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Static Dipole Polarizability of Ytterbium[†]

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The static dipole polarizability of the ground state ytterbium atom is calculated using full and approximate relativistic ab initio methods. Our recommended polarizability of 143 au is consistent with experimental atomic spectral data. The corresponding van der Waals coefficient C_6 of Yb_2, derived using Padé approximants, is 2062 (200) au.

Introduction

The rare earth atom ytterbium (Yb) is an interesting candidate for experimental studies of trapping of ultracold gas,[1] photoassociation spectroscopy,[2,3] Bose−Einstein condensation,[4] Fermi degeneracy,[5] and atomic clocks.[6] It has seven isotopes, five bosons, and two fermions. Its ground state (^{1}S) has the configuration [Xe]4f^{14}6s^2. It has low-lying metastable triplet P states and short-lived singlet P states. Its ionization potential is 6.25 eV. The ground state of the ion Yb$^+$ (^{2}S) has the configuration [Xe]4f^{14}6s^1. It also is a potential candidate for precision experiments.[7,8]

At the large internuclear distances R that strongly influence the collisions between two ground state Yb atoms at low temperatures, the interaction is the van der Waals term varying as the inverse sixth power of R. For Yb$^+$ with Yb it is the polarization term $-(1/2)\alpha/R^4$, where α is the dipole polarizability of Yb.

No measurement of α has been reported, but the van der Waals coefficient C_6 was recently derived by Enomoto et al. from precision spectroscopy of ^{174}Yb at 1 μK to be 2300 ± 250 au.[2] An early calculation of α with the Hartree−Fock approximation yielded a value of 266 au,[8] which is undoubtedly an overestimate. The calculation was improved by Porsev, Rakhlina, and Koslov,[9] who used a configuration interaction method to determine the contribution of valence−valence correlation and second-order many-body perturbation theory to account for the core−valence and core−core correlations. The resulting polarizability was 118 au with an uncertainty of 45 au. The large uncertainty stemmed from the evaluation of the matrix element connecting the ground 6s^2 $^1S_0$ state to the 6s6p $^1P_1$ state which makes by far the largest contribution to α, 95% according to Porsev et al.[9] A precise value of the square of the dipole matrix element C_3 has now been obtained from an analysis of the vibrational level structure of the excited $^1\Sigma_u$ state of Yb_2. It is 11.535 au,[3] differing from the calculated value of 12.9[9] by 12%. The polarizability is changed from 118 to 106 au. A similar but more elaborate calculation has been reported by Porsev and Derevianko,[6] who found $C_3 = 11.47$ and $\alpha = 111.3$ au. Because of the reliability of the value of C_3 and its large contribution to α, they claim a precision of 0.5% for α. Using Dirac−Fock density functional theory (DFT), Wang, Pan, and Schwarz obtained 131.6 au,[10] and with a nonrelativistic time-dependent DFT calculation Chu et al.[11] obtained 157.3 au. Two finite field calculations using the relativistic effective core potential approximation were reported by Wang and Dolg[12] and Buchachenko et al.[13] With different pseudopotentials, the values at the coupled cluster level of theory are 145.3 and 154.7 au.

For C_6, Buchachenko et al. used the relativistic effective core potential method and found $C_6 = 2568$ au and suggested that the correct value lies between 2400 and 2800 au.[14] Chu et al. used time-dependent DFT and found $C_6 = 2292$ au,[11] which agrees with the empirical value of 2300 ± 250 au derived from the intensity patterns in the photodissociation spectra of Yb_2 by Enomoto et al.[2]

To attempt to determine more precisely the polarizability α and the van der Waals coefficient C_6, we present in this paper further calculations of the polarizability and the van der Waals coefficient and compare them with previous theoretical and experimental values.

Computational Methods

Atomic optical properties depend largely on the structure of the valence electrons, and for heavy elements, relativistic effects may be important. Previous studies[15−19] showed that the approximate relativistic models, the Douglas−Kroll (DK) transformation[20−22] and the effective core potential (ECP),[23] are able to reproduce satisfactorily the four-component Dirac−Hartree−Fock and second-order many-body Rayleigh−Schrödinger perturbation results, although quantitative agreement with four-component calculations is not always obtained.[16] Therefore, in the present study, we employed both full four-component and approximate relativistic models. The comparisons between the full and approximate relativistic treatments and the examination of the influence of electron correlation will be instructive in the further applications of these methods.

A. Fully Four-Component Relativistic Formalism. A four-component relativistic Dirac−Hartree−Fock (DCHF) calculation was carried out using the standard Dirac−Coulomb Hamiltonian (in atomic units)

$$H_{\mathrm{DC}} = \sum_i [c\vec{\alpha}_i \vec{p}_i + c^2\beta_i + V_{\mathrm{ext}}(i)] + \sum_{i<j} r_{ij}^{-1}$$

where $\vec{\alpha}$ and $\vec{\beta}$ are the Dirac matrices and c is the speed of light. The DCHF equation was solved via a basis set expansion

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in a large uncontracted Gaussian basis set using the integral-direct DIRAC program.[24] A Gaussian nuclear model with the nuclear exponents given by Visscher and Dyall[25] was used. The DC Hamiltonian contains the spin-same-orbit two-particle interaction terms but omits the spin−other-orbit contributions. The absence of spin-other-orbit terms causes only small errors for heavy elements for which the one-electron spin−orbit contributions dominate.

Following the DCHF calculation, electron correlation was introduced at the level of second-order Møller−Plesset perturbation (MP2) theory. Forty-two valence electrons (4s4p4d5s5p4f6s) were correlated. Virtual orbitals with energies above 1000 au were deleted from the virtual active space.

Fægri's dual family even-tempered basis set[26] was used for the large component in all these calculations. The flexibility of the basis set was increased by adding 8g polarization functions. The final basis used in the calculation is 36*s*34*p*27*d*19*f*8*g*, denoted as DCB. Small component (ϕ_S) basis functions are automatically generated from the large components (ϕ_L) via the method of kinetic balance approximation by the following relation:

$$\phi_S = \frac{1}{2mc}\boldsymbol{\sigma}\cdot\vec{p}\phi_L$$

where $\boldsymbol{\sigma}$ is the 2 × 2 Pauli matrix.

Static electric dipole polarizabilities were obtained by using the finite electric field (FF) perturbation method followed by numerical differentiation of the field-dependent energies. The static dipole polarizability α of an atomic state is given by

$$\alpha = \left(\frac{\partial^2 E(\vec{f})}{\partial f_\mu\, \partial f_\mu}\right)_{f=0}$$

where $E(f)$ is the total electronic energy as a function of the electric field f. Field strengths of 0.001, 0.002, and 0.004 au were employed in the calculations. The differences in α are negligible, and the error in the linear fit was less than 0.05 au. We also performed linear response (LR) calculations[27] with the random phase approximation at the DCHF level as implemented in DIRAC.

B. All-Electron Douglas−Kroll Formalism. All-electron (AE) approximate relativistic calculations were carried out with the spin-averaged Douglas−Kroll−Hess (DKH) Hamiltonian.[20,28,29] DKH decouples the large and small components in the four-component Dirac formalism, and scalar relativistic effects are accounted for by modifying the one-electron integrals, which constitute the major contribution to physical observables.[28] Insight on the consequences of neglecting the electronic spin−orbit coupling can be obtained by comparison with full four-component relativistic results.

With the second-order Douglas−Kroll−Hess (DKH2) Hamiltonian and using linear response coupled cluster with singles and doubles (LR-CCSD)[30] theory as implemented in DALTON,[31] we calculated the static dipole polarizability and evaluated the Thomas−Reiche−Kuhn (TRK) sum rule $S(0)$ of oscillator strengths, which states that $S(0)$ should equal the number of electrons of the system. Deviations from the sum rule reflect the incompleteness of the basis set and of the cluster expansion of the wave function. The contributions from core electrons were systematically investigated by correlating 16 to 68 electrons. The transition dipole moment and transition energy to the 6s6p $^1P_1$ state were also examined at the same LR-CCSD level of theory. To check the validity of the finite field approach and to investigate the contribution beyond single and double excitations in the coupled cluster wave function and the higher order approximation to the relativistic effects, finite field calculations at CCSD(T) level of theory were performed with the third-order Douglas−Kroll−Hess (DKH3) Hamiltonian, which has been shown to yield the best approximation to the total exact energy for many-electron systems.[28]

A fully uncontracted relativistic Gaussian basis set (27*s*23*p*15*d*10*f*) developed by Tsuchiya et al.[32] was used. Five g-type polarization functions were added by scaling the last five *f*-type functions with a factor of 4/3. Two *h*-type and one *i*-type functions were added in the same way by scaling the last two *g*-type and one h-type functions with factors of 1.2 and 1.1, respectively. Diffuse functions were added in the even-tempered way with the factor of 2.0. In the later discussion, we designate 27*s*23*p*15*d*10*f*5*g* as DKB0. The point-charge model of the nucleus was employed throughout the AE DKH calculations. MOLPRO 2006.1[33] was used to perform the DKH3 finite field CCSD(T) calculations.

C. Effective Core Potential Approximation. The effective core potential (ECP) method incorporates relativistic effects through the parametrization of the potential generated by the core electron density. The energy-consistent Stuttgart ECP[23] is typically adjusted by means of a multielectron fit to a large number of states of the neutral atom and corresponding ions, with theoretical reference data determined at a level of theory similar to that at which the ECP is subsequently applied. Recent studies[15−17] on atomic and molecular properties using the energy-adjusted ECP have shown that the small-core ECP is capable of yielding results that are not significantly different from AE calculations.

In the present study, we employed two sets of pseudopotentials to replace the 1s−3d core orbitals. One is the quasirelativistic energy-adjusted ECP28MWB,[34] and the other is the fully relativistic energy-adjusted ECP28MDF.[12] As for the valence electrons, a fully uncontracted (14*s*13*p*10*d*8*f*6*g*) set,[35] referred to as ECPB0, was used along with ECP28MWB. A fully uncontracted (12*s*11*p*9*d*8*f*6*g*) set, denoted as ECPB1, was adopted for the ECP28MDF. As before, additional h-type and i-type and diffuse functions were added. The static dipole polarizability, transition dipole moment, and transition energy to the 6s6p $^1P_1$ state of Yb were obtained at the LR-CCSD level of theory.

In all the FF calculations, when the field was turned off the D_{2h} symmetry group was used, and C_{2v} symmetry was used with the field turned on due to the external field presented in the electronic Hamiltonian. Test calculations in the C_{2v} symmetry were performed when the field was turned off, and they produced the same energy as in the D_{2h} symmetry. In all calculations, the energies were converged to 1.0×10^{-10} au.

Results

The computed static dipole polarizabilities at various levels of theory are presented in Tables 1−4. Previous theoretical results are listed in Table 3. Atomic units will be used throughout the following discussion, unless otherwise specified.

A. Basis Set Effect and Electron Correlation. The basis set is an important factor in the determination of accurate polarizabilities.[36] The standard energy-optimized basis sets usually give poor results for the electric properties. Previous calculations[12,13] on the Yb atom have addressed this issue by adding extra tight *p* or *d* diffuse functions. In the current study, we systematically added polarization and diffuse functions until the calculations converged. Tables 1−3 show that the initial basis sets, DKB0, ECPB0, and ECPB1, all yield poor descriptions of the dipole polarizabilities at all levels of theory. The

TABLE 1: Static Dipole Polarizabilities $\alpha(0)$ (in atomic units) of the Ytterbium Atom Calculated Using Finite Field Method and with DKH3 Hamiltonian at Various Levels of Theory

		correlating 42 valence electrons			
	HF	MP2	SCSMP2	CCSD	CCSD(T)
DKB0	27.2	28.5	28.7	28.6	28.6
DKB0 + 1s1p1d1f1g	99.5	83.8	87.9	96.2	94.6
DKB0 + 2s2p2d2f2g	165.2	113.7	123.2	143.5	138.9
DKB0 + 3s3p3d3f3g	178.7	113.2	123.9	149.9	144.3
DKB0 + 4s4p4d4f4g	178.7	112.9	123.7	149.9	144.3
DKB0 + 3s3p3d3f3g + 3h2i	178.7	111.5	122.2	149.0	143.2

		correlating 52 valence electrons			
	HF	MP2	SCSMP2	CCSD	CCSD(T)
DKB0 + 3s3p3d3f3g + 3h2i	178.7	111.4	122.2	149.0	143.1

polarizabilities are smaller than 30 except for that of 95 in Table 3 from ECPB0, but it is still more than 30% smaller than those obtained with the largest basis functions. For both AE and ECP calculations, the polarizabilities converged after adding three or more sets of *spdfg* diffuse functions; the change with additional diffuse functions was less than 1%. Consistent with previous studies,[12] the *h* and higher angular momentum functions gave small usually negative contributions. By adding *h* and *i* functions, the polarizability was reduced by $\sim$1 or less. The converged calculations at the LR-CCSD level of theory using the ECP approach agree closely with calculations[12,13] with the FF method using ECP28MWB and ECP28MDF at the CCSD(T) level. The values converged to 153 for ECP28MWB and 143 for ECP28MDF. Note that the ECP28MWB was adjusted to the reference data from Wood−Boring (WB) scalar-relativistic AE calculations.[34] The ECP28MDF was adjusted to the reference data from fully relativistic multiconfiguration Dirac−Hartree−Fock calculations including a perturbative correction for the Breit interaction and some higher order quantum-electrodynamic effects.[12] With this improvement, the polarizability was reduced from 152.4 to 142.6, which is closer to our AE DKH3 CCSD(T) FF result of 143.1 obtained with the largest basis functions. Clearly, this change is due to the defect in the ECP adjusted from the WB reference.

Electron correlation effects on the dipole polarizability have been studied for alkali-metal and alkaline-earth-metal atoms[19,37−39] to which, with the addition of the fully filled 4f shell, Yb is closely related. It was shown that electron correlation is overestimated at the MBPT2 level of theory for heavy atoms due to the slow convergence of the many-body expansion,[39] which is also the case for Yb. Table 1 shows that MP2 underestimates the dipole polarizability by more than 20%. An improved description of MP2 electron correlation energy by scaling the so-called parallel and antiparallel components (SCSMP2),[40] which is closely related to Feenberg's scaling of the zero-order Hamiltonian and the corresponding perturbation operator,[41] improved the polarizability by about 10% at 122, but it is still more than 10% smaller than the coupled cluster results.

Within the coupled cluster framework, previous studies[19,39] on the alkaline-earth-metal atoms showed that the electron correlation from the triple excitations becomes more important with the increase of atomic nuclear charge. A similar situation is found in the current study. At the AE DKH3 level with the largest basis set and the correlation of 52 valence electrons, the triple excitations decrease the polarizability by 4% from 149.0 to 143.1 as shown in Table 1. Higher excitations would make small additional contributions. The consistent results between LR-CCSD and finite field AE DHK3 CCSD(T) calculations suggest that some cancellation of error has occurred.

The contributions from inner shell electrons were studied by correlating up to 68 electrons in the AE DKH2 LR-CCSD calculations, given in Table 2. Including only 4f6s shells (16 e) in the explicit correlation treatment is clearly not adequate. The calculated polarizability of 156.2 is about 10% higher than the converged value of 143.8 using the same basis function. Convergence is approached by including 34 valence electrons (4d5s5p4f6s). Adding an additional 18 electrons (3d4s4p) increased the polarizability by 0.4. Including further inner shells up to 2s2p (68 e) did not change the dipole polarizability. A similar convergence behavior was observed in the FF DHK3 calculations shown in Table 1. The change from correlating 42 electrons to 52 electrons is only 0.1 at the CCSD(T) level with the largest basis. A similar situation occurred for the ECP calculations, listed in Table 3. The difference in correlating 34 and all 42 valence electrons (4s4p4d5s5p4f6s) with the largest basis set is 0.5. Therefore, in molecular calculations, correlating 34 valence electrons would be sufficient.

The TRK sum rule $S(0)$, however, exhibited slow convergence with respect to the number of correlating electrons in the AE DKH2 LR-CCSD calculations. According to Table 2, $S(0)$ slowly increased to 69.7 from 27.8 with the increase of the number of explicitly correlated electrons from 16 to 68 with the basis DKB0 + 1s4p4d4f4g. The deviation from the exact value of 70 may be due to the lack of higher excitations, as suggested by the basis convergence. The $S(0)$ values in the ECP calculations, listed in Table 3, show rapid convergence, resulting from the replacement of inner electrons by an optimized effective potential. The small change of $S(0)$ with the increase of the basis set implies that the remaining deviation is due to the missing higher excitations in the cluster expansion of the wave function. Since we will use the calculated Cauchy moments to derive the dispersion coefficient C_6, the convergence of these calculations will be critical.

B. Relativistic Effects. Previous work[19,37−39] on the heavy alkali- and alkaline-metal atoms found a significant scalar relativistic effect and a negligible spin−orbit coupling effect on the static polarizability. Our calculations show a similar behavior for the Yb atom. The results from the fully four-component relativistic calculations are presented in Table 4. At the DCHF level, LR and FF calculations produced identical results. The LR-DCHF result of 178.6 is almost the same as the result of 178.7 from the FF DKH3 HF level in Table 1. A similar situation was observed at the MP2 level in correlating 42 valence electrons. The full relativistic value of 109.9 differs by less than 2% from the result of 111.5 evaluated at the FF DKH3 MP2 level of theory. Because of the large computational demand, we did not explore the polarizability at the relativistic CCSD(T) level. However, that similar results were found in the HF and MP2 calculations indicates that relativistic effects are well described by the approximate AE and ECP treatments.

Discussion

The calculated polarizabilities, obtained with the most extensive basis functions in which the oscillator strength sum rule is most nearly equal to the number of correlated electrons together with an average of published values, cluster about 143.

To gain some insights into the accuracy of this prediction, we attempt to analyze the spectral structure of α. The frequency-

TABLE 2: Static Dipole Polarizabilities α(0) (in atomic units) and TRK Sum Rule *S*(0) of the Ytterbium Atom Calculated at All-Electron DKH2 Linear Response CCSD Level of Theory

	α(0)					*S*(0)				
basis function	16 e	34 e	52 e	60 e	68 e	16 e	34 e	52 e	60 e	68 e
DKB0	29.2					38.6				
DKB0 + 1s3p3d3f3g	156.3	143.5	143.8	143.9	143.9	27.9	44.8	60.1	65.4	69.7
DKB0 + 1s4p4d4f4g	156.2	143.3	143.7	143.7	143.8	27.8	44.8	60.0	65.3	69.7
DKB0 + 1s3p3d3f3g + 2h1i					143.1					69.7

TABLE 3: Static Dipole Polarizabilities α(0) (in atomic units) and TRK Sum Rule *S*(0) of the Ytterbium Atom Calculated at the Linear Response CCSD Level of Theory along with Effective Core Potentials ECP28MWB and ECP28MDF

	α(0)		*S*(0)	
basis function	34 e	42 e	34 e	42 e
ECP28MWB				
ECPB0	94.8	94.9	41.5	44.6
ECPB0 + 2s2p2d2f2g	152.8	153.3	39.5	42.6
ECPB0 + 3s3p3d3f3g	152.7	153.3	39.5	42.6
ECPB0 + 3s3p3d3f3g + 6h4i	151.9	152.4	39.4	42.5
ECPB0 + 4s4p4d4f3g + 6h4i	151.9	152.4	39.4	42.5
ECP28MDF				
ECPB1	21.7	21.6	50.9	54.1
ECPB1 + 2s2p2d2f2g	120.3	120.7	39.7	42.3
ECPB1 + 3s3p3d3f3g	139.9	140.4	39.3	42.5
ECPB1 + 4s4p4d4f3g	142.9	143.4	39.3	42.5
ECPB1 + 5s5p5d5f3g	143.0	143.5	39.3	42.5
ECPB1 + 5s5p5d5f3g + 5h4i	142.1	142.6	39.2	42.4
other work	141.7,[a] 145.3,[b] 131.6,[c] 157.3,[d] 113.3,[e] 118,[f] 154.7[g]			

[a] Reference 59. Linear response relativistic density functional theory. [b] Reference 12. Finite field calculations at the CCSD(T) level of theory with relativistic effective core potential ECP28MDF. [c] Reference 10. Dirac−Fock density functional theory with Slater-type basis. [d] Reference 11. Nonrelativistic time-dependent density functional theory. [e] Reference 6. Relativistic valence CI + MBPT and random phase approximation. [f] Reference 9. Relativistic valence CI + MBPT and random phase approximation. [g] Reference 13. Finite field calculations at the CCSD(T) level of theory with relativistic effective core potential ECP28MWB.

TABLE 4: Static Dipole Polarizabilities α(0) (in Atomic Units) of the Ytterbium Atom Calculated with Four-Component Relativistic Theory

theory	method	basis functions	α(0)
DCHF	LR	DCB	178.6
DCHF	FF	DCB	178.6
DCHF-MP2[a]	FF	DCB	109.9

[a] Forty-two valence electrons (4s4p4d5s5p4f6s) were correlated in the MP2 calculations.

dependent polarizability α(*ω*) can be written as the sum of transition oscillator strengths:

$$\alpha(\omega) = \sum_{s} \frac{f_s}{{\omega_s}^2 - \omega^2}$$

where f_s is the oscillator strength of the dipole transition from the ground $^1S_0$ state to the excited P_1 states, the summation includes an integration over the continuum, and ω_s is the transition frequency and *ω* the applied frequency in atomic units. The static polarizability is α(0).

The major contribution to the summation for α comes from the transition $6s^2\ ^1S_0 \rightarrow 6s6p\ ^1P_1$ at a frequency of 25 068 cm^{-1} and a lifetime of 5.464 ± 0.005 ns.[3,42] The corresponding oscillator strength is 1.309. Table 5 compares the oscillator strength with values calculated at the LR-CCSD level of theory with DKH2 AE and ECP28MDF methods. The DKH2 AE method overestimates the oscillator strength, and the polarizabilities obtained from it are suspect. The oscillator strength calculation supports a polarizability from the ECP28MDF method between 140 and 143. The contribution to α of the $6s^2\ ^1S_0 \rightarrow 6s6p\ ^1P_1$ transition is 100.2 ± 0.1.

TABLE 5: $6s^2\ ^1S_0 \rightarrow 6s6p\ ^1P_1$ Transition Energies and Oscillator Strengths Calculated at the LR-CCSD Level of Theory with DKH2 AE and ECP28MDF Approaches

basis functions	electrons[a]	transition energy (cm^{-1})	oscillator strength
All-Electron DKH2 Calculations			
DKB0 + 1s3p3d3f3g	34	26 155	1.68
DKB0 + 1s3p4d4f4g	34	26 088	1.67
DKB0 + 1s3p3d3f3g	68	26 165	1.70
DKB0 + 1s3p4d4f4g	68	26 098	1.69
ECP28MDF Calculations			
ECPB1 + 4s4p4d4f3g	34	25 155	1.31
ECPB1 + 5s5p5d5f3g	34	25 138	1.31
ECPB1 + 5s5p5d5f3g + 5h4i	34	25 321	1.36
ECPB1 + 4s4p4d4f3g	42	25 329	1.41
ECPB1 + 5s5p5d5f3g	42	25 311	1.41
ECPB1 + 5s5p5d5f3g + 5h4i	42	25 465	1.44
experimental data		25 068.2[b]	1.309[c]

[a] Number of explicitly correlated electrons in the calculations. [b] From ref 42. [c] The latest experimental result from ref 3. For others, see ref 42 and references therein.

A lower limit to α can be obtained from experimental oscillator strength data. The contributions from the higher transitions of the $6s^2\ ^1S_0 \rightarrow 6snp\ ^1P_1$ series may be evaluated from the transition frequencies and radiative lifetimes listed by Blagoev and Komarovskii[42] and Jiang et al.,[43] who presented data for $6 \leq n \leq 21$ with the exception of $n = 9$ and 10 which may be interpolated. The total contribution of transitions from $n = 7$ to ∞ is 9.0 ± 0.3. The decrease of f_n is rapid, and extrapolation into the $6s\epsilon p\ ^1P_1$ continuum gives a negligible contribution. The total $6s^2\ ^1S_0 \rightarrow 6snp\ ^1P_1$ oscillator strength is 1.7 ± 0.2.

The lifetime of the spin-forbidden transition $6s^2\ ^1S_0 \rightarrow 6s6p\ ^3P_1$ measured in several experiments lies between 760 and 875 ns,[44−48] and theoretical calculations have yielded values ranging from 810 to 1294 ns.[9,49,50] The most recent experiment by Tojo et al.[51] yields a value of 874 ns. The transition frequency is 555.8 nm and the corresponding oscillator strength is 0.016, which leads to a contribution of 2.4 to the polarizability. Higher frequency transitions of this forbidden series will give a negligible contribution.

The radiative lifetimes of transitions including excitations of 4f shell electrons have been measured for ^1P states with the configuration $4f^{13}5d6s^2$ with a lifetime of 14.3 ± 0.9 ns or 17

TABLE 6: Effective Transition Frequencies (ω_i, in atomic units) and Oscillator Strengths (g_i) Derived Using Padé Approximants[a]

ω_i	0.11454	0.15066	0.18109	0.21972	0.33791	1.32280
g_i	1.313	0.654	0.211	0.064	0.142	8.789

[a] The Cauchy moments were evaluated at the linear response CCSD level of theory with ECP28MDF pseudopotential. Thirty-four valence electrons were correlated in the CCSD calculation, and the valence basis function is ECPB1 + 5s5p5d5f3g.

± 2 ns and with the configuration $4f^{13}5d6s6p$ with a lifetime of 125 ± 12 ns. They radiate at 346.4 and 210.2 nm, respectively. For the transition to $4f^{13}5d6s^2$, the corresponding oscillator strength is 0.35 ± 0.08[42] and the corresponding contribution to α is 20 ± 4. For $4f^{13}5d6s6p$, $f = 0.016 \pm 0.01$[52] and for α 0.34 ± 0.04. A transition at 267.3 nm has been observed by Lange et al.,[53] Blagoev et al.,[45] and Rambow and Schearer,[46] and its lifetime has been estimated to be 57.3 ± 4 ns, 82 ± 6 ns, or 77.4 ± 6 ns. It has been identified as the transition to the $5d^26s\ {}^1P$ state. It has an oscillator strength of 0.056 ± 0.004, 0.039 ± 0.003, or 0.041 ± 0.004. We adopted $f = 0.05$, which yields a contribution to α of 1.7. The oscillator strengths of transitions in which a 4f electron is excited are in general agreement with ab initio calculations of Beck.[54] The sum of contributions of the 4f shell electrons to α is 24 ± 4, and total oscillator strength is 0.5. The total contribution to α of these transitions and the $6s^2\ {}^1S_0 \rightarrow 6snp\ {}^1P_1$ and $6s^2\ {}^1S_0 \rightarrow 6s6p\ {}^3P_1$ transitions is 136.4 ± 4.

There are further contributions from photoionization resonances associated with inner shell transitions. Cross sections have been measured by Griesmann et al. with a limited range of energies.[55] These high-frequency transitions may be sufficient to explain the difference from our recommended polarizability of 143.

To evaluate the C_6 coefficient, we adopted the Padé approximant[56,57] using the Cauchy moments evaluated with the ECP28MDF at LR-CCSD level of theory. Table 6 lists the effective oscillator strengths g_i and transition frequencies ω_i for a six-term representation. They correspond to a polarizability of 143, and the first one closely reproduces the leading oscillator strength and transition frequency. The value of C_6 is 2062. Wang and Dolg[12] used the Slater−Kirkwood approximation. It leads to a C_6 of about 3400. Chu et al. applied time-dependent DFT and found $C_6 = 2292$.[11] For α they obtained 157. If we scale the C_6 by the polarizability ratio, we obtain $C_6 = 2090$ in agreement with our predicted value. In contrast, Buchachenko et al. derived C_6 from the calculation of the long-range interaction in the ${}^1\Sigma_g{}^+$ state of Yb_2 and concluded that C_6 lies between 2400 and 2800.[14] The experimental discrete oscillator strength distribution yields an extreme lower limit of about 1700. It ignores the inner shell and continuum contribution. The C_6 derived from an analysis of the intensity patterns in the photodissociation spectra of Yb_2 by Enomoto et al. is 2300 ± 250.[2] A more recent analysis[58] of measured vibrational levels leads to a value of about 1932 (30). Our theoretical prediction is 2062, to within an uncertainty tentatively estimated at 10%. The estimated uncertainty reflects the empirical lower limit and the larger values obtained in theoretical calculations. The corresponding uncertainty in the static polarizability is 5%.

Conclusion

The dipole polarizability of the ytterbium atom was studied using the full four-component relativistic, and the scalar Douglas−Kroll relativistic and relativistic pseudopotential approximations. Basis set dependence and electron correlation effects were shown to be critical to obtain an accurate polarizability. The comparison between full and approximate relativistic methods indicates that the scalar relativistic effects are dominant, and they can be well described by AE DKH and ECP approximations.

Our calculated results at the coupled cluster level of theory using both the linear response theory and the finite field method converged to a value about 143 au. The accuracy of the calculation was estimated through a comparison with the atomic spectral data, which leads to a lower limit of 136.4 ± 4 au contributed by transitions of $6s^2\ {}^1S_0 \rightarrow 6snp\ {}^1P_1$ and $6s^2\ {}^1S_0 \rightarrow 6s6p\ {}^3P_1$ and from three known 4f shell transitions. The remaining difference can be attributed to the contributions from the inner shells including the continuum.

The comparison of the calculated $6s^2\ {}^1S_0 \rightarrow 6s6p\ {}^1P_1$ transition with experiment suggests that the results from the pseudopotential approximation are reliable. The van der Waals coefficient C_6 of Yb_2 determined by the Cauchy moments from linear response coupled cluster theory with the pseudopotential approximation is 2062 (200) au.

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