Retarded dipole-dipole dispersion interaction potential for helium

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The retarded dipole-dipole dispersion interaction potential in helium is evaluated from a set of very accurate effective dipole transition frequencies and oscillator strengths already obtained from a variational calculation. The asymptotic form changes from the inverse sixth to the inverse seventh power of the nuclear separation as the atoms move apart. Simple representations of the potential are given for use in scattering and structure calculations.

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INTRODUCTION

Two widely separated atoms influence each other mainly through the long-range dipole-dipole dispersion interaction. In the absence of relativistic corrections, the interaction potential varies asymptotically as R^{-6} where R is the internuclear distance. When the atoms are sufficiently far apart that the time for an electromagnetic signal to travel from one to the other is comparable to the period of the lowest allowed dipole transition of either, retardation must be taken into account and the asymptotic variation of the potential becomes R^{-7}. The relativistic expression for the potential was first given by Casimir and Polder [1]. Retardation is a very small long-range effect. It is negligible in scattering calculations and unobservable in experiments at temperatures greater than a few degrees K. However, the rapidly expanding experimental field of ultra-low-temperature scattering measurements [2–9] may lead to detectable effects and has introduced the need for very low energy scattering and structure calculations which include retardation; a recent low-temperature experiment involving helium may be the first direct observation of retardation effects in neutral atom interactions [10]. The retarded potential for a pair of ground-state helium atoms has been calculated by Getzin and Karplus [11], Langhoff [12], and Luo *et al.* [13], using approximate dynamic polarizability data [14]. Below we present details of a very accurate calculation of the retarded potential for a pair of ground-state helium atoms, based on recent precise values of the polarizability [15].

CALCULATIONS

In atomic units (a.u.), which will be used throughout, the potential $V(R)$ is [1,13]

$$V(R) = -\frac{1}{R^6}\frac{1}{\pi}\int_0^\infty du\,\beta^2(iu)e^{-2uR\alpha}$$

$$\times[(uR\alpha)^4 + 2(uR\alpha)^3 + 5(uR\alpha)^2$$

$$+ 6uR\alpha + 3]\,,$$

where $\beta(iu)$ is the dipole polarizability at the imaginary frequency iu and $\alpha = 1/137.035\,9895$ is the fine structure constant. The value of $\beta(iu)$ was obtained by analytically continuing the expression for the dynamic polarizability $\beta(\omega)$, at frequency ω, in terms of a set of N effective dipole transition frequencies ω_i and oscillator strengths f_i which were obtained from a very precise variational calculation of Drake [15]

$$\beta(\omega) = \sum_{i=1}^{N}\frac{f_i}{\omega_i^2 - \omega^2}\,,$$

where $N = 197$ in these calculations. The method yields a lower bound to the magnitude of $V(R)$.

At small values of R

$$V(R) \approx \frac{-C_6}{R^6}\,,$$

where

$$C_6 = \frac{3}{\pi}\int_0^\infty du\,\beta^2(iu)\,.$$

At large values of R

$$V(R) \approx \frac{-C_7}{R^7}\,,$$

where

$$C_7 = \frac{23\beta^2(0)}{4\pi\alpha}\,.$$

With the variable of integration changed to $x = 2uR\alpha$, the potential is

BRIEF REPORTS

TABLE I. Retarded dipole-dipole dispersion interaction potential in helium.

R (bohr)	$-V(R)R^6/C_6$	$-V(R)R^7/C_7$	R (bohr)	$-V(R)R^6/C_6$	$-V(R)R^7/C_7$
0.0	1.000 000 0	0.000 000 0	0.2	0.999 999 0	0.000 608 9
0.4	0.999 996 2	0.001 217 8	0.6	0.999 991 4	0.001 826 7
0.8	0.999 984 7	0.002 435 6	1.0	0.999 976 2	0.003 044 5
1.2	0.999 965 8	0.003 653 4	1.4	0.999 953 7	0.004 262 2
1.6	0.999 939 7	0.004 871 0	1.8	0.999 923 9	0.005 479 8
2.0	0.999 906 3	0.006 088 6	2.2	0.999 886 9	0.006 697 3
2.4	0.999 865 9	0.007 306 0	2.6	0.999 843 0	0.007 914 6
2.8	0.999 818 5	0.008 523 2	3.0	0.999 792 3	0.009 131 8
3.5	0.999 719 3	0.010 653 0	4.0	0.999 636 0	0.012 173 8
4.5	0.999 542 6	0.013 694 3	5.0	0.999 439 3	0.015 214 3
6.0	0.999 203 7	0.018 252 9	7.0	0.998 930 8	0.021 289 2
8.0	0.998 621 9	0.024 323 0	9.0	0.998 278 4	0.027 354 0
10.0	0.997 901 6	0.030 381 8	20.0	0.992 536 4	0.060 436 9
30.0	0.984 859 1	0.089 954 2	40.0	0.975 495 2	0.118 798 5
50.0	0.964 886 7	0.146 883 3	60.0	0.953 359 0	0.174 154 1
70.0	0.941 158 8	0.200 579 7	80.0	0.928 476 5	0.226 145 0
90.0	0.915 461 5	0.250 846 8	100.0	0.902 231 8	0.274 690 8
110.0	0.888 881 6	0.297 688 9	120.0	0.875 486 5	0.319 857 6
130.0	0.862 106 9	0.341 216 8	140.0	0.848 791 7	0.361 788 8
150.0	0.835 580 1	0.381 597 3	160.0	0.822 503 4	0.400 667 1
170.0	0.809 586 8	0.419 023 5	180.0	0.796 850 0	0.436 691 9
190.0	0.784 308 6	0.453 697 7	200.0	0.771 974 5	0.470 066 1
300.0	0.661 069 2	0.603 801 5	400.0	0.571 958 7	0.696 547 4
500.0	0.500 774 1	0.762 321 0	600.0	0.443 452 0	0.810 072 5
700.0	0.396 734 2	0.845 519 5	800.0	0.358 168 3	0.872 374 8
900.0	0.325 935 5	0.893 100 1	1 000.0	0.298 683 5	0.909 363 0
2 000.0	0.159 772 8	0.972 879 1	3 000.0	0.108 108 0	0.987 427 3
4 000.0	0.081 523 4	0.992 815 2	5 000.0	0.065 386 4	0.995 367 0
6 000.0	0.054 565 4	0.996 769 3	7 000.0	0.046 810 3	0.997 620 4
8 000.0	0.040 981 8	0.998 175 1	9 000.0	0.036 442 2	0.998 556 5
10 000.0	0.032 806 9	0.998 829 8	20 000.0	0.016 417 9	0.999 706 7
30 000.0	0.010 947 0	0.999 869 6	40 000.0	0.008 210 7	0.999 926 6
50 000.0	0.006 568 8	0.999 953 0	60 000.0	0.005 474 0	0.999 967 4
70 000.0	0.004 692 1	0.999 976 0	80 000.0	0.004 105 6	0.999 981 7
90 000.0	0.003 649 4	0.999 985 5	100 000.0	0.003 284 5	0.999 988 3
∞	0.000 000 0	1.000 000 0			

$$V(R)=\frac{-1}{R^7}\frac{1}{2\pi\alpha}\int_0^\infty dx\,\beta^2\left[\frac{ix}{2R\alpha}\right]e^{-x}$$

$$\times\left[\frac{x^4}{16}+\frac{x^3}{4}+\frac{5x^2}{4}+3x+3\right]$$

and the polarizability is

$$\beta(iu)=\sum_{i=1}^N\frac{f_i}{\omega_i^2+u^2}.$$

Thus retardation becomes important if the time for propagating an electromagnetic signal between the atoms ($R\alpha$) is comparable with the period of the lowest dipole transition ($1/\omega_1$).

The quadrature was evaluated numerically by application of Romberg's method to trapezium rule estimates obtained with different step lengths. The range of x was taken as 0–35; $e^{-35}\approx 6\times 10^{-16}$ and the polynomial part of the integrand is approximately 10^5 at $x=35$. The range was divided into 35 subranges of unit length and the contribution of each was evaluated to within a rela-

tive accuracy of 10^{-9}. This partitioning reduced the effect of the modulation by the negative exponential factor; with a single partition the quadrature is forced into taking an unnecessarily large number of steps.

The value of C_6 was calculated directly from the nonretarded expression. We obtained a value of 1.460 978 a.u. To provide a check on the numerical procedures, C_6 was also evaluated by extrapolating to $R=0$ the values of $R^6V(R)$ calculated from the retardation expression. The value of C_7 was obtained from the static dipole polarizability. For the static dipole polarizability,

TABLE II. Coefficients for analytic fits to potential.

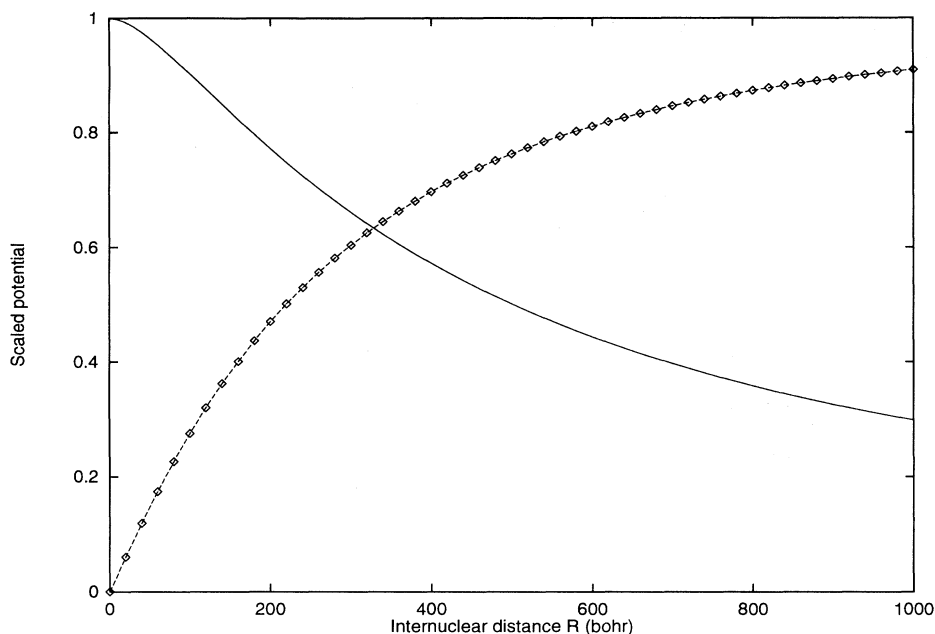| i	a_i	b_i
0	$-1.623\,43\times 10^{-3}$	$8.825\,06\times 10^{-2}$
1	$2.220\,97\times 10^{-3}$	$3.818\,46\times 10^{-2}$
2	$-1.173\,23\times 10^{-3}$	$-1.724\,21\times 10^{-3}$
3	$3.000\,12\times 10^{-4}$	
4	$-1.055\,12\times 10^{-5}$	$4.748\,97\times 10^{-7}$

FIG. 1. Full curve: $-R^6 V(R)/C_6$, dashed curve: $-R^7 V(R)/C_7$.

we obtained a value of 1.383 192 a.u. and for C_7 we obtained 479.8634 a.u. The results for C_6 and C_7 were calculated in the limit of infinite nuclear mass ignoring relativistic corrections and are accurate to the number of figures quoted. Finite mass corrections would modify the static polarizability to

$$\beta(0) = 1.383\,192 + 0.35626\,\mu/M \ ,$$

expressed in units of the cube of the reduced mass Bohr radius a_M^3, where μ/M is the ratio of the reduced electron mass to the nuclear mass. This value of $\beta(0)$ is in agreement with the calculations of Bhatia and Drachman [16]. Further relativistic corrections may be of the same order and are also negligible. A separate calculations with the four term data of Chan and Dalgarno [14] showed that the potential is insensitive to the details of the effective dipole transitions, as noted by Luo et al. [13] in their calculations of the retarded potential. The uncertainty in the results in Table I should be less than one in the fourth significant figures following the leading zeros or nines.

We derived analytic fits to the potential in the range 10–200 bohr. The dispersion potential is not appropriate for $R < 10$. For values at $R > 200$, interpolation of the tabulated values can be used. The analytic fits for R in the range 10–100 bohr are

$$V(R) = -\frac{C_6}{R^6}[1 - f(R)] \ ,$$

where

$$f(R) = a_0 + a_1 R^{1/2} + a_2 R + a_3 R^{3/2} + a_4 R^2$$

and for R in the range 100–200

$$V(R) = -\frac{C_6}{R^6}\frac{1 + g(R)}{1.2 + 0.8 R C_6/C_7} \ ,$$

where

$$g(R) = b_0 + b_1 R^{1/2} + b_2 R + b_4 R^2 \ ,$$

the values of a_i and b_i being given in Table II. The functions $f(R)$ and $g(R)$ were determined by least-squares fits to the calculated quantities $-[1 + V(R)R^6/C_6]$ and $-[1 + 1.2(V(R)R^6/C_6) + 0.8(V(R)R^7/C_7)]$, respectively; the latter quantity was found, by numerical experiment, to vary slowly over the range 100–200. The forms of the expansions of $f(R)$ and $g(R)$ were also determined by numerical experiment. Note the absence of a term $R^{3/2}$ in the expansion of $g(R)$; a better fit was obtained by omitting it. The analytic expressions reproduce the potential to within a relative accuracy of 10^{-5}.

We present our results graphically in Fig. 1 which shows how the effect of retardation changes the R dependence from R^{-6} to R^{-7} as R increases. Retardation becomes apparent as the signal propagation time approaches the period of the lowest dipole transition.

O'Carroll and Sucher [17] advanced the formula

$$-V(R)R^6/C_6 = (2/\pi)\tan^{-1}(d/R) \ ,$$

where d is a characteristic length

$$d = (\pi/2)C_7/C_6$$

as a representation of the retarded interaction that is free of disposable parameters. Langhoff [12] found that it yielded results within a few percent of his calculated values. We find that it underestimates our values by less than 3% for $R < 260$ and overestimates them by less than 2% for larger R, becoming exact in the asymptotic limit of large R.

ACKNOWLEDGMENTS

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