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Long-range potentials, including retardation, for the interaction of two alkali-metal atoms

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The retarded long-range potentials for the dispersion interaction arising from induced multipole moments of two ground-state alkali-metal atoms are evaluated as functions of the separation R for Li, Na, K, Rb, and Cs. Accurate atomic properties, determined using published model potentials, are utilized. Values for the potentials are given over a wide range of R. Results for H are also given. For small R the results reproduce the accepted values for the unretarded dispersion dipole-dipole (van der Waals), dipole-quadrupole, quadrupole-quadrupole, and dipole-octupole coefficients, while for $R \to \infty$ the Casimir-Polder potentials, due to retardation or effects due to the finite speed of light, are obtained. The overlap between the retardation potentials and terms arising from the Breit-Pauli Hamiltonian is explored.

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I. INTRODUCTION

The long-range interaction $V_{\mathrm{lr}}(R)$ between two spherically symmetric atoms, where R is the internuclear distance, occurs through the dispersion interaction of induced multipole moments, primarily electric dipole. For two ground-state spherically symmetric atoms for distances R sufficiently large that the exchange interaction is negligible [that is, for distances beyond the "LeRoy radius" [1] R_0, typically of the order of $\sim (15\text{–}30)a_0$], the dominant interaction is the van der Waals (electric dipole-dipole dispersion) interaction (cf. [2–4])

$$V_{\mathrm{lr}}(R) \sim -\frac{C_6(a,b)}{R^6}, \qquad R \gtrsim R_0, \tag{1.1}$$

where $C_6(a,b)$ is the van der Waals coefficient of the atoms a and b, while for asymptotically large distances the dominant interaction is modified by retardation giving rise to the Casimir-Polder potential. It is given by (cf. [5–7])

$$V_{\mathrm{lr}}(R) \sim -\frac{23}{4\pi\alpha}\frac{\alpha_{a1}(0)\alpha_{b1}(0)}{R^7}, \qquad R \to \infty, \tag{1.2}$$

where α is the fine-structure constant and $\alpha_{a1}(0)$ and $\alpha_{b1}(0)$ are the static electric dipole polarizabilities of, respectively, the atoms a and b.

A substantial amount of theoretical work has been devoted to the study of long-range diatomic forces—primarily to evaluating the small- and large-R limits of $V_{\mathrm{lr}}(R)$ and in particular to including terms arising from higher multipoles. The potentials arising from a given pair of induced moments can be expressed in a form valid over all R greater than several atomic units to infinity [5,8,9]. In this paper, values of $V_{\mathrm{lr}}(R)$ are given over a range $10a_0 < R < 10^5 a_0$ including retardation for the pairwise dispersion interactions of dipole, quadrupole, and octupole induced electrical moments. Here we apply a recently published procedure [10], for integrating the two coupled inhomogeneous differential equations for the dynamic multipole polarizabilities, with model potentials for the alkali-atom cores, to obtain the interactions for two alkali atoms (we will use the term alkali atom in reference to an alkali metal).

The results given are also of contemporary interest as improvements that have been achieved in the spectroscopy of laser-cooled atoms and in low-temperature surface physics have renewed interest in the empirical characterization of the long-range part of diatomic interaction potentials. Alkali atoms appear to be the most popular system for low-temperature experiments (though hydrogen [11] and helium [12] also have been studied). The present results are relevant to the current interest in the elastic scattering cross sections for alkali atoms, Li_2 and Na_2 [13,14], and Cs_2 [15,16], to the determination of the signs of scattering lengths for alkali-atom Bose gases [16,13] and to photoassociation spectroscopy [17].

II. FORM OF INTERACTIONS

For notational convenience the designations a and b identifying the atoms are suppressed. Although the expressions are written for like-atom interactions, they can be generalized readily. We use atomic units throughout. In 1948, Casimir and Polder [5] showed for the electric dipole interaction

$$V_{11}(R) \equiv -\frac{1}{\pi R^6}\int_0^\infty d\omega\, \alpha_1^2(i\omega)\exp(-2\omega\alpha R)P_1(\omega\alpha R), \tag{2.1}$$

where

$$P_1(x) = x^4 + 2x^3 + 5x^2 + 6x + 3. \tag{2.2}$$

Since then, Eq. (2.1) has been reproduced using many different theoretical methods; see for example, Refs. [18–22,6]. Equation (2.1) was generalized by Au and Feinberg [23] to all multipoles, electric and magnetic. They obtained for the electric multipoles

$$V_{NM}(R) = -\frac{4}{\pi R}\frac{1}{(2N)!(2M)!} \times \frac{d^{2(N+M-2)}}{dR^{2(N+M-2)}}\left[\frac{1}{R^5}\int_0^\infty d\omega\, \alpha_N(i\omega)\alpha_M(i\omega) \times \exp(-2\alpha\omega R)P_1(\alpha\omega R)\right], \tag{2.3}$$

where $\alpha_N(\omega)$ is the multipole dynamic polarizability of the atom and $N \geq 1$ and $M \geq 1$ represent, respectively, the order 2^N and 2^M of the electric multipole. Equation (2.3) may be written without derivatives. Recently, it has been applied with $N + M \leq 4$ to calculate V_{NM} for He_2 [24,25].

Some comments about Eq. (2.3) are in order at this point. The energy shift due to the magnetic multipoles is small; however, for specific atoms at large distances the retarded magnetic dipole interaction may be larger than the retarded electric dipole potential Eq. (1.2); for H_2, for example, this occurs at $R \sim 21$ cm [26]. Additionally, due to the appearance of a cross term between the retarded electric and magnetic dipole terms, the asymptotic potential describing the interaction between two different atoms need not be attractive [26]. The magnetic terms contribute for small R also. The magnetic dipole terms for H_2 contribute an additional energy of about 0.24% of C_6 [22].

Au and Feinberg [23] emphasized that Eq. (2.3) is *not* an exact expression because it is obtained by replacing the electric electromagnetic form factors $F_{E,N}$ for atomic Rayleigh scattering by the approximation

$$F_{E,N}(\omega) \sim \frac{8\pi\alpha_N(\omega)}{(2N)!} + O(\omega^2\alpha^2a^2)\alpha_{N+1}(\omega)/a^2 + \cdots, \tag{2.4}$$

and retaining the first term, where a is the atomic radius. Because $\omega a \sim 1$, this should be a good approximation; however, we are not aware of any more quantitative assessment of the error associated with this replacement for specific systems.

III. EVALUATION OF THE CASIMIR-POLDER FORMULAS

In this paper, we will evaluate the retarded potentials V_{11}, V_{12}, V_{13}, and V_{22}, for hydrogen and the alkali atoms, and

$$V(R) \equiv V_{11}(R) + 2V_{12}(R) + 2V_{13}(R) + V_{22}(R). \tag{3.1}$$

For numerical evaluation, it is convenient to express Eq. (2.3) relative to the small-R potential [27] for the electric dipole-dipole ($N = 1, M = 1$) or C_6, dipole-quadrupole ($N = 1, M = 2$) or C_8, and dipole-octupole ($N = 1, M = 3$) and quadrupole-quadrupole ($N = 2, M = 2$) or C_{10} dispersion terms

$$V_{sr}(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}}. \tag{3.2}$$

Thus we have

$$V(R) = -\frac{C_6 f_6(R)}{R^6} - \frac{C_8 f_8(R)}{R^8} - \frac{C_{10} f_{10}(R)}{R^{10}}, \tag{3.3}$$

where

$$f_6(R) = -R^6 V_{11}(R)/C_6 \tag{3.4}$$

with V_{11} given by Eq. (2.1),

$$f_8(R) = \frac{1}{3\pi C_8}\int_0^\infty d\omega\, B(\omega)\exp(-2\alpha\omega R)P_2(\alpha\omega R), \tag{3.5}$$

TABLE I. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$, Eqs. (3.4)–(3.6) for H_2 in atomic units. In the last row, labeled "Asymptotic," we give the values of f_6, f_8, and f_{10} calculated using the asymptotic forms, Eqs. (3.12)–(3.14). Numbers in square brackets represent powers of ten.

	C_6	C_8	C_{10}
	6.49903	1.24399[2]	3.28583[3]
R	f_6	f_8	f_{10}
1.0[1]	9.99641[-1]	9.99802[-1]	9.99870[-1]
1.5[1]	9.99213[-1]	9.99561[-1]	9.99711[-1]
2.0[1]	9.98635[-1]	9.99230[-1]	9.99492[-1]
2.5[1]	9.97919[-1]	9.98816[-1]	9.99214[-1]
3.0[1]	9.97072[-1]	9.98321[-1]	9.98881[-1]
5.0[1]	9.92545[-1]	9.95608[-1]	9.97034[-1]
7.0[1]	9.86506[-1]	9.91857[-1]	9.94434[-1]
1.0[2]	9.75304[-1]	9.84645[-1]	9.89325[-1]
1.5[2]	9.52727[-1]	9.69397[-1]	9.78230[-1]
2.0[2]	9.27221[-1]	9.51318[-1]	9.64673[-1]
2.5[2]	9.00233[-1]	9.31394[-1]	9.49351[-1]
3.0[2]	8.72675[-1]	9.10323[-1]	9.32769[-1]
5.0[2]	7.65880[-1]	8.22815[-1]	8.60494[-1]
7.0[2]	6.72699[-1]	7.39854[-1]	7.87663[-1]
1.0[3]	5.60851[-1]	6.33012[-1]	6.88435[-1]
1.5[3]	4.31138[-1]	4.99902[-1]	5.56957[-1]
2.0[3]	3.46222[-1]	4.07748[-1]	4.61155[-1]
2.5[3]	2.87601[-1]	3.41972[-1]	3.90527[-1]
3.0[3]	2.45180[-1]	2.93349[-1]	3.37184[-1]
5.0[3]	1.52655[-1]	1.84661[-1]	2.14809[-1]
7.0[3]	1.10273[-1]	1.33873[-1]	1.56367[-1]
1.0[4]	7.76721[-2]	9.44879[-2]	1.10625[-1]
1.5[4]	5.19570[-2]	6.32773[-2]	7.41830[-2]
2.0[4]	3.90144[-2]	4.75341[-2]	5.57530[-2]
2.5[4]	3.12289[-2]	3.80556[-2]	4.46456[-2]
3.0[4]	2.60320[-2]	3.17259[-2]	3.72243[-2]
5.0[4]	1.56260[-2]	1.90468[-2]	2.23517[-2]
7.0[4]	1.11628[-2]	1.36070[-2]	1.59689[-2]
1.0[5]	7.81445[-3]	9.52572[-3]	1.11795[-2]
		Asymptotic	
1.0[5]	7.81501[-3]	9.52658[-3]	1.11807[-2]

TABLE II. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for Li_2.

	C_6	C_8	C_{10}
	1.38830[3]	8.32365[4]	7.36482[6]
R	f_6	f_8	f_{10}
1.0[1]	9.99991[-1]	9.99992[-1]	9.99993[-1]
1.5[1]	9.99979[-1]	9.99982[-1]	9.99984[-1]
2.0[1]	9.99963[-1]	9.99968[-1]	9.99972[-1]
2.5[1]	9.99943[-1]	9.99950[-1]	9.99957[-1]
3.0[1]	9.99919[-1]	9.99928[-1]	9.99938[-1]
5.0[1]	9.99778[-1]	9.99803[-1]	9.99829[-1]
7.0[1]	9.99572[-1]	9.99620[-1]	9.99669[-1]
1.0[2]	9.99150[-1]	9.99239[-1]	9.99336[-1]
1.5[2]	9.98162[-1]	9.98342[-1]	9.98547[-1]
2.0[2]	9.96852[-1]	9.97143[-1]	9.97485[-1]
2.5[2]	9.95253[-1]	9.95668[-1]	9.96171[-1]
3.0[2]	9.93392[-1]	9.93942[-1]	9.94625[-1]
5.0[2]	9.83775[-1]	9.84908[-1]	9.86448[-1]
7.0[2]	9.71498[-1]	9.73218[-1]	9.75722[-1]
1.0[3]	9.49768[-1]	9.52284[-1]	9.56265[-1]
1.5[3]	9.08667[-1]	9.12206[-1]	9.18434[-1]
2.0[3]	8.65262[-1]	8.69478[-1]	8.77544[-1]
2.5[3]	8.21991[-1]	8.26631[-1]	8.36135[-1]
3.0[3]	7.80130[-1]	7.85020[-1]	7.95633[-1]
5.0[3]	6.35212[-1]	6.40287[-1]	6.53258[-1]
7.0[3]	5.26302[-1]	5.31122[-1]	5.44741[-1]
1.0[4]	4.12151[-1]	4.16450[-1]	4.29730[-1]
1.5[4]	2.97617[-1]	3.01117[-1]	3.12750[-1]
2.0[4]	2.30888[-1]	2.33777[-1]	2.43712[-1]
2.5[4]	1.87904[-1]	1.90340[-1]	1.98871[-1]
3.0[4]	1.58127[-1]	1.60223[-1]	1.67638[-1]
5.0[4]	9.62995[-2]	9.76253[-2]	1.02385[-1]
7.0[4]	6.90770[-2]	7.00389[-2]	7.35085[-2]
1.0[5]	4.84652[-2]	4.91423[-2]	5.15976[-2]
Asymptotic			
1.0[5]	4.85911[-2]	4.92669[-2]	5.17455[-2]

TABLE III. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for Na_2.

	C_6	C_8	C_{10}
	1.47220[3]	1.11877[5]	1.10655[7]
R	f_6	f_8	f_{10}
1.0[1]	9.99990[-1]	9.99992[-1]	9.99994[-1]
1.5[1]	9.99977[-1]	9.99983[-1]	9.99986[-1]
2.0[1]	9.99958[-1]	9.99969[-1]	9.99975[-1]
2.5[1]	9.99935[-1]	9.99952[-1]	9.99960[-1]
3.0[1]	9.99907[-1]	9.99931[-1]	9.99943[-1]
5.0[1]	9.99746[-1]	9.99811[-1]	9.99844[-1]
7.0[1]	9.99511[-1]	9.99633[-1]	9.99697[-1]
1.0[2]	9.99024[-1]	9.99264[-1]	9.99391[-1]
1.5[2]	9.97880[-1]	9.98390[-1]	9.98663[-1]
2.0[2]	9.96360[-1]	9.97215[-1]	9.97679[-1]
2.5[2]	9.94499[-1]	9.95764[-1]	9.96457[-1]
3.0[2]	9.92330[-1]	9.94057[-1]	9.95015[-1]
5.0[2]	9.81113[-1]	9.85055[-1]	9.87323[-1]
7.0[2]	9.66823[-1]	9.73291[-1]	9.77130[-1]
1.0[3]	9.41679[-1]	9.52051[-1]	9.58444[-1]
1.5[3]	8.94683[-1]	9.11036[-1]	9.21630[-1]
2.0[3]	8.45835[-1]	8.67047[-1]	8.81329[-1]
2.5[3]	7.97904[-1]	8.22807[-1]	8.40111[-1]
3.0[3]	7.52234[-1]	7.79810[-1]	7.99482[-1]
5.0[3]	5.99121[-1]	6.30718[-1]	6.55031[-1]
7.0[3]	4.88803[-1]	5.19405[-1]	5.44146[-1]
1.0[4]	3.77180[-1]	4.04044[-1]	4.26840[-1]
1.5[4]	2.68905[-1]	2.89915[-1]	3.08556[-1]
2.0[4]	2.07329[-1]	2.24185[-1]	2.39486[-1]
2.5[4]	1.68168[-1]	1.82122[-1]	1.94953[-1]
3.0[4]	1.41238[-1]	1.53096[-1]	1.64086[-1]
5.0[4]	8.57447[-2]	9.30781[-2]	9.99605[-2]
7.0[4]	6.14495[-2]	6.67329[-2]	7.17110[-2]
1.0[5]	4.30919[-2]	4.68060[-2]	5.03141[-2]
Asymptotic			
1.0[5]	4.31788[-2]	4.69062[-2]	5.04350[-2]

$$f_{10}(R) = \frac{1}{18\pi C_{10}} \int_0^\infty d\omega\, C(\omega) \exp(-2\alpha\omega R) P_3(\alpha\omega R), \tag{3.6}$$

where

$$B(\omega) = \alpha_1(i\omega)\alpha_2(i\omega), \tag{3.7}$$

with

$$P_2(x) = 2x^6 + 6x^5 + 19x^4 + 48x^3 + 84x^2 + 90x + 45, \tag{3.8}$$

and

$$C(\omega) = \tfrac{4}{5}\alpha_1(i\omega)\alpha_3(i\omega) + \alpha_2(i\omega)\alpha_2(i\omega), \tag{3.9}$$

with

$$\begin{aligned} P_3(x) = {} & 2x^8 + 8x^7 + 32x^6 + 114x^5 + 333x^4 \\ & +750x^3 + 1215x^2 + 1260x + 630. \end{aligned} \tag{3.10}$$

Knowledge of the various polarizabilities $\alpha_N(i\omega)$ allows one to evaluate the factors f_6, f_8, and f_{10} in Eqs. (3.4)–(3.6). The coefficients C_6,C_8,C_{10} for the alkali atoms Li, Na, K, Rb, and Cs have been evaluated using model potentials for the atomic properties and a set of coupled inhomogeneous differential equations to get $\alpha_N(i\omega)$ [10] and we follow the method of Ref. [10] to obtain the dynamic polarizabilities from the expression

$$\alpha_N(i\omega) = \frac{2}{2N+1} \mathrm{Re}[(0|r^N g_N(E_0 + i\omega) r^N|0)], \tag{3.11}$$

where (|) are radial matrix elements and g_N is the radial Green's function for states with angular momentum N.

In the tables numerical values of f_6, f_8, and f_{10} are given for H in Table I, Li in Table II, Na in Table III, K in Table IV, Rb in Table V, and Cs in Table VI. In the first row of Tables I–VI we give the values of C_6, C_8, and C_{10},

TABLE IV. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for K_2.

	C_6	C_8	C_{10}
	3.81250[3]	4.09609[5]	5.24761[7]
R	f_6	f_8	f_{10}
1.0[1]	9.99994[-1]	9.99996[-1]	9.99996[-1]
1.5[1]	9.99986[-1]	9.99991[-1]	9.99992[-1]
2.0[1]	9.99976[-1]	9.99983[-1]	9.99986[-1]
2.5[1]	9.99963[-1]	9.99974[-1]	9.99978[-1]
3.0[1]	9.99946[-1]	9.99962[-1]	9.99968[-1]
5.0[1]	9.99853[-1]	9.99896[-1]	9.99911[-1]
7.0[1]	9.99715[-1]	9.99797[-1]	9.99828[-1]
1.0[2]	9.99428[-1]	9.99591[-1]	9.99653[-1]
1.5[2]	9.98746[-1]	9.99098[-1]	9.99233[-1]
2.0[2]	9.97827[-1]	9.98428[-1]	9.98660[-1]
2.5[2]	9.96690[-1]	9.97593[-1]	9.97944[-1]
3.0[2]	9.95350[-1]	9.96601[-1]	9.97091[-1]
5.0[2]	9.88250[-1]	9.91249[-1]	9.92453[-1]
7.0[2]	9.78905[-1]	9.84036[-1]	9.86140[-1]
1.0[3]	9.61876[-1]	9.70554[-1]	9.74208[-1]
1.5[3]	9.28497[-1]	9.43229[-1]	9.49658[-1]
2.0[3]	8.92013[-1]	9.12334[-1]	9.21466[-1]
2.5[3]	8.54608[-1]	8.79758[-1]	8.91342[-1]
3.0[3]	8.17550[-1]	8.46708[-1]	8.60426[-1]
5.0[3]	6.83317[-1]	7.21590[-1]	7.40773[-1]
7.0[3]	5.76745[-1]	6.17195[-1]	6.38361[-1]
1.0[4]	4.59953[-1]	4.98484[-1]	5.19563[-1]
1.5[4]	3.37631[-1]	3.70003[-1]	3.88533[-1]
2.0[4]	2.64095[-1]	2.91012[-1]	3.06825[-1]
2.5[4]	2.15915[-1]	2.38648[-1]	2.52216[-1]
3.0[4]	1.82201[-1]	2.01757[-1]	2.13548[-1]
5.0[4]	1.11454[-1]	1.23788[-1]	1.31358[-1]
7.0[4]	8.00529[-2]	8.89922[-2]	9.45117[-2]
1.0[5]	5.62070[-2]	6.25107[-2]	6.64174[-2]
		Asymptotic	
1.0[5]	5.64007[-2]	6.27463[-2]	6.66894[-2]

TABLE V. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for Rb_2.

	C_6	C_8	C_{10}
	4.42548[3]	5.50605[5]	7.66476[7]
R	f_6	f_8	f_{10}
1.0[1]	9.99994[-1]	9.99996[-1]	9.99997[-1]
1.5[1]	9.99987[-1]	9.99991[-1]	9.99993[-1]
2.0[1]	9.99977[-1]	9.99985[-1]	9.99987[-1]
2.5[1]	9.99965[-1]	9.99976[-1]	9.99980[-1]
3.0[1]	9.99949[-1]	9.99966[-1]	9.99972[-1]
5.0[1]	9.99860[-1]	9.99906[-1]	9.99922[-1]
7.0[1]	9.99728[-1]	9.99818[-1]	9.99847[-1]
1.0[2]	9.99454[-1]	9.99633[-1]	9.99692[-1]
1.5[2]	9.98802[-1]	9.99190[-1]	9.99319[-1]
2.0[2]	9.97923[-1]	9.98588[-1]	9.98809[-1]
2.5[2]	9.96833[-1]	9.97835[-1]	9.98171[-1]
3.0[2]	9.95549[-1]	9.96940[-1]	9.97410[-1]
5.0[2]	9.88729[-1]	9.92092[-1]	9.93256[-1]
7.0[2]	9.79729[-1]	9.85527[-1]	9.87574[-1]
1.0[3]	9.63284[-1]	9.73187[-1]	9.76775[-1]
1.5[3]	9.30931[-1]	9.47975[-1]	9.54373[-1]
2.0[3]	8.95430[-1]	9.19218[-1]	9.28411[-1]
2.5[3]	8.58909[-1]	8.88653[-1]	9.00439[-1]
3.0[3]	8.22614[-1]	8.57413[-1]	8.71505[-1]
5.0[3]	6.90307[-1]	7.37266[-1]	7.57578[-1]
7.0[3]	5.84398[-1]	6.34940[-1]	6.57798[-1]
1.0[4]	4.67502[-1]	5.16475[-1]	5.39634[-1]
1.5[4]	3.44177[-1]	3.85941[-1]	4.06564[-1]
2.0[4]	2.69625[-1]	3.04609[-1]	3.22302[-1]
2.5[4]	2.20627[-1]	2.50295[-1]	2.65515[-1]
3.0[4]	1.86276[-1]	2.11860[-1]	2.25106[-1]
5.0[4]	1.14045[-1]	1.30245[-1]	1.38767[-1]
7.0[4]	8.19356[-2]	9.36901[-2]	9.99073[-2]
1.0[5]	5.75372[-2]	6.58322[-2]	7.02340[-2]
		Asymptotic	
1.0[5]	5.77454[-2]	6.61041[-2]	7.05480[-2]

which are in agreement with those of Ref. [10]. The integrals in Eqs. (3.4)–(3.6) were evaluated using a combination of Gauss-Laguerre and Gauss-rational quadrature methods. For H, our results for f_6 agree to within 10^{-4} with those of [28], while the other calculations of f_6 [22] and f_8 [23] lie, respectively, 0.16% and 0.25% above ours, but there does not appear to be a prior calculation of f_{10}, except for He [25]. We note that our value of C_6 is identical to the exact value [29]. The expressions have the expected asymptotic limits [5,23] for $R \sim \infty$,

$$f_6 \to \frac{23}{4\pi\alpha R}\frac{\alpha_1^2(0)}{C_6}, \tag{3.12}$$

$$f_8 \to \frac{161}{4\pi\alpha R}\frac{B(0)}{C_8}, \tag{3.13}$$

and

$$f_{10} \to \frac{483}{4\pi\alpha R}\frac{C(0)}{C_{10}}, \tag{3.14}$$

with B and C given, respectively, by Eqs. (3.7) and (3.9).

In the last row, labeled “Asymptotic,” of Tables I–VI, we give the values of f_6, f_8, and f_{10} calculated using the asymptotic forms above, Eqs. (3.12)–(3.14). O'Carroll and Sucher [9] have proposed a formula to approximate $f_6(R)$, the “arctangent formula,” which involves only numerical factors $\alpha_1(0)$, $\hbar$, c, and C_6. Au [22] has investigated the arctangent formula for the rare gases and found over a range of R that it differs by no more than 6% from a more accurate calculation using Eq. (2.1). It could be used here if one desires a less accurate, but easily parametrized, potential.

In Fig. 1 the retardation coefficients f_6,f_8,f_{10} for H are presented; plots of the values for a given alkali atom are similar to each other and to those for He given in Ref. [25]. In Fig. 2 the values of f_6 for the alkali atoms are presented. Note that the curve of f_6 for Na_2 is not in the expected order. It lies below that for Li_2 because the $3s$-$3p$ excitation energy for Na is larger than that of the $2s$-$2p$ excitation energy of Li, while the dipole matrix elements are about the same magnitude. We also find that for Na_2 the f_8 and f_{10} curves, respectively, lie below the Li_2 f_8 and f_{10} curves. We can also define retardation coefficients that measure the approach of the potentials

TABLE VI. Retardation coefficients $f_6(R)$, $f_8(R)$, and $f_{10}(R)$ for Cs_2.

	C_6	C_8	C_{10}
	6.32995[3]	9.62952[5]	1.52019[8]
R	f_6	f_8	f_{10}
1.0[1]	9.99995[-1]	9.99997[-1]	9.99998[-1]
1.5[1]	9.99990[-1]	9.99994[-1]	9.99995[-1]
2.0[1]	9.99982[-1]	9.99989[-1]	9.99990[-1]
2.5[1]	9.99972[-1]	9.99982[-1]	9.99985[-1]
3.0[1]	9.99959[-1]	9.99974[-1]	9.99978[-1]
5.0[1]	9.99888[-1]	9.99929[-1]	9.99940[-1]
7.0[1]	9.99782[-1]	9.99862[-1]	9.99883[-1]
1.0[2]	9.99560[-1]	9.99722[-1]	9.99764[-1]
1.5[2]	9.99032[-1]	9.99385[-1]	9.99478[-1]
2.0[2]	9.98317[-1]	9.98925[-1]	9.99085[-1]
2.5[2]	9.97427[-1]	9.98349[-1]	9.98592[-1]
3.0[2]	9.96373[-1]	9.97661[-1]	9.98003[-1]
5.0[2]	9.90723[-1]	9.93906[-1]	9.94766[-1]
7.0[2]	9.83177[-1]	9.88764[-1]	9.90297[-1]
1.0[3]	9.69206[-1]	9.78977[-1]	9.81709[-1]
1.5[3]	9.41240[-1]	9.58625[-1]	9.63619[-1]
2.0[3]	9.09990[-1]	9.34957[-1]	9.42292[-1]
2.5[3]	8.77330[-1]	9.09351[-1]	9.18948[-1]
3.0[3]	8.44414[-1]	8.82744[-1]	8.94440[-1]
5.0[3]	7.20939[-1]	7.76608[-1]	7.94650[-1]
7.0[3]	6.18416[-1]	6.81573[-1]	7.03030[-1]
1.0[4]	5.01582[-1]	5.66173[-1]	5.89302[-1]
1.5[4]	3.74212[-1]	4.32235[-1]	4.54190[-1]
2.0[4]	2.95238[-1]	3.45222[-1]	3.64746[-1]
2.5[4]	2.42574[-1]	2.85663[-1]	3.02823[-1]
3.0[4]	2.05324[-1]	2.42863[-1]	2.58001[-1]
5.0[4]	1.26232[-1]	1.50414[-1]	1.60384[-1]
7.0[4]	9.08067[-2]	1.08447[-1]	1.15775[-1]
1.0[5]	6.38120[-2]	7.62975[-2]	8.15070[-2]
		Asymptotic	
1.0[5]	6.40967[-2]	7.67211[-2]	8.19989[-2]

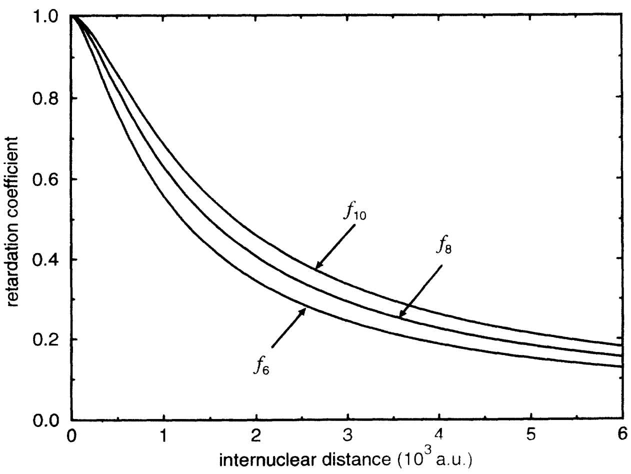

FIG. 1. For H, values of the retardation coefficients f_6, f_8, and f_{10}, Eqs. (3.4)–(3.6).

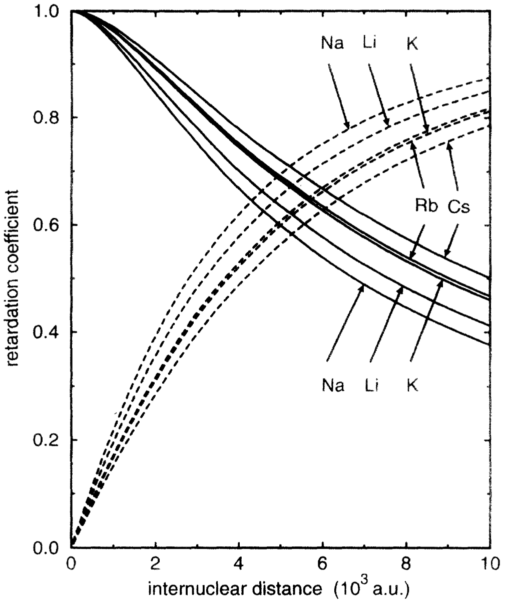

FIG. 2. For the alkali atoms Li, Na, K, Rb, and Cs, values of the retardation coefficients f_6 (solid lines), Eq. (3.4), and g_7 (dashed lines), Eq. (3.15), calculated as described in the text. Note that the Na coefficients are not in the expected order as discussed in the text.

to their asymptotic values. Thus, for the electric dipole potential V_{11} by analogy with Eq. (3.4), we define

$$g_7(R) = -R^7 V_{11}(R)/K_7, \tag{3.15}$$

where

$$K_7 = \frac{23}{4\pi\alpha}\alpha_1^2(0). \tag{3.16}$$

In Fig. 2 the values of g_7 for the alkali atoms are plotted.

IV. “SHORT-RANGE” LIMIT

The short-range limit needs to be properly characterized in order to match *ab initio* calculations of the diatomic potential. Relativistic corrections obtained from the Breit-Pauli equation are often simply added to the diatomic potential. We will investigate the consistency of this procedure with the inclusion of retardation effects.

A. Expansion of the retardation potential for small R

Rather than work with each of f_6, f_8, and f_{10}, Eqs. (3.4)–(3.6), we define the generating function

$$F_{2(s+2)}(R;N,M) = \frac{1}{\alpha R}\int_0^\infty dx\, \alpha_N(ix/\alpha R)\alpha_M(ix/\alpha R) \times \exp(-2x)P_s(x), \tag{4.1}$$

where α_N is given by Eq. (3.11). Then

$$f_6(R)C_6(R) = (1/\pi)F_6(R;1,1),$$
$$f_8(R)C_8(R) = (1/3\pi)F_8(R;1,2), \tag{4.2}$$

and

$$f_{10}(R)C_{10}(R) = (1/18\pi)[\tfrac{4}{5}F_{10}(R;1,3) + F_{10}(R;2,2)]. \tag{4.3}$$

Inserting the definition of the radial Green's function $g_N(E_0 + i\omega)$ into Eq. (3.11), we obtain, for the polarizability,

$$\alpha_N(ix/\alpha R) = \alpha R\frac{2}{2N+1}\sum_n (0|r^N|n)^2\frac{\tilde{\Delta}_n}{\tilde{\Delta}_n^2 + x^2}, \tag{4.4}$$

where the state $|n)$ and energy E_n correspond to the angular momentum N and $\tilde{\Delta}_n = \alpha R E_{n0}$, with $E_{n0} \equiv E_n - E_0$. Using Eq. (4.4) above for N and M in Eq. (4.1) we have

$$F_{2(s+2)}(R;N,M) = \frac{2}{2N+1}\frac{2}{2M+1} \times \sum_{n,m}(0|r^N|n)^2(0|r^M|m)^2\tilde{\Delta}_n\tilde{\Delta}_m \times T_s(\tilde{\Delta}_n,\tilde{\Delta}_m), \tag{4.5}$$

where

$$T_s(a,b) \equiv \alpha R\int_0^\infty d\omega\,\frac{e^{-2x}P_s(x)}{(a^2+x^2)(b^2+x^2)}. \tag{4.6}$$

Since P_s is a polynomial

$$P_s(x) = \sum_{l=0}^{2(s+1)}\beta_l x^l \tag{4.7}$$

and $a, b > 0$, we can write

$$T_s(a,b) = \alpha R\sum_{l=0}^{2(s+1)}\beta_l\mathcal{J}_l(a,b) \tag{4.8}$$

with

$$\mathcal{J}_l(a,b) \equiv \int_0^\infty dx\,\frac{x^l e^{-2x}}{(a^2+x^2)(b^2+x^2)}. \tag{4.9}$$

The integral $T_s(a,b)$ can be evaluated in closed form [5,8,21] through the use of the identity

$$\mathcal{J}_l = (b^2-a^2)^{-1}[\mathcal{I}_l(a) - \mathcal{I}_l(b)] \tag{4.10}$$

with

$$\mathcal{I}_l(a) = \int_0^\infty dx\,\frac{x^l e^{-2x}}{(a^2+x^2)}. \tag{4.11}$$

The analysis is standard using the integrals 3.356.1–2 of Ref. [30]. The final result is expressed in terms of the auxiliary functions f and g of the sine and cosine integrals [31] giving

$$\mathcal{I}_{2k}(a) = (-1)^k a^{2k-1}f(2a) + \frac{1}{2^{2k-1}}\sum_{l=1}^{k}(2k-2l)!(-4a^2)^{l-1}, \tag{4.12}$$

$$\mathcal{I}_{2k+1}(a) = (-1)^k a^{2k}g(2a) + \frac{1}{2^{2k}}\sum_{l=1}^{k}(2k-2l+1)!(-4a^2)^{l-1}. \tag{4.13}$$

Thus

$$T_s(a,b) = (b^2-a^2)^{-1}\alpha R\left[\sum_{l=0}^{2(s+1)}\beta_l\mathcal{I}_l(a) - \sum_{l=0}^{2(s+1)}\beta_l\mathcal{I}_l(b)\right] \equiv \frac{\alpha R}{b^2-a^2}\left[\mathcal{T}_s(a) - \mathcal{T}_s(b)\right]. \tag{4.14}$$

In order to obtain explicit forms for the potentials at small R we need the small-a expansions for Eq. (4.14),

$$\mathcal{T}_s(a) \sim \gamma_{s,1}a^{-1} + \gamma_{s,2} + \gamma_{s,3}a + \gamma_{s,4}a^2 + O(a^3). \tag{4.15}$$

In Table VII values of the $\gamma_{s,i}$, in agreement with Eq. (3.3) of [23], are given for $s = 1, 2, 3$ and $i = 1, ..., 4$.

Because $a = \tilde{\Delta}_n$ and $b = \tilde{\Delta}_m$ are small quantities, we may expand Eq. (4.14) to find

$$T_s(a,b) \sim \frac{\alpha R}{a^2-b^2}\left[\gamma_{s,1}\frac{a-b}{ab} + \gamma_{s,3}(a-b) - \gamma_{s,4}(a^2-b^2) + \cdots\right], \tag{4.16}$$

where the $\gamma_{s,2}$ terms cancel. Substituting the small-a expansion above, Eq. (4.16), into the generating function $F_{2(s+2)}(R;NM)$, Eq. (4.5), and using the definitions Eqs. (4.2) and (4.3) with the identities given in the Appendix, we obtain the final results

$$C_6 f_6 = C_6 - (\alpha R)^2 W_4 + (\alpha R)^3 U_3 + \cdots, \tag{4.17}$$

where

$$W_4 = \frac{1}{\pi}\int_0^\infty \alpha_1^2(i\omega)\omega^2 d\omega, \tag{4.18}$$

with $\alpha_1(i\omega)$ as defined in Eq. (3.11) and

TABLE VII. Values of coefficients $\gamma_{s,i}$ in the small-a expansions in Eq. (4.15).

s	$\gamma_{s,1}$	$\gamma_{s,2}$	$\gamma_{s,3}$	$\gamma_{s,4}$
1	$\frac{3}{2}\pi$	$-\frac{11}{4}$	$\frac{1}{2}\pi$	$-\frac{7}{6}$
2	$\frac{45}{2}\pi$	$-\frac{55}{2}$	3π	$-\frac{7}{2}$
3	315π	$-\frac{1155}{4}$	$\frac{45}{2}\pi$	$-\frac{35}{2}$

$$U_3 = \tfrac{7}{6\pi} S^2(1), \tag{4.19}$$

$$C_8 f_8 = C_8 - (\alpha R)^2 W_6 + (\alpha R)^3 U_5 + \cdots , \tag{4.20}$$

where

$$W_6 = \frac{2}{\pi} \int_0^\infty B(\omega)\omega^2 d\omega, \tag{4.21}$$

$$U_5 = \tfrac{7}{6\pi} S(1)S(2), \tag{4.22}$$

and

$$C_{10} f_{10} = C_{10} - (\alpha R)^2 W_8 + (\alpha R)^3 U_7 + \cdots , \tag{4.23}$$

where

$$W_8 = \frac{5}{2\pi} \int_0^\infty C(\omega)\omega^2 d\omega, \tag{4.24}$$

$$U_7 = \tfrac{35}{36\pi}[\tfrac{4}{5} S(1)S(3) + S^2(2)], \tag{4.25}$$

and we have defined a generalized-multipole sum and oscillator strength

$$S(N) = \sum_n f_{n0}^{(N)}, \tag{4.26}$$

$$f_{n0}^{(N)} = \frac{2}{2N+1} E_{n0} (0|r^N|n)^2. \tag{4.27}$$

We give expressions for the higher multipole terms in α^2 and α^3 because they are useful in making contact with relativistic and QED theory for small R. In the next section, the question of the numerical values of the coefficients is addressed. For atoms other than H, higher multipoles than the electric dipole term W_4, Eq. (4.17), are probably too small to be significant.

B. Relativistic dipole term W_4

The term W_4 is contained in $V_{11}(R)$, but it also can be obtained from a reduction of the Breit equation in the Pauli approximation, where it arises from the orbit-orbit term H_{oo}. (See Power and Zienau [32,33] and Meath and Hirschfelder [8].) Our W_6 and W_8 terms also could be obtained from higher electric multipoles in an analysis of the Breit equation similar to that of Ref. [8] or along the lines of the calculation of Hessels [34] for Rydberg states of helium. The effective potentials can be derived by expanding the "large" distance in the problem in multipoles and using perturbation theory with H_{oo}.

To introduce the notation, we give some relations, some old, some new, that can be used to obtain numerical values of C_6 and then we evaluate W_4, W_6, and W_8 for H. Our model potential method does not yield accurate values of the W coefficients for the alkali atoms. Numerical values of W_4 for Li and Na have been obtained in Refs. [35] and [36].

In atomic units, the dispersion coefficient can be written

$$C_6 = \frac{2}{3} \sum_{n,l} \frac{(0|r|l)^2 (0|r|n)^2}{E_{l0} + E_{n0}}, \tag{4.28}$$

where the intermediate states $|n)$ and $|l)$ are p states and $E_{l0} \equiv E_l - E_0$ and $E_{n0} \equiv E_n - E_0$. Using Eq. (A3) we obtain the well-known expression

$$C_6 = \frac{3}{\pi} \int_0^\infty \alpha_1^2(i\omega) d\omega. \tag{4.29}$$

Using Eq. (A8), another expression can be obtained,

$$C_6 = \frac{3}{\pi} \int_0^\infty \gamma^2(i\omega) d\omega, \tag{4.30}$$

where

$$\gamma(i\omega) = \tfrac{2}{3} \mathrm{Im}[(0|r g_1(E_0 + i\omega) r|0)]. \tag{4.31}$$

Although it has no advantage in the present work, this relation is useful if one atom is excited.

An alternative expression for W_4 is

$$W_4 = \frac{2}{9} \sum_{n,l} \frac{E_{l0} E_{n0}}{E_{l0} + E_{n0}} (0|r|l)^2 (0|r|n)^2, \tag{4.32}$$

which can be used to obtain the relation given in Eq. (4.18) using Eq. (A9). Using Eq. (A5), we obtain the equivalent formula

$$W_4 = \frac{1}{\pi} \int_0^\infty \beta^2(i\omega) d\omega, \tag{4.33}$$

where

$$\beta(i\omega) = \tfrac{2}{3}(0|r^2|0) - \omega\gamma(i\omega). \tag{4.34}$$

Again, this expression is useful if one atom is excited.

We used these expressions to evaluate W_4 for hydrogen and we obtained precise agreement with prior calculations [35,37]. Similar procedures yielded numerical values for W_6 and W_8, which are given in Table VIII. The numerical value of the coefficient $W_{LL,4;2}$ appearing in the potential of order α^2/R^6 obtained in Ref. [8] and evaluated in Ref. [37] for H is exactly 1.5 times our value for W_6. There are other terms entering at $O(\alpha^2/R^6)$—see, for example, Eq. (49) of Ref. [8]—but all these terms of $O(\alpha^2/R^6)$ are insignificant compared to the $\alpha^2 W_4/R^4$ term.

The matrix element $\epsilon_2(R)$ of H_{oo} has the form

$$\epsilon_2(R) = \alpha^2 W_4/R^4 + O(\alpha^2/R^6) \tag{4.35}$$

TABLE VIII. Numerical values for H of the coefficients W_4, W_6, and W_8 appearing in the small-R expansions.

W_4	W_6	W_8
0.462807	4.79533	234.702

for values of R that would be called "asymptotic" in a molecular calculation, but are in the present context—as described in the Introduction—in the small-R domain. It has been obtained by Kołos and Wolniewicz [38,39] by a direct evaluation of the matrix element using variationally determined nonrelativistic eigenfunctions of H_2. The calculated values have the same sign for $R > 5.8a_0$ as Eq. (4.35), but otherwise disagree qualitatively and quantitatively. Wolniewicz [39] noted that his results for $\epsilon_2(R)$ are sensitive to the expansion length of the representation of the eigenfunction. It appears that they are unreliable in the region beyond $10a_0$ where they are becoming small in magnitude.

The terms U_3, U_5, and U_7, which are of order α^3, presumably correspond to two-photon exchange effective potentials from QED [40,41] and would form a long-range approximation to the radiative shift E_L'', in the notation of [42]. While Wolniewicz [42,39] has estimated, using variationally determined nonrelativistic eigenfunctions of H_2, some terms of order $\alpha^3 \ln\alpha$ and α^3 at various internuclear distances, there do not appear to be available any values of E_L''.

V. CONCLUSIONS

The values of $V(R)$ calculated for H and alkali-atom–atom interactions and given in the tables are exact in the sense that given the semiempirical core potentials and the experimental values of the electric dipole polarizabilities, the dynamic multipole polarizabilities have been obtained with no approximations. We have also presented expressions for the small-R expansions of V and shown that they are related to the Breit-Pauli relativistic orbit-orbit term.

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APPENDIX

In this appendix we give some useful identities involving integrals that can be related to the frequency-dependent polarizabilities. Given the well-known integral representation

$$\frac{1}{a+b} = \frac{2ab}{\pi}\int_0^\infty \frac{d\omega}{(a^2+\omega^2)(b^2+\omega^2)}, \quad a,b>0 \qquad \text{(A1)}$$

and using the identity

$$I_1(a) \equiv \frac{a}{a^2+\omega^2} = \mathrm{Re}\left(\frac{1}{a-i\omega}\right), \qquad \text{(A2)}$$

we have, by substituting $I_1(a)$ and $I_1(b)$ into Eq. (A1),

$$\frac{1}{a+b} = \frac{2}{\pi}\int_0^\infty \mathrm{Re}\left(\frac{1}{a-i\omega}\right)\mathrm{Re}\left(\frac{1}{b-i\omega}\right). \qquad \text{(A3)}$$

Similarly, using

$$I_2(a) \equiv \frac{a^2}{a^2+\omega^2} = 1-\omega\mathrm{Im}\left(\frac{1}{a-i\omega}\right) \qquad \text{(A4)}$$

we have, by multiplying Eq. (A1) by ab and using $I_2(a)$ and $I_2(b)$, the identity

$$\frac{ab}{a+b} = \frac{2}{\pi}\int_0^\infty d\omega\left[1-\omega\mathrm{Im}\left(\frac{1}{a-i\omega}\right)\right] \times\left[1-\omega\mathrm{Im}\left(\frac{1}{b-i\omega}\right)\right]. \qquad \text{(A5)}$$

Analogous identities may be derived using the (less) well-known identity

$$\frac{1}{a+b} = \frac{2}{\pi}\int_0^\infty \frac{\omega^2 d\omega}{(a^2+\omega^2)(b^2+\omega^2)}, \quad a>0, b\geq 0 \text{ or } a\geq 0, b>0. \qquad \text{(A6)}$$

Given the definition

$$I_3(a) \equiv \frac{\omega}{a^2+\omega^2} = \mathrm{Im}\left(\frac{1}{a-i\omega}\right), \qquad \text{(A7)}$$

and substituting $I_3(a)$ and $I_3(b)$, Eq. (A7), into Eq. (A6) we get

$$\frac{1}{a+b} = \frac{2}{\pi}\int_0^\infty d\omega\mathrm{Im}\left(\frac{1}{a-i\omega}\right)\mathrm{Im}\left(\frac{1}{b-i\omega}\right) \qquad \text{(A8)}$$

and following a similar procedure using $I_1(a)$ and $I_1(b)$, Eq. (A2), into Eq. (A6) we get

$$\frac{ab}{a+b} = \frac{2}{\pi}\int_0^\infty d\omega\,\omega^2\,\mathrm{Re}\left(\frac{1}{a-i\omega}\right)\mathrm{Re}\left(\frac{1}{b-i\omega}\right). \qquad \text{(A9)}$$

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