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Dynamic multipole polarizability of atomic hydrogen

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Using an integral representation involving the radial Coulomb Green's function an analytic closed-form expression is derived for the dynamic multipole polarizability of atomic hydrogen in an arbitrary state. The application of the general expression to practical problems is discussed. Comparison is also made with other theoretical models.

I. INTRODUCTION

The exact evaluation of the dynamic 2^l-multipole polarizability of atomic hydrogen in an arbitrary $(n_i l_i m_i)$ state,

$$\beta_l^{n_i l_i m_i}(\omega)=\sum_{\substack{n'(\neq n_i)\\ l',m'}}\!\!\!\!\!\!\!\int \frac{|\langle \psi_{n_i l_i m_i}|r^l P_l(\cos\theta)|\psi_{n'l'm'}\rangle|^2}{E_{n'}-E_{n_i}-\omega}\,, \quad (1)$$

is of considerable interest in atomic physics. In Eq. (1), ω is the angular frequency of the electromagnetic field and E and ψ are the energy eigenvalue and eigenfunction of atomic hydrogen. $\sum\!\!\!\!\!\!\int$ represents a sum (excluding $n'=n_i$) over all discrete states and an integral over all continuous states.

The dynamic polarizability is an important quantity which describes the distortion of the electronic and charge distribution of an atom (or a molecule) in the presence of an oscillating electric field. It is directly related to the van der Waals constants,[1-4] the dynamic dipole shielding factor,[5] the Rayleigh scattering cross sections,[6] the Verdet constants,[7] the mean excitation energies,[8] and the frequency dependence of the refraction index.[9]

The problem of evaluating the dynamic polarizability in various forms has been studied by approximate or analytical methods by Karplus and Kolker,[9] Chan and Dalgarno,[10] Adamov, Kagan, and Orlov,[11] Vetchinkin and Khristenko,[12] Adamov, Balmakov, and Rebane,[13] Adamov, Orlov, and Rebane,[14] Deal and Young,[15] Shimamura,[16] and Au.[17] However, all these theoretical calculations are limited to the consideration of the dipole case, $l=1$, or of the spherical symmetric $n_i s$ state. The purpose of this paper is to derive a compact and analytic closed-form expression for Eq. (1) for the most general case of $l\geq 1$ and arbitrary $(n_i l_i m_i)$. Instead of using the Coulomb Green's function in three-dimensional momentum space,[17] we employ the one-dimensional radial Coulomb Green's function[18] in the derivation. The algebra involved is rather simple compared with that of other approaches.

Atomic units will be used unless otherwise stated.

II. ANALYTICAL EXPRESSION FOR $\beta_l^{n_i l_i m_i}(\omega)$

After calculating the angular part in Eq. (1), we have

$$\beta_l^{n_i l_i m_i}(\omega)=\sum_{l'=|l-l_i|}^{l+l_i}\left[(2l_i+1)(2l'+1)\begin{bmatrix} l_i & l & l' \\ 0 & 0 & 0\end{bmatrix}^2\begin{bmatrix} l_i & l & l' \\ -m_i & 0 & m_i\end{bmatrix}^2\right.$$
$$\left.\times\int_0^\infty dr\,dr'(rr')^{l+2}R_{n_i l_i}(r)R_{n_i l_i}(r')\sum_{\substack{n'(\neq n_i)\\ (n'>l')}}\!\!\!\!\!\!\!\int \frac{R_{n'l'}(r)R^*_{n'l'}(r')}{E_{n'}-(E_{n_i}+\omega)}\right], \quad (2)$$

where $\left(\begin{smallmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3\end{smallmatrix}\right)$ refers to the 3-j symbol.[19] In order to use the closure relation, we add and subtract a term with $n'=n_i$ inside $\sum\!\!\!\!\!\!\int$ in Eq. (2). Hence

$$\beta_l^{n_i l_i m_i}(\omega)=\sum_{l'=|l-l_i|}^{l+l_i}\left\{(2l_i+1)(2l'+1)\begin{bmatrix} l_i & l & l' \\ 0 & 0 & 0\end{bmatrix}^2\begin{bmatrix} l_i & l & l' \\ -m_i & 0 & m_i\end{bmatrix}^2\right.$$
$$\left.\times\left[\int_0^\infty\!\!\int dr\,dr'(rr')^{l+2}R_{n_i l_i}(r)R_{n_i l_i}(r')g_{l'}(r,r';E_{n_i}+\omega)+\frac{\epsilon_{n_i l'}}{\omega}\left[\int_0^\infty r^{l+2}R_{n_i l_i}(r)R_{n_i l'}(r)dr\right]^2\right]\right\}, \quad (3)$$

where

$$\epsilon_{n_i l'}=\begin{cases}1 & \text{for } n_i>l' \\ 0 & \text{for } n_i\le l' .\end{cases} \tag{4}$$

In Eq. (3), we define the radial Coulomb Green's function via

$$g_l(r,r';E)=\mathop{\sum\!\!\!\!\!\!\!\int}_{\substack{n\\(n>l)}}\frac{R_{nl}(r)R_{nl}^{*}(r')}{E_n-E} . \tag{5}$$

We now proceed to evaluate the terms appearing in Eq. (3). Since

$$R_{nl}=\sum_{k=0}^{n-l-1}B(n,l,k)r^{l+k}e^{-r/n} , \tag{6}$$

with

$$B(n,l,k)=(-1)^k\frac{[(n-l-1)!(n+l)!]^{1/2}\left[\dfrac{2}{n}\right]^{k+l+1}}{n(n-l-1-k)!(2l+1+k)!k!} , \tag{7}$$

the second integral in Eq. (3) may be done immediately

$$\int_0^\infty r^{l+2}R_{n_il_i}(r)R_{n_il'}(r)dr$$

$$=\sum_{k=0}^{n_i-l_i-1}\sum_{k'=0}^{n_i-l'-1}B(n_i,l_i,k)B(n_i,l',k')\times\frac{(l+l_i+l'+2+k+k')!}{\left[\dfrac{2}{n_i}\right]^{l+l_i+l'+3+k+k'}} . \tag{8}$$

We now consider the term with integral involving $g_{l'}$ in Eq. (3),

$$\Delta=\int_0^\infty\!\!\int dr\,dr'(rr')^{l+2}R_{n_il_i}(r)R_{n_il_i}(r')g_{l'}(r,r';E_{n_i}+\omega). \tag{9}$$

Substituting Eq. (6) into Eq. (9), we obtain

$$\Delta=\sum_{k,k'=0}^{n_i-l_i-1}\int_0^\infty\!\!\int B(n_i,l_i,k)B(n_i,l_ik')r^{l_i+l+2+k}r'^{l_i+l+2+k'}e^{-(r+r')/n_i}g_{l'}(r,r';E_{n_i}+\omega)$$

$$=\sum_{k,k'=0}^{n_i-l_i-1}(-1)^{k+k'}B(n_i,l_i,k)B(n_i,l_i,k')\nu^{2(l_i+l+1-l')+k+k'}$$

$$\times 2\left[\frac{\partial^{l_i+l+1+k-l'}}{\partial\mu^{l_i+l+1+k-l'}}\frac{\partial^{l_i+l+1+k'-l'}}{\partial(\mu')^{l_i+l+1+k'-l'}}\left[\tfrac{1}{2}\int_0^\infty\!\!\int dr\,dr'(rr')^{l'+1}e^{-(\mu r+\mu' r')/\nu}g_{l'}(r,r';E_{n_i}+\omega)\right]\Bigg|_{\mu=\mu'=\nu/n_i}\right] , \tag{10}$$

where

$$\nu=\left[\frac{-1}{2(E_{n_i}+\omega)}\right]^{1/2} . \tag{11}$$

A useful integral representation involving g_l, which is exactly the integral inside the square brackets in Eq. (10), has been introduced and derived by Rapoport and Zon:[18]

$$J_l(\mu,\mu';\nu)=\tfrac{1}{2}\int_0^\infty\!\!\int dr\,dr'(rr')^{l+1}e^{-(\mu r+\mu' r')/\nu}g_l(r,r';\nu)$$

$$=\frac{2^{2l+1}(2l+1)!\nu^{2l+3}}{(l+1-\nu)[(\mu+1)(\mu'+1)]^{2l+2}}\,{}_2F_1\left[2l+2,l+1-\nu,l+2-\nu;\frac{(\mu-1)(\mu'-1)}{(\mu+1)(\mu'+1)}\right] , \tag{12}$$

where ${}_2F_1$ is the usual hypergeometric function. Thus

$$\Delta=[\hat{\mathscr{D}}(\mu,\mu';n_i,l_i,l,l')J_{l'}(\mu,\mu';\nu)]\,|_{\mu=\mu'=\nu/n_i} , \tag{13}$$

where we define $\hat{\mathscr{D}}$ via

$$\hat{\mathscr{D}}(\mu,\mu';n_i,l_i,l,l')=\sum_{k,k'=0}^{n_i-l_i-1}(-1)^{k+k'}2B(n_i,l_i,k)B(n_i,l_i,k')\nu^{2(l_i+l+1-l')+k+k'}\frac{\partial^{l_i+l+1+k-l'}}{\partial\mu^{l_i+l+1+k-l'}}\frac{\partial^{l_i+l+1+k'-l'}}{\partial(\mu')^{l_i+l+1+k'-l'}} . \tag{14}$$

TABLE I. Numerical values of $\beta_1^{100}(\omega)$ and $\beta_1^{200}(\omega)$. Numbers in parentheses represent powers of ten.

ω	β_1^{100}	ω	β_1^{200}
0	2.25 (exact)	0	60 (exact)
1.00(−1)	2.965 629 367(0)	1.0(−2)	6.902 615 499(1)
2.00(−1)	4.412 861 310(0)	2.0(−2)	8.145 239 227(1)
3.00(−1)	9.243 864 448(0)	3.0(−2)	9.974 929 997(1)
3.60(−1)	3.970 254 842(1)	4.0(−2)	1.296 491 409(2)
3.70(−1)	1.139 414 878(2)	5.0(−2)	1.883 930 241(2)
3.80(−1)	−1.077 201 814(2)	6.0(−2)	3.649 203 288(2)
3.90(−1)	−3.332 873 142(1)	6.5(−2)	7.422 018 480(2)
4.00(−1)	−1.798 482 633(1)	7.0(−2)	−5.592 296 525(3)
4.10(−1)	−1.084 034 918(1)	7.1(−2)	−1.867 816 216(3)
4.20(−1)	−5.975 051 251(0)	7.3(−2)	−8.323 988 400(2)
4.30(−1)	−8.449 198 716(−1)	7.5(−2)	−5.115 798 355(2)
4.40(−1)	1.516 330 769(1)	7.7(−2)	−3.578 112 255(2)
4.41(−1)	2.117 971 322(1)	7.9(−2)	−2.654 149 208(2)
4.42(−1)	3.195 252 453(1)	8.0(−2)	−2.310 010 690(2)
4.43(−1)	5.736 037 886(1)	9.0(−2)	2.985 439 865(1)
4.44(−1)	1.961 844 023(2)	9.1(−2)	9.170 418 468(1)
4.45(−1)	−1.640 137 061(2)	9.2(−2)	2.138 654 772(2)
4.46(−1)	−6.082 900 378(1)	9.3(−2)	6.394 191 594(2)
4.47(−1)	−3.822 816 597(1)	9.4(−2)	−2.275 872 225(3)
4.48(−1)	−2.821 422 869(1)	9.5(−2)	−5.142 744 415(2)
4.49(−1)	−2.249 382 364(1)		
4.50(−1)	−1.874 375 308(1)		

TABLE II. Numerical values of $\alpha_1^{100}(\omega)$ defined in Sec. III B. Numbers in parentheses represent powers of ten.

ω	Adamov, Kagan, and Orlov (Ref. 11)	Vetchinkin and Khristenko (Ref. 12)	Adamov, Orlov, and Rebana (Ref. 14)		This work
			Variational lower bound	Variational upper bound	
0		4.500(0)			4.5 (exact)
1.00(−1)	4.7843(0)	4.784(0)	4.784 300 3(0)	4.784 300 3(0)	4.784 300 342(0)
2.00(−1)	5.9417(0)	5.942(0)	5.941 674 8(0)	5.941 674 8(0)	5.941 674 860(0)
3.00(−1)	1.0564(1)	1.056(1)	1.056 388 8(1)	1.056 388 8(1)	1.056 388 886(1)
3.60(−1)	4.0923(1)	4.092(1)	4.092 300 0(1)	4.092 302 9(1)	4.092 302 283(1)
3.70(−1)	1.1515(2)	1.152(2)	1.151 461 7(2)	1.151 461 7(2)	1.151 468 376(2)
3.80(−1)	−1.0653(2)	−1.065(2)	−1.065 296(2)	−1.065 296(2)	−1.065 295 795(2)
3.90(−1)	−3.2153(1)	−3.215(1)	−3.215 259(1)	−3.215 259(1)	−3.215 251 467(1)
4.00(−1)	−1.6823(1)	−1.682(1)	−1.682 282(1)	−1.682 218(1)	−1.682 264 535(1)
4.10(−1)	−9.6918(0)	−9.692(0)	−9.6924(0)	−9.6908(0)	−9.691 867 337(0)
4.20(−1)	−4.8399(0)	−4.840(0)	−4.8427(0)	−4.8371(0)	−4.839 944 009(0)
4.30(−1)	2.9713(−1)	2.971(−1)	2.7547(−1)	3.0913(−1)	2.971 257 640(−1)
4.40(−1)	1.6273(1)	1.627(1)	1.5491(1)	1.6396(1)	1.627 259 373(1)
4.41(−1)	2.2288(1)	2.229(1)	2.0913(1)	2.2474(1)	2.228 773 951(1)
4.42(−1)	3.3059(1)	3.306(1)	2.9905(1)	3.3353(1)	3.305 929 397(1)
4.43(−1)	5.8466(1)	5.847(1)	4.9103(1)	5.9029(1)	5.846 589 434(1)
4.44(−1)	1.9729(2)	1.973(2)	1.1687(2)	1.9942(2)	1.972 886 667(2)
4.45(−1)	−1.6291(2)	−1.629(2)	−1.6484(2)	−5.9152(1)	−1.629 106 899(2)
4.46(−1)	−5.9727(1)	−5.973(1)	−6.0532(1)	−3.5238(1)	−5.972 723 290(1)
4.47(−1)	−3.7128(1)	−3.713(1)	−3.7689(1)	−2.5145(1)	−3.712 763 757(1)
4.48(−1)	−2.7114(1)	−2.711(1)	−2.7586(1)	−1.9565(1)	−2.711 493 992(1)
4.49(−1)	−2.1396(1)	−2.140(1)	−2.1836(1)	−1.5960(1)	−2.139 577 167(1)
4.50(−1)	−1.7647(1)	−1.765(1)	−1.8060(1)	−1.3348(1)	−1.764 693 509(1)

TABLE III. Numerical values of $\alpha_1^{200}(\omega)$ defined in Sec. III B. Numbers in parentheses represent powers of ten.

ω	Adamov, Balmakov, and Rebene (Ref. 13)	This work
0	120	120 (exact)
1.0(−2)	1.221 538 97(2)	1.221 538 981(2)
2.0(−2)	1.291 625 12(2)	1.291 625 120(2)
3.0(−2)	1.430 725 26(2)	1.430 725 265(2)
4.0(−2)	1.693 436 79(2)	1.693 436 800(2)
5.0(−2)	2.250 335 9(2)	2.250 335 905(2)
6.0(−2)	3.989 533 9(2)	3.989 533 921(2)
6.5(−2)	7.750 686(2)	7.750 686 566(2)
7.0(−2)	−5.5605(3)	−5.560 516 933(3)
7.1(−2)	−1.936 245(3)	−1.936 245 295(3)
7.3(−2)	−8.012 37(2)	−8.012 369 621(2)
7.5(−2)	−4.808 163(2)	−4.808 163 013(2)
7.7(−2)	−3.274 357(2)	−3.274 357 563(2)
7.9(−2)	−2.354 17(2)	−2.354 176 361(2)
8.0(−2)	−2.011 89(2)	−2.011 892 902(2)
9.0(−2)	5.793(1)	5.793 232 174(1)
9.1(−2)	1.196(2)	1.196 199 725(2)
9.2(−2)	2.416(2)	2.416 210 295(2)
9.3(−2)	6.67(2)	6.670 163 782(2)
9.4(−2)	−2.248(3)	−2.248 431 579(3)
9.5(−2)	−4.87(2)	−4.869 885 303(2)

Substituting Eqs. (8) and (13) into Eq. (3), we ultimately find that the dynamic polarizability is given by

$$\beta_l^{n_i l_i m_i}(\omega)=(2l_i+1)\sum_{l'=|l-l_i|}^{l+l_i}\left\{(2l'+1)\begin{bmatrix} l_i & l & l' \\ 0 & 0 & 0\end{bmatrix}^2\begin{bmatrix} l_i & l & l' \\ -m_i & 0 & m_i\end{bmatrix}^2 \times\left[[\hat{\mathscr{D}}(\mu,\mu';n_i,l_i,l,l')J_{l'}(\mu,\mu';\nu)]\,|_{\mu=\mu'=\nu/n_i} + \frac{\epsilon_{n_i l'}}{\omega}\left[\sum_{k=0}^{n_i-l_i-1}\sum_{k'=0}^{n_i-l'-1}B(n_i,l_i,k)B(n_i,l_i,k')\frac{(l+l_i+l'+k+k'+2)!}{\left[\dfrac{2}{n_i}\right]^{l+l_i+l'+k+k'+3}}\right]^2\right]\right\}. \tag{15}$$

Notice that as ω→0, the first and second terms in Eq. (15), both behave as $1/\omega$, and exactly cancel out each other for the case of $l'<n_i$. Thus there is no singularity problem in Eq. (15). In view of Eq. (12), the final expression for the dynamic polarizability, Eq. (15), is a finite summation of hypergeometric functions and is analytical in real or imaginary ω.

III. APPLICATIONS

In Sec. II we managed to obtain an analytical and closed-form expression, Eq. (15), for the dynamic polarizability. The result holds for arbitrary l (the multiple order) and arbitrary state (n_i,l_i,m_i). For simplicity and for the purpose of illustration we focus our attention on the $n_i s$ state ($n_i=1$ and 2).

A. β_1^{100} and $\beta_1^{200}(\omega)$

Substituting $n_i=1$, $l_i=0$, and $l=1$ into Eq. (15), we obtain

$$\beta_1^{100}(\omega)=\frac{2^{11}\nu^7}{(2-\nu)(\nu+1)^{10}}\left[{}_2F_1\left[4,2-\nu;3-\nu;\left[\frac{\nu-1}{\nu+1}\right]^2\right]+\frac{(2-\nu)(5-4\nu)}{(3-\nu)(\nu+1)^2}{}_2F_1\left[5,3-\nu;4-\nu;\left[\frac{\nu-1}{\nu+1}\right]^2\right]\right.$$
$$\left.+\frac{5(2-\nu)(\nu-1)^2}{(4-\nu)(\nu+1)^4}{}_2F_1\left[6,4-\nu;5-\nu;\left[\frac{\nu-1}{\nu+1}\right]^2\right]\right], \tag{16}$$

where

$$\nu=\left[\frac{1}{1-2\omega}\right]^{1/2}. \tag{17}$$

Similarly, one has for $n_i=2$,

$$\beta_1^{200}(\omega)=2^6\nu^7\left[\frac{1}{(2-\nu)(1+\mu)^{10}}\left[4-\frac{20\nu}{1+\mu}+\frac{25\nu^2}{(1+\mu)^2}\right]{}_2F_1\left[4,2-\nu;3-\nu;\left[\frac{\mu-1}{\mu+1}\right]^2\right]\right.$$
$$+\frac{4}{(3-\nu)(1+\mu)^{12}}\left[5-4\mu+\frac{10\nu(3\mu-4)}{1+\mu}+\frac{25\nu^2(3-2\mu)}{(1+\mu)^2}\right]{}_2F_1\left[5,3-\nu;4-\nu;\left[\frac{\mu-1}{\mu+1}\right]^2\right]$$
$$+\frac{20}{(4-\nu)(1+\mu)^{14}}\left[(\mu-1)^2+\frac{2\nu(\mu-1)(9-7\mu)}{1+\mu}+\frac{\nu^2(35\mu^2-90\mu+57)}{(1+\mu)^2}\right]{}_2F_1\left[6,4-\nu;5-\nu;\left[\frac{\mu-1}{\mu+1}\right]^2\right]$$
$$+\frac{240\nu(\mu-1)^2}{(5-\nu)(1+\mu)^{17}}\left[\mu-1+\frac{\nu(7-5\mu)}{1+\mu}\right]{}_2F_1\left[7,5-\nu;6-\nu;\left[\frac{\mu-1}{\mu+1}\right]^2\right]$$
$$\left.\left.+\frac{840\nu^2(\mu-1)^4}{(6-\nu)(1+\mu)^{20}}{}_2F_1\left[8,6-\nu;7-\nu;\left[\frac{\mu-1}{\mu+1}\right]^2\right]\right]\right|_{\mu=\nu/2}+\frac{9}{\omega}, \tag{18}$$

where

$$\nu=\frac{2}{(1-8\omega)^{1/2}}. \tag{19}$$

A general explicit expression for $\beta_l^{n00}(\omega)$ in nature units was previously derived by Au[17] using a different Green's-function representation. Hence the corresponding and equivalent expressions for $\beta_1^{100}(\omega)$ and $\beta_1^{200}(\omega)$ are easily obtained from Au's Eq. (50).

In Table I, we have listed numerically $\beta_1^{100}(\omega)$ and $\beta_1^{200}(\omega)$ for ω from 0 (static polarizability) to 0.45. We have also used the implicit technique of Dalgarno and Lewis,[20,21] which reduces the calculation of the infinite sums in Eq. (1) to the numerical integration of a first-order inhomogeneous differential equation, to evaluate $\beta_1^{100}(\omega)$ and $\beta_1^{200}(\omega)$. Our theoretical results of both calculations match to at least the tenth decimal place for all ω. Thus the reliability of our numerical codes is established. The numerical values in Table I are therefore accurate at least up to ten significant figures.

B. $\alpha_1^{100}(\omega)$ and $\alpha_1^{200}(\omega)$

In literature, the quantity $\alpha_l^{n_il_im_i}(\omega)$, which is also referred to as the dynamic polarizability, is related to $\beta_l^{n_il_im_i}(\omega)$ of Eq. (1) via

$$\alpha_l^{n_il_im_i}(\omega)=\beta_l^{n_il_im_i}(\omega)+\beta_l^{n_il_im_i}(-\omega). \tag{20}$$

We have used Eqs. (16)–(20) to compute $\alpha_1^{100}(\omega)$ and $\alpha_1^{200}(\omega)$ for various ω. A comparison of our theoretical results with other calculations is presented in Tables II and III. Although the agreement among various theoretical models is satisfactory, we believe that our numerical values are more accurate. Our confidence in the present calculation is based on the fantastic agreement between the Green's-function method and the implicit technique. Both methods are exact and completely independent.

C. van der Waals constants

Chan and Dalgarno[10] in 1965, and later Deal and Young[22] in 1970 pointed out that the long-range interaction energy between two atomic systems is related to their multipole polarizabilities. In particular, they showed that the long-range interaction energy between two hydrogenic atoms in n_is and $n_i's$ states, respectively, is quite simple and is given in rydbergs by

$$E(R)=-\left[\frac{C_6}{R^6}+\frac{C_8}{R^8}+\frac{C_{10}^{(1)}+C_{10}^{(2)}}{R^{10}}\right], \tag{21}$$

where R is the separation of the atoms. The van der Waals constants in Eq. (21) are defined via

$$C_6=\frac{3}{\pi}\int_0^\infty \alpha_{\mathrm{CD},1}^{n_is}(\omega)\alpha_{\mathrm{CD},1}^{n_i's}(\omega)d\omega, \tag{22}$$

$$C_8=\frac{15}{2\pi}\int_0^\infty [\alpha_{\mathrm{CD},1}^{n_iS}(\omega)\alpha_{\mathrm{CD},2}^{n_i's}(\omega)+\alpha_{\mathrm{CD},2}^{n_is}(\omega)\alpha_{\mathrm{CD},1}^{n_i's}(\omega)]d\omega, \tag{23}$$

$$C_{10}^{(1)}=\frac{14}{\pi}\int_0^\infty [\alpha_{\mathrm{CD},1}^{n_is}(\omega)\alpha_{\mathrm{CD},3}^{n_i's}(\omega)+\alpha_{\mathrm{CD},3}^{n_is}(\omega)\alpha_{\mathrm{CD},1}^{n_i's}(\omega)]d\omega, \tag{24}$$

TABLE IV. Numerical values of $\alpha^{100}_{\text{CD},l}(\omega)$ defined in Sec. III. Numbers in parentheses represent powers of ten.

ω	Chan and Dalgarno (Ref. 10) $\alpha^{100}_{\text{CD},1}$	$\alpha^{100}_{\text{CD},2}$	$\alpha^{100}_{\text{CD},3}$	This work $\alpha^{100}_{\text{CD},1}$	$\alpha^{100}_{\text{CD},2}$	$\alpha^{100}_{\text{CD},3}$
0	4.500(0)	1.504(1)	1.313(2)	4.5 (exact)	15 (exact)	131.25 (exact)
1.0(−1)	4.250(0)	1.452(1)	1.280(2)	4.250 298(0)	1.451 859(1)	1.280 169(2)
3.0(−1)	2.978(0)	1.164(1)	1.075(2)	2.978 326(0)	1.163 549(1)	1.074 714(2)
5.0(−1)	1.905(0)	8.477(0)	8.251(1)	1.905 388(0)	8.469 799(0)	8.241 280(1)
7.0(−1)	1.258(0)	6.107(0)	6.184(1)	1.258 016(0)	6.106 514(0)	6.183 497(1)
9.0(−1)	8.747(−1)	4.496(0)	4.681(1)	8.745 551(−1)	4.495 649(0)	4.680 811(1)
1.0(0)	7.427(−1)	3.903(0)	4.101(1)	7.424 407(−1)	3.897 303(0)	4.100 637(1)
1.4(0)	4.247(−1)	2.352(0)	2.543(1)	4.245 466(−1)	2.351 598(0)	2.543 334(1)
1.8(0)	2.720(−1)	1.549(0)	1.700(1)	2.719 919(−1)	1.549 272(0)	1.699 972(1)
2.5(0)	1.481(−1)	8.646(−1)	9.605(0)	1.482 516(−1)	8.649 416(−1)	9.607 193(0)
3.5(0)	7.800(−2)	4.618(−1)	5.164(0)	7.806 725(−2)	4.619 300(−1)	5.166 048(0)
4.5(0)	4.791(−2)	2.853(−1)	3.200(0)	4.794 121(−2)	2.853 881(−1)	3.200 471(0)
6.0(0)	2.727(−2)	1.630(−1)	1.831(0)	2.727 334(−2)	1.630 035(−1)	1.831 107(0)
8.0(0)	1.546(−2)	9.256(−2)	1.041(0)	1.545 065(−2)	9.253 795(−2)	1.040 390(0)
1.0(1)	9.929(−3)	5.950(−2)	6.692(−1)	9.924 092(−3)	5.949 012(−2)	6.690 518(−1)
1.2(1)	6.910(−3)	4.142(−2)	4.659(−1)	6.906 132(−3)	4.141 640(−2)	4.658 543(−1)
2.5(1)	1.598(−3)	9.585(−3)	1.080(−1)	1.597 637(−3)	9.586 114(−3)	1.078 432(−1)
5.0(1)	3.999(−4)	2.399(−3)	2.699(−2)	3.998 364(−4)	2.399 115(−3)	2.699 015(−2)

and

$$C^{(2)}_{10}=\frac{35}{\pi}\int_0^\infty \alpha^{n_is}_{\text{CD},2}(\omega)\alpha^{n_i's}_{\text{CD},2}(\omega)d\omega\ , \tag{25}$$

where $\alpha^{n_is}_{\text{CD},1}(\omega)$, $\alpha^{n_is}_{\text{CD},2}(\omega)$, and $\alpha^{n_is}_{\text{CD},3}(\omega)$ are the frequency-dependent dipole, quadrupole, and octopole polarizabilities of the isolated n_is-state atom, respectively. They are defined by Chan and Dalgarno[10]

$$\alpha^{n_is}_{\text{CD},l}=2\sum_{\substack{n'(\neq n_i),\\ l',m'}}\frac{(E_{n'}-E_{n_i})\,|\langle\psi_{n_i00}\,|\,r^lP_l(\cos\theta)\,|\,\psi_{n'l'm'}\rangle|^2}{(E_{n'}-E_{n_i})^2+\omega^2}\ , \tag{26}$$

which is related to $\beta^{n_is}_l(\omega)$ via

$$\begin{aligned}\alpha^{n_is}_{\text{CD},l}(\omega)&=\beta^{n_is}_l(i\omega)+\beta^{n_is}_l(-i\omega)\\ &=2\,\text{Re}[\beta^{n_is}_l(i\omega)]\ .\end{aligned} \tag{27}$$

Explicit expression of $\alpha^{n_is}_{\text{CD},l}(\omega)$ for $l=1,2,3$ and $n_i=1,2$ are available upon request. In Tables IV and V we have tabulated our numerical data for $\alpha^{n_is}_{\text{CD},l}(\omega)$ for various ω. We have also listed the results of Chan and Dalgarno for $n_i=1$ in Table IV for comparison. Note that our $\alpha^{100}_{\text{CD},l}(\omega=0)$ is an exact analytical result. The overall picture of Table IV indicates that the numerical results of Chan and Dalgarno are reliable at least up to the third decimal place. For $n_i=2$ no other calculation has yet been reported in literature. Although we have confidence in our computer codes, algebraic mistakes are still possible in the mathematical formula for $\alpha^{n_is}_{\text{CD},l}(\omega)$ owing to the complexity of the expressions. Considerable effort was devoted to finding another independent method to check the results. While direct application of the implicit technique cannot be used here, we have employed a term-by-term summation method[23–25] (a brief summary is available upon request) to evaluate $\alpha^{n_is}_{\text{CD},l}(\omega)$. Since the summation method requires numerical integration, it is not as accurate as the Green's-function method which deals only with hypergeometric functions. However, the agreement between the two methods is good at least to four significant figures and is regarded as satisfactory.

We have also evaluated the van der Waals constants via Eqs. (22)–(25) and have listed the numerical values in Table VI. Note that the interaction energy is very large for the 1s-2s pair and is very much stronger for the 2s-2s pair (this is not surprising in view of the large polarizabilities for the 2s hydrogenic atom). The large van der Waals interaction energy and the long lifetime of the metastable 2s hydrogen make this conclusion very interesting and may have experimental implications in further van der Waals spectroscopy investigation.

In conclusion, we would like to point out that all numerical computations reported in this paper are carried out on an IBM XT personal computer, thus demonstrating the utility and practicality of the technique presented in this paper. To test the theoretical predictions of this paper, dedicated experimental investigation especially concerned with 2s atomic hydrogen would be of great value.

TABLE V. Numerical values of $\alpha^{200}_{\mathrm{CD},l}(\omega)$ defined in Sec. III C.

ω	$\alpha^{200}_{\mathrm{CD},1}$	$\alpha^{200}_{\mathrm{CD},2}$	$\alpha^{200}_{\mathrm{CD},3}$
0	120 (exact)	16 320 (exact)	823 200 (exact)
1.0(−1)	4.643 156 03(1)	5.386 450 96(3)	4.139 442 41(5)
2.0(−1)	1.777 525 06(1)	1.807 612 77(3)	1.685 467 20(5)
3.0(−1)	9.046 787 72(0)	8.626 707 32(2)	8.511 671 07(4)
4.0(−1)	5.425 279 70(0)	4.994 555 11(2)	5.032 421 77(4)
5.0(−1)	3.601 039 93(0)	3.244 658 06(2)	3.299 859 17(4)
6.0(−1)	2.559 264 88(0)	2.273 379 23(2)	2.322 908 73(4)
7.0(−1)	1.910 220 96(0)	1.679 936 26(2)	1.720 954 17(4)
8.0(−1)	1.479 224 62(0)	1.291 362 22(2)	1.324 885 07(4)
9.0(−1)	1.178 740 99(0)	1.023 296 48(2)	1.050 832 65(4)
1.0(0)	9.610 522 62(−1)	8.306 714 53(1)	8.535 284 99(3)
1.2(0)	6.736 598 02(−1)	5.785 818 80(1)	5.948 888 11(3)
1.4(0)	4.980 397 84(−1)	4.258 971 50(1)	4.380 332 41(3)
1.6(0)	3.830 026 40(−1)	3.265 046 68(1)	3.358 578 06(3)
1.8(0)	3.036 076 01(−1)	2.582 201 91(1)	2.656 361 64(3)
2.0(0)	2.465 329 15(−1)	2.093 029 61(1)	2.153 211 02(3)
2.5(0)	1.584 354 30(−1)	1.341 023 18(1)	1.379 598 78(3)
3.0(0)	1.102 989 76(−1)	9.318 551 99(0)	9.586 426 29(2)
3.5(0)	8.116 786 82(−2)	6.848 990 21(0)	7.045 710 14(2)
4.0(0)	6.221 414 15(−2)	5.245 141 15(0)	5.395 680 54(2)
4.5(0)	4.919 688 95(−2)	4.145 074 68(0)	4.263 965 10(2)
5.0(0)	3.987 377 65(−2)	3.357 961 90(0)	3.454 225 09(2)
6.0(0)	2.771 334 81(−2)	2.332 334 39(0)	2.399 142 35(2)
7.0(0)	2.037 178 27(−2)	1.713 740 27(0)	1.762 801 74(2)
8.0(0)	1.560 287 41(−2)	1.312 177 44(0)	1.349 728 00(2)

TABLE VI. van der Waals constants C_6, C_8, and $C_{10}=C^{(1)}_{10}+C^{(2)}_{10}$.

	Chan and Dalgarno (Ref. 10)	This work		
	1*s*-1*s*	1*s*-1*s*	1*s*-2*s*	2*s*-2*s*
C_6	6.499 05	6.500 82	56.7999	931.505
C_8	124.4	124.417	17 746.7	600 248.8
C_{10}	3285.5	3286.095	2 422 680	$2.473\,81\times 10^8$

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