Accurate calculations of the dissociation energy, equilibrium distance and spectroscopic constants for the Yb dimer

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Abstract. The dissociation energy, equilibrium distance, and spectroscopic constants for the $^{1}\Sigma_{g}^{+}$ ground state of the Yb$_{2}$ molecule are calculated. The relativistic effects are introduced through generalized relativistic effective core potentials with very high precision. The scalar relativistic coupled cluster method particularly well suited for closed-shell van-der-Waals systems is used for the correlation treatment. Extensive generalized correlation basis sets were constructed and employed. The relatively small corrections for high-order cluster amplitudes and spin-orbit interactions are taken into account using smaller basis sets and the spin-orbit density functional theory.

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1. Introduction.

Several groups are working on the development of a new generation of frequency and time standards based on atomic optical transitions [1, 2, 3]. Neutral ytterbium atoms loaded into a laser lattice are very promising candidates for constructing such high-performance atomic clock [4, 5]. The properties of Yb$_2$ are necessary to assess the feasibility of using laser cooled and trapped Yb atomic species for ultraprecise optical clocks or quantum information-processing devices [6].

Unfortunately, reliable experimental data on the dissociation energy, equilibrium distance, and spectroscopic constants of the Yb$_2$ molecule are unknown; e.g., the uncertainty of the experimental dissociation energy estimate from [7], 0.17 eV, is comparable to the value itself. A series of papers was devoted to their calculation. Dolg and co-workers reported the values 400 [8], 470 [9], and 740 cm$^{-1}$ [10] for the dissociation energy. The coupled electron pair approximation, density functional theory (DFT), configuration interaction method with single and double excitations (CISD), and coupled cluster method with single, double (and non-iterative triple) cluster amplitudes, CCSD(T), were used to account for the correlation effects. Ytterbium core shells were replaced by scalar (spin-averaged) energy-consistent pseudopotentials (PPs) generated for 2, 10, and 42 explicitly treated electrons. Their latest result [10] of 740 cm$^{-1}$ should be considered the most reliable, because the basis set used was larger than that in the previous calculations and 42 electrons were treated explicitly for each Yb atom (42e-PP).

In [11], the scalar DFT approach and a 24-electron relativistic effective core potential (RECP) model for ytterbium were used. The dissociation energy estimates ranging from 500 to 1400 cm$^{-1}$ were obtained with different exchange-correlation functionals. In [12], the Yb dimer was studied within the averaged quadratic coupled cluster, CCSD(T), and DFT approximations. The Yb atom was described by a 42-electron energy-consistent PP. It was emphasized that the “incomplete convergency, most clearly seen for Yb$_2$ results, indicated the need for more advanced ab initio schemes”. In addition to the evident problem of the incompleteness of the one-electron basis set, it is not clear whether the truncation of the cluster expansion after the three-body terms provides a good approximation for the Yb$_2$ ground state, which could be considered as a perturbed four-electron system. Furthermore, almost all calculations mentioned above were done within the scalar relativistic approximation. In spite of the closed-shell-like nature of the system under study, the contribution of spin-dependent interactions to the bond energy can still be significant (cf. [13]). The only attempt [8] to estimate the role of spin-orbit interactions in Yb$_2$ was made within a somewhat simplistic four-electron CI scheme using a very restricted basis set that can hardly be used to reliably reproduce the van-der-Waals behaviour of the potential curve.

In the present paper, we report our results of improving the accuracy of the calculated dissociation energy, equilibrium distance and spectroscopic constants for Yb$_2$ using extremely flexible generalized correlation basis sets, contributions from high-order cluster amplitudes and spin-dependent relativistic effects. Such improvements
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were successfully applied to accurate calculation of $Hg_2$ when giving a few times better agreement with the experimental data than the other earlier performed studies [14].

2. Calculations and discussion.

Scalar relativistic calculations were performed within the generalized relativistic effective core potential (GRECP) model [15, 16, 17, 18] using the CCSD(T) method (implemented in the MOLCAS program package [19]) for correlation treatment. The high accuracy and reliability of this approach has been demonstrated in similar calculations (see, e.g., [13]). The $4f_{5/2}$, $4f_{7/2}$, and $6s_{1/2}$ spinors of the Yb atom have the one-electron energies of -0.54, -0.49, and -0.20 a.u., respectively, and are usually considered as valence ones. The average radii of the $4f_{5/2}$, $4p_{1/2}$, $4p_{3/2}$, $4d_{3/2}$, and $4d_{5/2}$ spinors are very close to those of the $4f_{5/2}$ and $4f_{7/2}$ spinors. Therefore, excitations of electrons from the latter spinors will lead to strong relaxation of the former spinors which, therefore, should be considered as the outercore ones for the GRECP generation procedure and “valence-type” property calculations [15]. Thus, we use the GRECP with 42 explicitly treated electrons for each Yb atom. In series of preliminary calculations, we have estimated the contributions from correlations with different shells of Yb to the dissociation energy of $Yb_2$ (some of them are presented in table 3). The main contribution is provided by the $6s$ shell whereas the contributions from the $4f$, $5s$, and $5p$ shells are relatively small. It is clear that the corresponding contributions from the innermore $4d$, $4p$, $4s$, etc. shells will be significantly smaller. Thus, we “freeze” the $4s, 4p, 4d$ or $4s, 4p, 4d, 4f, 5s, 5p$ shells in 48- and 4-electron calculations, respectively, to reduce computational expenses in the present calculations. Generalized correlation basis sets comprising (19, 17, 7, 17, 6, 1)/[7, 8, 5, 4, 3, 1] functions, basis C (core), in the former and (38, 22, 24, 14, 7, 1)/[11, 10, 9, 7, 5, 1], basis L (large), (38, 22, 24, 14)/[5, 6, 4, 3], basis M (medium, with the $g$ and $h$ harmonics removed from the previous uncontracted basis set), (38, 22, 24, 14)/[5, 5, 3, 2], basis S (small), in the latter cases were generated by the procedure developed previously [20, 21]. Calculations were carried out for internuclear distances from 6 to 14 a.u. All our results were rectified using the counterpoise corrections (CPC) [22, 23] calculated for the Yb $6s^2$ state with one more Yb atom treated as the ghost one. The energies of the rovibrational levels were obtained by solving the rovibrational Schrödinger equation with the numerical interatomic potential by the second order finite-difference method [24]. The stage of calculation of the molecular constant [24] begins with fitting the numerical potential curve for the dimer by polynomials with the help of the quasi-Hermitian method. Appropriate derivatives of the potential curve at the equilibrium point are calculated by recurrence relations. Then rovibrational Schrödinger equation is solved by the Dunham method to express the Dunham coefficients in terms of these derivates.

The $^1\Sigma_g^+$ closed-shell ground state of the $Yb_2$ molecule dissociates into two Yb atoms in the $4f^{14}6s^2(^1S)$ ground state. The computed ground-state potential energy curves for the $Yb_2$ molecule are shown in table 1 and figure 1; the energies of the
Calculated lowest rovibrational levels for the ground electronic state are collected in table 2. Our estimates for the dissociation energy, equilibrium distance, and main spectroscopic constants are listed in table 3. We started from 4-electron scalar relativistic CCSD(T) (denoted as 4e-CCSD(T) below) calculations with rather large basis set L, which gave $D_e = 706 \text{ cm}^{-1}$. The negligible CPC (0.3 cm$^{-1}$ for dissociation energy) indicates a good quality of the basis set used. Subsequent calculations of the effects of the difference between the iterative and non-iterative triple cluster amplitudes (CCSDT-CCSD(T) or contribution from iteration of triples) as well as of quadruple cluster amplitudes (these two contributions are denoted further as the iTQ contribution), valence–outer core correlations (OC), and the spin-orbit interaction (SO) described below have shown that the corresponding contributions to the Yb–Yb interaction energy are within 15% (with respect to the final dissociation energy estimate of 786 cm$^{-1}$), thus justifying the choice of the 4e-CCSD(T) scheme as a good initial approximation. Note that the 4-electron FCI or 48-electron CCSD(T) calculations with considerably smaller basis sets M or C have given much lower $D_e$ estimates ($D_e = 536$ or $353 \text{ cm}^{-1}$, correspondingly). Thus, the quality of the basis set is of crucial importance for accurate calculations of the ytterbium dimer.

The contribution from the quadruple cluster amplitudes as well as the difference between the iterative and non-iterative triple amplitudes was estimated as the difference between the total energies obtained in the 4e-FCI and 4e-CCSD(T) calculations with basis set M for each of the above mentioned internuclear distances. This difference was then added to the total energy obtained in the 4e-CCSD(T) calculation with basis set L. The derived correction from the iTQ amplitudes to the dissociation energy, 117 cm$^{-1}$, is 15% with respect to our final value for $D_e$. We expect that the contribution from the iTQ amplitudes calculated with basis set M will change very slightly (with respect to the final $D_e$ value, etc.) if this basis set is replaced by basis L. It should be noted that the 4e-CCSD energy difference for $R_e = 100$. a.u. and $R_e = 9$. a.u. (the latter is close to the equilibrium distance) changes by 229 and 215 cm$^{-1}$ in going from basis set S to M and from basis set M to L, respectively. The corresponding contributions from the non-iterative triple cluster amplitudes are 94 and 81 cm$^{-1}$, whereas the former contribution from the iTQ amplitudes is only 18 cm$^{-1}$. Thus, extrapolation to the infinite basis set limit should only slightly increase the dissociation energy estimate.

The contribution from the correlations with the 4f, 5s, and 5p outer-core electrons was estimated as the difference between the total energies found in the 48e-CCSD(T) and 4e-CCSD(T) calculations with basis set C for each of the above mentioned internuclear distances. The only difference between these two calculations is the number of correlated electrons, therefore, the lowerings in the total energies give the contribution of the OC correlations. These lowerings were then added to the 4e-CCSD(T) and 4e-CCSD(T)+iTQ total energies derived above. The 4e-CCSD(T)+OC and 4e-CCSD(T)+iTQ+OC dissociation energy, equilibrium distance and spectroscopic constants were calculated with the obtained potential curves. The dissociation energy was decreased by $56 \text{ cm}^{-1}$, whereas the corresponding CPC contribution was about
Calculations of $\text{Yb}_2$ of 100 cm$^{-1}$. It should be noted that the level of the approximations made in calculations\cite{10,12} most closely correspond to our 4e-CCSD(T)+OC approximation (see table 3). The difference (of 82–98 cm$^{-1}$ for $D_e$) between the results of the above calculations can be assigned to the insufficient flexibility of the basis set functions from the “outer-core” region in \cite{10,12}. Unfortunately, calculations for 4 correlated electrons, which are necessary to check this conjecture, were not reported in the cited works.

The effect of spin-dependent (effective spin-orbit) interactions was taken from Ref. \cite{25} as the difference between the ground-state potential curves obtained in two-component relativistic DFT calculations\cite{26} with full RECPs and in scalar relativistic DFT calculations with spin-averaged RECPs. The details of the employed procedure can be found elsewhere\cite{27}. We only note that effects of electronic correlations are taken into account within DFT, so the additivity of the correlations and spin-orbit effects is irrelevant to (is not exploited in) our present study. An uncontracted Gaussian basis set\cite{25} (10s11p8d9f4g) was used to expand auxiliary one-electron spinors in the Kohn-Sham scheme. Two generalized gradient approximations for exchange-correlation functionals were employed, a rather universal Perdew-Burke-Erzernhof (PBE) model\cite{28} and the Perdew-Wang approximation (PW91\cite{29}), which is often believed to be particularly well suited for the description of van-der-Waals bonds\cite{30}.

Scalar relativistic DFT dissociation energy is about 1.6 times higher than that of the corresponding \textit{ab initio} 4e-CCSD(T)+iTQ+OC approximation. Nevertheless, we believe that the spin-orbit contribution is rather correctly extracted from the DFT calculations because the spin-orbit interaction is described by the the one-electron operator and the one-electron parts are the same for Kohn-Sham and Schrödinger (including Hartree-Fock) Hamiltonians. Despite the potential energy functions obtained in the relativistic DFT calculations with PBE and PW91 functionals are slightly different in shape (dissociation energy estimates in two-component calculations are 1238 and 1298 cm$^{-1}$, respectively), the corresponding spin-orbit corrections to bond energies as functions of the internuclear separation almost coincide. The addition of these corrections to the results of accurate scalar relativistic calculations has increased $D_e$ by 19 cm$^{-1}$.

3. Conclusions.

We predict the exact $D_e$ and $w_e$ to be slightly higher than 786 cm$^{-1}$ and 24.1 cm$^{-1}$ and the exact $R_e$ to be slightly lower than 4.582 Å , because all contributions (taken into account in our calculations with a good accuracy) except for the OC correlations change these constants correspondingly. We expect that the reported estimates of the dissociation energy, equilibrium distance and spectroscopic constants of Yb$_2$ obtained by the CCSD(T) technique with very extensive basis sets and the incorporation of corrections for higher-order cluster amplitudes and spin-orbit interactions are the most reliable up to date. Our analysis has revealed a non-negligible role of quadruple amplitudes as well as the significant contribution from iteration of triple amplitudes in the cluster expansion (which were not taken into account in \cite{8,9,10,12}) and small
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but non-negligible contributions from spin-dependent relativistic effects.

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Tables and table captions

**Table 1.** Potential energy functions for the Yb\(_2\) ground state calculated with the help of the GRECP and different correlation methods. Internuclear distances \(R\) and total energy lowerings \(E(R) - E(\infty)\) are in a.u.

| \(R\) | \(4\text{e-CCSD(T)}+\text{OC}\) | \(4\text{e-CCSD(T)}+\text{OC+iTQ}\) | \(4\text{e-CCSD(T)}+\text{OC+iTQ+SO}\) |
|------|-------------------------------|-------------------------------|----------------------------------|
| 6    | 0.02783884                    | 0.02661730                    | 0.02244608                       |
| 7    | 0.00432099                    | 0.00334087                    | 0.00280762                       |
| 8    | -0.00206658                   | -0.00281218                   | -0.00299103                      |
| 9    | -0.00290975                   | -0.00343593                   | -0.00349171                      |
| 10   | -0.00236798                   | -0.00271825                   | -0.00273208                      |
| 11   | -0.00166549                   | -0.00188952                   | -0.00189083                      |
| 12   | -0.00110258                   | -0.00124272                   | -0.00124178                      |
| 13   | -0.00070971                   | -0.00079694                   | -0.00079630                      |
| 14   | -0.00045218                   | -0.00050694                   | -0.00050653                      |
| 100  | 0.00000000                    | 0.00000000                    | 0.00000000                       |

**Table 2.** The energies of the lowest rovibrational levels for the \(^1\Sigma_g^+\) ground state of the \(^{171}\)Yb\(_2\) molecule from the GRECP/4\text{e-CCSD(T)}+\text{iTQ+OC+SO} potential curve are in cm\(^{-1}\). \(J\) and \(v\) are the rotational and vibrational quantum numbers.

| \(v=0\) | \(J=0\) | \(J=1\) | \(J=2\) | \(J=3\) | \(J=4\) | \(J=5\) | \(J=6\) | \(J=7\) | \(J=8\) |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| v=1    | 36.23   | 36.25   | 36.29   | 36.34   | 36.42   | 36.51   | 36.62   | 36.75   | 36.90   |
| v=2    | 59.45   | 59.47   | 59.51   | 59.56   | 59.64   | 59.73   | 59.84   | 59.97   | 60.11   |
| v=3    | 82.15   | 82.17   | 82.21   | 82.26   | 82.34   | 82.43   | 82.54   | 82.66   | 82.81   |
| v=4    | 104.44  | 104.46  | 104.49  | 104.55  | 104.62  | 104.71  | 104.82  | 104.94  | 105.09  |
| v=5    | 126.33  | 126.35  | 126.39  | 126.44  | 126.51  | 126.60  | 126.71  | 126.83  | 126.97  |
| v=6    | 147.85  | 147.87  | 147.90  | 147.96  | 148.03  | 148.12  | 148.22  | 148.35  | 148.49  |
| v=7    | 169.00  | 169.02  | 169.05  | 169.10  | 169.17  | 169.26  | 169.37  | 169.49  | 169.63  |
| v=8    | 189.77  | 189.79  | 189.82  | 189.87  | 189.94  | 190.03  | 190.14  | 190.26  | 190.40  |
### Table 3.
The dissociation energy, equilibrium distance, and spectroscopic constants of the $^1\Sigma^+_g$ ground state of the $^{171}\text{Yb}_2$ molecule. $R_e$ is in Å, $B_e$ in $10^{-3}$ cm$^{-1}$, $\alpha_e$ in $10^{-5}$ cm$^{-1}$, $Y_{02}$ in $10^{-9}$ cm$^{-1}$, and other values in cm$^{-1}$.

| Method | $D_e$ | $R_e$ | $w_e$ | $D_0^0$ | $B_e$ | $w_ex_e$ | $\alpha_e$ | $Y_{02}$ |
|--------|-------|-------|-------|---------|-------|----------|------------|---------|
| Present GRECP calculations: |       |       |       |         |       |          |            |         |
| 4e-CCSD(T) | 706   | 4.767 | 22.9  | 694     | 8.67  | 0.20     | 7.5        | 5.0     |
| 4e-CCSD(T)+OC | 642   | 4.683 | 21.5  | 631     | 8.99  | 0.19     | 8.3        | 6.3     |
| 4e-CCSD(T)+iTQ | 823   | 4.708 | 24.7  | 811     | 8.89  | 0.20     | 7.1        | 4.6     |
| 4e-CCSD(T)+iTQ+OC | 767   | 4.615 | 23.5  | 756     | 9.25  | 0.19     | 7.8        | 5.8     |
| 4e-CCSD(T)+iTQ+OC +SO | 786   | 4.582 | 24.1  | 774     | 9.39  | 0.23     | 8.3        | 5.7     |
| Previous calculations: |       |       |       |         |       |          |            |         |
| 42e-GRECP/ DFT(PW91) | 1261  | 4.274 | 33.2  | 1244    | 10.79 | 0.19     | 6.3        | 4.5     |
| 10e-PP/CISD | 400   | 5.308 | 13    |         |       |          |            |         |
| 10e-PP/20e-CCSD(T) | 470   | 4.861 | 18    |         |       |          |            |         |
| 42e-PP/CCSD(T) | 740   | 4.549 | 25    |         |       |          |            |         |
| 42e-PP/CCSD(T) | 724   | 4.472 |       |         |       |          |            |         |
Figure 4. Calculated potential energy functions for the Yb$_2$ ground state.
Curve (a) corresponding to the computational scheme 4e-CCSD(T)+OC provides an approximation for all-electron scalar CCSD(T), that obtained at the 4e-CCSD(T)+OC+iTQ level (b) should approach the scalar relativistic limit whereas curve (c) presents our best full relativistic results (4e-CCSD(T)+OC+iTQ+SO).