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Retardation long-range potentials between two helium atoms

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The retardation long-range potentials between two 1 ^1S (or 2 ^3S) helium atoms are calculated. The complex dynamic multipole polarizabilities of 1 ^1S and 2 ^3S states of helium are obtained through a variation-perturbation approach with B-spline and Slater-type basis functions in a configuration-interaction scheme. They are used to calculate the retardation long-range potentials. The retardation coefficients are examined. Their relative magnitudes are different for different systems. The possibility of an excited state of helium dimer from the 1 ^1S–2 ^3S He$_2$ state is estimated.

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I. INTRODUCTION

The helium dimer has been a fascinating subject of research for several decades [1–14]. A good review of the theoretical works is given by Chalasiński and Gutowski [15]. It is only seen in the experiment recently [16]. The system is very weakly bound with the binding energy of about 1 mK. Theoretical calculations indicate that the zero-point energy is very close to the well depth of the potential. Hence, a very accurate potential is needed in order to predict correctly the binding energy of the helium dimer. One of the most sophisticated analytic He$_2$ potentials, the Hartree-Fock plus damped dispersion model [HFD-B2(HE)], is developed by Aziz and Slaman [17] using experimental data [18,19] as well as *ab initio* calculation results [20–22]. An important part of the potential is the van der Waal two-body dispersion coefficients C_n's ($n=6$, 8, and 10), i.e., the long-range potential, in the multipole expansion. The accuracy of these coefficients is very important in the prediction of the existence of the helium dimer. In addition, the influence of retardation on the long-range potential is also found to be very significant [23,24]. We will provide accurate data for the long-range part of the potential in the present work.

Recently, Jamieson *et al.* [25] have calculated the dominant long-range potential, the dipole-dipole dispersion interaction including retardation, for the ground-state heliums. Luo *et al.* [23,24] have shown that the influence of the retardation corrections for the higher-order dispersion terms is about an order of magnitude smaller than that of the leading dipole-dipole term. Hence, it is necessary to calculate the higher-order terms for more accurate determination and a complete description of the helium dimer potentials.

In this work, we will calculate the C_6, C_8, and C_{10} coefficients using two types of wave functions, the Slater orbitals, and B-spline basis function. The results of calculation will be compared with those in the literature. The retardation effect will also be calculated. In this work, the complex dynamic polarizability is calculated using a variation perturbation method [26,27]. Our purpose is to provide a set of highly accurate parameters for future refinement of the helium dimer potential. Since 2 ^3S state of helium has a long lifetime, it is possible that an excited state of helium dimer may be formed from the interaction of 1 ^1S and 2 ^3S. The range of higher multipole dispersion terms for excited heliums decreases slower than that for the ground-state heliums, so the influence of the dispersion terms and retardation on the binding energies on the excited helium is expected to be more significant. For these reasons we have also computed the dispersion coefficients of the 1 ^1S–2 ^3S and 2 ^3S–2 ^3S He$_2$ systems.

II. THEORY

For the long-range interactions between atoms, Casimir and Polder [28] have obtained the electric dipole interaction

$$V_{11}(R)=\frac{-1}{\pi R^6}\int_0^\infty d\omega\,\alpha_1^2(i\omega)\exp(-2\omega R/c)P_1(\omega R/c), \tag{1}$$

where P_1 is a polynomial given by

$$P_1(x)=x^4+2x^3+5x^2+6x+3, \tag{2}$$

and $\alpha_1(i\omega)$ is the dipole dynamic polarizability.

Au and Feinberg [29] generalized the electric dipole interaction to all electric and magnetic multipoles by using the method of Feinberg and Sucher [30]. They gave the electric multipole interactions as

$$V_{NM}(R)=-\frac{4}{\pi R(2N)!(2M)!}\frac{d^{2(N+M-2)}}{dR^{2(N+M-2)}}\times\left[\frac{1}{R^5}\int_0^\infty d\omega\,\alpha_N(i\omega)\alpha_M(i\omega)\times\exp(-2\omega R/c)P_1(\omega R/c)\right], \tag{3}$$

where $\alpha_N(i\omega)$ is the dynamic 2^N polarizability.

The retardation potentials between two helium atoms can be expressed [31,32] as follows:

$$V(R)=-\frac{C_6f_6(R)}{R^6}-\frac{C_8f_8(R)}{R^8}-\frac{C_{10}f_{10}(R)}{R^{10}}-\cdots, \tag{4}$$

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where R is the separation distance between the charge centers which is sufficiently large that the overlap of the two atoms' charge distributions can be neglected. C_6, C_8, and C_{10} are the dispersion coefficients. $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ are retardation coefficients. We have

$$C_6=\frac{3}{\pi}\int_0^\infty d\omega\alpha_1(i\omega)\alpha_1(i\omega), \tag{5}$$

$$C_8=\frac{15}{\pi}\int_0^\infty d\omega\alpha_1(i\omega)\alpha_2(i\omega), \tag{6}$$

$$C_{10}=\frac{14}{\pi}\int_0^\infty d\omega\alpha_1(i\omega)\alpha_3(i\omega)+\frac{35}{\pi}\int_0^\infty d\omega\alpha_2^2(i\omega), \tag{7}$$

and

$$f_6(R)=\frac{1}{\pi C_6}\int_0^\infty d\omega\alpha_1^2(i\omega)\exp(-2\omega R/c)P_1(\omega R/c), \tag{8}$$

$$f_8(R)=\frac{1}{3\pi C_8}\int_0^\infty d\omega\alpha_1(i\omega)\alpha_2(i\omega)\times\exp(-2\omega R/c)P_2(\omega R/c), \tag{9}$$

$$f_{10}(R)=\frac{1}{18\pi C_{10}}\int_0^\infty d\omega\left(\frac{4}{5}\alpha_1(i\omega)\alpha_3(i\omega)+\alpha_2^2(i\omega)\right)\times\exp(-2\omega R/c)P_3(\omega R/c), \tag{10}$$

where the polynomials P_2 and P_3 are given by

$$P_2(x)=2x^6+6x^5+19x^4+48x^3+84x^2+90x+45 \tag{11}$$

and

$$P_3(x)=2x^8+8x^7+32x^6+114x^5+333x^4+750x^3+1215x^2+1260x+630. \tag{12}$$

The long-range interactions between atoms can be calculated by evaluating the electric dynamic multipole polarizabilities at imaginary frequencies using the time-dependent variation-perturbation theory [33].

Let us consider a spherical symmetric atom which is placed in an oscillatory electromagnetic field of frequency ω and strength F. Its time-dependent Schrödinger equation is given as

$$i\frac{\partial}{\partial t}\Psi(\vec{r},t)=[H_0+V(\vec{r},t)]\Psi(\vec{r},t), \tag{13}$$

where H_0 is the unperturbed Hamiltonian in the nonrelativistic approximation. We expand the wave function Ψ in powers of field strength F,

$$\Psi(\vec{r},t)=\Psi_0(\vec{r},t)+\sum_{n=1}^{\infty}F^n\Psi_n(\vec{r},t). \tag{14}$$

The field-free Schrödinger equation is

$$H_0\psi_0(\vec{r})=E_0\psi_0(\vec{r}) \tag{15}$$

and the perturbation potential, $V(\vec{r},t)$, is given as

$$V(\vec{r},t)=F[\exp(i\omega t)+\exp(-i\omega t)]v(\vec{r}). \tag{16}$$

For a helium atom, $v(\vec{r})$ can be taken as z_1+z_2 in the electric dipole approximation.

In writing the time-dependent first-order perturbed wave function as

$$\Psi_1(\vec{r},t)=\psi_+^1(\vec{r})e^{i(\omega-E_0)t}+\psi_-^1(\vec{r})e^{-i(\omega+E_0)t}, \tag{17}$$

we have the first-order perturbation equation

$$(H_0-E_0+\omega)\psi_+^1+v(\vec{r})\psi_0=0, \tag{18}$$

$$(H_0-E_0-\omega)\psi_-^1+v(\vec{r})\psi_0=0. \tag{19}$$

The dynamic dipole polarizability [26,27,33,34] is

$$\alpha(\omega)=\alpha_{1+}(\omega)+\alpha_{1-}(\omega), \tag{20}$$

where

$$\alpha_{1\pm}(\omega)=\langle\psi_\pm^1(\vec{r})|H_0-E_0\pm\omega|\psi_\pm^1(\vec{r})\rangle. \tag{21}$$

Note that because of the definition of v in Eq. (16), the $\psi_\pm^1$ has an extra dimension of (electric field)$^{-1}$. $\alpha_{1\pm}$ has the same dimension [(energy)/(field)^2] as that of the static polarizability. The dynamic 2^l polarizabilities (α_l) for $l>1$ are defined the same as in Eqs. (20) and (21) except the perturbation $v(\vec{r})$ becomes

$$v(\vec{r})=r_1^lY_{l,0}(\vec{r_1})+r_2^lY_{l,0}(\vec{r_2}), \tag{22}$$

where $Y_{l,0}$ is the spherical harmonics.

We calculate the dynamic multipole polarizabilities at imaginary frequencies by solving the first-order perturbation equations [Eqs. (18) and (19)] to obtain $\psi_\pm^l$ with the variation-perturbation method [35], minimizing the functional

$$\langle\psi_\pm^1(\vec{r})|H_0-E_0\pm\omega|\psi_\pm^1(\vec{r})\rangle+2\langle\psi_\pm^1(\vec{r})|v(\vec{r})|\psi_0(\vec{r})\rangle. \tag{23}$$

III. COMPUTATIONAL ASPECT

We construct the unperturbed ψ_0 and the perturbed wave functions $\psi_\pm^l$, with B-spline basis functions and Slater-type basis functions in the configuration-interaction scheme.

In the present work, eight angular partial waves are used to determine the $1\,^1S$ and $2\,^3S$ unperturbed wave functions with B-spline basis functions. As in our previous work [36], the B-spline basis functions are defined in terms of the order K and the total number N between the two end points $r_{\min}=0$ and $r_{\max}=R$. The orders of the B-spline basis functions in this work are either 9 or 10. We obtained the nonrelativistic energies, −2.903 654 94 a.u. for $1\,^1S$ and −2.175 229 16 a.u. for $2\,^3$S. The most accurate nonrelativistic energies are −2.903 724 377 034 1 a.u. for $1\,^1S$ and −2.175 229 378 2 a.u. for $2\,^3S$ at present [37,38]. Our

TABLE I. Static multipole polarizabilities for 1 ^1S and 2 ^3S He (in a.u.).

	1 ^1S			2 ^3S		
	α_1	α_2	α_3	α_1	α_2	α_3
This work (*B* spline)	1.38328	2.44549	10.6237	315.630	2707.89	88377.4
This work (Slater)	1.38327	2.44566	10.6252	315.611	2707.81	88356.2
Bishop & Pipin [41,42]	1.383192	2.445083	10.620360	315.631	2707.85	88377.2
Caffarel *et al.* [39,40]	1.3827	2.4066	10.36	315.92	2662.02	–
Thakkar [21]	1.38312	2.44344	10.6144	–	–	–
Chung & Hurst [45]	1.384			315.63		

present results are better than our previous ones [36], which were calculated with less partial waves or less basis functions. The R is 30 a.u. as before [36]. We use seven partial waves for the perturbed wave functions of P, D, and F symmetries. The number of basis functions and partial waves are sufficiently large to ensure the static and dynamic multipole polarizabilities (at imaginary frequencies) converged to within an uncertainty of 0.003% for dipole polarizability, and at least 0.007% for quadrupole and octupole polarizabilities.

By constructing the radial wave functions with Slater-type basis functions, we used 7 and 8 partial waves to obtain the 1 ^1S and 2 ^3S unperturbed wave functions, respectively. The energies are $-2.903\,630\,92$ a.u. and $-2.175\,229\,09$ a.u. The perturbed wave functions of P, D, and F symmetries are calculated with 7, 8, and 9 partial waves, respectively. The convergence of the multipole polarizability calculation for Slater function is similar to that of the B-spline basis function calculation.

The convergence of the dynamic multipole polarizabilities at imaginary frequencies is similar to those of the corresponding static polarizabilities. The values of $\alpha_1(i\omega)$, $\alpha_2(i\omega)$, and $\alpha_3(i\omega)$ decrease monotonically as ω increases. They are 10^{-6} smaller than the corresponding static polarizabilities for ω up to 1500 a.u. In calculating the integrals for the dispersion coefficients C_6, C_8, and C_{10} and the retardation coefficients f_6, f_8, and f_{10} we divide the range $\omega = 0$ to 1500 a.u. into hundreds of sections and carry out the integral by 32-point and 64-point Gauss-Legendre integrations in each section. These results are converged to about 5 digits.

IV. RESULTS AND DISCUSSION

The static multipole polarizability results are given in Table I and they are compared with others in the literature [21,39–42]. Our results, which are calculated with B-spline and Slater-type basis functions, agree with each other to about 4–5 digits except for α_3 of 2 ^3S He. The agreement of α_l tends to be better for smaller l and for 1 ^1S He. The results show that the agreement does not depend sensitively on the energy of ψ_0. Our polarizabilities agree very well with those of Bishop and Pipin [41,42], especially for smaller l. For 2 ^3S He, our B-spline results agree closely with those of Bishop and Pipin.

In Table II, we compare the results for C_6, C_8, and C_{10} with the existing results in the literature. Our two sets of

TABLE II. Comparison of dispersion coefficients of helium dimer potentials (in a.u.).

State	Author (Ref.)	C_6	C_8	C_{10}
1 ^1S–1 ^1S	Thakkar [21]	1.46082	14.1118	183.600
	Bishop & Pipin [41,42]	1.4609778	1.4117855[1]	1.8369125[2]
	Davison [46]	1.4586	1.4094[1]	
	Glover & Weinhold [47]	1.4610		
	Luyckx *et al.* [48]	1.458	1.406[1]	1.822[2]
	Bartolotti [49]	1.4638	1.4131[1]	1.8347[2]
	Jamieson *et al.* [25]	1.46098		
	This work (*B* spline)	1.46108	1.41202[1]	1.83744[2]
	This work (Slater orbital)	1.46106	1.41208[1]	1.83765[2]
1 ^1S–2 ^3S	Bishop & Pipin [41,42]	2.9082914[1]	1.7002700[3]	1.3638030[5]
	Glover & Weinhold [47]	2.906[1]		
	This work (*B* spline)	2.90710[1]	1.70051[3]	1.36399[5]
	This work (Slater orbital)	2.90680[1]	1.70047[3]	1.36382[5]
2 ^3S–2 ^3S	Bishop & Pipin [41,42]	3.2766770[3]	2.1056399[5]	2.1786484[7]
	Glover & Weinhold [47]	3.268[3]		
	This work (*B* spline)	3.27610[3]	2.10518[5]	2.17838[7]
	This work (Slater orbital)	3.27590[3]	2.10507[5]	2.17802[7]

TABLE III. Retardation coeffiients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for 1 ^1S–1 ^1S He$_2$ [with *B*-spline basis functions and with Slater-type basis functions. f_i's are from *B*-spline calculation and $\Delta f_i = f_i(B\text{ spline}) - f_i(\text{Slater})$].

R	f_6	f_8	f_{10}	Δf_6	Δf_8	Δf_{10}
1.0[0]	9.99976[−1]	9.99989[−1]	9.99993[−1]	1.8[−8]	−5.3[−8]	1.3[−8]
1.5[0]	9.99947[−1]	9.99975[−1]	9.99985[−1]	1.6[−8]	−2.4[−8]	1.3[−8]
2.0[0]	9.99906[−1]	9.99955[−1]	9.99973[−1]	4.9[−8]	1.0[−9]	1.7[−8]
2.5[0]	9.99855[−1]	9.99930[−1]	9.99958[−1]	6.5[−8]	1.7[−8]	2.2[−8]
3.0[0]	9.99792[−1]	9.99900[−1]	9.99940[−1]	1.0[−7]	3.5[−8]	2.5[−8]
5.0[0]	9.99440[−1]	9.99727[−1]	9.99835[−1]	2.2[−7]	1.0[−7]	5.4[−8]
7.0[0]	9.98931[−1]	9.99474[−1]	9.99680[−1]	4.1[−7]	1.6[−7]	1.0[−7]
1.0[1]	9.97903[−1]	9.98951[−1]	9.99358[−1]	7.8[−7]	3.7[−7]	1.8[−7]
1.5[1]	9.95560[−1]	9.97726[−1]	9.98595[−1]	1.2[−6]	7.7[−7]	4.2[−7]
2.0[1]	9.92539[−1]	9.96102[−1]	9.97567[−1]	2.0[−6]	1.2[−6]	7.0[−7]
2.5[1]	9.88946[−1]	9.94118[−1]	9.96295[−1]	2.9[−6]	1.7[−6]	1.0[−6]
3.0[1]	9.84864[−1]	9.91811[−1]	9.94798[−1]	3.5[−6]	2.4[−6]	1.5[−6]
5.0[1]	9.64894[−1]	9.79934[−1]	9.86873[−1]	5.2[−6]	4.2[−6]	2.9[−6]
7.0[1]	9.41168[−1]	9.64891[−1]	9.76462[−1]	5.5[−6]	4.9[−6]	4.0[−6]
1.0[2]	9.02242[−1]	9.38576[−1]	9.57531[−1]	5.7[−6]	4.6[−6]	3.9[−6]
1.5[2]	8.35593[−1]	8.89761[−1]	9.20580[−1]	5.4[−6]	3.1[−6]	2.5[−6]
2.0[2]	7.71989[−1]	8.39414[−1]	8.80433[−1]	4.8[−6]	2.0[−6]	−5.6[−7]
2.5[2]	7.13666[−1]	7.90330[−1]	8.39555[−1]	4.1[−6]	6.6[−7]	−2.6[−6]
3.0[2]	6.61086[−1]	7.43817[−1]	7.99359[−1]	3.7[−6]	−4.9[−7]	−3.4[−6]
5.0[2]	5.00792[−1]	5.89422[−1]	6.56525[−1]	1.7[−6]	−3.5[−6]	−8.7[−6]
7.0[2]	3.96750[−1]	4.79419[−1]	5.46468[−1]	1.3[−6]	−4.4[−6]	−1.0[−5]
1.0[3]	2.98697[−1]	3.68982[−1]	4.29425[−1]	7.0[−7]	−4.6[−6]	−1.0[−5]
1.5[3]	2.08968[−1]	2.62541[−1]	3.10808[−1]	3.5[−7]	−4.0[−6]	−8.2[−6]
2.0[3]	1.59781[−1]	2.02249[−1]	2.41338[−1]	2.3[−7]	−3.3[−6]	−6.8[−6]
2.5[3]	1.29046[−1]	1.63977[−1]	1.96495[−1]	1.8[−7]	−2.8[−6]	−5.6[−6]
3.0[3]	1.08114[−1]	1.37685[−1]	1.65399[−1]	1.3[−7]	−2.5[−6]	−4.8[−6]
5.0[3]	6.53901[−2]	8.35622[−2]	1.00771[−1]	1.2[−7]	−1.5[−6]	−3.0[−6]
7.0[3]	4.68129[−2]	5.98817[−2]	7.22959[−2]	4.6[−8]	−1.1[−6]	−2.2[−6]
1.0[4]	3.28088[−2]	4.19905[−2]	5.07269[−2]	3.1[−8]	−7.6[−7]	−1.5[−6]
1.5[4]	2.18867[−2]	2.80199[−2]	3.38609[−2]	2.1[−8]	−5.1[−7]	−1.0[−6]
2.0[4]	1.64188[−2]	2.10219[−2]	2.54070[−2]	1.5[−8]	−3.8[−7]	−7.6[−7]
2.5[4]	1.31364[−2]	1.68201[−2]	2.03298[−2]	1.3[−8]	−3.1[−7]	−6.1[−7]
3.0[4]	1.09476[−2]	1.40179[−2]	1.69434[−2]	1.0[−8]	−2.6[−7]	−5.0[−7]
5.0[4]	6.56913[−3]	8.41175[−3]	1.01677[−2]	6.1[−9]	−1.5[−7]	−2.9[−7]
7.0[4]	4.69234[−3]	6.00859[−3]	7.26298[−3]	4.2[−9]	−1.1[−7]	−2.1[−7]
1.0[5]	3.28468[−3]	4.20609[−3]	5.08421[−3]	3.0[−9]	−7.7[−8]	−1.5[−7]
1.5[5]	2.18980[−3]	2.80408[−3]	3.38952[−3]	2.0[−9]	−5.1[−8]	−1.0[−7]
2.0[5]	1.64236[−3]	2.10307[−3]	2.54215[−3]	1.5[−9]	−3.9[−8]	−7.1[−8]
2.5[5]	1.31389[−3]	1.68246[−3]	2.03373[−3]	1.2[−9]	−3.1[−8]	−5.6[−8]

results agree with each other to about 4–5 digits for the 1 ^1S and 1 ^1S–2 ^3S helium dimers but only 4 digits for the 2 ^3S helium dimer. For C_6 of the 1 ^1S helium dimer, the results of Glover and Weinhold [47], Bishop and Pipin [41,42], and Jamieson *et al.* [25] all agree closely with ours. For others, the results from Bishop and Pipin [41,42] are the closest to ours. They differ by no more than 1 at the fourth digit.

In Tables III–V, we show the retardation coefficients f_n ($n=6$, 8, and 10) calculated from *B*-spline basis functions, and the difference, Δf_n, between those of the *B*-spline and Slater-type basis functions for every separation R. In Table III, the retardation corrections become smaller with increasing n for 1 ^1S He$_2$ as in Luo *et al.* [24]. The differences between our *B*-spline and Slater-function results are 10^{-8} when R is a few bohr radii, and they increase to 10^{-6} at $R \leqslant 20$ a.u. But, this difference decreases monotonically when R is larger than a few hundreds of bohr radii. We also find the differences in percentage become a constant at large R, and they are larger for larger n. Jamieson *et al.* [25] have calculated f_6 with Hylleraas basis functions and expressed the dynamic dipole polarizability with oscillator strengths for ground-state helium atoms. Our results agree with their results [25] in the first 6–4 digits as R increases from 0 to 10^5 a.u.

In Table IV, we show the retardation coefficients for 1 ^1S–2 ^3S He$_2$. The coefficient f_6 is smaller than f_8 at $R \leqslant 3\times 10^2$ a.u. f_6 and f_8 are smaller than f_{10} at

TABLE IV. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for $1\ {}^1S\text{–}2\ {}^3S$ He_2 [with B-spline basis functions and with Slater-type basis functions. f_i's are from B-spline calculation and $\Delta f_i = f_i(B\text{-spline}) - f_i(\text{Slater})$].

R	f_6	f_8	f_{10}	Δf_6	Δf_8	Δf_{10}
1.0[1]	9.99847[−1]	9.99904[−1]	9.99930[−1]	−1[−7]	−5[−8]	−5[−8]
1.5[1]	9.99670[−1]	9.99787[−1]	9.99846[−1]	−2[−7]	−4[−8]	−2.4[−8]
2.0[1]	9.99437[−1]	9.99629[−1]	9.99729[−1]	−3[−7]	−3[−8]	−1.0[−8]
2.5[1]	9.99153[−1]	9.99431[−1]	9.99581[−1]	−6[−7]	−2[−8]	2[−9]
3.0[1]	9.98823[−1]	9.99194[−1]	9.99405[−1]	−9[−7]	−1[−8]	2.7[−8]
5.0[1]	9.97122[−1]	9.97905[−1]	9.98426[−1]	−2.4[−6]	−3[−9]	1.5[−7]
7.0[1]	9.94946[−1]	9.96136[−1]	9.97051[−1]	−3.5[−6]	−5[−8]	3.0[−7]
1.0[2]	9.91057[−1]	9.92744[−1]	9.94354[−1]	−8.2[−6]	−2[−7]	5.0[−7]
1.5[2]	9.83511[−1]	9.85577[−1]	9.88476[−1]	−1.5[−5]	−5.3[−7]	8.6[−7]
2.0[2]	9.75200[−1]	9.77037[−1]	9.81257[−1]	−2.2[−5]	−9.0[−7]	1.3[−6]
2.5[2]	9.66493[−1]	9.67541[−1]	9.73029[−1]	−2.8[−5]	−1.2[−6]	1.7[−6]
3.0[2]	9.57598[−1]	9.57379[−1]	9.64040[−1]	−3.3[−5]	1.5[−6]	2.3[−6]
5.0[2]	9.22034[−1]	9.13514[−1]	9.23678[−1]	−4.7[−5]	−2.6[−6]	4.5[−6]
7.0[2]	8.88154[−1]	8.68779[−1]	8.80728[−1]	−5.4[−5]	−2.9[−6]	6.8[−6]
1.0[3]	8.41495[−1]	8.05080[−1]	8.17587[−1]	−5.8[−5]	−3.3[−6]	1.0[−5]
1.5[3]	7.73764[−1]	7.12219[−1]	7.22976[−1]	−5.8[−5]	−3.0[−6]	1.2[−5]
2.0[3]	7.16081[−1]	6.35282[−1]	6.43279[−1]	−5.5[−5]	−2.5[−6]	1.7[−5]
2.5[3]	6.66189[−1]	5.71461[−1]	5.76714[−1]	−5.0[−5]	−2.0[−6]	1.9[−5]
3.0[3]	6.22502[−1]	5.18082[−1]	5.20918[−1]	−4.7[−5]	−1.6[−6]	2.0[−5]
5.0[3]	4.90766[−1]	3.72781[−1]	3.69510[−1]	−3.3[−5]	−5[−7]	2.0[−5]
7.0[3]	4.02408[−1]	2.88495[−1]	2.82749[−1]	−2.5[−5]	−8[−8]	1.7[−5]
1.0[4]	3.14275[−1]	2.13953[−1]	2.07230[−1]	−1.8[−5]	1.8[−7]	1.4[−5]
1.5[4]	2.27662[−1]	1.48546[−1]	1.42270[−1]	−1.1[−5]	3.3[−7]	1.0[−5]
2.0[4]	1.77248[−1]	1.13381[−1]	1.07951[−1]	−7.9[−6]	3.4[−7]	8.1[−6]
2.5[4]	1.44626[−1]	9.15375[−2]	8.68589[−2]	−6.2[−6]	3.2[−7]	2.5[−6]
3.0[4]	1.21926[−1]	7.66893[−2]	7.26185[−2]	−5.0[−6]	2.9[−7]	5.5[−6]
5.0[4]	7.45031[−2]	4.64024[−2]	4.37875[−2]	−3.1[−6]	2.1[−7]	3.3[−6]
7.0[4]	5.35039[−2]	3.32270[−2]	3.13212[−2]	−2.0[−6]	1.5[−7]	2.4[−6]
1.0[5]	3.75627[−2]	2.32905[−2]	2.19417[−2]	−1.4[−6]	1.1[−7]	1.7[−6]
1.5[5]	2.50815[−2]	1.55384[−2]	1.46339[−2]	−9.3[−7]	7.5[−8]	1.2[−6]
2.0[5]	1.88216[−2]	1.16568[−2]	1.09770[−2]	−6.9[−7]	5.7[−8]	8.4[−7]
2.5[5]	1.50611[−2]	9.32657[−3]	8.78219[−3]	−5.6[−7]	4.5[−8]	6.8[−7]
3.0[5]	1.25526[−2]	7.77265[−3]	7.31876[−3]	−4.6[−7]	3.8[−8]	5.6[−7]
5.0[5]	7.53306[−3]	4.66402[−3]	4.39149[−3]	−2.7[−7]	2.3[−8]	3.4[−7]
7.0[5]	5.38103[−3]	3.33153[−3]	3.13682[−3]	−2.0[−7]	1.6[−8]	2.4[−7]
1.0[6]	3.76682[−3]	2.33210[−3]	2.19579[−3]	−1.5[−7]	1.1[−8]	1.7[−7]
1.5[6]	2.51124[−3]	1.55474[−3]	1.46387[−3]	−9.2[−8]	7[−9]	1.1[−7]
2.0[6]	1.88344[−3]	1.16606[−3]	1.09790[−3]	−6.9[−8]	5[−9]	8.5[−8]
2.5[6]	1.50675[−3]	9.32850[−4]	8.78322[−4]	−5.6[−8]	4.5[−9]	6.8[−8]
3.0[6]	1.25563[−3]	7.77375[−4]	7.31936[−4]	−4.7[−8]	3.9[−9]	5.6[−8]
5.0[6]	7.53377[−4]	4.66425[−4]	4.39162[−4]	−2.8[−8]	2.3[−9]	3.4[−8]

$R \leqslant 7\times10^2$ a.u. As R increases, we have the relation $f_6 > f_{10} > f_8$. For the retardation coefficients of $2\ {}^3S$ He_2, we have $f_6 > f_8 \geqslant f_{10}$ for all R as shown in Table V. The relation among f_n of $1\ {}^1S\text{–}2\ {}^3S$ He_2 is similar to that of $1\ {}^1S$ He_2 at smaller R and that of $2\ {}^3S$ He_2 at larger R. The influence of retardation corrections on the binding energy of the $1\ {}^1S\text{–}2\ {}^3S$ He_2 (or $2\ {}^3S$ He_2) is different from that of the $1\ {}^1S$ helium dimer.

The retardation corrections for $1\ {}^1S\text{–}2\ {}^3S$ and $2\ {}^3S$ He_2 potential are smaller than those for $1\ {}^1S$ He_2. At large internuclear separations, the coefficients f_6, f_8, and f_{10} for the $1\ {}^1S\text{–}2\ {}^3S$ He_2 are 11.4, 5.5, and 4.3 times as large as those for $1\ {}^1S$ He_2 (in the case of $2\ {}^3S$ He_2, they are 29, 21, and 18 times). We therefore expect an excited state of helium dimer from $1\ {}^1S\text{–}2\ {}^3S$ state very likely. Although we did not calculate the binding energy of $1\ {}^1S\text{–}2\ {}^3S$ helium dimer, we can say its binding energy will be much larger than that of $1\ {}^1S$ He_2 based on the result of the long-range potential.

In examing the retardation coefficients f_n at large distances, we find $f_n(R) \propto R^{-1}$ as $n=6$ at $R \geqslant 3\times10^3$ a.u., $n=8$ at $R \geqslant 5\times10^3$ a.u., $n=10$ at $R \geqslant 7\times10^3$ a.u. for the $1\ {}^1S$ helium dimer, as $n=6$ at $R \geqslant 2.5\times10^4$ a.u., and as $n=8$ or

TABLE V. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for 2 ^3S–2 ^3S He$_2$ [with B-spline basis functions and with Slater-type basis functions, f_i's are from B-spline calculation. $\Delta f_i = f_i(B$ spline) $- f_i$ (Slater)].

R	f_6	f_8	f_{10}	Δf_6	Δf_8	Δf_{10}
1.0[1]	9.99995[−1]	9.99995[−1]	9.99995[−1]	−4[−9]	6[−9]	−1.6[−8]
1.5[1]	9.99988[−1]	9.99988[−1]	9.99989[−1]	1[−10]	4[−9]	6[−9]
2.0[1]	9.99980[−1]	9.99979[−1]	9.99981[−1]	−5[−9]	1[−10]	4[−9]
2.5[1]	9.99968[−1]	9.99968[−1]	9.99971[−1]	−1.4[−8]	−4[−9]	3[−9]
3.0[1]	9.99955[−1]	9.99954[−1]	9.99958[−1]	−2.2[−8]	−1.0[−8]	1[−9]
5.0[1]	9.99879[−1]	9.99874[−1]	9.99885[−1]	−7.1[−8]	−4.1[−8]	−9[−9]
7.0[1]	9.99770[−1]	9.99758[−1]	9.99777[−1]	−1.4[−7]	−9.0[−8]	−2.5[−8]
1.0[2]	9.99548[−1]	9.99517[−1]	9.99553[−1]	−2.6[−7]	−1.8[−7]	−6.0[−8]
1.5[2]	9.99036[−1]	9.98953[−1]	9.99022[−1]	−5.0[−7]	−3.8[−7]	−1.4[−7]
2.0[2]	9.98360[−1]	9.98201[−1]	9.98307[−1]	−7.4[−7]	−6.9[−7]	−2.3[−7]
2.5[2]	9.97537[−1]	9.97276[−1]	9.97422[−1]	−1.0[−6]	−8.8[−7]	−3.4[−7]
3.0[2]	9.96578[−1]	9.96193[−1]	9.96377[−1]	−1.2[−6]	−1.1[−6]	−4.4[−7]
5.0[2]	9.91581[−1]	9.90496[−1]	9.90812[−1]	−1.9[−6]	−2.2[−6]	−8.3[−7]
7.0[2]	9.85076[−1]	9.83038[−1]	9.83421[−1]	−2.3[−6]	−3.1[−6]	−1.0[−6]
1.0[3]	9.73229[−1]	9.69448[−1]	9.69788[−1]	−2.4[−6]	−4.1[−6]	−1.0[−6]
1.5[3]	9.49760[−1]	9.42661[−1]	9.42581[−1]	−1.7[−6]	−4.8[−6]	−2.7[−7]
2.0[3]	9.23562[−1]	9.13069[−1]	9.12257[−1]	−4.6[−7]	−4.8[−6]	1.1[−6]
2.5[3]	8.96032[−1]	8.82347[−1]	8.80643[−1]	1.1[−6]	−4.3[−6]	2.7[−6]
3.0[3]	8.68040[−1]	8.51501[−1]	8.48865[−1]	2.7[−6]	−3.6[−6]	4.5[−6]
5.0[3]	7.60125[−1]	7.35907[−1]	7.30399[−1]	8.7[−6]	3.0[−7]	1.1[−5]
7.0[3]	6.66338[−1]	6.39080[−1]	6.32598[−1]	1.3[−5]	3.6[−6]	1.9[−5]
1.0[4]	5.54100[−1]	5.26671[−1]	5.20806[−1]	1.6[−5]	6.6[−6]	1.8[−5]
1.5[4]	4.24502[−1]	4.00399[−1]	3.96748[−1]	1.7[−5]	8.2[−6]	1.9[−5]
2.0[4]	3.40091[−1]	3.19626[−1]	3.17641[−1]	1.5[−5]	8.2[−6]	1.7[−5]
2.5[4]	2.82054[−1]	2.64579[−1]	2.63597[−1]	1.4[−5]	7.7[−6]	1.6[−5]
3.0[4]	2.40184[−1]	2.25055[−1]	2.24656[−1]	1.3[−5]	7.0[−6]	1.4[−5]
5.0[4]	1.49231[−1]	1.39596[−1]	1.39917[−1]	8.5[−6]	4.9[−6]	1.0[−5]
7.0[4]	1.07722[−1]	1.00720[−1]	1.01104[−1]	6.4[−6]	3.7[−6]	7.2[−6]
1.0[5]	7.58433[−2]	7.08955[−2]	7.12306[−2]	4.5[−6]	2.7[−6]	5.2[−6]
1.5[5]	5.07215[−2]	4.74066[−2]	4.76554[−2]	3.0[−6]	1.8[−6]	3.4[−6]
2.0[5]	3.80832[−2]	3.55928[−2]	3.57864[−2]	2.3[−6]	1.4[−6]	2.6[−6]
2.5[5]	3.04821[−2]	2.84883[−2]	2.86458[−2]	1.8[−6]	1.1[−6]	2.1[−6]
3.0[5]	2.54087[−2]	2.37465[−2]	2.38791[−2]	1.5[−6]	9.0[−7]	1.75[−6]
5.0[5]	1.52512[−2]	1.42534[−2]	1.43340[−2]	9.2[−7]	5.4[−7]	1.05[−6]
7.0[5]	1.08948[−2]	1.01820[−2]	1.02398[−2]	6.5[−7]	3.9[−7]	7.5[−7]
1.0[6]	7.62674[−3]	7.12778[−3]	7.16831[−3]	4.6[−7]	2.7[−7]	5.3[−7]
1.5[6]	5.08462[−3]	4.75198[−3]	4.77903[−3]	3.1[−7]	1.8[−7]	3.5[−7]
2.0[6]	3.81349[−3]	3.56401[−3]	3.58431[−3]	2.3[−7]	1.4[−7]	2.6[−7]
2.5[6]	3.05080[−3]	2.85122[−3]	2.86746[−3]	1.8[−7]	1.1[−7]	2.1[−7]
3.0[6]	2.54234[−3]	2.37602[−3]	2.38955[−3]	1.5[−7]	9.1[−8]	1.6[−7]
5.0[6]	1.52540[−3]	1.42561[−3]	1.43374[−3]	8.8[−8]	5.8[−8]	1.06[−7]

10 at $R \geqslant 2\times10^4$ a.u. for the 1 ^1S–2 ^3S helium dimer, and as $n=6$ at $R \geqslant 7\times10^4$ a.u. and as $n=8$ or 10 at $R \geqslant 5\times10^4$ a.u. for the 2 ^3S helium dimer. It is interesting that R is smaller if f_n is smaller at large distances.

At small internuclear distances, the retardation potential can be expanded as [32]

$$C_6 f_6(R) = C_6 - (R/c)^2 W_4 + \cdots, \tag{24}$$

where

$$W_4 = \frac{1}{\pi}\int_0^\infty d\omega\, \alpha_1^2(i\omega)\,\omega^2, \tag{25}$$

$$C_8 f_8(R) = C_8 - (R/c)^2 W_6 + \cdots, \tag{26}$$

where

$$W_6(R) = \frac{2}{\pi}\int_0^\infty d\omega\, \alpha_1(i\omega)\,\alpha_2(i\omega)\,\omega^2 \tag{27}$$

and

TABLE VI. Coefficients W_4, W_6, and W_8 (in a.u.).

	W_4	W_6	W_8
1^1S-1^1S	6.6284[−1]	3.0174[0]	2.3442[1]
$1\ ^1S$–$2\ ^3S$	9.2558[−1]	3.2057[1]	1.8322[3]
$2\ ^3S$–$2\ ^3S$	3.3006[0]	2.0945[2]	1.94835[4]

$$C_{10}f_{10}(R)=C_{10}-(R/c)^2W_8+\cdots, \tag{28}$$

where

$$W_8=\frac{5}{2\pi}\int_0^\infty d\omega\left(\frac{4}{5}\alpha_1(i\omega)\alpha_3(i\omega)+\alpha_2^2(i\omega)\right)\omega^2. \tag{29}$$

Marinescu *et al.* [32] have pointed out that the term W_4 can be obtained from the Breit-Pauli relativistic orbit-orbit term [43], and the terms W_6 and W_8 can also be obtained from the higher electric multipoles in a similar analysis of the Breit equation [43] or along the lines of Hessels' work for Rydberg states of He [44] .

We have also calculated the coefficients W_4, W_6, and W_8, with B-spline basis functions. They are given in Table VI. In checking the expansion $f_n=1-(R/c)^2W_n/C_n$ with the data of Tables III, IV, and V, we find that it is a good approximation for f_6 at R $\leqslant 10$ a.u., for f_8 at R $\leqslant 15$ a.u., and for f_{10} at R $\leqslant 20$ a.u. for the 1 ^1S helium dimer. It is also a good approximation for f_6 at $R\leqslant 20$ a.u., f_8 at $R\leqslant$ 30 a.u., and f_{10} at $R\leqslant 50$ a.u. for the 1 ^1S–2 ^3S helium dimer. For the 2 ^3S helium dimer, it is a good approximation for f_6 at $R\leqslant 70$ a.u., f_8 at $R\leqslant 150$ a.u., and f_{10} at $R\leqslant 200$ a.u. The values of W_n/C_n decrease as n increases.

It appears that the retardation effects decrease as n increases and Eqs. (25), (27), and (29) are good approximations at small internuclear distances for the 1 ^1S and 1 ^1S–2 ^3S helium dimers. We also find the retardation effects decrease as n increases for the 2 ^3S helium dimer at $R\leqslant 3.0$ a.u. For example, they are 0.999 999 88, 0.999 999 885, and 0.999 999 893 at $R=1.5$ a.u. and 0.999 999 524, 0.999 999 525, and 0.999 999 573 at $R=3.0$ a.u. for f_6, f_8, and f_{10}, respectively. However, as the distance increases, the relative magnitude of the retardation coefficients are different for different systems, e.g., they are $f_6<f_8<f_{10}$ for the 1 ^1S helium dimer, $f_6>f_8>f_{10}$ for the 1 ^1S–2 ^3S helium dimer, and $f_6<f_{10}<f_8$ for the 2 ^3S helium dimer. It appears that the retardation effects at intermediate and large internuclear distances depend sensitively on the structure of the system.

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