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Long-range dispersion interactions. II. Alkali-metal and rare-gas atoms

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The dispersion coefficients for the van der Waals interactions between the rare gases Ne, Ar, Kr, and Xe and the low-lying states of Li, Na, K, and Rb are estimated using a combination of *ab initio* and semiempirical methods. The rare-gas oscillator strength distributions for the quadrupole and octupole transitions were derived by using high-quality calculations of rare-gas polarizabilities and dispersion coefficients to tune Hartree-Fock single-particle energies and expectation values.

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I. INTRODUCTION

Recently a formalism [1] was presented that allows the van der Waals interaction between two atoms [2,3], e.g.,

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots \quad (1)$$

to be computed in a relatively straightforward manner. The C_n parameters in Eq. (1) are the dispersion coefficients while R is the distance between the two nuclei.

In this previous work, the dispersion coefficients for ground and excited states of alkali-metal atoms interacting with helium and atomic hydrogen were presented [1]. The present work extends the calculations to encompass the heavier rare gases, namely, neon, argon, krypton, and xenon, to give improved descriptions of the interaction potential at large distances.

One of the main applications of this work lies in the area of pressure broadening [4–6]. The theory of spectral line broadening relies on an accurate description of the potential curves between the two states undergoing the transition and the perturbing atom. The size of the dispersion parameters has a major influence upon the broadening since many of the collisions occur at large impact parameters. While there have been a number of investigations of the dispersion interaction between ground state alkali-metal atoms and the rare gases [2,7–12], this is not true for the alkali-metal-atom excited states which have received only the most cursory attention [12].

This is surprising since the alkali-metal–rare-gas combination represents an almost ideal laboratory in which to investigate the general theory of pressure broadening of radiation by a perturbing atom or molecule. There have been a number of laboratory investigations of broadening for lithium [13–15], sodium [16–21], potassium [22], and rubidium [23,24]. In addition, there have been a number of theoretical investigations of alkali metal spectral line broadening caused by the rare gases [15,25–30]. Knowledge of the van der Waals interaction is also important for the determination of the refractive index of alkali-metal-atom matter waves traveling through rare gases [31–33]. The present paper gives the dispersion coefficients between the two lowest alkali-metal s states and the rare gases. In addition, dispersion coefficients between lowest lying p and d states and the rare gases are also given. All dispersion coefficients are reported in atomic units (a.u.).

II. GENERATION OF THE TRANSITION MOMENT ARRAYS

A. Theoretical overview

The approach used to generate the dispersion coefficients is based on the work of Dalgarno who originally derived expressions in terms of oscillator strength sum rules [2,3]. This reduced the calculation of the C_n parameters for two spherically symmetric atoms to sums over the products of the absorption oscillator strengths (originating in the ground state) divided by an energy denominator. The sums should include contributions from all discrete and continuum excitations. In practice a pseudostate representation is used which gives a discrete representation of the continuum [1,34]. The sum over oscillator strengths needs to be rewritten in terms of a sum over the reduced matrix elements of the electric multipole operator in cases where one (or both) of the atoms is in a state with $L>0$ [1].

The major part of any calculation involves the generation of lists of reduced transition matrix elements for the two atomic states. This involves quite lengthy calculations to generate the excitation spectrum of the pseudostate representation. It is then a relatively straightforward calculation to use the formalism outlined in Zhang and Mitroy [1] to process the lists of matrix elements and generate the dispersion coefficients.

B. The alkali-metal atoms

The transition arrays for the alkali-metal atoms are those which were used in calculations of the dispersion interactions between these atoms and the ground states of hydrogen and helium [1]. These are computed by diagonalizing the fixed core Hamiltonian in a large basis of Laguerre-type orbitals. The core Hamiltonian is based upon an HF description of the core with a semiempirical core polarization potential tuned to reproduce the energies of low-lying spectrum.

Core excitations are included in the dispersion parameter calculation. Oscillator strength distributions were constructed by using independent estimates of the core polarizabilities to constrain the sum rules [34–37]. The methodology of using constrained sum rules is also used for the rare gases and is discussed more fully in the next section.

C. The rare gases

The rare-gas transition arrays that contribute to the dispersion parameter calculation are obtained from constrained

TABLE I. Multipole oscillator strength ($f^{(l)}$) distributions and corresponding excitation energies for the rare gases. The numbers in the square brackets denote powers of 10.

$l=2$		$l=3$	
ΔE	$f^{(2)}$	ΔE	$f^{(3)}$
	Ne		
33.9925	0.133878	33.6045	1.75422[−2]
3.15043	3.86864	2.76243	11.2038
2.07044	12.2909	1.68244	58.9965
0.759537	2.45818	0.772737	11.7993
	Ar		
119.209	3.98387[−2]	119.162	1.53543[−3]
12.9212	8.04905[−1]	12.8742	4.31731[−1]
10.1705	2.09210	10.1235	1.14016
1.87635	9.39598	1.82935	56.1225
1.19002	33.1090	1.14302	314.699
0.497717	6.62181	0.475217	62.9399
	Kr		
520.604	9.64829[−3]	520.610	8.88348[−5]
70.3421	1.65122[−1]	70.3471	1.76317[−2]
63.44877	3.84045[−1]	63.4538	3.68588[−2]
11.28845	1.32692	11.2936	1.03610
8.77049	4.12244	8.77559	3.53790
4.26423	7.42956	4.26933	8.61329
1.59193	12.1612	1.59703	90.0166
0.963181	44.5482	0.968281	528.064
0.445401	8.90964	0.401311	105.613
	Xe		
1224.66	4.23665[−3]	1224.61	1.70417[−5]
189.625	6.86382[−2]	189.582	3.00160[−3]
178.067	1.54981[−1]	178.024	5.88693[−3]
40.4602	4.63478[−1]	40.4172	1.21755[−1]
35.5061	1.32979	35.4631	3.49418[−1]
26.4033	1.85270	26.3603	4.64015[−1]
8.14081	2.50232	8.09781	3.42416
6.29285	8.22655	6.24985	12.7347
3.06236	17.5948	3.01936	38.5874
1.22936	17.7446	1.18636	1.81736[2]
0.742226	62.4884	0.699226	9.51970[2]
0.380326	12.4977	0.372196	1.90394[2]

sum rules. The data for the dipole transitions come from a set of previously published pseudo-excitation-energies and dipole oscillator strengths [38]. The pairs of (f_{0i},E_{0i}) were constrained to give f-value sum rules in agreement with empirical estimates of these sum rules [39]. For all practical purposes, these sets of empirical estimates (f_{0i},E_{0i}) are expected to give estimates of dispersion coefficients that are accurate to about 1% [38,39].

The data for the quadrupole and octupole transitions were derived by tuning an f-value distribution obtained from Hartree-Fock calculations to high-accuracy calculations of the polarizabilities and the dispersion coefficients between two identical rare-gas atoms [34,37]. We use the sum rule for the multipole polarizability $\alpha^{(l)}$

$$\alpha^{(l)} = \sum_i \frac{f_{0i}^{(l)}}{\epsilon_{0i}^2} \tag{2}$$

and

$$lN\langle r^{2l-2}\rangle = \sum_i f_i^{(l)} = S^{(l)}(0) \tag{3}$$

[40] to help estimate an $f^{(l)}$-value distribution function of reasonable accuracy. Equation (3) reduces to the well known Thomas-Reiche-Kuhn sum rule

$$N = \sum_i f_i^{(1)} = S^{(1)}(0) \tag{4}$$

for $l=1$. In these equations, N is the total number of electrons, and $\langle r^{2l-2}\rangle$ is a radial expectation value of the ground-state wave function.

The other sum rules used to constrain the $(f_i^{(l)},\epsilon_i)$ distributions are those for the dispersion coefficients C_8 and C_{10}. These are

$$C_8 = \frac{15}{4}\sum_{ij}\frac{f_{0i}^{(1)}f_{0j}^{(2)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})} + \frac{15}{4}\sum_{ij}\frac{f_{0i}^{(2)}f_{0j}^{(1)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})} \tag{5}$$

and

$$C_{10} = 7\sum_{ij}\frac{f_{0i}^{(1)}f_{0j}^{(3)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})} + 7\sum_{ij}\frac{f_{0i}^{(3)}f_{0j}^{(1)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})} + \frac{35}{2}\sum_{ij}\frac{f_{0i}^{(2)}f_{0j}^{(2)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})}. \tag{6}$$

First, we assume that the contribution from each closed subshell is equal to the number of electrons in the subshell (N_i) multiplied by the mean value of r^{2l-2} for the subshell. The $\langle r^{2l-2}\rangle$ expectation value for each subshell is computed by using the Hartree-Fock (HF) wave function. These expectation values are expected to be accurate at the level of 1–2 % (ignoring relativistic effects) for the systems under consideration.

Next, the excitation energy for each subshell is set to the Koopmans energy ϵ_i (i.e., the single-particle energy coming from a HF calculation) plus an energy shift $\Delta_1^{(l)}$. The motivation for this is the expectation that the HF single-particle energies will give a reasonable initial approximation to the oscillator strength distribution originating from each shell [34,37]. The overall purpose of the energy shift is to refine the distribution so that it is consistent with the results of some sum rules for quantities such as the quadrupole polarizability for which reasonably accurate values are known.

For the valence np shell there are two energy shifts. Five of the six electrons are given energy shifts of $\Delta_1^{(l)}$, while one electron is given a different energy shift of $\Delta_2^{(l)}$. The multipole polarizability computed with this oscillator strength distribution is

TABLE II. The polarizabilities (in a.u.) and homonuclear dispersion coefficients (in a.u.) computed from the $f^{(\ell)}$-value distributions of Table I and Ref. [38] are in the row labeled present. The reference values used to tune the $f^{(2)}$ and $f^{(3)}$ oscillator strength distributions are discussed in the text. Values from nonrelativistic MBPT calculations [41] and relativistic MP2 calculations (TDMP2) [42] are also given. The notation $a[b]$ represents $a \times 10^b$.

System	Method	$\alpha^{(1)}$	$\alpha^{(2)}$	$\alpha^{(3)}$	C_6	C_8	C_{10}
Ne	Present	2.669	7.518	42.07	6.383	90.27	1.533[3]
	MBPT	2.656	7.328	42.07	6.553	90.34	1.536[3]
	TDMP2				6.543	91.79	1.589[3]
Ar	Present	11.08	52.80	536.4	64.30	1.621[3]	4.903[4]
	MBPT	11.06	51.86	536.4	64.30	1.623[3]	4.906[4]
	TDMP2	11.15	52.78	553.1	64.80	1.644[3]	5.024[4]
Kr	Present	16.79	98.20	1.255[3]	129.6	4.040[3]	1.501[5]
	MBPT	17.21	99.30	1.273[3]	135.1	4.187[3]	1.555[5]
	TDMP2	16.85	96.75	1.241[3]	130.1	3.981[3]	1.474[5]
Xe	Present	27.16	213.7	3455	285.9	1.200[4]	5.882[5]
	MBPT	28.22	223.3	3640.6	302.3	1.281[4]	6.198[5]
	TDMP2	27.17	202.8		288.4	1.139[4]	

$$\alpha^{(l)} = \sum_{i \neq np} \frac{N_i l r_i^{2l-2}}{(\epsilon_i + \Delta_1^{(l)})^2} + \frac{5 l r_{np}^{2l-2}}{(\epsilon_{np} + \Delta_1^{(l)})^2} + \frac{l r_{np}^{2l-2}}{(\epsilon_{np} + \Delta_2^{(l)})^2}. \qquad (7)$$

The parameters $\Delta_1^{(2)}$ and $\Delta_2^{(2)}$ are adjusted until $\alpha^{(2)}$ and C_8 agree with the reference values of these quantities. The C_8 dispersion parameter also requires knowledge of the dipole oscillator strength distribution which is taken from the empirical distributions of Kumar and Meath [38]. Once the quadrupole oscillator strength distribution has been fixed, the process can be repeated using $\alpha^{(3)}$ and C_{10} to fix the values of $\Delta_1^{(3)}$ and $\Delta_2^{(3)}$.

A tabulation of the $f^{(l)}$ distributions derived from this process are given in Table I. Table II gives the polarizabilities and C_n values (for homo-nuclear dimers) computed with these $f^{(l)}$ distributions. Once the oscillator strengths have been determined, the reduced matrix elements needed for the evaluation of the dispersion parameters are obtained from

$$f_{0n}^{(l)} = \frac{2|\langle \psi_0; L_0 \| r^l \mathbf{C}^l(\hat{\mathbf{r}}) \| \psi_n; L_n \rangle|^2 \Delta E_{n0}}{(2l+1)(2L_0+1)}, \qquad (8)$$

where $\Delta E_{n0} = E_n - E_0$. This expression can be inverted and the positive square root taken without any loss of generality since the rare-gas ground states have an angular momentum of zero.

The usefulness of this approach does depend on using accurate reference values of the quadrupole and octupole polarizabilities, and accurate values of C_8 and C_{10} to fix $\Delta_i^{(l)}$. These are now discussed.

1. Neon

Using the oscillator strength distributions of Kumar and Meath [38] gave $\alpha^{(1)} = 2.669 a_0^3$ and $C_6 = 6.383$ a.u. A reference value of $7.52 a_0^5$ was adopted for $\alpha^{(2)}$. This was taken from a coupled cluster calculation with full allowance for single and double excitations and with an estimate of the impact of triple excitations [CCSD(T)] [43]. This calculation gave $\alpha^{(1)} = 2.68 a_0^3$. An independent CCSD(T) calculation gave $\alpha^{(2)} = 7.525 a_0^5$ [44].

The reference value for the octupole polarizability $42.07 a_0^5$ was taken from a many-body perturbation theory (MBPT) calculation [41]. This MBPT calculation gave $\alpha^{(1)} = 2.656 a_0^3$. The reference values for the Ne-Ne dispersion coefficients $C_8 = 90.344$ a.u. and $C_{10} = 1535.6$ a.u. were also taken from an MBPT calculation [41].

2. Argon

Using the oscillator strength distributions of Kumar and Meath [38] gave $\alpha^{(1)} = 11.08 a_0^3$ and $C_6 = 64.30$ a.u. The value of $52.8 a_0^5$ was adopted for $\alpha^{(2)}$. This was derived from a coupled cluster calculation with full allowance for single and double excitations and with an estimate of the impact of triple excitations [43]. This calculation also gave $\alpha^{(1)} = 11.12 a_0^3$. This is a light atom and relativistic effects have a small impact upon the polarizabilities [a CCSD(T) calculation using a pseudopotential for the core gave a relativistic correction of only $-0.1 a_0^5$ to $\alpha^{(2)}$ [45]].

The reference value for the octupole polarizability, $536.4 a_0^7$ was taken from a MBPT calculation [41]. The MBPT calculation gave $\alpha^{(1)} = 11.06 a_0^3$ and $\alpha^{(2)} = 51.86 a_0^5$. The reference Ar-Ar dispersion coefficients $C_8 = 1623.2$ a.u. and $C_{10} = 40963$ a.u. were also taken from this MBPT calculation [41].

3. Inclusion of relativistic effects

Relativistic effects have a larger impact upon the structure and excitation spectrum for krypton and xenon than they do for neon and argon. Preferably, one would choose reference values for krypton and xenon directly from relativistic calculations, but the problem with this is that the best nonrelativistic calculations usually have a better treatment of electron

TABLE III. The dispersion coefficients (in a.u.) between two ground-state rare-gas atoms. Values from nonrelativistic MBPT calculations [41] and relativistic MP2 calculations (TDMP2) [42] are also listed. The numbers in the square brackets denote powers of ten.

System	Method	C_6	C_8	C_{10}
Ne-Ne	Present	6.383	90.27	1.533[3]
	MBPT	6.5527	90.344	1.5356[3]
	TDMP2	6.543	91.79	1.589[3]
Ne-Ar	Present	19.50	3.889[2]	9.335[3]
	MBPT	19.753	3.9012[2]	9.3352[3]
	TDMP2	19.85	3.965[2]	9.618[3]
Ne-Kr	Present	27.30	627.38	1.740[4]
	MBPT	28.009	6.3814[2]	1.7658[4]
	TDMP2	27.74	6.270[2]	1.768[4]
Ne-Xe	Present	39.66	1.128[3]	3.857[4]
	MBPT	40.518	1.1623[3]	3.8978[4]
	TDMP2	40.54	1.094[3]	
Ar-Ar	Present	64.30	1.621[3]	4.903[4]
	MBPT	64.543	1.6232[3]	4.9063[4]
	TDMP2	64.80	1.644[3]	5.024[4]
Ar-Kr	Present	91.13	2571.1	8.677[4]
	MBPT	93.16	2.6167[3]	8.8260[4]
	TDMP2	91.16	2.566[3]	8.685[4]
Ar-Xe	Present	134.5	4.527[3]	1.807[5]
	MBPT	137.97	4.6694[3]	1.8425[5]
	TDMP2	135.7	4.403[3]	
Kr-Kr	Present	129.6	4.040[3]	1.501[5]
	MBPT	135.08	4.1873[3]	1.5545[5]
	TDMP2	130.1	3.981[3]	1.474[5]
Kr-Xe	Present	191.9	7.026[3]	3.035[5]
	MBPT	201.27	7.3891[3]	3.1603[5]
	TDMP2	193.2	6.774[3]	
Xe-Xe	Present	285.9	1.200[4]	5.882[5]
	MBPT	302.29	1.2807[4]	6.1984[5]
	TDMP2	288.4	1.139[4]	

TABLE IV. The dispersion coefficients (in a.u.) between the ground states of alkali-metal atoms and rare-gas atoms. The data from the Standard and Certain (SC) tabulation [8] are also listed; the two numbers represent the estimates of lower and upper bounds for the coefficients. The numbers in the square brackets denote powers of ten.

System	Method	C_6	C_8	C_{10}
Li-Ne	Present	43.79	2.229[3]	1.531[5]
	SC	42.9–44.8	2.00[3]–2.20[3]	1.21[5]–1.47[5]
Li-Ar	Present	174.0	9.493[3]	6.781[5]
	SC	171–177	8.63[3]–9.49[3]	5.53[5]–6.69[5]
Li-Kr	Present	259.6	1.476[4]	1.087[6]
	SC	255–262	1.34[4]–1.48[4]	8.92[5]–1.08[6]
Li-Xe	Present	410.7	2.521[4]	1.957[6]
	SC	402–414	2.30[4]–2.54[4]	1.63[6]–1.97[6]
Na-Ne	Present	50.41	2.721[3]	1.993[5]
	SC	46–137	2.40[3]–3.19[3]	1.57[5]–1.94[5]
Na-Ar	Present	196.8	1.153[3]	8.769[5]
	SC	184–508	1.03[4]–1.53[4]	7.11[5]–9.30[5]
Na-Kr	Present	292.7	1.787[4]	1.398[6]
	SC	273–737	1.59[4]–2.48[4]	1.14[6]–1.53[6]
Na-Xe	Present	460.9	3.033[4]	2.496[6]
	SC	430–1130	2.71[4]–4.52[4]	2.05[6]–2.90[6]
K-Ne	Present	77.44	5.309[3]	4.936[5]
	SC	73.8–83.9	4.57[3]–5.04[3]	3.71[5]–4.38[5]
K-Ar	Present	299.3	2.228[4]	2.132[6]
	SC	292–318	1.95[4]–2.16[4]	1.65[6]–1.94[6]
K-Kr	Present	444.1	3.431[4]	3.352[6]
	SC	432–469	3.01[4]–3.33[4]	2.60[6]–3.06[6]
K-Xe	Present	697.9	5.751[4]	5.836[6]
	SC	680–737	5.07[4]–5.64[4]	4.60[6]–5.42[6]
Rb-Ne	Present	88.00	6.355[3]	6.231[5]
	SC	78.0–94.2	5.33[3]–5.99[3]	4.94[5]–5.63[5]
Rb-Ar	Present	336.4	2.656[4]	2.681[6]
	SC	310–352	2.27[4]–2.56[4]	2.16[6]–2.48[6]
Rb-Kr	Present	498.0	4.083[4]	4.203[6]
	SC	460–518	3.50[4]–3.93[4]	3.40[6]–3.89[6]
Rb-Xe	Present	780.1	6.819[4]	7.281[6]
	SC	725–813	5.87[4]–6.63[4]	5.92[6]–6.84[6]

correlations than the best relativistic calculations. The strategy adopted is to use estimates of the relativistic corrections to the $\alpha^{(l)}$ and C_n coefficients to adjust the best nonrelativistic values.

4. Krypton

The oscillator strength distributions of Kumar and Meath [38] gave $\alpha^{(1)}=16.79a_0^3$ and $C_6=129.6$ a.u. The value of $98.2a_0^5$ was adopted for $\alpha^{(2)}$. This was derived from a CCSD(T) calculation which gave 99.86 [43]. An independent CCSD(T) calculation using a pseudopotential for the core estimated the decrease in $\alpha^{(2)}$ due to relativistic effects to be $1.65a_0^5$ [45]. The CCSD(T) calculation gave $\alpha^{(1)}=17.07a_0^3$ if a correction of $0.01a_0^3$ is made for relativistic effects [45].

The reference value adopted for the octupole polarizability was $\alpha^{(3)}=1254.8a_0^7$. This was determined by adding a relativistic correction of $-17.8a_0^7$ (taken from a second order Moller-Plesset calculation [42]) to a value of $1272.6a_0^3$ taken from a large basis MBPT calculation [41] (this MBPT calculation gave $\alpha^{(1)}=17.21a_0^3$).

The reference values for the Kr-Kr dispersion coefficients were $C_8=4040$ a.u. and $C_{10}=1.501\times10^5$ a.u. These values were derived from the relativistic second order Moller-Plesset perturbation theory calculations (MP2) of Hattig and Hess [42] (note the data that is quoted was identified as TDMP2 in this paper). This calculation gave estimates of $C_6=130.1$ a.u. and $\alpha^{(1)}=16.85a_0^3$ which are in very good agreement with those of Kumar. However, the MP2 values of $\alpha^{(2)}=96.8a_0^5$ and $\alpha^{(3)}=1241a_0^7$ are, respectively, 1.5 and

TABLE V. The dispersion coefficients (in atomic units) for the Σ and Π symmetries, between the resonant *np* excited state of alkali-metal atoms and the ground-state atoms of rare gases. The numbers in the square brackets denote powers of ten.

System	Σ			Π		
	C_6	C_8	C_{10}	C_6	C_8	C_{10}
Li-Ne	9.822[1]	1.549[4]	1.849[6]	5.492[1]	7.522[2]	3.586[4]
Li-Ar	4.011[2]	6.379[4]	7.846[6]	2.201[2]	3.969[3]	1.949[5]
Li-Kr	6.049[2]	9.690[4]	1.216[7]	3.296[2]	6.818[3]	3.529[5]
Li-Xe	9.728[2]	1.584[5]	2.062[7]	5.244[2]	1.351[4]	7.578[5]
Na-Ne	1.492[2]	3.112[4]	4.739[6]	8.511[1]	1.395[3]	8.680[4]
Na-Ar	6.088[2]	1.283[5]	1.998[7]	3.413[2]	7.032[3]	4.354[5]
Na-Kr	9.187[2]	1.947[5]	3.078[7]	5.120[2]	1.186[4]	7.562[5]
Na-Xe	1.479[3]	3.171[5]	5.160[7]	8.167[2]	2.294[4]	1.539[6]
K-Ne	2.006[2]	5.065[4]	9.204[6]	1.187[2]	2.328[3]	1.670[5]
K-Ar	8.127[2]	2.089[5]	3.866[7]	4.717[2]	1.122[4]	8.022[5]
K-Kr	1.223[3]	3.169[5]	5.937[7]	7.060[2]	1.858[4]	1.358[6]
K-Xe	1.964[3]	5.151[5]	9.887[7]	1.123[3]	3.500[4]	2.664[6]
Rb-Ne	2.290[2]	6.289[4]	1.239[7]	1.379[2]	2.971[3]	2.256[5]
Rb-Ar	9.241[2]	2.595[5]	5.197[7]	5.451[2]	1.403[4]	1.066[6]
Rb-Kr	1.390[3]	3.934[5]	7.969[7]	8.150[2]	2.301[4]	1.785[6]
Rb-Xe	2.229[3]	6.391[5]	1.324[8]	1.295[3]	4.2797[4]	3.448[6]

1.1 % smaller than the reference values adopted for these polarizabilities. Accordingly, the effective $f^{(l)}$-value distributions of Hattig and Hess [42] for $l=2$ and 3 were rescaled by 1.015 and 1.011 and used in conjunction with their $f^{(1)}$ distributions to recompute C_8 and C_{10} resulting in the values listed at the start of this paragraph.

5. Xenon

The oscillator strength distributions of Kumar and Meath [38] gave $\alpha^{(1)}=27.16a_0^3$ and $C_6=285.9$ a.u. A value of $\alpha^{(2)}=213.7a_0^5$ was adopted as the reference. This was determined by adding a relativistic correction of $-9.64a_0^5$ (taken from a second order Moller-Plesset calculation [42]) to a value of $223.29a_0^3$ taken from a large basis MBPT calculation [41] (this MBPT calculation gave $\alpha^{(1)}=28.23a_0^3$). The C_8 reference values for the Xe-Xe interaction were determined by a procedure similar to that used for the Kr-Kr case. The relativistic MP2 $f^{(2)}$-value distribution of Hattig and Hess [42] was rescaled by 1.054 (=213.7/202.8) and used in conjunction with their $f^{(1)}$ distribution to give $C_8=1.200\times10^4$.

This procedure could not be adopted for $\alpha^{(3)}$ and C_{10} because Hattig and Hess did not report any calculations for this case. Accordingly, the relativistic correction was estimated by assuming it was the same relative size as the correction for the quadrupole transition. Using the data from Hattig and Hess, one gets a correction of 0.949=202.8/213.7. Scaling the MBPT octupole polarizability of 3640.6 by 0.949 gave a reference value of $\alpha^{(3)}=3455a_0^7$. (Note that the scale factors for the relativistic correction for $\alpha^{(2)}$ and $\alpha^{(3)}$ were roughly similar in size, e.g., for krypton they were 0.985 and 0.989, respectively.) The value of C_{10} was estimated by simply rescaling the MBPT value of 6.198×10^5 by 0.949 giving 5.882×10^5 as the reference value. This probably underestimates the size of the relativistic correction since the quadrupole-quadrupole sum in C_{10} should be rescaled by $(0.949)^2$ while the dipole-octupole sums are rescaled by 0.949.

III. CALCULATIONS AND RESULTS

A. Dispersion parameters

The dispersion coefficients were computed using the formalism presented in Ref. [1]. This formalism reduces the dispersion coefficients to sums over sets of reduced matrix elements of the two atoms. The oscillator strengths for the rare gases can be converted to reduced matrix elements without any error since the expressions for the dispersion relations involving one atom in an *S* state only involve squares of the reduced matrix elements for the *S*-state atom.

B. The heteronuclear rare-gas combinations

The complete set of dispersion coefficients for all the possible rare-gas combinations are listed in Table III. The ultimate accuracy of the tabulated coefficients is largely limited by the accuracy of the many-body calculations used to derive the reference values. Most of the dispersion coefficients were based on the MBPT dispersion coefficients of Thakkar *et al.* [41]. The present values of the dispersion coefficients for combinations involving Kr or Xe should be regarded as more accurate than the MBPT values since the impact of relativistic effects have been incorporated as corrections.

The other set of dispersion coefficients listed in Table IV are the TDMP2 values of Hattig and Hess [42]. The TDMP2

TABLE VI. The dispersion coefficients (in a.u.) between the $(n+1)s$ excited state of an alkali-metal atom and a rare-gas atom in its ground state. The data from the Proctor and Stwalley tabulation [7] are also listed. The numbers in the square brackets denote powers of ten.

System	Method	C_6	C_8	C_{10}
Li-Ne	Present	310.4	8.185[4]	2.578[7]
	PS	308.4	8.106[4]	2.545[7]
Li-Ar	Present	1.280 [3]	3.410[5]	1.077[8]
	PS	1.273 [3]	3.377[5]	1.062[8]
Li-Kr	Present	1.934 [3]	5.189[5]	1.645[8]
	PS	1.921 [3]	5.090[5]	1.597[8]
Li-Xe	Present	3.118 [3]	8.480[5]	2.710[8]
	PS	3.091 [3]	8.149[5]	2.546[8]
Na-Ne	Present	337.0	9.427[4]	3.153[7]
	PS	331.1	9.286[4]	3.095[7]
Na-Ar	Present	1.386 [3]	3.926[5]	1.317[8]
	PS	1.368 [3]	3.868[5]	1.291[8]
Na-Kr	Present	2.095 [3]	5.973[5]	2.010[8]
	PS	2.064 [3]	5.831[5]	1.943[8]
Na-Xe	Present	3.375 [3]	9.756[5]	3.306[8]
	PS	3.322 [3]	9.431[5]	3.099[8]
K-Ne	Present	435.5	1.488[5]	6.064[7]
	PS	417.6	1.443[5]	5.877[7]
K-Ar	Present	1.786 [3]	6.192[5]	2.529[8]
	PS	1.727 [3]	6.031[5]	2.450[8]
K-Kr	Present	2.697 [3]	9.413[5]	3.855[8]
	PS	2.607 [3]	9.096[5]	3.690[8]
K-Xe	Present	4.341 [3]	1.534[6]	6.319[8]
	PS	4.199 [3]	1.459[6]	5.898[8]
Rb-Ne	Present	469.6	1.685[5]	7.237[7]
	PS	444.1	1.630[5]	6.973[7]
Rb-Ar	Present	1.921 [3]	7.009[5]	3.017[8]
	PS	1.838 [3]	6.787[5]	2.907[8]
Rb-Kr	Present	2.899 [3]	1.065[6]	4.597[8]
	PS	2.773 [3]	1.024[6]	4.378[8]
Rb-Xe	Present	4.665 [3]	1.736[6]	7.530[8]
	PS	4.468 [3]	1.643[6]	7.001[8]

C_n coefficients are consistently smaller for interactions involving either krypton or xenon. This is expected since relativistic effects generally lead to contractions of the orbitals which result in smaller polarizabilities and dispersion interactions. The present values of the dispersion coefficients generally lie between the TDMP2 and MBPT values for interactions involving krypton or xenon.

C. The alkali-metal–rare-gas coefficients

The dispersion constants between the rare gases and the alkali-metal-atom ground states are given in Table III and compared with the compilation of Standard and Certain (SC) [8]. The values of SC were determined by constructing f-value distributions using a combination of experimental and theoretical information about polarizabilities, sum rules, and transition energies to give bounded estimates of the polarizabilities and thus the dispersion coefficients using Pade approximates [8,10]. It can be seen from Table III that many of the bounds given in the SC tabulation are quite loose, and in the case of interactions involving sodium, the variation between the upper and lower bounds is more than a factor of 2. Some older compilations of dispersion coefficients for the alkali-metal–rare-gas combinations [2,7,10–12] are not listed for reasons of brevity.

The present values should be regarded as superior to the SC compilation for three reasons. The pseudo-oscillator-strength distributions for the higher multipoles of the rare gases and alkali-metal cores should be better than the essentially one-term expressions for the dynamic polarizabilities used by SC [8,10]. In addition, the data used to bound the pseudo-f-value distributions is in many cases better. Finally, the dipole f-value distributions for the rare gases [38] and the valence f-value distributions used for the alkali-metal atoms [36] represent an update of the data that was available to SC in 1985 [8].

The C_8 and C_{10} dispersion coefficients were usually larger than the upper bounds given by SC. The only alkali-metal atom for which this does not occur is sodium, but the spread quoted by SC for the sodium upper and lower bounds is significantly larger than the spreads given for lithium, potassium, and cesium.

In addition to the ground state, the dispersion coefficients between the np alkali-metal excited state and the rare gases are given in Table V. Apart from the early work of Mahan [12], these values represent the only calculations of the dispersion coefficients between the alkali-metal np states and the rare gases from neon onward (note that there have been some calculations of the dispersion coefficients for helium [1,46]). Data on the excited state potentials do exist [47–52] but almost nothing is known about the long-range forms of the potentials. The present calculations rectify this omission. The obvious trend in the table is the tendency for the dispersion coefficients to get larger as either the alkali-metal atom or the rare-gas atom increases in size.

The dispersion coefficients for the interaction of atoms in excited $(n+1)s$ states with the rare gases are listed in Table VI. The results of Proctor and Stwalley (PS) [7] are presented for comparison. The PS results were derived by using various constraints on oscillator strength sum rules (based on experimental and theoretical data) to determine the oscillator strength distribution as a function of excitation energy. Although PS quoted uncertainties, these are not given here since their uncertainties in many cases seem to be overoptimistic. The present C_n are all larger than those of PS. This is not surprising since PS did not include any contribution from the alkali-metal-atom cores in the calculation. Therefore it would be expected that the differences from the PS values would get larger as the size of the alkali-metal atom increases, and this is the case. The difference between the present and PS C_6 for the Li-Ne combination was 2.0 out of 310 a.u. For the Rb-Ne case, the difference for C_6 was 25.6 out of 469.6 a.u. This situation was reminiscent of the comparison with PS for the alkali-metal–He C_n coefficients of

TABLE VII. The dispersion coefficients (in atomic units) for the Σ, Π, and Δ symmetries, between the lowest *nd* excited state of the alkali-metal atoms with the ground state of rare-gas atoms. The numbers in the square brackets denote powers of ten.

System	Σ			Π			Δ		
	C_6	C_8	C_{10}	C_6	C_8	C_{10}	C_6	C_8	C_{10}
Li-Ne	428.3	3.132[5]	1.800[8]	380.4	1.138[5]	1.087[7]	236.5	−1.609[4]	−2.874[5]
Li-Ar	1.770[3]	1.299[6]	7.474[8]	1.571[3]	4.723[5]	4.755[7]	972.9	−6.199[4]	−1.395[6]
Li-Kr	2.678[3]	1.969[6]	1.135[9]	2.376[3]	7.173[5]	7.481[7]	1.469[3]	−8.975[4]	−2.209[6]
Li-Xe	4.323[3]	3.193[6]	1.848[9]	3.834[3]	1.168[6]	1.303[8]	2.365[3]	−1.325[5]	−3.815[6]
Na-Ne	422.7	3.035[5]	1.725[8]	375.7	1.104[5]	1.043[7]	234.7	−1.552[4]	−2.770[5]
Na-Ar	1.743[3]	1.259[6]	7.164[8]	1.548[3]	4.578[5]	4.566[7]	961.5	−5.969[4]	−1.341[6]
Na-Kr	2.636[3]	1.908[6]	1.088[9]	2.340[3]	6.954[5]	7.188[7]	1.451[3]	−8.634[4]	−2.121[6]
Na-Xe	4.253[3]	3.094[6]	1.772[9]	3.773[3]	1.133[6]	1.252[8]	2.334[3]	−1.272[5]	−3.652[6]
K-Ne	310.3	1.763[5]	8.399[7]	276.9	6.427[4]	5.172[6]	176.7	−8.498[3]	−1.423[5]
K-Ar	1.267[3]	7.310[5]	3.489[8]	1.128[3]	2.667[5]	2.289[7]	712.0	−3.190[4]	−6.713[5]
K-Kr	1.911[3]	1.109[6]	5.303[8]	1.701[3]	4.054[5]	3.630[7]	1.070[3]	−4.534[4]	−1.034[6]
K-Xe	3.073[3]	1.799[6]	8.648[8]	2.733[3]	6.617[5]	6.408[7]	1.711[3]	−6.432[4]	−1.694[6]
Rb-Ne	258.2	1.252[5]	5.305[7]	231.4	4.583[4]	3.321[6]	151.0	−5.600[3]	−8.989[4]
Rb-Ar	1.044[3]	5.190[5]	2.204[8]	932.9	1.901[5]	1.483[7]	599.1	−2.054[4]	−4.107[5]
Rb-Kr	1.571[3]	7.873[5]	3.352[8]	1.402[3]	2.892[5]	2.364[7]	896.7	−2.867[4]	−6.128[5]
Rb-Xe	2.518[3]	1.278[6]	5.473[8]	2.245[3]	4.728[5]	4.212[7]	1.427[3]	−3.899[4]	−9.364[5]

helium [1]. Part of the difference between the present and PS C_n can be attributed to the core. For example, omission of the core for the Rb(5*s*)-Ne interaction results in $C_6=449.7$ and $C_8=1.681\times10^3$ a.u., both of these values are still larger than the PS values.

The PS dispersion coefficients for the Li–rare-gas systems were recently utilized in a combined experimental and theoretical analysis of the noble gas pressure broadening of the ^{7}Li 2*s*−3*s* transition by Rosenberry *et al.* [15]. Rosenberry *et al.* were not able to get detailed quantitative agreement for either the pressure broadening or pressure shift. The present values of C_6 for the Li–rare-gas case agree with those of PS to better than 1%, and to within 5% for C_8, so any inaccuracies in the PS C_n coefficients are unlikely to be a major contributor to any error.

Table VII reports the dispersion coefficients between the lowest *nd* state of the alkali-metal atoms with the rare-gas ground states. The C_6 coefficients for a given alkali-metal atom show a tendency to get larger as the rare-gas atom gets larger. This behavior is expected. The C_n coefficients exhibit one pattern that is unexpected. The dispersion coefficients for a given rare gas tend to be largest for Li and smallest for rubidium; for example, the C_6 dispersion coefficients for the Σ, Π, and Δ states of Li-Ar decrease steadily as the Li is substituted by Na, K, and Rb. This behavior is caused by the nature of the downward transition from the *nd* state to the resonant *np* excited state. The oscillator strength for this transition is negative. As the alkali-metal atoms get larger, the negative contribution from this transition to C_6 gets larger leading to a reduction in the value of C_6. It is worth noting that the static dipole polarizability of the lowest *nd* state decreases as the alkali-metal atom gets larger [36].

One of the larger sources of error in the present calculations will be the oscillator strength distributions for the alkali-metal-atom cores since these were defined with a single $\Delta^{(l)}$ shift. The coefficient with the largest core contribution is C_6 for Rb-Ne, where 23% of C_6 arises from the core. Calculations of C_6 for the positronium–rare-gas and hydrogen–rare-gas interactions suggest the error involved in using a single $\Delta^{(1)}$ does not exceed 5% [37]. So the influence of the errors in the core $f^{(l)}$-value distributions could result in C_6 being too large by about 1–2 %. The influence of the core decreases as the excitation level of the alkali-metal atom increases (e.g., the core has a 4% effect on the Rb(6*s*)-Ne C_6), or the multipolarity of C_n increases (e.g., the core has a 6% effect on the Rb(5*s*)-Ne C_8), and decreases as the size of the rare-gas atom increases (e.g., the core has a 16% effect on the Rb(5*s*)-Xe C_6).

IV. SUMMARY

The van der Waals coefficients between the rare gases and some low-lying excited states of the alkali-metal atoms have been determined using sum rules over oscillator strengths and transition moments. The dipole oscillator strength distributions for the rare gases were taken from the empirical tabulations of Kumar and Meath [38]. The oscillator strength distributions for the higher multipoles were determined by tuning distributions derived from HF wave functions to expectation values taken from sophisticated many-body calculations.

The most recent previous compilation of the alkali-metal–rare-gas dispersion interactions is the one by SC [8]. The present values should be regarded as superseding the SC values. The underlying *f*-value distributions for the rare gases and alkali-metal atoms give dipole polarizabilities and dispersion interactions that are generally accurate to about 1% for the rare-gas–rare-gas and alkali-metal–alkali-metal cases [1,34,53–55]. The present C_8 and C_{10} dispersion coefficients are generally larger than the SC values or near the high end of allowable range indicated by SC.

The scope of the present article has been restricted to the *ns*, $(n+1)s$, and *np* and lowest *md* states of the alkali-metal atoms, mainly to keep the length of the present article to a reasonable size. However, generating tables of dispersion coefficients for other low-lying excited states of alkali-metal atoms would be relatively straightforward.

[1] J. Y. Zhang and J. Mitroy, Phys. Rev. A **76**, 022705 (2007).
[2] A. Dalgarno and W. D. Davison, Adv. At. Mol. Phys. **2**, 1 (1966).
[3] A. Dalgarno, Adv. Chem. Phys. **12**, 143 (1967).
[4] S. Chen and M. Takeo, Rev. Mod. Phys. **29**, 20 (1956).
[5] G. Peach, Adv. Phys. **30**, 367 (1981).
[6] N. Allard and J. Kielkopf, Rev. Mod. Phys. **54**, 1103 (1982).
[7] T. R. Proctor and W. C. Stwalley, J. Chem. Phys. **66**, 2063 (1977).
[8] J. M. Standard and P. R. Certain, J. Chem. Phys. **83**, 3002 (1985).
[9] N. A. Lima and M. J. Caldas, Phys. Rev. B **72**, 033109 (2005).
[10] K. T. Tang, J. M. Norbeck, and P. R. Certain, J. Chem. Phys. **64**, 3063 (1976).
[11] P. Huxley, D. B. Knowles, J. N. Murrell, and J. D. Watts, J. Chem. Soc., Faraday Trans. 2 **80**, 1349 (1984).
[12] G. D. Mahan, J. Chem. Phys. **50**, 2755 (1969).
[13] A. Gallagher, Phys. Rev. A **12**, 133 (1975).
[14] R. Kachru, T. J. Chen, T. W. Mossberg, and S. R. Hartmann, Phys. Rev. A **25**, 1546 (1981).
[15] M. A. Rosenberry, K. M. Burgess, and B. Stewart, J. Phys. B **40**, 77 (2007).
[16] F. Biraben, B. Cagnac, E. Giacobino, and G. Grynberg, J. Phys. B **10**, 2369 (1976).
[17] W. P. West and A. Gallagher, Phys. Rev. A **17**, 1431 (1978).
[18] R. H. Chatham, A. Gallagher, and E. L. Lewis, J. Phys. B **13**, L7 (1980).
[19] J. F. Kielkopf, J. Phys. B **13**, 3813 (1980).
[20] J. Huennekens, H. J. Park, T. Colbert, and S. C. McClain, Phys. Rev. A **35**, 2892 (1987).
[21] M. J. Jongerius, J. Phys. B **20**, 3345 (1987).
[22] J. P. Hohimer and J. Gee, Phys. Rev. A **25**, 1404 (1982).
[23] M. D. Rotondaro and G. P. Perram, J. Quant. Spectrosc. Radiat. Transf. **57**, 497 (1997).
[24] D. Aumiler, T. Ban, and G. Pichler, Phys. Rev. A **70**, 032723 (2004).
[25] C. Bottcher, A. Dalgarno, and E. L. Wright, Phys. Rev. A **7**, 1606 (1973).
[26] W. Behmenburg, A. Ermers, and F. Rebentrost, Z. Phys. D **18**, 93 (1991).
[27] K. J. Nieuwesteeg, J. A. Leegwater, T. Hollander and C. T. J. Alkemade, J. Phys. B **20**, 3345 (1987).
[28] W. S. Lobb and D. G. McCartan, J. Phys. B **21**, L723 (1988).
[29] C. Zhu, J. F. Babb, and A. Dalgarno, Phys. Rev. A **71**, 052710 (2005).
[30] C. Y. Robert Wu and W. C. Stwalley, Phys. Rev. A **18**, 1066 (1978).
[31] C. Champenois, E. Eudouard, P. Duplaa, and J. Vigue, J. Phys. II **7**, 523 (1997).
[32] S. Blanchard, D. Civello, and R. C. Forrey, Phys. Rev. A **67**, 013604 (2003).
[33] T. D. Roberts, A. D. Cronin, D. A. Kokorowski, and D. E. Pritchard, Phys. Rev. Lett. **89**, 200406 (2002).
[34] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 052714 (2003).
[35] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **70**, 052503 (2004).
[36] J. Y. Zhang, J. Mitroy, and M. W. J. Bromley, Phys. Rev. A **75**, 042509 (2007).
[37] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 035201 (2003).
[38] A. Kumar and W. J. Meath, Mol. Phys. **54**, 823 (1985).
[39] A. Kumar and W. J. Meath, Can. J. Chem. **63**, 1616 (1985).
[40] D. Rosenthal, R. P. McEachran, and M. Cohen, Proc. R. Soc. London, Ser. A **337**, 365 (1974).
[41] A. J. Thakkar, H. Hetterna, and P. E. S. Wormer, J. Chem. Phys. **97**, 3252 (1992).
[42] C. Hattig and B. A. Hess, J. Phys. Chem. **100**, 6243 (1996).
[43] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **100**, 2975 (1994).
[44] G. Maroulis and A. J. Thakkar, Chem. Phys. Lett. **156**, 87 (1989).
[45] A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **102**, 8942 (1995).
[46] C. Zhu, A. Dalgarno, S. G. Porsev, and A. Derevianko, Phys. Rev. A **70**, 032722 (2004).
[47] R. Duren and G. Moritz, J. Chem. Phys. **73**, 5155 (1980).
[48] E. Zanger, V. Schmatloch, and D. Zimmermann, J. Chem. Phys. **88**, 5396 (1988).
[49] M. B. El Hadj Rhouma, H. Berriche, Z. B. Lakhdar, and F. Spiegelman, J. Chem. Phys. **116**, 1839 (2002).
[50] C. Figl, J. Grosser, O. Hoffmann, and F. Rebentrost, J. Phys. B **37**, 3369 (2004).
[51] F. Masnou-Seeuws, J. Phys. B **15**, 883 (1982).
[52] W. Behmenburg, A. Kaiser, F. Rebentrost, M. Jungen, M. Smit, M. Luo, and G. Peach, J. Phys. B **31**, 689 (1998).
[53] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 062710 (2003).
[54] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **71**, 019902(E) (2005); **71**, 019903(E) (2005).
[55] S. G. Porsev and A. Derevianko, JETP **129**, 227 (2006).