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Pseudopotential study of the ground and excited states of Yb_2*

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Abstract The ground state of the van der Waals-type lanthanide dimer Yb_2 has been studied by means of relativistic energy-consistent ab initio pseudopotentials using three different core definitions. Electron correlation was treated by coupled-cluster theory, whereby core-valence correlation effects have been accounted for either explicitly by correlating the energetically highest coreorbitals or implicitly by means of an effective core-polarization potential. Results for the first and second atomic ionization potentials, the atomic dipole polarizability, and the spectroscopic constants of the molecular ground state are reported. Low-lying excited states have been investigated with spin-orbit configuration interaction calculations. It is also demonstrated for the whole lanthanide series that correlation effects due to the atomic-like, possibly open $4f$-shell in lanthanides can be modeled effectively by adding a core-polarization potential to pseudopotentials attributing the $4f$-shell to the core.

Key words: Core-polarization potential – Pseudopotential – Lanthanides – Ytterbium – Van der Waals interaction

1 Introduction

The $^1S_0$ ground state of the ytterbium atom Yb ($Z = 70$) predominantly arises from a closed-shell $[Xe]4f^{14}6s^2$ configuration [1] and Yb, together with Eu, is sometimes considered to be a lanthanide analogue to alkaline earth elements like Sr or Ba. Owing to the "inert" character of the Yb $6s^2$ shell the homonuclear dimer Yb_2 should only have a rather weakly bound $^1\Sigma_g^+(0_g^+)$ ground state, but several low-lying metastable excited states resulting from a $6s^2 \rightarrow 6s^1 6p^1$ excitation on one center in the limit of the separated atoms. Formally the situation for Yb_2 is not only analogous to the one for Ba_2 and the lighter Group 2 dimers, but also to the one for Hg_2 and its lighter Group 12 homologues Cd_2 and Zn_2. Whereas Ba and Yb differ by 14 units of nuclear charge and the filled $4f$-shell, Yb and Hg differ by 10 units of nuclear charge and the filled $5d$-shell. A comparison of Yb_2 to Ba_2 gives information on the effects of the lanthanide contraction, whereas a comparison to Hg_2 is of interest since the "maximum of relativistic effects" in the Periodic Table is usually considered to occur close to Hg, i.e. at Au, at least when properties related to the $6s$ valence orbital are considered [2].

The ground and excited states of both Group 2 and Group 12 dimers have been investigated previously by experimental and theoretical methods [3–9, and references cited therein]; however, only very little information is available for Yb_2 [10–13]. In 1972, Guido and Balducci [10] identified the ytterbium dimer for the first time by mass spectrometry and estimated the dissociation energy of the ground state using classical statistical thermodynamics to be 0.17 eV, with an estimated maximum uncertainty comparable to the value itself. In order to obtain this result a vibrational frequency of $\omega_e = 33\ cm^{-1}$ was deduced for Yb_2 from the vibrational frequency of the Group 2 dimer Ca_2 and the Debye temperatures of the Ca and Yb metals, which have the same crystal structure; the bond distance was estimated to be 4.19 Å, assuming that the interatomic distances for the Yb_2 and Ca_2 molecules are in the same ratio as the respective covalent radii. Later, the vibrational frequency of the Yb_2 dimer in its ground state was estimated empirical to be $21.9\ cm^{-1}$ by Goodfriend [11] using an empirial relationship, i.e. a value only 2/3 of the one used by Guido and Balducci [10]. Clearly, the estimates for the bond length and vibrational frequency are so rough, and the error bar of the dissociation energy is so large, that the experimental numbers can only be a guide to theoretical work. The UV-visible absorption spectrum of Yb_2 in rare gas matrices (Ar, Kr, Xe) de-

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* Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

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termined by Suzer and Andrews [12] shows extensive vibrational structures around 550 nm with a spacing of $48\,\mathrm{cm}^{-1}$. The authors assigned this absorption to a $6s^2(^1\mathrm{S}_0)6s^2(^1S_0)^1\Sigma_\mathrm{g}^+ \rightarrow 6s^16p^1(^1\mathrm{P}_1)6s^2(^1\mathrm{S}_0)^1\Sigma_\mathrm{u}^+$ transition similar to the ones observed for Group 2 metal dimers [14]. The dissociation energy for the $^1\Sigma_\mathrm{u}^+$ excited state of Yb_2 has been determined to be 0.936 eV with respect to the $^1\mathrm{S}_0 +^1 \mathrm{P}_1$ separated atoms limit. To our knowledge this is the only excited state for which this information exists.

The spectroscopic properties of the Yb_2 ground state have been theoretically determined in previous work by one of the present authors [13]. A scalar-relativistic energy-consistent 10-valence-electron pseudopotential (PP) [15] together with a $(7s6p5d1f)/[5s4p3d1f]$ valence basis set has been applied in single-reference configuration interaction calculations including all single and double substitutions (CISD) and the size-consistency correction of Langhoff and Davidson (+SCC [16]) ($D_\mathrm{e} = 0.05$ eV, $R_\mathrm{e} = 5.308$ Å, $\omega_\mathrm{e} = 13\,\mathrm{cm}^{-1}$) as well as coupled electron-pair approximation calculations (CEPA-1 [17]) ($D_\mathrm{e} = 0.05$ eV, $R_\mathrm{e} = 5.203$ Å, $\omega_\mathrm{e} = 14\,\mathrm{cm}^{-1}$). Whereas the binding energy is within the experimental error bars, the vibrational constant is significantly lower and the bond length significantly larger than the empirical estimates discussed above. A recalculation of the properties of the Yb_2 ground state and a corresponding study of the excited states therefore seemed to be desirable.

Recently, our group has studied the ground-state properties of the Group 12 dimers $\mathrm{Zn}_2, \mathrm{Cd}_2$, and Hg_2 at the coupled-cluster level with single and double excitation operators and a perturbative estimate of triple excitations [CCSD(T)] using relativistic 20-valence-electron ab initio PPs and large valence basis sets containing up to *g* functions [7, 8]. The derived spectroscopic data agree excellently with the available experimental values and encouraged us to perform a similar PP CCSD(T) study for the Yb_2 ground state. The Yb atom was modelled as a 2-, 10-, and 42-valence-electron system in order to investigate the errors related to the choice of the core. The 2-valence-electron PP is of special interest here since it would also allow study of small clusters of ytterbium atoms (cf. related work on mercury clusters [18]).

For the ground states of the Group 12 dimers, besides the dominating van der Waals interaction, quite significant covalent contributions to bonding have been found [6–8]. We will compare the situation for Yb_2 to the previous findings for the Group 12 dimers. Another important goal of the present work, besides the accurate calculation of spectroscopic parameters for the ground state and the interpretation of bonding, is to investigate the potential curves for the low-lying excited states of Yb_2 in order to give some guidance for future experimental studies.

2 Method

All scalar-relativistic calculations reported here were performed with the MOLPRO program package [19], whereas for the calculations including spin-orbit coupling the program RELMOL [20] was used. All-electron and pseudopotential atomic calculations within the finite difference scheme were carried out with the program GRASP [21].

2.1 Pseudopotentials and valence basis sets

The energy-consistent PP method applied here was described previously [15, 22]. In the current investigation we used relativistic 42-, 10-, and 2-valence-electron ab initio pseudopotentials, which will be denoted as PP(42), PP(10), and PP(2) in the following. In brief, the parameters were adjusted to total valence energies of a multitude of low-lying electronic states of the neutral atom and its cations. The reference data were obtained from fully relativistic multi-configuration Dirac-Hartree-Fock (DHF) calculations including a perturbative correction for the Breit interaction (+B) and some higher-order quantum-electrodynamic effects (+QED). In the scalar-relativistic calculations we apply PPs adjusted directly to valence energies which were averaged over all states of a nonrelativistic configuration, whereas for the relativistic calculations the adjustment was performed with respect to the valence energies of the individual states within the intermediate coupling scheme [23]. The parameters for the recommended PP(10) (vide infra) are listed in Table 1 [24]. The functional form of the PP is

Table 1. Parameters (in au) for the 10-valence-electron pseudopotentials [PP(10)] for Yb; dipole polarizability $\alpha_\mathrm{D} = 4.2745$; cutoff parameter $\delta = 0.3875$

l	A_l	a_l	$A_{l,l+1/2}$	$A_{l,l-1/2}$	a_{lj}
0	592.068431	9.043610	333.151069		9.299265
0	−37.940692	4.518599	−27.460975		4.502357
0	0.019535	1.499985	−1.840753		2.249997
0	−0.023856	0.494386	3.009259		1.120000
1	334.845502	7.564260	387.941705	302.188582	7.443154
1	−13.863816	3.811792	−109.889518	−89.308571	3.742253
1	0.066082	1.199008	31.870092	24.031666	2.374609
1	−0.040081	0.398656	−0.344358	0.2204440	1.180000
2	90.540081	4.739704	301.870026	247.778061	4.750370
2	−6.633788	2.382664	−14.770908	−13.514895	2.375153
2	0.006005	1.100005	−3.1962505	−2.9351721	1.185133
2	−0.013732	0.297450	−0.0076174	−0.0057031	0.589758
3	7.0165100	1.386400	7.0165100	7.0165100	1.386400

$$V_{\mathrm{PP}} = -\frac{Q}{r} + \sum_{l,j,k} A_{ljk} \exp(-a_{ljk} r^2) \mathscr{P}_{lj} \tag{1}$$

where $\mathscr{P}_{lj}$ denotes the projector onto angular-momentum symmetry lj. For comparison we consider also PPs adjusted to reference data from Wood-Boring (WB) scalar-relativistic all-electron calculations (PP(42) [22], PP(10) [15]). A core-polarization potential (CPP) [25, 26] accounting for both static and dynamic polarization of the PP core was added to PP(10) and PP(2). The form of the CPP used here is

$$V_{\mathrm{CPP}} = -\tfrac{1}{2}\alpha_{\mathrm{D}} \mathbf{f}^2 \tag{2}$$

$$\mathbf{f} = \sum_i \frac{\mathbf{r}_i}{r_i^3} \omega(r_i) - Q_\mu \frac{\mathbf{r}_\mu}{r_\mu^3} \omega(r_\mu) \tag{3}$$

$$\omega(r) = (1 - \exp(-\delta r^2)) \tag{4}$$

Here α_{D} is the dipole polarizability of the Yb^{10+} respectively Yb^{2+} core and $\mathbf{f}$ is the electric field generated at the site of this core ($\mathbf{r} = \mathbf{0}$) by the valence electrons (at positions $\mathbf{r}_i$) and the other Yb core ($Q_\mu = 10$ respectively 2, at position $\mathbf{r}_\mu$). The cutoff factor ω was parametrized by adjusting δ at the CCSD(T) level to the experimental first and second ionization potential of the neutral atom. In case of the PP(2) the Hamiltonian had to be augmented by a core-core repulsion correction (CCRC) in order to account for deviations from the point charge repulsion between the large Yb^{2+} cores. The CCRC was derived for every internuclear distance of interest using PP(10) for Yb_2^{4+} at the Hartree-Fock level with frozen atomic orbitals taken from a calculation of Yb^{2+}.

In case of the scalar-relativistic DHF + B + QED-adjusted PPs the following basis sets were applied: for PP(42) a $(12s11p9d8f6g)/[5s5p4d4f3g]$ basis set using a generalized atomic natural orbital contraction and augmented by a diffuse $(3s3p3d3f2g)$ set; for PP(10) an uncontracted $(9s9p8d6f2g)$ basis set based on a $(7s6p5d)$ set Hartree-Fock optimized for the $6s^2$ and $6s^1 5d^1$ configurations and augmented by a diffuse $(2s3p3d)$ set and a $(6f2g)$ correlation set roughly optimized in CCSD(T) calculations; for PP(2) an uncontracted $(6s6p5d3f1g)$ basis set based on a $(5s5p5d)$ set with s-, p-, and d-exponents from state-averaged Hartree-Fock calculations for the $6s^2$, $6s^1 6p^1$ and $6s^1 5d^1$ configurations, respectively, augmented by a diffuse $(1s1p)$ set and a $(3f1g)$ correlation set. For the scalar-relativistic WB-adjusted PPs, basis sets of similar size and quality have been used: for PP(42) the basis set size and derivation is identical to the one described above for the DHF + B + QED-adjusted PP(42); for PP(10) an uncontracted $(9s8p7d6f2g)$ basis set was generated by augmenting a $(7s6p5d)$ Hartree-Fock optimized set by a diffuse $(2s2p2d)$ set and a $(6f2g)$ correlation set.

2.2 Spectroscopic constants and bonding analysis for the ground state

The single reference CCSD(T) method was used to calculate the ground-state potential energy curve for all three kinds of PPs. The basis set superposition error (BSSE) was found to be significant in previous investigations of Group 12 dimers [4, 7, 8] and therefore was corrected by means of the counterpoise method of Boys and Bernardi [27]. In the case of the 42-valence-electron PP, calculations both with the $4f^{14}5s^2 5p^6 6s^2$ (48 electrons) and $5s^2 5p^6 6s^2$ (20 electrons) configuration of each atom correlated were carried out in order to investigate the effect of correlating the $4f$ shell, e.g., to check the neccessity of adding a CPP to PP(10). Similarly, for the PP(10) calculations with the $5s^2 5p^6 6s^2$ (20 electrons) and $6s^2$ (4 electrons) configuration of each atom correlated have been performed to establish the need of a CPP in the PP(2) case. The spectroscopic constants were obtained by fitting a fifth-order polynomial in R times a factor $1/R$ for seven points around the equilibrium distance. A spacing of 0.1 bohr between the points was used. The accuracy of $D_{\mathrm{e}}, R_{\mathrm{e}}$, and ω_{e} as estimated from various (reasonable) choices of the calculated points as well as different orders of the polynomial is better than 0.001 eV, 0.001 Å, and $1\,\mathrm{cm}^{-1}$.

For Group 12 dimers a significant covalent bonding contribution was found besides the dominating van der Waals interaction in several previous studies [6–8]. Using the method of Mödl et al. [28] we performed an analysis of the bonding for the ground state on the basis of the complete active space multi-configuration self-consistent field (CASSCF) wavefunction with the $6s$ and $6p$ orbitals as active space. The charge fluctuation $\sqrt{\langle \delta N^2 \rangle}$ defined by

$$N = \sum_{i,\sigma} d_{i\sigma}^+ d_{i\sigma} \quad \text{and} \quad \delta N^2 = N^2 - \langle N \rangle^2 \tag{5}$$

well reflects the bonding characteristics. Here $d_{i\sigma}^+$ and $d_{i\sigma}$ are the creation and annihilation operators for the localized spin orbital $i\sigma$, and N a local occupation number operator for the valence orbitals localized on one of the two atoms. For a pure van der Waals molecule like He_2 the charge fluctuations vanish since only simultaneous intra-atomic excitations on both centers are present, whereas for an ideal covalent single bond one has, in the molecular orbital picture, a value of $\sqrt{2}/2$.

2.3 CASSCF and MRCI calculations for the excited states

The excited states of Yb_2 considered here are those resulting from the separated atoms limits ${}^1\mathrm{S} + {}^3\mathrm{P}$ and ${}^1\mathrm{S} + {}^1\mathrm{P}$, i.e., ${}^{1,3}\Sigma_{\mathrm{u}}^+$, ${}^{1,3}\Sigma_{\mathrm{g}}^+$, ${}^{1,3}\Pi_{\mathrm{g}}$, and ${}^{1,3}\Pi_{\mathrm{u}}$ in the absence of spin-orbit interaction. The CASSCF method was used to generate the orbitals for the subsequent multi-reference configuration interaction calculations (MRCI) which were corrected for size-consistency errors by means of the Siegbahn correction [29]. The active space consisted of the valence $6s$ and $6p$ atomic orbitals (4 electrons in 8 orbitals), i.e., in the case of PP(10) the $5s$ and $5p$ orbitals were kept doubly occupied in the CASSCF. The number of reference CSFs (configuration state functions)\the size of the MRCI matrix after contraction for the states examined here were in D_{2h}

symmetry: 60\2377916 ($^1\Sigma_g^+$), 48\3282920 ($^3\Sigma_u^+$), 44\2240032 ($^1\Sigma_u^+$), 48\3237864 ($^3\Pi_g, ^3\Pi_u$), 40\2186720 ($^1\Pi_g$, $^1\Pi_u$), and 42\2932658 ($^3\Sigma_g^+$).

Spin-orbit interaction was considered in case of the large-core PP(2) including the CPP. This approach has the advantage that core-valence correlation effects are taken into account quite accurately at low cost as long as states with occupied 5*d* orbitals are not considered. As above, the valence 6*s* and 6*p* orbitals were used as active space to generate the zeroth-order wavefunction from which single and double excitations were performed [20]. Owing to program limitations, small $(6s6p)/[4s4p]$ basis sets were used. The states corresponding to gerade and ungerade parity as well as odd and even angular momentum quantum number Ω were diagonalized separately. The number of reference determinants\the size of the CI matrix was 121\37964 for even parity and even Ω and 108\36208 in all other cases. Since the ground-state potential curve in this approach shows too little bonding, we extracted only the excitation energies and added them to the PP(10) + CPP CCSD(T) ground-state potential curve obtained with the big basis set. Corrections of this type lead to reliable results in a study of I_2 by Teichteil and Pélissier [30].

3 Results and discussion

3.1 Ionization potentials and dipole polarizability of the neutral atom

Before discussing the calculations of Yb_2 , the first and second ionization potentials and the dipole polarizability of the neutral atom Yb will be reported in order to check the accuracy of the applied methods and to select the optimal PP for the molecular calculations. The results are summarized in Table 2. In the case of the small-core PP [42 valence electrons, PP(42)] the DHF + B + QED-adjusted PP performs clearly better than the WB-adjusted one at all levels of theory. The inclusion of the 4*f* subshell in the CCSD(T) calculation increases the ionization potentials by 0.14 eV for IP_1 and 0.27 eV for IP_2, whereas the further inclusion of the 4*s*4*p*4*d* subshell leads only to negligible changes. This implies that the medium-core PP [10 valence electrons, PP(10)] should be augmented by a CPP. In contrast to PP(42), for PP(10) the DHF + B + QED- and WB-adjusted PP give essentially results of the same quality, both with and without CPP. The CPP effects for IP_1 and IP_2 at the CCSD(T) level of 0.17 eV and 0.40 eV, respectively, are larger than the corrections obtained by explicitly correlating the 4*f* shell. Since the IPs of both approaches without correlation of the 4*f* shell respectively without CPP are in quite good agreement [6.08 eV, 11.78 eV for PP(42), 6.05 eV, 11.81 eV for PP(10)], but the results for PP(10) including the CPP (6.22 eV, 12.21 eV) are in better overall agreement with the experimental values (6.25 eV, 12.18 eV) than those obtained with PP(42) and explicit correlation of the 4*f* shell (6.23 eV, 12.08 eV), we suppose that the correlation treatment in the latter case might still be insufficient. Since a further increase of the *spdfg* basis set did not result in any substantial improvements, one possible reason might be the lack of *h*-type functions for the correlation treatment of the 4*f* shell. However, since *g*-type functions contribute only with 0.04 eV and 0.07 eV to IP_1 and IP_2, respectively, and *h*-type functions will most likely contribute less, other reasons are also possible, e.g., PP errors, incompleteness of the many-particle basis, or errors due to the perturbative estimate of triples in CCSD(T). The corresponding triple corrections to the CCSD result are 0.07 eV and 0.03 eV when only the 5*s*5*p*6*s* valence space is correlated, but they increase to 0.12 eV both for IP_1 and IP_2 when the 4*f* and 4*d* shells are also included. The results obtained with the large-core PP [2 valence electrons, PP(2)] including the CPP (6.28 eV, 12.21 eV) are also in very good agreement with the experimental values.

No decisive answers concerning the quality of the DHF + B + QED-adjusted PPs can be drawn from the results for the dipole polarizability of the Yb atom. The CCSD(T) results for PP(10) + CPP (137.3 au), PP(2) + CCP (143.1 au), and PP(42) (145.3 au) are within 3% of the recommended value given by Miller

Table 2. First and second ionization potentials $IP_i (i = 1, 2)$ (eV) and dipole polarizability α (au) of Yb calculated with scalar-relativistic 42-, 10-, and 2-valence-electron pseudopotentials [PP(42), PP(10), PP(2)] based on reference data from Dirac-Hartree-Fock calculations including perturbative corrections for the Breit interaction and quantum electrodynamics (DHF + B + QED). The results for corresponding pseudopotentials based on Wood-Boring (WB) calculations are given in parentheses

Method	Active	IP_1	IP_2	α
PP(42), SCF		5.16 (5.10)	11.26 (11.08)	178.4 (190.1)
PP(42), CCSD	5*s*5*p*6*s*	6.01 (5.96)	11.75 (11.53)	157.8 (169.0)
PP(42), CCSD(T)	5*s*5*p*6*s*	6.08 (6.02)	11.78 (11.55)	155.6 (162.9)
PP(42), CCSD	4*f*5*s*5*p*6*s*	6.09 (6.05)	11.95 (11.72)	155.8 (170.3)
PP(42), CCSD(T)	4*f*5*s*5*p*6*s*	6.22 (6.17)	12.05 (11.83)	149.1 (162.9)
PP(42), CCSD	4*d*4*f*5*s*5*p*6*s*	6.11 (6.06)	11.96 (11.74)	153.1 (172.6)
PP(42), CCSD(T)	4*d*4*f*5*s*5*p*6*s*	6.23 (6.18)	12.08 (11.85)	145.3 (159.5)
PP(10), SCF		5.13 (5.10)	11.24 (11.17)	177.3 (181.9)
PP(10), CCSD	6*s*	5.80 (5.75)	11.24 (11.17)	180.3 (188.4)
PP(10), CCSD	5*s*5*p*6*s*	5.98 (5.93)	11.77 (11.69)	155.4 (161.9)
PP(10), CCSD(T)	5*s*5*p*6*s*	6.05 (6.00)	11.81 (11.73)	152.5 (159.9)
PP(10), CPP, CCSD	5*s*5*p*6*s*	6.20 (6.18)	12.20 (12.19)	137.6 (141.2)
PP(10), CPP, CCSD(T)[a]	5*s*5*p*6*s*	6.22 (6.20)	12.21 (12.20)	137.3 (141.0)
PP(2), SCF		5.17	11.27	178.4
PP(2), CCSD	6*s*	5.88	11.27	178.7
PP(2), CPP, CCSD	6*s*	6.28	12.21	143.1
Exp. [1, 31]		6.25	12.18	141.9

[a] The nonrelativistic values for IP_1, IP_2 and α are 5.81 eV, 11.36 eV, and 185.2 au, respectively

(141.9 au [31]). Since the contribution of g-type functions in case of PP(42) is a reduction of the polarizability by 2.5 au and h-type functions will contribute less, we assume that the same reasons as mentioned previously for the ionization potentials are responsible for the slightly too high dipole polarizability in this case. Note that the SCF results as well as the CCSD and CCSD(T) results for PP(42) without correlation of the $4f$ shell and PP(10) without CPP agree within 3 au. The problems in the explicit treatment of core-valence correlation in Yb appear to be due to the existence of shells of three different main quantum numbers ($n = 4, 5, 6$) which, on the basis of energetic or spatial arguments, have to be correlated simultaneously: orbital energies obey the order $6s > 4f > 5p > 5s$, whereas the radial expectation values are in the order $6s > 5p > 5s > 4f$. The use of a CPP therefore seems to be a computationally attractive alternative to an explicit correlation treatment. In case of the WB-adjusted pseudopotentials, PP(42) (159.5 au) seems to give too high dipole polarizabilities owing to a PP defect already present at the uncorrelated level, whereas the value for PP(10) + CPP (141.0 au) is in excellent agreement with Miller's recommended value (141.9 au).

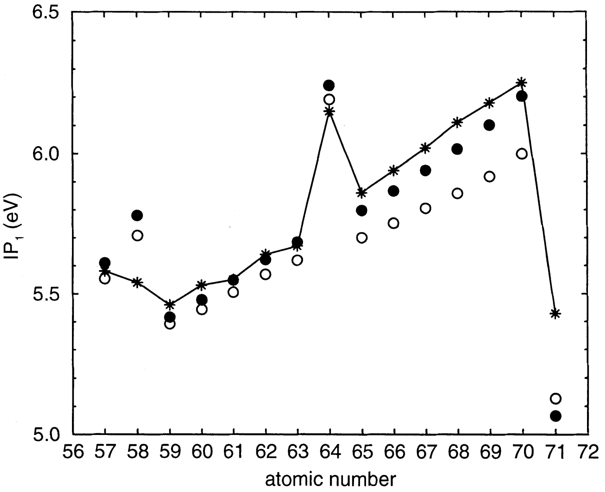

Fig. 1. First ionization potentials IP_1 of the lanthanide atoms from pseudopotential (PP) CCSD(T) calculations without (*empty circles*) and with (*filled circles*) inclusion of a core-polarisation potential (CPP). Experimental values (*stars on solid line*) from Martin et al. [1]

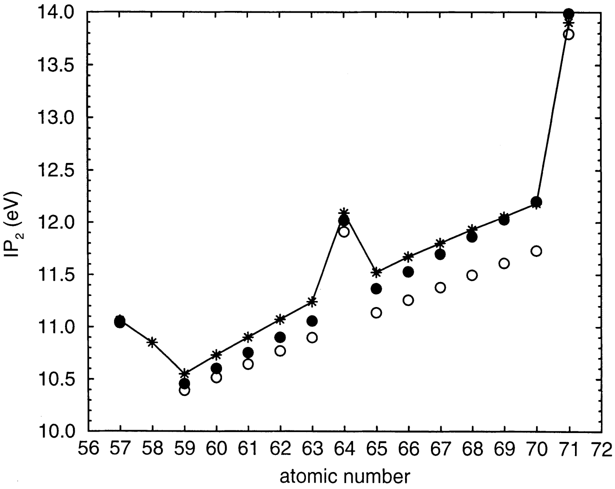

Fig. 2. Second ionization potentials IP_2 of the lanthanide atoms from PP CCSD(T) calculations without (*empty circles*) and with (*filled circles*) inclusion of a CPP. Experimental values (*stars on solid line*) from Martin et al. [1]

In order to check the previous findings also for the other lanthanide elements, we investigated the first and second ionization potentials of the elements La to Lu using PPs which treat the (open) $4f$ shell as part of the core [15] and have been augmented by a CPP. A major difficulty for the CPP generation is the lack of (accurate) experimental ionization potentials for the one-valence electron systems Ln^{9+} and Ln^{10+}. Therefore, we performed only a relatively crude CPP adjustment. The DHF dipole polarizabilities α_D of Ba^{10+} (0.5631 au), Yb^{10+} (4.2745 au) and La^{11+} (0.4777 au), Lu^{11+} (1.9812 au) were used to interpolate those of the Ln^{10+} and respectively Ln^{11+} cores of the other lanthanide elements. The cutoff parameters δ have been fitted at the CCSD(T) level to the experimental $6s^2 \rightarrow 6s^1$ and $6s^1 \rightarrow 6s^0$ ionization potentials, i.e., the first and second ionization potentials of Yb ($\delta = 0.4589$) and respectively the second and third ionization potentials of Lu ($\delta = 0.5592$). The resulting parameters have also been used for the 10- and 11-valence-electron PPs of all other lanthanide elements. The uncontracted standard basis sets of ($7s6p5d$) quality were augmented by three diffuse s, p, and d functions each (exponents 0.01, 0.005, 0.0025) and seven f and g functions each (exponents 9, 3, 1, 0.33, 0.11, 0.037, 0.012). The CCSD(T) results are displayed in Figs. 1 and 2. It is seen that the addition of the CPP improves the calculated values in almost all cases, especially for the second half of the series. The relatively large errors in the first ionization potential of Ce and Lu can be explained, at least partially, by spin-orbit effects, which have not been considered in our calculations but may be estimated from experimental data [1]. For Lu the $^2\mathrm{D}_{3/2}$ ground state is 0.15 eV below the $^2\mathrm{D}$ spin-orbit average, whereas for Lu^+ $^1\mathrm{S}_0$ and respectively $^1\mathrm{S}$ no correction is needed [1], i.e., the calculated IP_1 should be increased by 0.15 eV to yield 5.22 eV (exp. 5.43 eV [1]). In case of La the $^2\mathrm{D}_{3/2}$ ground state is 0.08 eV below the $^2\mathrm{D}$ spin-orbit average, for La^+ $^3\mathrm{F}_2$ it is 0.15 eV below $^2\mathrm{F}$, and for La^{2+} $^2\mathrm{D}_{3/2}$ it is 0.12 eV below $^2\mathrm{D}$. The calculated IP_1 should be decreased by 0.07 eV yielding 5.54 eV (exp. 5.58 eV [1]), whereas the calculated IP_2 should be increased by 0.03 eV to give 11.07 eV (exp. 11.06 eV [1]). The most difficult case is Ce: no correction arises for the $^1\mathrm{G}_4$ and respectively $^1\mathrm{G}$ ground state, whereas the $^4\mathrm{H}_{7/2}$ ground state of Ce^+ is 0.34 eV below the $^4\mathrm{H}$ spin-orbit average. This implies that the calculated IP_1 has to be reduced by 0.34 eV to yield 5.44 eV (exp. 5.54 eV [1]). We note, however, that the coupling between the f and d shells has changed from low spin in Ce to high spin in Ce^+, an effect which is not taken into account by the applied PP. It is also not possible to evaluate IP_2 for Ce since the f occupation changes during this ionization process. For all other cases considered in Figs. 1 and 2 the ionization occurs from the 6*s* orbital and spin-orbit effects are negligible.

The dipole polarizability of Yb (142 au [31]) is roughly a factor of two smaller than that of Ba (256 au [31], 270 au [32]), but it is about a factor of four higher than that of Hg (34 au [33, 34]). The marked decrease of the dipole polarizabilities in the sixth row may be attributed to the increase of relativistic effects, especially for the 6*s* orbital [2]. The relativistic dipole polarizability decrease for Yb (26% ; nonrelativistic value 185.2 au for PP(10) + CPP + CCSD(T)) is significantly smaller than for Hg (41%; nonrelativistic value 58.1 au for PP(20) + CCSD(T) [8]). The coupling between relativistic and electron correlation effects is also weaker for Yb than for Hg, i.e., the ratio of the nonrelativistic dipole polarizability to the relativistic result is 1.30 and 1.35 at the PP(10) SCF and PP(10) + CPP CCSD(T) levels, respectively, compared to corresponding values of 1.83 and 1.70 for Hg.

As preparation for a study of the excited molecular states it is necessary to check the performance of the PPs for the excited states of the Yb atom. Tables 3 and 4 summarize selected excitation and ionization energies obtained without and with considering electron correlation, respectively. It is obvious that both PP(2) and PP(10) yield values in close agreement with the DHF all-electron results, except for the $^3D_1$-$^1D_2$ splitting of the $5d^1\,6s^1$ configuration from PP(2) (Table 3). We attribute the 12% too large value to the altered nodal structure of the pseudoorbitals and the resulting overestimation of corresponding exchange integrals. This deficiency of large-core PPs was first discussed by Pittel and Schwarz [35] and later quantitatively investigated by one of the present authors [36]. It should also be noted that in many cases the effects of the Breit term are larger than the PP errors. The correlated results clearly demonstrate the need to include core-valence correlation by means of a CPP, both for the spin-orbit averaged ionization and excitation energies and the fine-structure splittings (Table 4).

3.2 Spectroscopic parameters of the ground state

The results for bond length, binding energy, and vibrational frequency of Yb_2 are listed in Table 5. The comparison of corresponding results without and with correction for the BSSE clearly indicates that, except for the large-core PP, it is important to include a BSSE correction. In the case of the CCSD(T) results for PP(42), the BSSE is of the same magnitude as the corrected binding energy itself (up to 0.07 eV); the BSSE

Table 3. Spin-orbit-averaged atomic excitation and ionization energies of Yb from finite-difference all-electron Dirac-Hartree-Fock (DHF, DHF + B + QED) [21] and corresponding pseudopotential [PP(2), PP(10)] calculations. The spin-orbit splittings are also given (cm^{-1})

Configuration	States	DHF	DHF + B + QED	PP(2)	PP(10)
Yb $6s^2$	$^1S_0$	0	0	0	0
Yb $6s^1 6p^1$	avg.	15356	15343	15150	15383
	$^3P_0$-$^3P_1$	741	735	692	738
	$^3P_0$-$^3P_2$	2226	2206	2094	2217
	$^3P_0$-$^1P_1$	16149	16136	16805	16037
Yb $5d^1 6s^1$	avg.	23142	23079	22916	23078
	$^3D_1$-$^3D_2$	51	41	43	40
	$^3D_1$-$^3D_3$	128	103	108	101
	$^3D_1$-$^1D_2$	7761	7747	8690	7721
Yb^+ $6s^1$	$^2S_{1/2}$	41546	41519	41480	41490
Yb^+ $6p^1$	avg.	68343	68295	68292	68263
	$^2P_{1/2}$-$^2P_{3/2}$	2822	2790	2803	2804
Yb^+ $5d^1$	avg.	65428	65306	65249	65304
	$^2D_{3/2}$-$^2D_{5/2}$	532	485	488	485
Yb^{2+}	$^1S_0$	132586	132498	132421	132542

Table 4. Spin-orbit-averaged atomic excitation and ionization energies of Yb from DHF + B + QED pseudopotential [PP(2), PP(10)] configuration interaction calculations without and with core-polarization potential (CPP) in comparison to experimental values [1] and all-electron (AE) coupled-cluster results based on the Dirac-Coulomb-Breit (DCB) Hamiltonian [41]. The corresponding spin-orbit splittings are also given (cm^{-1})[a]

Configuration	States	Exp.	AE DCB	PP(2) + CPP	PP(2)	PP(10) + CPP	PP(10)
Yb $6s^2$	$^1S_0$	0	0	0	0	0	0
Yb $6s^1 6p^1$	avg.	20418	21051	20897	17801	21011	19828
	$^3P_0$-$^3P_1$	704	730	651	620	724	697
	$^3P_0$-$^3P_2$	2422	2477	2242	2032	2585	2138
	$^3P_0$-$^1P_1$	7780	9912	8670	10438	8637	12692
Yb^+ $6s^1$	$^2S_{1/2}$	50441	51109	50385	47395	49731	48098
Yb^+ $6p^1$	avg.	79723	81274	80954	74143	80562	76983
	$^2P_{1/2}$-$^2P_{3/2}$	3330	3442	3423	2778	3536	2874
Yb^{2+}	$^1S_0$	148710[b]	148985	148555	138263	147957	142736

[a] Basis sets: AE $(31s26p21d15f10g6h)$; PP(2) $(6s6p5d2f)$; PP(10) $(8s8p5d)/[6s6p5d]$

[b] Uncertainty ±50 cm^{-1}

Table 5. Bond lengths R_e (Å), binding energies D_e (eV), and vibrational constants ω_e(cm^{-1}) for the Yb$_2$ ground-state from calculations using DHF + B + QED 42-, 10-, and 2-valence-electron pseudopotentials [PP(42), PP(10), PP(2)]. Results without counterpoise correction of the basis set superposition error are given in parentheses

Method	Active	R_e	D_e	ω_e
PP(42), CCSD(T)	$4f5s5p6s$	4.653 (4.500)	0.076 (0.143)	22 (27)
PP(42), CCSD	$4f5s5p6s$	4.895 (4.699)	0.044 (0.099)	16 (21)
PP(42), CCSD(T)	$5s5p6s$	4.735 (4.670)	0.076 (0.098)	22 (23)
PP(42), CCSD	$5s5p6s$	4.956 (4.872)	0.044 (0.062)	16 (18)
PP(10), CPP, CCSD(T)	$5s5p6s$	4.861 (4.836)	0.058 (0.064)	18 (19)
PP(10), CPP, CCSD	$5s5p6s$	5.009 (4.983)	0.041 (0.046)	15 (16)
PP(10), CCSD(T)	$5s5p6s$	4.922 (4.901)	0.060 (0.066)	19 (19)
PP(10), CCSD	$5s5p6s$	5.158 (5.134)	0.035 (0.040)	14 (14)
PP(10), CCSD(T)	$6s$	4.964 (4.958)	0.067 (0.070)	19 (20)
PP(10), CCSD	$6s$	5.188 (5.178)	0.038 (0.041)	15 (15)
PP(2), CPP, CCSD(T)	$6s$	4.445 (4.433)	0.092 (0.095)	25 (25)
PP(2), CPP, CCSD	$6s$	4.551 (4.540)	0.066 (0.069)	22 (22)
PP(2), CCSD(T)	$6s$	4.598 (4.594)	0.103 (0.104)	26 (26)
PP(2), CCSD	$6s$	4.799 (4.794)	0.057 (0.057)	19 (20)
Est. [10]		4.19	0.17 ± 0.17	33
Est. [11]				22

correction also leads to a significant bond lengthening (up to 0.2 Å) and a reduction of the vibrational frequency (up to 5 cm^{-1}). The corrections are smaller for PP(10), but especially for the binding energy (up to 10%) are still not negligible. Scalar-relativistic effects were investigated at the CCSD(T) level with the 5*s*, 5*p*, and 6*s* orbitals in the active space for PP(10). Relativity leads to a destabilization of Yb$_2$, i.e., a bond length expansion of 0.20 Å, a decrease of the binding energy by 0.036 eV, and a reduction of the vibrational constant by 6 cm^{-1}. We attribute this destabilization mainly to the strong relativistic reduction of the Yb dipole polarizability, since the first ionization potential slightly increases (cf. Table 2) and the 6*s* orbital contracts (cf. [2]). Note that a simple estimate for the dispersion interaction in a homonuclear dimer is given by an approximation to London's formula, i.e.

$$\Delta E^{\mathrm{disp}} = -3\mathrm{IP}_1\alpha^2/(4R^6) \tag{6}$$

With a ratio between relativistic and nonrelativistic values of 1.07 for the first ionization potential and 0.74 for the dipole polarizability [CCSD(T) values for PP(10) + CPP from Table 2], the reduction of the dipole polarizability clearly dominates. An estimate of the bond length based only upon the 6*s* radial expectation values [37] would lead to a 7% bond length contraction instead of the observed expansion.

Despite the differences observed for the atoms, the molecular BSSE-corrected CCSD(T) results for the DHF + B + QED-adjusted PP(42) ($R_e = 4.653$ Å, $D_e = 0.076$ eV, $\omega_e = 22$ cm^{-1}) are almost identical to those for the WB-adjusted PP(42) ($R_e = 4.666$ Å, $D_e = 0.076$ eV, $\omega_e = 22$ cm^{-1}). The corresponding BSSE-corrected CCSD(T) results obtained for PP(10) including a CPP are rather similar for the DHF + B + QED adjustment ($R_e = 4.861$ Å, $D_e = 0.058$ eV, $\omega_e = 18$ cm^{-1}) and the WB adjustment ($R_e = 4.789$ Å, $D_e = 0.062$ eV and $\omega_e = 19$ cm^{-1}); however, the bond is substantially weaker and longer than in case of PP(42). Finally, for the DHF + B + QED-adjusted PP(2) augmented by a CPP, the strongest and shortest bond is obtained ($R_e = 4.445$ Å, $D_e = 0.092$ eV and $\omega_e = 25$ cm^{-1}). Since the range of the calculated values for different core definitions is larger than observed, e.g., for the Group 12 dimers [7, 9], some further analysis is necessary.

The BSSE-corrected CCSD(T) results obtained with PP(42) show that the inclusion of the 4*f* shell into the correlation treatment leads to a bond length contraction of 0.08 Å and to virtually no change of the binding energy and the vibrational constant. In case of PP(10) the addition of a CPP also leads to a small bond length contraction (0.06 Å) as well as an almost negligible decrease of the binding energy (0.002 eV) and the vibrational constant (1 cm^{-1}). In this case, without CPP, a bond length contraction of about 0.04 Å is due to the correlation of the 5*s* and 5*p* orbitals, whereas the binding energy is slightly decreased by 0.007 eV (10%) and the vibrational constant remains unchanged. The total bond length decrease of 0.10 Å resulting from the correlation of the 4*f*, 5*s* and 5*p* orbitals is overestimated by 50% by the addition of a CPP to PP(2); however, the bond appears to be too short and too strong in this approximation compared to the results obtained with PP(10).

Which of the three sets of molecular constants obtained with the three DHF + B + QED-adjusted PP at the highest computational level, i.e., CCSD(T) including the BSSE correction, should one consider to be the most reliable? On one hand, based on the previously discussed results for the atom and the relatively large BSSE-corrections resulting for the molecule, we suppose that the values for PP(42) are not to be recommended, although from the choice of the core this approach is certainly the most reliable. On the other hand, judged from the quality of the pseudopotential the PP(2) approach is certainly inferior to the PP(10) treatment, although the atomic results are indeed excellent (Table 2). Large-core PPs tend to lead to a too short bond distance, especially when unoccupied orbitals of higher angular quantum number and lower main quantum number (5*d*, 5*f*) than the actual valence orbitals (6*s*, 6*p*) are present. One reason is the cutoff function of the CPP which cannot be adjusted simultaneously to reproduce accurately core-valence correlation effects for these orbitals [38], and, when adjusted to the experimental ionization potentials of Yb$^+$ 6s^1 and 6p^1, gives a much too attractive term for

Yb^+ $5d^1$ and $5f^1$. Another source of error might be the electron-electron interaction which is calculated with nodeless pseudoorbitals of different main quantum numbers [35, 36], i.e., $6s$ and $6p$ with $5d$ and $5f$ (compare, for example, the too large ^3D-^1D splitting in Table 4). Although the results obtained for the PP(2) + CPP and PP(42) are closer to the empirical estimates mentioned in the introduction, we assume that the results for the PP(10) augmented by a CPP are the most reliable, i.e., the ground state spectroscopic constants of Yb_2 should be close to $R_e = 4.861$ Å, $D_e = 0.058$ eV, and $\omega_e = 18\ \mathrm{cm}^{-1}$.

In our previous work we found a nonnegligible stabilizing contribution of spin-orbit interaction to the ground state of Hg_2 [7], i.e., a 0.003 eV (10%) increase of the binding energy and a 0.035 Å contraction of the bond. Using PP(2) + CPP and a $(6s6p4d)/[4s4p2d]$ valence basis set at the averaged coupled-pair functional (ACPF) and linear coupled-cluster (LCC) level for Yb_2, we find only a 0.010 Å bond length contraction and less than 0.001 eV and 0.1 cm^{-1} increase in the binding energy and vibrational constant, respectively [20]. Spin-orbit contributions are therefore negligible for the ground state of Yb_2.

3.3 Covalent bonding contributions in the ground state

Finally, we want to address the question of covalent bonding contributions in the Yb_2 ground state besides the dominating van der Waals interaction. Similar to the previous studies of the Group 12 dimers [7, 8], we assume that the major covalent contributions, if present, could be treated at the CASSCF level with a $6s$ and $6p$ active orbital space and would result in nonzero charge fluctuations $\sqrt{\langle \delta N^2 \rangle}$, when N denotes the occupation number operator for a subset of orbitals localized on one of the two atoms. The charge fluctuations and the square of the local spin $\langle S^2 \rangle$ on one atom are compared to the ones of Be_2 and the Group 11 and 12 dimers in Fig. 3. H_2 and He_2 have also been included as typical cases for a single covalent bond and a pure van der Waals interaction, respectively. Owing to the shorter bond length obtained for PP(2), we observe a larger charge fluctuation and local spin on Yb than in case of PP(10). Despite the longer bond distance the covalent contributions to bonding are slightly stronger in Yb_2 than in the Group 12 dimers, but they are much smaller than in Be_2, where also a significant local spin on one atom is observed. As discussed recently by Stärck and Meyer [5], the interaction between the Hartree-Fock determinant and a configuration obtained by spin-pairing two atomic $2s^12p^1$ triplet valence states leads to a significant stabilization of Be_2. The present analysis supported this picture for Be_2 [8]; however, no significant stabilization of Yb_2 due to spin-pairing two atomic $6s^16p^1$ triplet valence states was observed.

3.4 Excited states

The low-lying excited states of Yb_2 are expected to result from the $^3P + {}^1S$ (spin-orbit averaged experimental term energy 18 869 cm^{-1} [1]) and $^1P + {}^1S$ (25 068 cm^{-1}) asymptotes of the separated atoms. In contrast to the Group 2 and Group 12 homonuclear dimers the situation is much more complicated for Yb_2 owing to the low-lying $5d$ orbitals, i.e., the $^3D + {}^1S$ (24 942 cm^{-1}) and $^1D + {}^1S$ (27 678 cm^{-1}) asymptotes are in the same region of energy (cf. Table 3). For accurate theoretical work this alone would require at least an active space of 4 electrons in 18 orbitals ($6s$, $6p$, $5d$ on each center) to generate the appropriate reference wavefunctions; however, even at this computationally quite demanding level of theory one would not account for the asymptotes arising from $4f^{13}5d^16s^2 + 6s^2$ ($\geq$23 189 cm^{-1}). In order to reduce the computational effort to a reasonable amount we restricted ourselves to the discussion of the $^3P + {}^1S$ asymptote, which is about 0.5 eV lower than the other ones mentioned above. Nevertheless, the results for $^1P + {}^1S$ are included since the only experimentally observed excited state ($^1\Sigma_u^+$) has this dissociation limit.

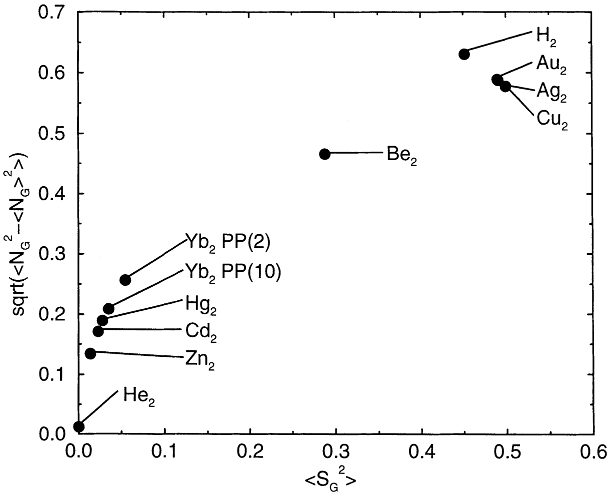

Fig. 3. Charge fluctuations $\sqrt{\langle \delta N^2 \rangle}$ and square of the local spin $\langle S^2 \rangle$ for *ns* and *np* localized valence orbitals on one of the two atoms of M_2 (M = H, He, Be, Cu, Zn, Ag, Cd, Yb, Au, Hg). The limiting value of the charge fluctuation is 0.707 for a covalent single bond, whereas a pure van der Waals interaction corresponds to a value of zero. The value of the square of the local spin on each of the separated atoms is zero for $S = 0$ and 0.866 for $S = 1/2$

The CASSCF reference wavefunction of the scalar-relativistic PP(10) + CPP calculations was built from 4 valence electrons in 8 orbitals ($6s, 6p$). The potential curves obtained at the CASSCF + MRCI level are displayed in Fig. 4. The corresponding curves from PP(2) + CPP MRCI calculations including spin-orbit coupling are given in Fig. 5. The spectroscopic constants are listed in Tables 6 and 7, respectively. It is seen from Fig. 5 and Table 7 that spin-orbit coupling has only a relatively small influence on the potential curves of the low-lying states. The most marked effects besides the splitting of the asymptote $^1S + {}^3P$ are the avoided crossing between the 1_g components of $^3\Sigma_g^+$ and $^1\Pi_g$ near 8.5 bohr and the strong repulsion between the 1_g components of $^3\Pi_g$ and $^1\Pi_g$ near their minima at 6.5 bohr. Since the only experimentally known excited state is $^1\Sigma_u^+$, where spin-orbit contributions are small, we will

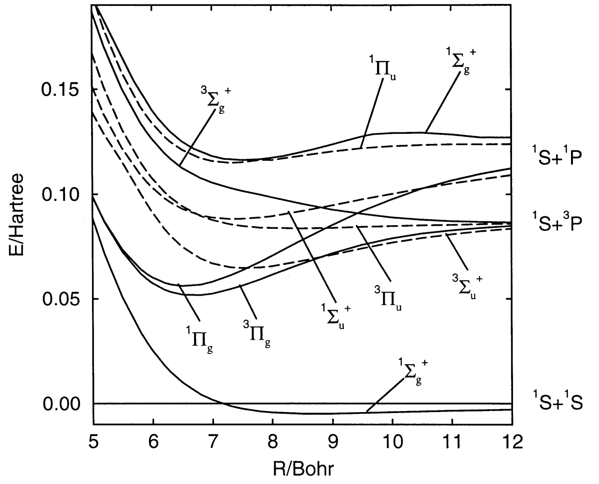

Fig. 4. Low-lying electronic states of Yb_2 from scalar-relativistic PP multireference configuration interaction (MRCI) calculations

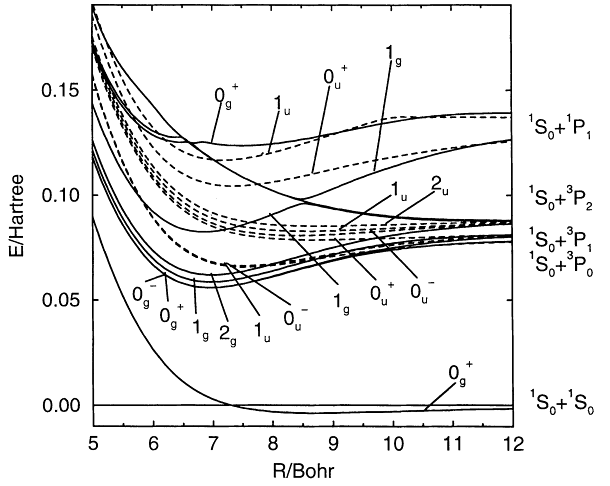

Fig. 5. Low-lying electronic states of Yb_2 from relativistic PP MRCI calculations

Table 6. Bond lengths R_e (Å), vibrational constants ω_e (cm^{-1}), adiabatic term energies T_e (eV), and dissociation energies D_e (eV) (with respect to the given separated atoms limit) for low-lying bound excited states of Yb_2 from scalar-relativistic CASSCF + MRCI calculations with PP(10) + CPP

State	R_e	ω_e	T_e	D_e	Dissociation limit
$^3\Pi_g$	3.535	77	1.54	1.00	$^3P+^1S$
$^1\Pi_g$	3.464	84	1.66	1.84	$^1P+^1S$
$^3\Sigma_u^+$	4.000	58	1.90	0.64	$^3P+^1S$
$^3\Pi_u$	4.415	24	2.41	0.13	$^3P+^1S$
$^1\Sigma_u^+$	3.894	53	2.53	0.97	$^1P+^1S$
$^1\Pi_u$	3.873	56	3.26	0.24	$^1P+^1S$
$^1\Sigma_g^+$	3.984	58	3.30	0.20	$^1P+^1S$

discuss in the remainder only the results of the calculations without spin-orbit coupling, since these are based on a better correlation treatment.

Table 7. Bond lengths R_e (Å), vibrational constants ω_e (cm^{-1}), adiabatic term energies T_e (eV), and dissociation energies D_e (eV) (with respect to the given separated atoms limit) for low-lying bound excited states of Yb_2 from relativistic MRCI calculations with PP(2) + CPP

State	R_e	ω_e	T_e	D_e	Dissociation limit
$0_g^-(^3\Pi_g)$	3.688	65	1.63	0.59	$^3P_0+^1S_0$
$0_g^+(^3\Pi_g)$	3.689	66	1.63	0.67	$^3P_1+^1S_0$
$1_g(^3\Pi_g)$	3.696	65	1.70	0.60	$^3P_1+^1S_0$
$2_g(^3\Pi_g)$	3.703	66	1.79	0.69	$^3P_2+^1S_0$
$0_u^-(^3\Sigma_u^+)$	3.992	54	1.89	0.33	$^3P_0+^1S_0$
$1_u(^3\Sigma_u^+)$	3.978	56	1.91	0.39	$^3P_1+^1S_0$
$0_u^+(^3\Pi_u)$	4.611	26	2.24	0.06	$^3P_1+^1S_0$
$0_u^-(^3\Pi_u)$	4.447	31	2.30	0.18	$^3P_2+^1S_0$
$1_u(^3\Pi_u)$	4.549	27	2.35	0.13	$^3P_2+^1S_0$
$2_u(^3\Pi_u)$	4.633	27	2.42	0.06	$^3P_2+^1S_0$
$1_g(^1\Pi_g, ^3\Sigma_g^+)$	3.618	76	2.34	0.14	$^3P_2+^1S_0$
$1_g(^3\Sigma_g^+, ^1\Pi_g)$	4.484	115	2.78	1.12	$^1P_1+^1S_0$
$0_u^+(^1\Sigma_u^+)$	3.888	59	2.94	0.96	$^1P_1+^1S_0$
$1_u(^1\Pi_u)$	3.794	68	3.28	0.62	$^1P_1+^1S_0$
$0_g^+(^1\Sigma_g^+)$	3.976	51	3.46	0.44	$^1P_1+^1S_0$

Our calculated binding energy of the $^1\Sigma_u^+$ state with respect to the $^1P+^1S$ separated atoms limit of 0.97 eV agrees very well with the experimental value of 0.936 eV given by Suzer and Andrews [12] (Table 6). Similarly, our calculated vibrational constant of 53 cm^{-1} for this state is in line with the vibrational spacing of 48 cm^{-1} observed in the 550 nm transition. However, we derive a vertical (adiabatic) transition energy of 21 451 (20 376) cm^{-1} which is significantly higher than the experimental value of 18 346 cm^{-1} [12]. This result is consistent with the fact that we derive at a bond distance of 60 bohr a ^1S-^1P atomic excitation energy of 27 236 cm^{-1} in comparison to the experimental value of 25 068 cm^{-1} [1]. The main reason for this deficiency of the current calculations is probably the neglect of the 5*d* orbitals in the active space and the importance of intermediate coupling: Migdalek and Baylis [39] found in atomic relativistic MCSCF calculations a lowering of the $^1S_0$-$^1P_1$ energy difference by 3344 cm^{-1} when configurations of the type $5d^16p^1$ were included for $^1P_1$; moreover, the interpretation of the experimental spectrum leads to the conclusion that the ^1P state contributes with only 73% to $^1P_1$ [1]. Unfortunately, CASSCF + MRCI calculations with a correspondingly extended active space $(6s, 6p, 5d)$ are currently not feasible.

4 Conclusions

Relativistic energy-consistent ab initio PPs with three different core definitions were used to study the ground and excited states of the ytterbium dimer Yb_2. The spectroscopic constants of the $^1\Sigma_g^+$ ground state are estimated to be $R_e = 4.861$ Å, $D_e = 0.058$ eV, and $\omega_e = 18\ \mathrm{cm}^{-1}$ on the basis of CCSD(T) calculations using a medium-core pseudopotential with 10 valence electrons and a corresponding core-polarization potential. The bonding is found to be substantially weaker than suggested by previous empirical estimates. Covalent bonding contributions, as measured by the charge fluctuations and the local spin on one atom, are found to be slightly larger than for the Group 12 dimers Zn_2, Cd_2, and Hg_2. The calculated binding energy of the excited $^1\Sigma_u^+$ state with respect to the $^1P + {}^1S$ separated atoms limit of 0.97 eV as well as the vibrational constant of $53\ \mathrm{cm}^{-1}$ agree very well with the experimental values of 0.936 eV and $48\ \mathrm{cm}^{-1}$, respectively. The calculation of excited states is more complicated than for the corresponding Group 2 or Group 12 dimers owing to the possible low-energy excitations into the unoccupied 5*d* shell and from the occupied 4*f* shell in addition to the 6*s* to 6*p* excitations. The addition of a core-polarization potential is found to improve the performance of the previously published medium-core lanthanide PPs [15] for the first and second ionization potential of the atoms, especially for the second half of the series, and is recommended for future investigations. The still quite acceptable performance of the large-core pseudopotential with 2 valence electrons in connection with a CPP allows the investigation of size-dependent properties as well as the analysis of bonding for small Yb clusters [40] in analogy to previous work on Hg clusters [18].

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