his calculations rests in the non-adiabatic corrections. As the present non-BO calculations have been converged to a very high accuracy at the non-relativistic level and the finite-mass effects (both adiabatic and non-adiabatic) have been explicitly accounted for in the variational energy and the

wave function, these effects are automatically included in our results to a very high precision. The finite-mass effects are also explicitly included in the calculations of the relativistic effects. We believe that our transition energies are converged to within 0.001 cm^{-1} or better (the estimate comes from the convergence pattern obtained when optimizing the non-linear variational parameters and from our previous systematic calculations on similar systems, such as H_2 and HD). This leaves the quantum electro-dynamic (QED) corrections as the only source of an error in our calculations.

The results presented in Table 3 show that adding the relativistic correction makes the agreement between the experimental transition energy of D_2 worse than without that correction. For a clue why this happens we went to the work of Piszczatowski et al. on H_2 [19]. In that work the $v = 0 \rightarrow 1$ transition was calculated with inclusion of the leading relativistic (α^2) and QED (the α^3 correction and the one-loop term of the α^4 correction). Their value for the α^2 of 0.0235(3) cm^{-1} is almost cancelled by the $\alpha^3 + \alpha^4$ 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 D_2 of 0.0176 cm^{-1} is by 0.0059 cm^{-1} smaller that for H_2, it is reasonable to expect that the QED correction is also less negative for this system than for H_2. Thus, the D_2 $v = 0 \rightarrow 1$ 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 T_2 suggests that the $v = 0 \rightarrow 1$ 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 D_2 $v = 0 \rightarrow 1$ 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
Lowest pure vibrational transition frequencies of D_2 and T_2 calculated using the non-relativistic ($E_{nonrel}^{v=1} - E_{nonrel}^{v=0}$) and relativistic ($E_{rel}^{v=1} - E_{rel}^{v=0}$) total energies. All values are in cm^{-1}.

	D_2	T_2
$E_{nonrel}^{v=1} - E_{nonrel}^{v=0}$	2993.6150(1)	2464.5022(1)
$E_{rel}^{v=1} - E_{rel}^{v=0}$	2993.6326(10)	2464.5171(10)
Wolniewicz [18]	2993.609	2464.497
Experiment (see Table 1)	2993.6108(30), 2993.6130(19)	

Table 4
Some expectation values calculated for the $v = 0$ and 1 pure vibrational states of the D_2 and T_2 molecules with the wave functions expanded in terms of 10000 explicitly correlated Gaussians. As in the $\langle 1/r_{N-e}\rangle$ expectation value, N is used to denote a nucleus, while e denotes an electron. All values are in a.u.

	D_2 ($v = 0$)	D_2 ($v = 1$)	T_2 ($v = 0$)	T_2 ($v = 1$)
$\langle 1/r_{N-N}\rangle$	0.703846	0.684680	0.705667	0.689942
$\langle 1/r_{N-e}\rangle$	0.904959	0.890653	0.906353	0.894605
$\langle 1/r_{e-e}\rangle$	0.581653	0.570874	0.582673	0.573867
$\langle r_{N-N}\rangle$	1.434562	1.502127	1.428359	1.483304
$\langle r_{N-e}\rangle$	1.567223	1.602852	1.563908	1.592899
$\langle r_{e-e}\rangle$	2.191855	2.236727	2.187730	2.224135
$\langle r_{N-N}^2\rangle$	2.077687	2.316156	2.056241	2.248689
$\langle r_{N-e}^2\rangle$	3.113364	3.265511	3.099443	3.222635
$\langle r_{e-e}^2\rangle$	5.754556	5.997527	5.732488	5.928941
$\langle \delta(\mathbf{r}_{N-e})\rangle$	0.226936	0.222025	0.227455	0.223404
$\langle \delta(\mathbf{r}_{e-e})\rangle$	0.016328	0.015565	0.016402	0.015776

In the last step the non-relativistic wave functions obtained for the $v = 0$ and $v = 1$ 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 $v = 0$ and $v = 1$ 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 α^2 relativistic corrections, which were added to the non-relativistic energies. These energies were then used to calculate the $v = 0 \rightarrow 1$ 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 α^3.

Acknowledgments

References

[1] W.E. Coswell, G.P. Lepage, Phys. Lett. B 167 (1986) 437.
[2] T. Kinoshita, M. Nio, Phys. Rev. D 53 (1996) 4909.
[3] H.A. Bethe, E.E. Salpeter, Quantum Mechanics of One- and Two-Electron, Publishing Corporation, New York, 1977.
[4] M. Cafiero, S. Bubin, L. Adamowicz, Phys. Chem. Chem. Phys. 5 (2003) 1491.
[5] S. Bubin, M. Cafiero, L. Adamowicz, Adv. Chem. Phys. 131 (2005) 377.
[6] D.B. Kinghorn, L. Adamowicz, J. Chem. Phys. 110 (1999) 7166.
[7] D.B. Kinghorn, L. Adamowicz, J. Chem. Phys. 113 (2000) 4203.
[8] S.F. Boys, Proc. Royal Soc. Lond., Ser. A 258 (1294) (1960) 402.
[9] J.V.L. Longstaff, K. Singer, Proc. Royal Soc. Lond., Ser. A 258 (1294) (1960) 421.
[10] L. Adamowicz, A.J. Sadlej, J. Chem. Phys. 67 (1977) 4298.
[11] W. Cencek, J. Komasa, J. Rychlewski, Chem. Phys. Lett. 246 (1995) 417.
[12] J. Rychlewski, Adv. Quant. Chem. 31 (1999) 173.
[13] S. Bubin, M. Stanke, L. Adamowicz, J. Chem. Phys. 131 (2009) 044128.
[14] M. Stanke, S. Bubin, L. Adamowicz, Phys. Rev. 79 (2009) 060501.
[15] D. Kędziera, M. Stanke, S. Bubin, M. Barysz, L. Adamowicz, J. Chem. Phys. 125 (2006) 014318.
[16] M. Stanke, D. Kędziera, S. Bubin, M. Molski, L. Adamowicz, J. Chem. Phys. 128 (2008) 114313.
[17] D. Kędziera, M. Stanke, S. Bubin, M. Barysz, L. Adamowicz, J. Chem. Phys. 125 (2006) 084303.
[18] L. Wolniewicz, J. Chem. Phys. 99 (1993) 1851.
[19] K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki, B. Jeziorski, J. Chem. Theory Comput. 5 (2009) 3039.
[20] Y.P. Zhang, C.H. Cheng, J.T. Kim, J. Stanojevic, E.E. Eyler, Phys. Rev. Lett. 92 (2004) 203003.
[21] See CODATA 2002 Recommended Values and NIST Physical.
[22] G.W.F. Drake, Z.C. Yan, Can. J. Phys. 86 (2008) 45.
[23] M. Puchalski, K. Pachucki, Phys. Rev. A 78 (2008) 052511.
[24] V.I. Korobov, Phys. Rev. A 77 (2008) 022509.
[25] S. Bubin, F. Leonarski, M. Stanke, L. Adamowicz, Chem. Phys. Lett. 477 (2009) 12.
[26] E.C. Looi, J.C. Stryland, H.L. Welsh, Can. J. Phys. 56 (1978) 1102.
[27] A.R.W. McKellar, T. Oka, Can. J. Phys. 56 (1978) 1310.
[28] M.A. Henesian, M.D. Duncan, R.L. Byer, A.D. May, Opt. Lett. 1 (1977) 149.
[29] D.W. Ferguson, K.N. Rao, M.E. Mickelson, L.W. Larson, J. Mol. Spectrosc. 160 (1993) 315.
[30] P.J. Brannon, C.H. Church, C.W. Peters, J. Mol. Spectrosc. 27 (1968) 44.
[31] D.K. Veris, G.M. Rosenblatt, J. Mol. Spectrosc. 121 (1987) 401.
[32] B.P. Stoicheff, Can. J. Phys. 35 (1975) 730.
[33] J.L. Dunham, Phys. Rev. 41 (1932) 713.
[34] J.L. Dunham, Phys. Rev. 41 (1932) 721.
[35] D.E. Jennings, A. Weber, J.W. Brault, J. Mol. Spectrosc. 126 (1987) 19.
[36] D.E. Jennings, A. Weber, W. Brault, Appl. Opt. 25 (1986) 284.
[37] K.L. Bak, S.P.A. Sauer, J. Oddershedec, J.F. Ogilvie, Phys. Chem. Chem. Phys. 7 (2005) 1747.
[38] J. Liu, D. Sprecher, C. Jungen, W. Ubachs, F. Merkt, J. Chem. Phys. 132 (2010) 154301.