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High precision calculation of multipolar dynamic polarizabilities and two- and three-body dispersion coefficients of atomic hydrogen

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Abstract In this paper we investigate a variationally stable procedure for multipolar dynamic polarizabilities calculation as well as the two- and three-body van der Waals coefficients of the hydrogen atom. This approach provides precise, fast convergent values for real and imaginary frequency-dependent 2^L -pole dynamic polarizabilities. Highly accurate two- and three-body van der Waals dispersion coefficients are calculated from dynamic polarizabilities at imaginary photon frequencies. The present approach is also precise for higher interaction orders. The results are compared with previous calculations found in the literature.

1 Introduction

The large variety of applications for the polarizabilities has motivated researches to develop increasingly more precise and efficient calculation methods [1–7]. The main emphasis has been given to analytical and approximate procedures for the determination of static and dynamic electric dipole polarizabilities [3].

Multipolar polarizabilities have also become subject of investigation [8–10], especially for its use in the evaluation of two- and three-body van der Waals dispersion coefficients, obtained from polarizabilities at complex photon frequencies. The dispersion coefficients are related to multipole–multipole interactions among atomic species, appearing in the van der Waals interaction potential of dipole–dipole, dipole–quadrupole, quadrupole–octupole order and so on.

Long distance interactions among atomic species are important for many areas of physics and chemistry. In the last decades, this subject has received increasing attention due to laser trapping investigations and the realization of Bose–Einstein condensation for some elements such as the hydrogen and a few alkali and alkaline-earth atoms [9, 11]. The hydrogen atom has been an important investigation subject, for which there are precise results in the literature. Its importance as a prototypical system is also owed to a whole family of atoms and ions, whose properties are described by one-electron potential models for the electrons in the atomic valence shell. Hydrogen and one-electron ions trapped in nanostructures such as fullerene molecules (C_{60})

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[12, 13], are systems emerging from quantum confinement technology, which may also benefit from stable and efficient calculation procedures for multipolar polarizabilities and van der Waals coefficients.

Considerable calculation efforts are focused on analytical procedures that solve a set of inhomogeneous differential equations by power series expansions or similar methods, which are able to express multipolar polarizabilities in powers of the photon frequency [4–8]. This work makes use of an efficient approach that provides high precision, fast convergent calculation of one electron multipolar dynamic polarizabilities at real and imaginary photon frequencies. The method is based on a variationally stable procedure of Gao–Starace [14–16] that has the advantage of fast convergence with respect to the number of terms of a basis set. Within this approach, contrary to the classic perturbative approximation, the electronic transition energies are obtained only with the knowledge of the ground-state wave function. Moreover, it can be easily generalized for model potential systems [17–20]. Two- and three-body dispersion coefficients (C_n up to $n = 40$ and Z_{L_1, L_2, L_3} up to $L_i = 5$) of the hydrogen atom are presented and compared with the most precise results available in the literature. Contrary to the usual techniques, the variationally stable procedure employed does not suffer from lack of precision for higher interaction orders. In fact, the results have shown increasing convergence and significant figures, which eventually turn the present results into benchmarks for other methods.

In this work, Sect. 2 is dedicated to present the variationally stable approach and the main equations for the dispersion coefficients. Our results are discussed in Sect. 3, followed by the conclusions.

2 Theory

2.1 Variationally stable procedure

The multipolar dynamic polarizabilities are a two-photon ($N = 2$) process expressed as a function of the transition matrix $T_{i \rightarrow i}^{(N=2)}$ (cf. Refs. [14–16]), that is,¹

$$\alpha_L(\omega) = - \left[T_{i \rightarrow i}^{(N=2)}(\omega) + T_{i \rightarrow i}^{(N=2)}(-\omega) \right]. \quad (1)$$

In this expression, the transition matrix elements are defined as

$$T_{i \rightarrow i}^{(N=2)}(\omega) = \left\langle i \left| \hat{d}_L \frac{1}{E_i + \omega - \hat{H}} \hat{d}_L \right| i \right\rangle, \quad (2)$$

where $|i\rangle$ is the initial-state wave function, E_i is the corresponding energy, \hat{H} is the atomic Hamiltonian, ω is the multipolar field frequency and \hat{d}_L is the 2^L -pole operator, expressed by

$$\hat{d}_L = \sqrt{\frac{4\pi}{2L+1}} y_{L0}(\theta, \phi) r^L, \quad (3)$$

in which $y_{L0}(\theta, \phi)$ are the usual spherical harmonics. In the limit $\omega \rightarrow 0$, one has the static multipolar polarizabilities.

In the variational form of Gao–Starace [14–20], Eq. (2) becomes

$$T_{i \rightarrow i}^{(N=2)}(\omega) = 2 \langle i | \hat{d}_L | \lambda \rangle - \langle \lambda | E_i + \omega - \hat{H} | \lambda \rangle, \quad (4)$$

where $|\lambda\rangle$ is an intermediate state defined as

$$|\lambda\rangle = \frac{1}{E_i + \omega - \hat{H}} \hat{d}_L |i\rangle. \quad (5)$$

It is convenient to express this intermediate state as an expansion in terms of Slater type orbitals (STOs) Φ_μ as follows,

$$|\lambda\rangle = \frac{y_{\ell' m'}(\theta, \phi)}{r} \sum_{\mu=1}^M a_\mu \Phi_\mu(r), \quad (6)$$

¹ Atomic units (a.u.) will be used throughout.

where the STOs are explicitly given by,

$$\Phi_\mu(r) = N_\mu r^{\ell'+\mu} e^{-r}, \quad (7)$$

in which N_μ is a normalization factor,

$$N_\mu^2 = \frac{2^{2\mu+2\ell'+3}}{(2\mu+2\ell'+2)!}. \quad (8)$$

In Eq. (6), M is the basis size. In the variationally stable form, i.e., in Eq. (4), the first order errors in the transition matrix due to the determination of intermediate states $|\lambda\rangle$ are canceled out [14, 15], providing additional stability and convergence to the numerical calculations.

For the hydrogen atom, all matrix elements are analytically derived. Thus, if one sets $|i\rangle \equiv |\psi_{n\ell m}\rangle$, with $\psi_{n\ell m} \rightarrow y_{\ell m}(\theta, \phi) R_{n\ell}(r)$, the matrix elements can be expressed as,

$$\langle i | \hat{d}_L | \lambda \rangle = \sum_\mu a_\mu N_\mu D_\mu, \quad (9)$$

with

$$D_\mu = \varepsilon^\ell (n+\ell)! I(\ell m L 0 \ell' m') \times \sum_{k=0}^{n-\ell-1} \frac{(-\varepsilon)^k}{(n-\ell-1-k)!(2\ell+1+k)!k!} \frac{(k+\mu+\beta)!}{(1+\varepsilon)^{k+\mu+\beta+1}}, \quad (10)$$

where $\beta = \ell + L + \ell' + 1$ and $\varepsilon = 2Z/n$. In Eq. (9), the angular integral is given as a function of the 3- j symbols by

$$I(\ell m L 0 \ell' m') = (-1)^m \sqrt{(2\ell+1)(2\ell'+1)} \begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & L & \ell' \\ -m & 0 & m' \end{pmatrix}. \quad (11)$$

The Hamiltonian matrix elements become

$$\langle \lambda | E_i + \omega - \hat{H} | \lambda \rangle = \sum_{\mu, \mu'} a_\mu a_{\mu'} N_\mu N_{\mu'} (A_{\mu\mu'} + B_{\mu\mu'} + C_{\mu\mu'}), \quad (12)$$

where

$$A_{\mu\mu'} = \left(E_i + \omega + \frac{1}{2} \right) \frac{\bar{\mu}!}{2^{\bar{\mu}+1}}, \quad (13)$$

$$B_{\mu\mu'} = (\mu + \ell + 1) \frac{(\bar{\mu} - 1)!}{2^{\bar{\mu}}}, \quad (14)$$

$$C_{\mu\mu'} = \frac{(\mu + 2\ell)(\mu - 1)}{2} \frac{(\bar{\mu} - 2)!}{2^{\bar{\mu}-1}}, \quad (15)$$

and

$$\bar{\mu} = \mu + \mu' + 2\ell. \quad (16)$$

At this point, the coefficients a_μ , in Eqs. (9) and (12), are attained by imposing the variational principle to Eq. (4) with respect to the variations of the coefficients. Therefore, the coefficients are obtained solving the linear equation system

$$\sum_{\mu=1}^M a_\mu N_\mu (A_{\mu\mu'} + B_{\mu\mu'} + C_{\mu\mu'}) = N_{\mu'} D_{\mu'}. \quad (17)$$

The multipolar polarizabilities are further obtained by substituting the coefficients a_μ into Eq. (1).

Table 1 Convergence of dynamic dipole polarizability for selected real photon frequencies with respect to basis size of the first-order perturbative wave function

ω (a.u.)	Basis size, M	$\alpha_1(\omega)$ (a.u.)
0.00	1	4.000 000 000 000 000 000 000 000 000(+0)
	2	4.500 000 000 000 000 000 000 000 000(+0)
0.10	5	4.784 300 342 722 324 171 375 431 626 688(+0)
	10	4.784 300 342 997 543 878 886 124 116 451(+0)
	15	4.784 300 342 997 543 878 886 370 964 401(+0)
	20	4.784 300 342 997 543 878 886 370 964 401(+0)
0.20	10	5.941 674 860 994 533 869 360 260 237 262(+0)
	15	5.941 674 860 994 536 844 346 057 234 793(+0)
	20	5.941 674 860 994 536 844 346 065 187 034(+0)
	25	5.941 674 860 994 536 844 346 065 187 034(+0)
0.30	20	1.056 388 886 715 500 418 065 714 145 587(+1)
	30	1.056 388 886 715 500 418 065 810 983 502(+1)
	40	1.056 388 886 715 500 418 065 810 983 502(+1)
0.40	20	−1.682 264 535 461 978 136 858 198 683 099(+1)
	40	−1.682 264 535 449 368 290 443 700 189 001(+1)
	60	−1.682 264 535 449 368 290 443 700 184 201(+1)
	80	−1.682 264 535 449 368 290 443 700 184 201(+1)
0.45	40	−1.764 693 509 509 963 564 584 740 163 537(+1)
	60	−1.764 693 509 509 922 593 624 005 195 155(+1)
	80	−1.764 693 509 509 922 593 624 002 913 792(+1)
	100	−1.764 693 509 509 922 593 624 002 913 792(+1)

Table 2 Dipole dynamic polarizability $\alpha_1(\omega)$ (a.u.) of the hydrogen atom for selected real photon frequencies

ω (a.u.)	This work	Tang and Chan [3]	Figari and Magnasco [7]
0.000	4.500 000 000 000 000 000 000 000 000(+0)	4.5 (exact)	
0.100	4.784 300 342 997 543 878 886 370 964 400(+0)	4.784 300 342(+0)	4.784 300 343(+0)
0.200	5.941 674 860 994 536 844 346 065 187 034(+0)	5.941 674 860(+0)	5.941 674 861(+0)
0.300	1.056 388 886 715 500 418 065 810 983 502(+1)	1.056 388 886(+1)	1.056 388 886 7(+1)
0.360	4.092 302 283 532 768 331 344 690 828 105(+1)	4.092 302 283(+1)	
0.370	1.151 468 376 111 127 394 699 436 291 973(+2)	1.151 468 376(+2)	
0.380	−1.065 295 795 332 715 467 859 461 841 368(+2)	−1.065 295 795(+2)	
0.390	−3.215 251 467 325 941 405 107 831 594 748(+1)	−3.215 251 467(+1)	
0.400	−1.682 264 535 449 368 290 443 700 184 201(+1)	−1.682 264 535(+1)	
0.410	−9.691 867 337 715 159 495 485 081 574 908(+0)	−9.691 867 337(+0)	
0.420	−4.839 944 009 063 621 807 808 460 221 187(+0)	−4.839 944 009(+0)	
0.430	2.971 257 640 123 292 630 759 458 126 752(−1)	2.971 257 640(−1)	
0.440	1.627 259 373 972 931 674 591 953 377 475(+1)	1.627 259 373(+1)	
0.441	2.228 773 951 409 198 207 025 774 473 480(+1)	2.228 773 951(+1)	
0.442	3.305 929 397 029 205 614 992 646 701 105(+1)	3.305 929 397(+1)	
0.443	5.846 589 434 878 751 173 439 469 175 807(+1)	5.846 589 434(+1)	
0.444	1.972 886 667 397 881 423 311 054 682 477(+2)	1.972 886 667(+2)	
0.445	−1.629 106 899 513 480 212 546 648 873 002(+2)	−1.629 106 899(+2)	
0.446	−5.972 723 290 793 189 358 159 075 511 041(+1)	−5.972 723 290(+1)	
0.447	−3.712 763 757 157 969 386 069 775 174 396(+1)	−3.712 763 757(+1)	
0.448	−2.711 493 992 356 807 654 482 798 922 045(+1)	−2.711 493 992(+1)	
0.449	−2.139 577 167 337 679 119 256 142 744 743(+1)	−2.139 577 167(+1)	
0.450	−1.764 693 509 509 922 593 624 002 913 792(+1)	−1.764 693 509(+1)	

The results were evaluated with 100 STOs basis functions

2.2 Two- and three-body dispersion coefficients

A detailed description of the van der Waals dispersion coefficients may be found elsewhere in Refs. [21–23]. In short, those are the coefficients of the long-range interaction potential between two or three atoms. The van der Waals interatomic potential is an asymptotic expansion in the internuclear distance, where the leading term

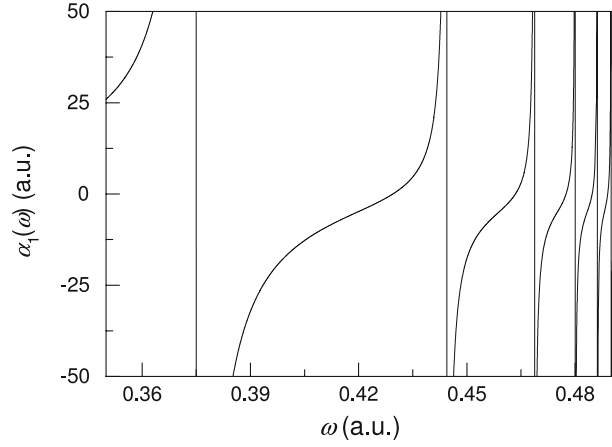


Fig. 1 Resonances of the hydrogen atom for the dipole transitions $1s \rightarrow np$ with $n = 2, \dots, 7$. $\alpha_1(\omega)$ is calculated with 10^{-5} a.u. frequency step, a basis configuration of 100 STOs

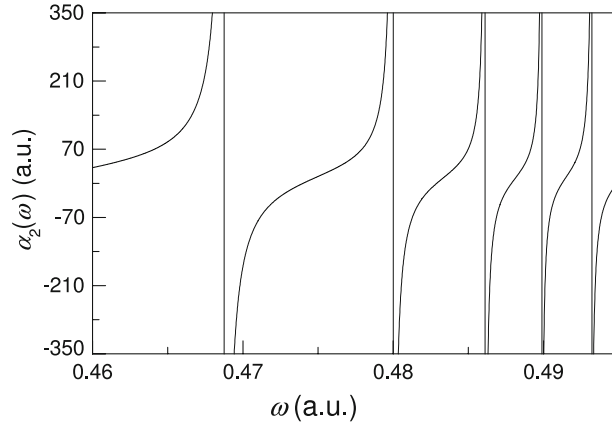


Fig. 2 Dynamic quadrupole polarizability of the hydrogen atom in the ground state. $\alpha_2(\omega)$ is calculated with 10^{-5} a.u. frequency step, a basis configuration of 100 STOs

is of sixth order. The two-body dispersion coefficients for hydrogen are given by [8]

$$C_{2n} = \frac{(2n-2)!}{2\pi} \sum_{L_1=1}^{n-2} \frac{1}{(2L_1)!(2L_2)!} \int_0^\infty \alpha_{L_1}(i\omega) \alpha_{L_2}(i\omega) d\omega, \quad (18)$$

in which L_1 and L_2 stand for two interacting hydrogen atoms, $n = L_1 + L_2 + 1$ and $\alpha_L(i\omega)$ are the multipolar dynamic polarizabilities at imaginary frequencies. For the interaction among three atoms, aside the two-body interaction, there exist higher order three-body dispersion coefficients, which are expressed as [8, 23]

$$Z_{L_1, L_2, L_3} = \frac{1}{\pi} \int_0^\infty \alpha_{L_1}(i\omega) \alpha_{L_2}(i\omega) \alpha_{L_3}(i\omega) d\omega. \quad (19)$$

This equation represents the part of the interaction that does not depend on the geometrical configuration of the three interacting atoms.

3 Results and discussion

In this section, we present and discuss the numerical results of our calculations. Our codes use FORTRAN language with REAL*16 (quadruple) precision in order to minimize numerical error propagation. In order to

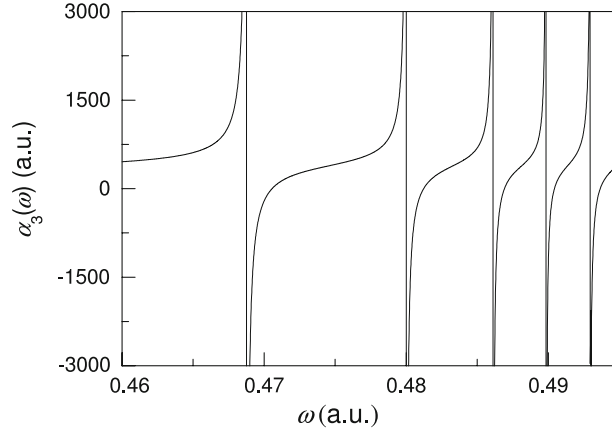


Fig. 3 Dynamic octupole polarizability of the hydrogen atom in the ground state. $\alpha_3(\omega)$ is calculated with 10^{-5} a.u. frequency step, a basis configuration of 100 STOs

Table 3 Convergence of dynamic dipole polarizability for selected imaginary photon frequencies with respect to basis size of the first-order perturbative wave function

ω (a.u.)	Basis size, M	$\alpha_1(i\omega)$ (a.u.)
0.5	10	1.905 388 437 075 874 437 228 121 101 722
	20	1.905 388 437 076 072 909 047 335 163 667
	30	1.905 388 437 076 072 909 047 335 063 272
	40	1.905 388 437 076 072 909 047 335 063 272
50	30	0.00039983640185
	40	0.00039983639553
	50	0.00039983639515
	60	0.00039983639521
500	30	0.00000399998107
	40	0.00000399998066
	50	0.00000399998049
	60	0.00000399998044

assure the reliability of our calculation, some representative results were double-checked using the algebraic manipulation package Maple. As it will be further discussed, a basis set size M is chosen in accordance with a desired precision. All numerical integrations had been carried out using a quadrature method known as Tanh-Sinh [24, 25]. This method has been proved highly accurate [26, 27] due to a quadratic convergence [28]. Thus, our results are only hampered by the round-off errors in the calculation of the multipolar polarizabilities.

The convergence for selected values of ω can be observed in Table 1, which lists the calculated values of the dynamic polarizability as the number M of STO basis functions increases. Convergence of at least 30 significant digits is achieved for ω values ranging from the static limit up to close to the ionization energy. Note that, as ω approaches the excitation energies, a larger basis set is needed to maintain the same precision level. Such behavior is expected, considering the divergences in the transition matrix element (cf. Eq. (2)). The precision loss in calculations at photon frequencies around the excitation energies is amended by increasing the size of the basis set. Such improvement is attained within manageable numerical efforts. The implementations of the algorithms are quite fast, even using desktop computers (we have tested a 1.5 GHz Pentium based machine running FORTRAN with quadruple precision codes and the Maple software). It is interesting to notice that, for a fixed value of the basis size M and using symbolic computation (Maple), it is possible to obtain a closed expression for the polarizability as a function of ω , allowing high precision computation of numerical values even faster. In this work, analytical expressions for the multipolar polarizabilities have been obtained using basis sets with sixty terms ($M = 60$). Those closed form expressions have been used to double-check the results. In Table 2 we present the dipole dynamic polarizability converged values obtained with 100 basis terms. The results show very good precision when compared with other accurate theoretical predictions [3, 7].

Table 4 Dipole dynamic polarizability $\alpha_1(i\omega)$ (a.u.) of the hydrogen atom for selected imaginary photon frequencies

ω (a.u.)	This work	Figari and Magnasco [7]
0.0	4.500 000 000 000 000 000 000 000 000 000	4.500 000 0
0.1	4.250 298 264 792 239 372 519 409 065 945	
0.2	3.653 832 590 032 246 022 371 399 368 849	
0.3	2.978 325 539 101 585 901 105 635 533 968	2.978 325 6
0.4	2.381 754 586 944 033 351 040 109 840 350	
0.5	1.905 388 437 076 072 909 047 335 063 273	
0.75	1.143 219 730 398 506 840 610 715 752 413	
1.0	0.742 440 752 952 082 847 124 047 159 867	
2.0	0.224 473 608 918 335 601 158 613 394 066	0.224 473 68
4.0	0.060 293 160 804 414 708 747 921	0.060 27
6.0	0.027 273 343 987 303 414 009	0.027 24
8.0	0.015 450 652 399 001 753	0.015 42
10.0	0.009 924 092 240 704	0.009 90
12.0	0.006 906 132 628 892	0.006 9
14.0	0.005 080 609 642 850	0.005 07
16.0	0.003 893 317 990 25	0.003 88
18.0	0.003 078 148 897 21	0.003 07
20.0	0.002 494 460 769 51	0.002 49
30.0	0.001 109 936 873 4	
40.0	0.000 624 612 210 1	
50.0	0.000 399 836 395 2	
100.0	0.000 099 988 981	
250.0	0.000 015 999 698	
500.0	0.000 003 999 980	

The results were evaluated with a 60 STO basis size

Table 5 Convergence of selected two-body dispersion coefficients

Coefficient	Basis size, M	Value
C_6	1	6.482 142 857 142 857 14(+00)
	5	6.499 026 596 235 597 39(+00)
	10	6.499 026 705 386 888 53(+00)
	15	6.499 026 705 405 762 29(+00)
	20	6.499 026 705 405 837 99(+00)
	25	6.499 026 705 405 839 26(+00)
	29	6.499 026 705 405 839 30(+00)
C_{18}	1	3.229 205 929 695 528 826 106(+10)
	5	3.234 218 640 285 225 259 669(+10)
	10	3.234 218 715 848 367 819 595(+10)
	15	3.234 218 715 849 377 633 222(+10)
	20	3.234 218 715 849 377 825 796(+10)
	25	3.234 218 715 849 377 826 066(+10)
	27	3.234 218 715 849 377 826 068(+10)
C_{40}	1	1.679 493 010 395 217 257 268 28(+36)
	5	1.680 697 894 955 493 412 142 51(+36)
	10	1.680 697 910 378 362 070 115 08(+36)
	15	1.680 697 910 378 430 221 708 98(+36)
	20	1.680 697 910 378 430 222 688 44(+36)
	23	1.680 697 910 378 430 222 688 49(+36)

The results for $\alpha_1(\omega)$, $\alpha_2(\omega)$ and $\alpha_3(\omega)$ at real photon frequencies are shown in Figs. 1, 2 and 3, where the vertical lines (asymptote) represent the excitation energies. The exact determination of transition energies from dynamic polarizabilities is of special interest since the only information needed from the system is the ground-state wave function [19]. The precision in the computation of such transitions is also related to the discretization of ω within the numerical calculations. In our calculations, we have discretized the photon frequencies with a fine step size of 10^{-5} a.u. to assure an accurate description at photon energies in the vicinity of the resonances. It is worth mentioning that root finding algorithms may be used to calculate ω when the polarizability is obtained using a fixed value M of STO basis functions, which allows an exact solution of the variational procedure, solved by algebraic manipulation programs.

Table 6 Two-body dispersion coefficients of atomic hydrogen with $L_i^{\max} = 18$

Coefficient	This work	Other calculations
C_6	6.499 026 705 405 839 304 858 5(+00)	6.499 026 705 405 9(+00) ^a 6.499 026 705 405 839 313 128 194 6(+00) ^b 6.499 026 705 405 840 5(+00) ^c
C_8	1.243 990 835 836 223 436 095 9(+02)	1.243 990 835 836 2(+02) ^a 1.243 990 835 836 2(+02) ^b 1.243 990 835 836 223 5(+02) ^c
C_{10}	3.285 828 414 967 421 697 803 2(+03)	3.285 828 414 967 4(+03) ^a 3.285 828 414 967 4(+03) ^b 3.285 828 414 967 421 7(+03) ^c
C_{12}	1.214 860 208 968 610 991 158 8(+05)	1.214 860 208 968 6(+05) ^a 1.214 860 208 968 6(+05) ^b 1.214 860 208 968 611 0(+05) ^c
C_{14}	6.060 772 689 192 124 908 987 1(+06)	6.060 772 689 191 7(+06) ^a 6.060 772 689 192 1(+06) ^b 6.060 772 689 192 124 9(+06) ^c
C_{16}	3.937 506 393 999 179 696 399 3(+08)	3.937 506 393 998 5(+08) ^a 3.937 506 393 999 2(+08) ^b 3.937 506 393 999 179 7(+08) ^c
C_{18}	3.234 218 715 849 377 826 068 3(+10)	3.234 218 716(+10) ^a 3.234 218 715 849 377 8(+10) ^c
C_{20}	3.278 573 440 416 621 670 609 6(+12)	3.278 573 440(+12) ^a 3.278 573 440 416 621 7(+12) ^c
C_{22}	4.021 082 847 685 359 832 651 6(+14)	4.021 082 848(+14) ^a 4.021 082 847 685 359 8(+14) ^c
C_{24}	5.868 996 334 559 957 342 896 1(+16)	5.868 996 335(+16) ^a 5.868 996 334 559 957 3(+16) ^c
C_{26}	1.005 294 993 336 294 160 242 0(+19)	1.005 294 993(+19) ^a 1.005 294 993 336 294 2(+19) ^c
C_{28}	1.996 944 940 887 575 822 677 4(+21)	1.996 944 941(+21) ^a 1.996 994 940 887 575 8(+21) ^c
C_{30}	4.553 288 866 634 735 129 437 4(+23)	4.553 288 866(+23) ^a 4.553 288 866 634 735 1(+23) ^c
C_{32}	1.181 107 088 344 316 248 277 7(+26)	1.181 107 088(+26) ^a
C_{34}	3.458 184 040 146 051 464 675 3(+28)	
C_{36}	1.134 965 083 356 195 352 381 0(+31)	
C_{38}	4.149 550 460 735 782 445 306 3(+33)	
C_{40}	1.680 697 910 378 430 222 688 5(+36)	

Results are compared with the most precise previous calculations

^a Mitroy and Bromley [10]

^b Yan and Dalgarno [23]

^c Thakkar [5]

In calculating the multipolar polarizabilities at imaginary photon frequencies, one just substitutes ω by $i\omega$ where required. Since the polarizabilities are obtained using the transition matrix calculated at $\pm i\omega$ (cf. Eqs. (1) and (2)), the final result is a real quantity.

Similarly to Tables 1, 3 shows the convergence of the dipole dynamic polarizability calculated at imaginary photon frequencies, up to $M = 60$ STO basis functions. In Table 4, an extensive range of converged results is listed for the dipole polarizability at imaginary frequencies. Also shown are the results from the literature [7]. Our values converged with more significant digits than those from Ref. [7], especially for larger values of ω , for which there is an increasing difficulty in the calculations. As shown in this table, larger values of ω require larger basis sets, although, in practice, the calculations do not require intensive numerical efforts for the range presented. The accuracy can be improved by increasing the basis set size [29].

Out of many physical quantities calculated from dynamic polarizabilities are the van der Waals dispersion coefficients. In Table 5 is shown the convergence of few selected two-body van der Waals dispersion coefficients of H as the number M of basis functions in the expansions is systematically increased. It is noteworthy that, for higher interaction orders, the number of significant figures actually increases. Table 6 provides a comparison between our converged results for the two-body van der Waals coefficients (C_n) and accurate theoretical calculations from other authors [5, 10, 23]. Except for the C_6 and C_8 coefficients, our converged results have more significant digits than those from the literature. Hence, it is suggested that this approach can be used as benchmark for other calculation methods.

Table 7 Convergence of selected three-body dispersion coefficients with respect to the intermediate basis set size

L_1, L_2, L_3	Basis size, M	Z_{L_1, L_2, L_3}
1, 1, 1	1	7.196 747 448 979 591 837(+00)
	2	7.214 361 104 176 351 417(+00)
	3	7.214 185 759 003 997 581(+00)
	4	7.214 156 808 713 584 871(+00)
	5	7.214 154 956 481 653 440(+00)
	10	7.214 154 836 880 446 809(+00)
	15	7.214 154 836 878 660 941(+00)
	20	7.214 154 836 878 659 455(+00)
	25	7.214 154 836 878 659 446(+00)
	29	7.214 154 836 878 659 446(+00)
2, 2, 3	1	3.274 300 359 061 093 980 1(+03)
	2	3.282 123 137 201 174 508 9(+03)
	3	3.282 130 617 476 201 472 6(+03)
	4	3.282 118 478 278 485 810 0(+03)
	5	3.282 117 307 859 825 447 3(+03)
	10	3.282 117 205 607 264 693 3(+03)
	15	3.282 117 205 606 176 843 5(+03)
	20	3.282 117 205 606 176 559 9(+03)
	25	3.282 117 205 606 176 559 2(+03)
	28	3.282 117 205 606 176 559 2(+03)
5, 5, 5	1	2.273 926 101 731 219 067 126(+13)
	2	2.276 878 586 552 011 942 469(+13)
	3	2.276 895 585 121 866 561 237(+13)
	4	2.276 893 048 760 435 761 904(+13)
	5	2.276 892 790 102 947 842 740(+13)
	10	2.276 892 768 106 067 387 365(+13)
	15	2.276 892 768 105 969 688 125(+13)
	20	2.276 892 768 105 969 684 187(+13)
	25	2.276 892 768 105 969 684 185(+13)
	26	2.276 892 768 105 969 684 185(+13)

The three-body coefficients (Z_{L_1, L_2, L_3}) were also obtained. The convergence of the computation is shown in Table 7. Analogously to the results for the two-body coefficients, there is an increasing accuracy for higher interaction orders. The converged results are listed in Table 8 and compared with the most precise results found in the literature [5].

As a last remark, further improvements in the numerical calculations can be accomplished [29] by using extended arithmetics, employing arbitrary precision subroutines [30,31]. A key point is that the achieved accuracy, permitted by our computational constraints (finite arithmetics), is sufficient in obtaining competitive predictions for both the dynamic polarizabilities and the van der Waals coefficients. Furthermore, in most cases, the present accuracy surpasses the best available calculations.

4 Conclusions

Highly accurate two- and three-body, van der Waals dispersion coefficients C_n (n up to 40) and Z_{L_1, L_2, L_3} (L_i up to 5), were calculated for the hydrogen atom. For this purpose, the atomic multipole, frequency-dependent polarizabilities (L_i up to 18) were obtained using the variationally stable approach of Gao–Starace. The calculation showed very good convergence and, for higher interaction orders, exhibited significant improvements over existing calculations. Thus, the present data may be used as a benchmark for other theoretical methodologies and/or computational procedures. The calculation shown in this work can be extended to other diatomic and triatomic molecules, provided the dynamic multipole polarizabilities are calculated for such systems. The calculation of polarizabilities of other atomic and molecular species, using the Gao–Starace method, has been presented in the literature for real photon frequencies [16–20], which opens perspectives for calculation at imaginary frequencies in order to achieve the van der Waals dispersion coefficients.

Table 8 Three-body dispersion coefficients Z_{L_1, L_2, L_3} of the hydrogen atom with $L_i^{\max} = 5$

L_1, L_2, L_3	This work	Thakkar [5]
1, 1, 1	7.214 154 836 878 659 446 047(+00)	7.214 154 836 878 659 4(+00)
1, 1, 2	2.623 572 212 844 463 429 580(+01)	2.623 572 212 844 463 4(+01)
1, 1, 3	2.373 443 263 079 563 275 306(+02)	2.373 443 263 079 563 2(+02)
1, 1, 4	3.914 797 915 212 531 233 549(+03)	3.914 797 915 212 531 2(+03)
1, 1, 5	1.016 264 085 751 231 556 149(+05)	1.016 264 085 751 231 5(+05)
1, 2, 2	9.645 706 352 308 603 614 855(+01)	9.645 706 352 308 603 6(+01)
1, 2, 3	8.766 748 094 499 075 941 380(+02)	8.766 748 094 499 075 9(+02)
1, 2, 4	1.449 816 353 248 769 904 764(+04)	1.449 816 353 248 769 9(+04)
1, 2, 5	3.770 097 793 839 280 994 468(+05)	3.770 097 793 839 281 0(+05)
1, 3, 3	7.983 980 420 693 903 024 519(+03)	7.983 980 420 693 903 0(+03)
1, 3, 4	1.321 888 252 429 620 460 132(+05)	1.321 888 252 429 620 5(+05)
1, 3, 5	3.440 020 106 065 453 322 306(+06)	3.440 020 106 065 453 3(+06)
1, 4, 4	2.190 066 438 824 243 019 707(+06)	2.190 066 438 824 243 0(+06)
1, 4, 5	5.701 791 079 045 648 161 996(+07)	5.701 791 079 045 648 2(+07)
1, 5, 5	1.484 869 244 935 850 133 777(+09)	1.484 869 244 935 850 1(+09)
2, 2, 2	3.591 579 298 442 920 157 864(+02)	3.591 579 298 442 920 2(+02)
2, 2, 3	3.282 117 205 606 176 559 215(+03)	3.282 117 205 606 176 6(+03)
2, 2, 4	5.444 675 443 581 831 412 036(+04)	5.444 675 443 581 831 4(+04)
2, 2, 5	1.418 681 464 756 161 954 778(+06)	1.418 681 464 756 162 0(+06)
2, 3, 3	3.006 448 973 144 702 567 288(+04)	3.006 448 973 144 702 6(+04)
2, 3, 4	4.994 156 252 686 642 743 643(+05)	4.994 156 252 686 642 7(+05)
2, 3, 5	1.302 448 320 872 365 967 522(+07)	1.302 448 320 872 365 9(+07)
2, 4, 4	8.302 513 672 007 483 906 595(+06)	8.302 513 672 007 483 9(+06)
2, 4, 5	2.166 356 287 661 398 259 771(+08)	2.166 356 287 661 398 3(+08)
2, 5, 5	5.654 517 127 290 032 691 877(+09)	5.654 517 127 290 032 7(+09)
3, 3, 3	2.760 922 957 772 705 614 623(+05)	2.760 922 957 772 705 6(+05)
3, 3, 4	4.592 966 812 146 163 573 521(+06)	4.592 966 812 146 163 6(+06)
3, 3, 5	1.198 957 248 225 472 655 308(+08)	1.198 957 248 225 472 7(+08)
3, 4, 4	7.647 067 550 033 841 578 742(+07)	7.647 067 550 033 841 6(+07)
3, 4, 5	1.997 296 911 169 497 589 184(+09)	1.997 296 911 169 497 6(+09)
3, 5, 5	5.218 501 618 198 915 493 769(+10)	5.218 501 618 198 915 5(+10)
4, 4, 4	1.274 303 087 606 323 576 162(+09)	1.274 303 087 606 323 6(+09)
4, 4, 5	3.330 172 209 781 951 888 168(+10)	3.330 172 209 781 951 9(+10)
4, 5, 5	8.706 067 248 106 873 282 478(+11)	
5, 5, 5	2.276 892 768 105 969 684 185(+13)	

Results are compared with the most precise previous calculations

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