

Three-body dispersion coefficients for excited hydrogen atoms

Shi-Zhong Huang* and Qiu-Feng Sun

Department of Physics, Anhui Normal University, Wuhu 241000, China

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Abstract. The three-body van der Waals dispersion coefficients $Z(l_1 l_2 l_3)$ (up to $l_i = 5$) for the H(1s)-H(1s)-H(1s) and H(2s)-H(2s)-H(2s) systems are calculated by virtue of the dynamic polarizabilities at imaginary photon frequencies. The expression for the 2^l -pole dynamic polarizabilities of atomic hydrogen is derived by application of the integration properties of the one-dimensional radial Coulomb Green's function. The results for the H(1s)-H(1s)-H(1s) system are consistent with previous calculation in the literature, while the results for the H(2s)-H(2s)-H(2s) systems are reported for the first time, and they are the main contribution of this work.

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1 Introduction

In the last decades, the van der Waals interaction between atoms 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 [1, 2]. The hydrogen atom has been an important investigation subject, because it is 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}) [3, 4], are systems emerging from quantum confinement technology, which may also benefit from efficient calculation procedures for van der Waals dispersion coefficients.

The van der Waals dispersion coefficients are directly related to dynamic polarizabilities [5], which describes the distortion of electronic and charge distribution of an atom in the presence of an oscillating electric field. The problem of evaluating the dynamic polarizabilities and dispersion coefficients for atomic hydrogen have been widely studied by different

*Corresponding author. *Email address:* huangsz@mail.ahnu.edu.cn (S. Z. Huang)

methods in various forms [6–15]. The most recent studies have been carried out by Masili and Gentil [16] and Groote *et al.* [17]. They make use of an efficient approach that provides high precision calculation of one electron multipolar dynamic polarizabilities and two- and three-body dispersion coefficients. The method is based on a variationally stable procedure of Gao-Starace [18–20] that has the advantage of fast convergence with respect to the number of terms of a basis set. However, this approach is limited to the ground-state and is not valid for the excited states.

It is known that the dispersion coefficients for excited alkali-metal atoms have been calculated [21]. To our knowledge, however, the dispersion coefficients for excited hydrogen atoms have not been evaluated. The purpose of this paper is to calculate the three-body van der Waals dispersion coefficients for H(1s)-H(1s)-H(1s) and H(2s)-H(2s)-H(2s) systems by virtue of the dynamic polarizabilities at imaginary photon frequencies [5]. The expression for the multipolar polarizabilities of atomic hydrogen is derived analytically by application of the integration properties of the one-dimensional radial Coulomb Green's function [22]. The results for the H(1s)-H(1s)-H(1s) system are compared with that previously calculated by Cebim, Masili and Groote [17], while the results for the H(2s)-H(2s)-H(2s) system are reported for the first time, and they are the main contribution of this work. It is found that the interaction energy is very much stronger for the H(2s)-H(2s)-H(2s) system. This large van der Waals interaction energy and the long lifetime of the metastable 2s hydrogen make this work very interesting and might have experimental implications in further quantum confinement investigation. On the other hand, the present approach is also valid for higher interaction orders and can be easily generalized for other excited states and for model potential systems [23–27].

2 Theory

2.1 Dispersion coefficient

A detail description of the van der Waals dispersion coefficients may be found elsewhere [5]. In short, those are the coefficients of the long-range interaction potential of dipole-dipole, dipole-quadrupole, quadrupole-octupole order and so on, between two atoms. The van der Waals interatomic potential is an asymptotic expansion in the internuclear distance R and expressed as

$$V(R) = - \sum_{k=3} \frac{C_{2k}}{R^{2k}}, \quad (1)$$

where C_{2k} are the two-body dispersion coefficients. For two hydrogen atoms, which are in state $\psi_{n_a 00}$ and $\psi_{n_b 00}$ respectively, the two-body dispersion coefficients are given by [28]

$$C_{2k}^{(n_a s, n_b s)} = \frac{(2k-2)!}{2\pi} \sum_{l_a=1}^{k-2} \frac{1}{(2l_a)! (2l_b)!} \int_0^\infty \alpha_{l_a}^{n_a 00}(i\omega) \alpha_{l_b}^{n_b 00}(i\omega) d\omega,$$

in which l_b is limited by $l_a + l_b + 1 = k$ and $\alpha_{l_a}^{n_a 00}(i\omega)$ is the 2^{l_a} -dipole polarizability of the hydrogen atom in the $\psi_{n_a 00}$ state at imaginary frequency.

For the interaction among three atoms, in addition to the interaction potential of each pair of atoms, there exists a higher-order term given by [5]

$$V(R_{12}, R_{13}, R_{23}) = - \sum_{l_1 l_2 l_3} \frac{Z(l_1 l_2 l_3)}{(R_{12} R_{13} R_{23})^3}, \quad (2)$$

where R_{ij} is the separation between each pair of atoms, and $Z(l_1 l_2 l_3)$ are the three-body dispersion coefficients. For three hydrogen atoms, which are in state $\psi_{n_1 0 0}$, $\psi_{n_2 0 0}$ and $\psi_{n_3 0 0}$ respectively, $Z(l_1 l_2 l_3)$ can be expressed as [16, 17, 28, 29]

$$Z(l_1 l_2 l_3) = \frac{1}{\pi} \int_0^\infty \alpha_{l_1}^{n_1 0 0}(i\omega) \alpha_{l_2}^{n_2 0 0}(i\omega) \alpha_{l_3}^{n_3 0 0}(i\omega) d\omega. \quad (3)$$

2.2 Multipole polarizability

The basic expression of the 2^l -pole dynamic polarizability of atomic hydrogen in an arbitrary state $\psi_{n_i l_i m_i}$ is [5]

$$\alpha_l^{n_i l_i m_i}(\omega) = \frac{8\pi}{(2l+1)} \mathbf{S}_{\substack{n' l' m' \\ (n' \neq n_i)}} \frac{(E_{n'} - E_{n_i}) \left| \left\langle \psi_{n_i l_i m_i} \left| r^l Y_0^{(l)}(\hat{r}) \right| \psi_{n' l' m'} \right\rangle \right|^2}{(E_{n'} - E_{n_i})^2 - \omega^2}, \quad (4)$$

where ω is the angular frequency of the electromagnetic field and E_{n_i} is the eigenvalue of atomic hydrogen in state $\psi_{n_i l_i m_i} = R_{n_i l_i}(r) Y_{l_i m_i}(\theta, \varphi)$. \mathbf{S} represents a sum (excluding $n' = n_i$) over all the negative energy (discrete spectrum) wavefunctions and an integral over all positive energy (continuous spectrum) wavefunctions. Eq. (4) can be rewritten as

$$\alpha_l^{n_i l_i m_i}(\omega) = \beta_l^{n_i l_i m_i}(\omega) + \beta_l^{n_i l_i m_i}(-\omega), \quad (5)$$

where

$$\beta_l^{n_i l_i m_i}(\omega) = \frac{4\pi}{2l+1} \mathbf{S}_{\substack{n' l' m' \\ (n' \neq n_i)}} \frac{\left| \left\langle \psi_{n_i l_i m_i} \left| r^l Y_0^{(l)}(\hat{r}) \right| \psi_{n' l' m'} \right\rangle \right|^2}{(E_{n'} - E_{n_i})^2 - \omega^2}. \quad (6)$$

After calculating the angular part in Eq. (6) by utilizing the irreducible tensor theory, we have

$$\beta_l^{n_i l_i m_i}(\omega) = \sum_{l'=|l-l_i|}^{l+l_i} (2l_i+1)(2l'+1) \begin{pmatrix} l_i & l & l' \\ -m_i & 0 & m_i \end{pmatrix}^2 \begin{pmatrix} l_i & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \times \int_0^\infty \int_0^\infty dr dr' R_{n_i l_i}(r) R_{n_i l_i}(r') (rr')^{l+2} \mathbf{S}_{n' \neq n_i} \frac{R_{n' l'}(r) R_{n' l'}(r')}{(E_{n'} - E_{n_i}) - \omega}, \quad (7)$$

where $\begin{pmatrix} l_i & l & l' \\ -m_i & 0 & m_i \end{pmatrix}$ refers to the 3- j symbol. In order to use the integration properties of the one-dimensional radial Coulomb Green's function, we add and subtract a term with $n'=n_i$ inside $S_{n' \neq n_i}$ in Eq. (7). Hence

$$\begin{aligned} \beta_l^{n_i l_i m_i}(\omega) = & \sum_{l'=|l-l_i|}^{l+l_i} (2l_i+1)(2l'+1) \begin{pmatrix} l_i & l & l' \\ -m_i & 0 & m_i \end{pmatrix}^2 \begin{pmatrix} l_i & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \\ & \times \int_0^\infty \int_0^\infty dr dr' R_{n_i l_i}(r) R_{n_i l_i}(r') (rr')^{l+2} S_{n'} \frac{R_{n' l'}(r) R_{n' l'}(r')}{E_{n'} - (E_{n_i} + \omega)} \\ & + \frac{1}{\omega} \sum_{l'=|l-l_i|}^{l+l_i} (2l_i+1)(2l'+1) \begin{pmatrix} l_i & l & l' \\ -m_i & 0 & m_i \end{pmatrix}^2 \\ & \times \begin{pmatrix} l_i & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \left(\int_0^\infty dr R_{n_i l_i}(r) R_{n_i l'}(r) r^{l+2} \right)^2. \end{aligned} \quad (8)$$

The second term in Eq. (8) is cancelled out with the similar term in $\beta_l^{n_i l_i m_i}(-\omega)$ in Eq. (5), thus the 2^l -pole dynamic polarizability of atomic hydrogen in state $\psi_{n_i l_i m_i}$ can be simplified as

$$\alpha_l^{n_i l_i m_i}(\omega) = \gamma_l^{n_i l_i m_i}(\omega) + \gamma_l^{n_i l_i m_i}(-\omega), \quad (9)$$

with

$$\begin{aligned} \gamma_l^{n_i l_i m_i}(\omega) = & \sum_{l'=|l-l_i|}^{l+l_i} (2l_i+1)(2l'+1) \begin{pmatrix} l_i & l & l' \\ -m_i & 0 & m_i \end{pmatrix}^2 \begin{pmatrix} l_i & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \\ & \times \int_0^\infty \int_0^\infty dr dr' R_{n_i l_i}(r) R_{n_i l_i}(r') (rr')^{l+2} g_{l'}(r, r', E_{n_i} + \omega). \end{aligned} \quad (10)$$

where $g_{l'}(r, r', E_{n_i} + \omega)$ is the radial Coulomb Green's function defined by

$$g_{l'}(r, r'; \xi) = S_{n'} \frac{R_{n' l'}(r) R_{n' l'}(r')}{E_{n'} - \xi}. \quad (11)$$

By using the well-known expression for the radial functions

$$R_{n_i l_i}(r) = \sum_{k=0}^{n_i - l_i - 1} \left((-1)^k \frac{((n_i - l_i - 1)! (n_i + l_i)!)^{1/2} (2/n_i)^{k+l_i+1}}{n_i (n_i - l_i - 1 - k)! (2l_i + 1 + k)! k!} \right) r^{l_i+k} e^{-r/n_i}, \quad (12)$$

it is not difficult to find that the integral in Eq. (10) can be rewritten as

$$\begin{aligned}
 & \int_0^\infty \int_0^\infty dr dr' R_{n_i l_i}(r) R_{n_i l_i}(r') (rr')^{l+2} g_{l'}(r, r', E_{n_i} + \omega) \\
 = & 2 \sum_{k=0}^{n_i - l_i - 1} \sum_{k'=0}^{n_i - l_i - 1} \left(\frac{((n_i - l_i - 1)! (n_i + l_i)!)^{1/2} (2/n_i)^{k+l_i+1}}{n_i (n_i - l_i - 1 - k')! (2l_i + 1 + k)! k!} \right) \\
 & \times \left(\frac{((n_i - l_i - 1)! (n_i + l_i)!)^{1/2} (2/n_i)^{k'+l_i+1}}{n_i (n_i - l_i - 1 - k')! (2l_i + 1 + k')! k'!} \right) (\nu)^{2(l_i + l' + 1) + k + k'} \\
 & \times \left(\left(\frac{\partial^{l_i + l' + 1 + k}}{\partial \mu^{l_i + l' + 1 + k}} \left(\frac{\partial^{l_i + l' + 1 + k} I_l(\mu, \mu'; \nu)}{\partial (\mu')^{l_i + l' + 1 + k'}} \right) \right) \right) \Big|_{\mu = \mu' = \nu / n_i} \quad (13)
 \end{aligned}$$

where

$$I_l(\mu, \mu'; \nu) \equiv \frac{1}{2} \int_0^\infty \int_0^\infty dr dr' (rr')^{l+1} e^{-(\mu r + \mu' r')/\nu} g_l(r, r', E_{n_i} + \omega). \quad (14)$$

It is found by Rapoport [22] that

$$\begin{aligned}
 I_l(\mu, \mu'; \rho) & \equiv \frac{1}{2} \int_0^\infty \int_0^\infty dr dr' (rr')^{l+1} e^{-(\mu r + \mu' r')/\rho} g_l(r, r'; \xi) \\
 & = \frac{2^{2l+1} (2l+1)! \rho^{2l+3}}{(l+1-\rho) (\mu+1) (\mu'+1)^{2l+2}} {}_2F_1 \left(2l+2, l+1-\rho, l+2-\rho; \frac{(\mu-1)(\mu'-1)}{(\mu+1)(\mu'+1)} \right) \quad (15)
 \end{aligned}$$

with

$$\rho = \sqrt{-1/2\xi}, \quad (16)$$

where ${}_2F_1$ is the usual hypergeometric function. Thus the integral in Eq. (13), namely $I_l(\mu, \mu'; \nu)$, can be worked out as

$$\begin{aligned}
 I_l(\mu, \mu'; \nu) & = \frac{2^{2l+1} (2l+1)! \nu^{2l+3}}{(l+1-\nu) (\mu+1) (\mu'+1)^{2l+2}} \\
 & \quad \times {}_2F_1 \left(2l+2, l+1-\nu, l+2-\nu; \frac{(\nu-1)(\nu'-1)}{(\nu+1)(\nu'+1)} \right) \quad (17)
 \end{aligned}$$

with

$$\nu = \sqrt{-1/2(E_{n_i} + \omega)}. \quad (18)$$

Using Eqs. (10), (13), (17) and (18), and keeping in mind that

$$\frac{\partial}{\partial z} {}_2F_1(\alpha, \beta, \gamma; z) = \frac{\alpha\beta}{\gamma} {}_2F_1(\alpha+1, \beta+1, \gamma+1; z),$$

after some length and careful arithmetic works, we have found that the dynamic 2^l -multipole polarizability of atomic hydrogen in state ψ_{100} is

$$\alpha_l^{100}(\omega) = \gamma_l^{100}(\omega) + \gamma_l^{100}(-\omega) \quad (19)$$

with

$$\begin{aligned} \gamma_l^{100}(\omega) = & \frac{2^{2l+7}(2l)!(l+1)v^{2l+5}}{(\mu+1)^{4l+6}} \left(\frac{(l+1)}{2(l+1-v)} {}_2F_1(2l+2, l+1-v, l+2-v; y) \right. \\ & + \frac{((2l+3)-2(l+1)v)}{(l+2-v)(v+1)^2} {}_2F_1(2l+3, l+2-v, l+3-v; y) \\ & \left. + \frac{(2l+3)(v-1)^2}{(l+3-v)(v+1)^4} {}_2F_1(2l+4, l+3-v, l+4-v; y) \right), \end{aligned} \quad (20)$$

where

$$y = \left((v-1)/(v+1) \right)^2, \quad v = \frac{1}{\sqrt{1-2\omega}}, \quad (21)$$

and that the dynamic 2^l -multipole polarizability of atomic hydrogen in state ψ_{200} is

$$\alpha_l^{200}(\omega) = \gamma_l^{200}(\omega) + \gamma_l^{200}(-\omega) \quad (22)$$

with

$$\begin{aligned} \gamma_l^{200}(\omega) = & \frac{2^{2l+1}(2l)!(l+1)^2v^{2l+5}}{(l+1-v)(\mu+1)^{4l+6}} {}_2F_1(2l+2, l+1-v, l+2-v; x) \\ & \times \left(4 - \frac{4(2l+3)v}{(v+1)} + \frac{(2l+3)^2v^2}{(v+1)^2} + \frac{2^{2l+4}(2l)!(l+1)v^{2l+5}}{(l+2-v)(\mu+1)^{4l+8}} {}_2F_1(2l+3, l+2-v, l+3-v; x) \right. \\ & \times \left(2(l+1)(1-\mu) + 1 - \frac{(2l+3)(3(l+1)(1-\mu)+2)v}{(\mu+1)} + \frac{(2l+3)^2((l+1)(1-\mu)+1)v^2}{(\mu+1)^2} \right) \\ & + \frac{2^{2l+2}(2l+3)!v^{2l+5}}{(l+3-v)(\mu+1)^{4l+10}} {}_2F_1(2l+4, l+3-v, l+4-v; x) \\ & \times \left(2(\mu-1)^2 + \frac{4((3l+4)(1-\mu)+2)(\mu-1)v}{(\mu+1)} \right. \\ & \left. + \frac{((12l^2+35l+25)(1-\mu)^2+2(7l+11)(1-\mu)+(l+1)(1-\mu^2)+4)v^2}{(\mu+1)^2} \right) \\ & + \frac{2^{2l+4}(2l+4)!v^{2l+6}}{(l+4-v)(2l+1)(\mu+1)^{4l+13}} {}_2F_1(2l+5, l+4-v, l+5-v; x) \\ & \times \left((\mu-1)^3 + \frac{((2l+3)(1-\mu)+2)(\mu-1)^2v}{(\mu+1)} \right) \\ & + \frac{2^{2l+3}(2l+5)!v^{2l+7}(\mu-1)^4}{(l+5-v)(2l+1)(\mu+1)^{4l+16}} {}_2F_1(2l+6, l+5-v, l+6-v; x), \end{aligned} \quad (23)$$

where

$$x = \left(\frac{\mu - 1}{\mu + 1} \right)^2, \quad \mu = \nu/2, \quad \nu = \frac{2}{\sqrt{1 - 8\omega}}. \quad (24)$$

It can be easily checked that for the dipole case ($l = 1$), Eq. (20) is equivalent to that derived by Szmytkowski [30]. This makes us confident of the expression (23) for the multipolar dynamic polarizabilities of the hydrogen atom in the first excited state.

Table 1: Three-body dispersion coefficients $Z(l_1 l_2 l_3)$ for H(1s)-H(s)-H(s) and H(2s)-H(2s)-H(2s) systems.

$l_1 l_2 l_3$	Cebim, Masili and Groote [17]		This work	
	H(1s)-H(s)-H(s)	H(1s)-H(s)-H(s)	H(1s)-H(s)-H(s)	H(2s)-H(2s)-H(2s)
1,1,1	7.214154836878659446047(0)	7.2141548368785690(0)	2.51755295221607230(4)	
1,1,2	2.623572212844463429580(1)	2.6235722128444340(1)	3.29955685513518840(6)	
1,1,3	2.373443263079563275306(2)	2.3734432630795274(2)	1.86666672072725530(8)	
1,1,4	3.914797915212531233549(3)	3.9147979152124670(3)	1.7926267279916924(10)	
1,1,5	1.016264085751231556149(5)	1.0162640857512153(5)	2.5597766745528633(12)	
1,2,2	9.645706352308603614855(1)	9.6457063523084290(1)	4.33480217905111500(8)	
1,2,3	8.766748094499075941380(2)	8.7667480944988620(2)	2.4365181135086796(10)	
1,2,4	1.449816353248769904764(4)	1.4498163532487373(4)	2.3324835695723760(12)	
1,2,5	3.770097793839280994468(5)	3.7700977938392095(5)	3.3242991896933144(14)	
1,3,3	7.983980420693903024519(3)	7.9839804206937020(3)	1.3940236050719280(12)	
1,3,4	1.321888252429620460132(5)	1.3218882524295954(5)	1.3456858222168964(14)	
1,3,5	3.440020106065453322306(6)	3.4400201060654107(6)	1.9274001578036572(16)	
1,4,4	2.190066438824243019707(6)	2.1900664388242206(6)	1.3043826805191634(16)	
1,4,5	5.701791079045648161996(7)	5.7017910790456320(7)	1.8729137091332370(18)	
1,5,5	1.484869244935850133777(9)	1.4848692449358570(9)	2.6933743387734514(20)	
2,2,2	3.591579298442920157864(2)	3.5915792984427840(2)	5.7069914279553320(10)	
2,2,3	3.282117205606176559215(3)	3.2821172056060636(3)	3.1890799066670166(12)	
2,2,4	5.444675443581831412036(4)	5.4446754435817080(4)	3.0443042092678440(14)	
2,2,5	1.418681464756161954778(6)	1.4186814647561447(6)	4.3314528083750664(16)	
2,3,3	3.006448973144702567288(4)	3.0064489731446450(4)	1.8112687450840253(14)	
2,3,4	4.994156252686642743643(5)	4.9941562526866350(5)	1.7421723731700308(16)	
2,3,5	1.302448320872365967522(7)	1.3024483208723813(7)	2.4898359624357440(18)	
2,4,4	8.302513672007483906595(6)	8.3025136720076330(6)	1.6819060799662140(18)	
2,4,5	2.166356287661398259771(8)	2.1663562877194527(8)	2.4090598639513895(20)	
2,5,5	5.654517127290032691877(9)	5.6545171272902690(9)	3.4552820249609814(22)	
3,3,3	2.760922957772705614623(5)	2.7609229577727267(5)	1.0492575486186550(16)	
3,3,4	4.592966812146163573521(6)	4.5929668121462990(6)	1.0187050273912055(18)	
3,3,5	1.198957248225472655308(8)	1.1989572482255244(8)	1.4639823374591851(20)	
3,4,4	7.647067550033841578742(7)	7.6470675500342320(7)	9.9362313119812550(19)	
3,4,5	1.997296911169497589184(9)	1.9972969111696215(9)	1.4319483786052915(22)	
3,5,5	5.218501618198915493769(10)	5.218501618199280(10)	2.0671949480574613(24)	
4,4,4	1.2743030876063235761620(9)	1.2743030876064124(9)	9.7413604204552800(21)	
4,4,5	3.330172209781951888168(10)	3.330172209782207(10)	1.4082545836934342(24)	
4,5,5	8.706067248106873282478(11)	8.706067248107562(11)	2.0397583237547210(26)	
5,5,5	2.276892768105969684185(13)	2.276892768106143(13)	2.9605222240090640(28)	

3 Results and discussion

By using Eqs. (3), (19)-(24), the three-body van der Waals dispersion coefficients for H(1s)-H(1s)-H(1s) and H(2s)-H(2s)-H(2s) systems are calculated and the results are listed in Table 1 (where the number in the parentheses after each value, such as (1), means $\times 10^1$). The results for the H(1s)-H(1s)-H(1s) system are consistent with that previously calculated by Cebim, Masili and Groote [17]. There are, however, systematic differences, which are resulted from two sources. One is from the truncate approximation that employed by Cebim, Masili and Groote. The other is from the ground-state energy of atomic hydrogen. The approximate theoretical value $E_1 = -1/2$ (a.u.) has been used in this work, while the accurate experimental value was used by Cebim, Masili and Groote. Because our main purpose is to estimate the three-body dispersion coefficients for the H(2s)-H(2s)-H(2s) system purely theoretically, we intentionally avoid using any experimental value.

It is noted that the interaction energy is very much stronger for the H(2s)-H(2s)-H(2s) system. This is reasonable in view of the large polarizabilities for the 2s hydrogen atom, which can be easily tabulated from Eqs. (22)-(24). This large van der Waals interaction energy and the long lifetime of the metastable 2s hydrogen make this work very interesting and might have experimental implications in further quantum confinement investigation.

In conclusion, three-body van der Waals dispersion coefficients $Z(l_1 l_2 l_3)$ (l_i up to 5) for the H(1s)-H(1s)-H(1s) and H(2s)-H(2s)-H(2s) systems are calculated by virtue of the dynamic polarizabilities at imaginary photon frequencies, the later is derived by application of the integration properties of the one-dimensional radial Coulomb Green's function. The results for the H(1s)-H(1s)-H(1s) system are consistent with that previously calculated by Cebim, Masili and Groote, while the results for the H(2s)-H(2s)-H(2s) system are contributed in this work, which might be used as standard for other calculation methods. The present approach is also precise for higher interaction orders, for higher excited states, and for model potential systems.

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