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Semiempirical calculation of van der Waals coefficients for alkali-metal and alkaline-earth-metal atoms

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The van der Waals coefficients, C_6, C_8, and C_{10} for the alkali-metal (Li, Na, K, and Rb) and alkaline-earth-metal (Be, Mg, Ca, and Sr) atoms are estimated by a combination of *ab initio* and semiempirical methods. Polarizabilities and atom-wall coefficients are given as a diagnostic check, and the lowest order nonadiabatic dispersion coefficient, D_8 and the three-body coefficient, C_9 are also presented. The dispersion coefficients are in agreement with the available relativistic many-body perturbation theory calculations. The contribution from the core was included by using constrained sum rules involving the core polarizability and Hartree-Fock expectation values to estimate the *f*-value distribution.

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I. INTRODUCTION

One of the most startling recent achievements in physics has been the realization of Bose-Einstein condensation (BEC) for the alkali-metal atoms, Li, Na, Rb, and atomic hydrogen [1,2]. This has naturally stimulated interest in whether other atomic gases can achieve a BEC. Recent interest has focused on the alkaline-earth-metal atoms, Mg, Ca, and Sr and it has recently proved possible to cool and trap these atoms [3,4]. For a number of reasons (e.g., these atoms all have isotopes with zero nuclear spin) a BEC consisting of alkaline-earth-metal atoms is more amenable to analysis.

One consequence of the realization of the BEC has been the increased importance in determining the interaction potentials in alkali-metal and alkaline-earth-metal atoms. For example, the stability and structure of BECs depends on the sign (and magnitude) of the scattering length, and the scattering length depends on the precise values of the dispersion constants [5,6]. The long-range interaction between two spherically symmetric atoms can be written in the general form

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \dots, \tag{1}$$

where the C_n parameters are the van der Waals dispersion coefficients.

The importance of this topic is demonstrated by the high degree of recent activity aimed at determining the dispersion constants for the alkali and alkaline-earth metals. This has consisted of experimental [3,4,7–9] and theoretical [10–14] investigations. Of particular importance from the theoretical perspective have been the investigations using relativistic many-body perturbation theory (MBPT) [10–13] since this method is believed to give dispersion coefficients accurate to order 1%.

In this paper, the C_n dispersion coefficients and related parameters are computed using a semiempirical approach for a number of alkali and alkaline-earth atoms by directly summing the appropriate oscillator strength sum rules. This approach to the evaluation of the sum rules was pioneered by Dalgarno and collaborators [15–17]. We have recently completed a series of investigations on a number of positronic atoms [18,19] (these are neutral atoms that have a bound positron [20–22]). The realistic description of positronic atom structure requires a model that is able to describe the polarization response of the atom to the Coulomb field of the positron. Since the available evidence suggests that our semiempirical model can describe these polarization responses quite accurately it is natural to apply it to the determination of the dispersion coefficients, C_6, C_8, and C_{10}. Comparisons of the present dispersion coefficients with those derived from relativistic MBPT calculations [10–12] reveals an excellent level of agreement and confirms that the semiempirical potential method used in the present work is capable of achieving a level of accuracy comparable with the more computationally intensive MBPT approach. Once the *f*-values distributions have been constructed, it is a simple matter to determine other dispersion parameters, such as the nonadiabatic parameter D_8 [23,24], and the three-body parameter C_9 [25,26]. It is noted a compendium of recommended dispersion parameters for the alkali and alkaline-earth calculations does exist [27]. However, the primary data used to establish the upper and lower bounds on the dispersion parameters is rather dated.

II. CALCULATIONS USING OSCILLATOR STRENGTH SUM-RULES

All of the polarization parameters that are reported were computed from their respective oscillator strength sum-rules with the dipole, quadrupole, and octupole oscillator strengths $f_{0i}^{(\ell)}$ from the ground state (with orbital and spin angular momentum equal zero) to the ith excited state defined as

$$f_{0i}^{(\ell)} = \frac{2|\langle \psi_0 \| r^\ell \mathbf{C}^\ell(\hat{\mathbf{r}}) \| \psi_i \rangle|^2 \epsilon_{0i}}{(2\ell+1)}. \tag{2}$$

In this expression $\mathbf{C}^\ell$ is the spherical tensor of rank ℓ while ϵ_{0i} is the excitation energy of the transition. The sum rule for the adiabatic multipole polarizability, $\alpha^{(\ell)}$ is

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$$\alpha^{(\ell)} = \sum_i \frac{f_{0i}^{(\ell)}}{\epsilon_{0i}^2} = S^{(\ell)}(-2), \tag{3}$$

while the nonadiabatic polarizability, $\beta^{(\ell)}$ is given by

$$\beta^{(\ell)} = \frac{1}{2}\sum_i \frac{f_{0i}^{(\ell)}}{\epsilon_{0i}^3} = \frac{1}{2} S^{(\ell)}(-3). \tag{4}$$

The dipole-dipole dispersion parameter, C_6 is

$$C_6 = \frac{3}{2}\sum_{ij} \frac{f_{0i}^{(1)} f_{0j}^{(1)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})}, \tag{5}$$

the dipole-quadrupole dispersion parameter, C_8 is

$$C_8 = \frac{15}{2}\sum_{ij} \frac{f_{0i}^{(1)} f_{0j}^{(2)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})} + \frac{15}{2}\sum_{ij} \frac{f_{0i}^{(2)} f_{0j}^{(1)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})} \tag{6}$$

and the dispersion parameter, C_{10}

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

The sum rules are a generalized sum which implicitly includes a sum over excitations to bound states and an integration taking into account excitations to continuum states. In the present work the sum rule is explicitly discretized. It is known that C_6 parameters derived from pseudostate calculations generally converge very quickly as the dimension of the pseudostate basis is increased [28,29].

Besides the standard atom-atom adiabatic dispersion parameters, the atom-wall dispersion parameter C_3

$$C_3 = \frac{1}{8}\sum_i \frac{f_{0i}^{(1)}}{\epsilon_{0i}} = \frac{1}{8} S^{(1)}(-1), \tag{8}$$

the nonadiabatic atom-atom dispersion parameter, D_8 [23,24]

$$D_8 = \frac{45}{2}\sum_{ij} \frac{f_{0i}^{(1)} f_{0j}^{(1)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})^2}, \tag{9}$$

and the three-body dispersion parameter, C_9

$$C_9 = \frac{3}{2}\sum_{ijk} \frac{f_{0i}^{(1)} f_{0j}^{(1)} f_{0k}^{(1)}(\epsilon_{0i}+\epsilon_{0j}+\epsilon_{0k})}{\epsilon_{0i}\epsilon_{0j}\epsilon_{0k}(\epsilon_{0i}+\epsilon_{0j})(\epsilon_{0i}+\epsilon_{0k})(\epsilon_{0j}+\epsilon_{0k})} \tag{10}$$

were determined. Equations (9) and (10) were written down by reference to similar equations presented in Marinescu, and Dalgarno [24], Yan *et al.* [25], and Maninescu and Starace [26].

All of the sum rules involve contributions from both core and valence excitations. The valence contributions were evaluated by simply diagonalizing the model Hamiltonian in a very large basis. This is essentially a brute-force evaluation of the sum rules. Determination of the *f*-value distribution for the core is more problematic and is handled by using the properties of *f*-value sum rules. The programs used to compute the dispersion coefficients were checked by reference to the data of Yan *et al.* [25].

A. Core contributions

The contribution from the core was calculated using an approximation designed to give a reasonable estimate of the *f*-value distribution with a minimum of computation. We use the sum rule for the polarizability, Eq. (3) and

$$\ell N \langle r^{2\ell-2} \rangle = \sum_i f_i^{(\ell)} = S^{(\ell)}(0), \tag{11}$$

Ref. [39] to estimate an $f^{(\ell)}$-value distribution function of reasonable accuracy. This expression reduces to the well known Thomas-Reiche-Kuhn sum rule

$$N = \sum_i f_i^{(1)} = S^{(1)}(0), \tag{12}$$

for $\ell = 1$. In these expressions N is the total number of electrons and $\langle r^{2\ell-2} \rangle$ is an expectation value of the ground state wave function.

First, we assume that the contribution from each closed subshell (N_i) is equal to the number of electrons in the subshell multiplied by the mean value of $r^{2\ell-2}$ for the subshell. The $\langle r^{2\ell-2} \rangle$ expectation value is computed using the Hartree-Fock (HF) wave function for the core and is 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 Koopman energy, ϵ_i (i.e., the single particle energy coming from a HF calculation) plus an energy shift. Then, the expression

$$\alpha_{\text{core}}^{(\ell)} = \sum_i \frac{\ell N_i r_i^{2\ell-2}}{(\epsilon_i + \Delta^{(\ell)})^2}, \tag{13}$$

is used to fix $\Delta^{(\ell)}$ so that the computed polarizability is equal to the experimentally known core polarizability, $\alpha_{\text{core}}^{(\ell)}$. A tabulation of the values assigned to $\Delta^{(\ell)}$ and the underlying quadrupole and octupole polarizabilities used to fix $\Delta^{(\ell)}$ is given in Table I.

Once the $\Delta^{(\ell)}$ are fixed, the dispersion parameters are easily evaluated. For example, the dipole atom-wall dispersion parameter C_3 is

$$C_3 = \sum_{i \in \text{core}} \frac{N_i}{(\epsilon_i + \Delta)} + \sum_{i \in \text{val}} \frac{f_{0i}^{(1)}}{\epsilon_{0i}}, \tag{14}$$

As a more complicated case, the C_6 parameter for two atoms *a* and *b* can be partitioned into

$$C_6 = C_6^{\text{c}} + C_6^{\text{v}} + C_6^{\text{cv}}, \tag{15}$$

TABLE I. Atomic multipole polarizabilities, $\alpha^{(\ell)}_{\text{core}}$ (given in a.u.) for the singly charged cores of the alkali-metal atoms and the doubly charged cores of the alkaline-earth-metal atoms. The $\Delta^{(\ell)}$ parameters (in Hartree) needed for the Koopman model to reproduce the known polarizabilities are also listed.

System	$\alpha^{(1)}_{\text{core}}$	$\Delta^{(1)}$	$\alpha^{(2)}_{\text{core}}$	$\Delta^{(2)}$	$\alpha^{(3)}_{\text{core}}$	$\Delta^{(3)}$
Li^+	0.1925 [30]	0.745	0.1139 [31]	1.398	0.1684 [30]	1.878
Na^+	0.99 [32]	1.12	1.521 [33]	1.198	7.5 [13]	0.531
K^+	5.47 [34,35]	0.156	16.27 [33]	0.457	110 [13]	0.419
Rb^+	9.076 [33]	0.0689	35.41 [33]	0.330	314 [13]	0.301
Be^{2+}	0.0523 [35,36]	1.451	0.015 32 [31]	3.066		
Mg^{2+}	0.4814 [37]	1.5445	0.5183 [33]	1.741		
Ca^{2+}	3.16 [35,38]	0.1319	6.936 [33]	0.5881		
Sr^{2+}	5.813 [33]	0.009 99	17.15 [33]	0.3972		

where

$$C_6^{\text{c}}=\frac{3}{2}\sum_{\substack{i\in\text{core:a}\\ j\in\text{core:b}}}\frac{N_iN_j}{(\epsilon_i+\Delta_a^{(1)})(\epsilon_j+\Delta_b^{(1)})(\epsilon_i+\Delta_a^{(1)}+\epsilon_j+\Delta_b^{(1)})},\tag{16}$$

$$C_6^{\text{cv}}=\frac{3}{2}\sum_{\substack{i\in\text{core:a}\\ j\in\text{val:b}}}\frac{N_if_{0j}^{(1)}}{(\epsilon_i+\Delta_a^{(1)})\epsilon_{0j}(\epsilon_i+\Delta_a^{(1)}+\epsilon_{0j})}+\frac{3}{2}\sum_{\substack{i\in\text{val:a}\\ j\in\text{core:b}}}\frac{f_{0i}^{(1)}N_j}{\epsilon_{0i}(\epsilon_j+\Delta_b^{(1)})(\epsilon_{0i}+\epsilon_j+\Delta_b^{(1)})},\tag{17}$$

and

$$C_6^{\text{v}}=\frac{3}{2}\sum_{i,j\in\text{val}}\frac{f_{0i}^{(1)}f_{0j}^{(1)}}{\epsilon_{0i}\epsilon_{0j}(\epsilon_{0j}+\epsilon_{0i})}.\tag{18}$$

Similar expressions for the other dispersion parameters are easily derived. In practice, expressions such as the above are not used explicitly in the calculations, rather the $f^{(\ell)}$-value distributions are constructed incorporating the appropriate entries for the core, and all dispersion parameters are then determined using Eqs. (3)–(10). The expressions above are most useful in understanding how the core contributes to the different dispersion parameters.

The relative contributions of the core to $\alpha^{(\ell)}$ get smaller as ℓ increases because of the $\ell r_i^{(2\ell-2)}$ weighting factors. This has implications for the core contribution to the C_8 and C_{10} dispersion parameters. The part of the $f^{(2)}$ and $f^{(3)}$ distributions arising from the core make a rather small contribution to the final values of C_8 and C_{10}. It must also be noted that the contribution to C_6 from the core *f*-value distribution were 10% or less for every system studied in this paper. Detailed discussions of the reliability of the core oscillator strengths distributions occur later.

B. Valence contributions

For the valence electron(s), a model potential calculation was used to determine the wave function of the ground state and the $L=1$ excited states. The model potential adds a semi-empirical polarization potential to the direct and exchange interactions of the Hartree-Fock (HF) core. This method has been described in numerous other calculations [34,38,40,41] and does not need to be recapitulated here in any detail. Instead Tables II and III summarize some of the crucial atomic parameters such as the resonance oscillator strength and static multipole polarizabilities that can be used to assess the overall accuracy of the model.

The calculations for the alkali atoms were straightforward. The ℓ-dependent polarization potentials were tuned so that they reproduced the binding energies of the ns ground state and the np, nd, and nf excited states. The energies of the excited states were assigned to the statistical average of their respective spin-orbit doublets. The model one-body Hamiltonian was then diagonalized in a very large orbital basis (e.g., 20–40 Laguerre type orbitals for each ℓ-value) and the oscillator strengths computed using a dipole operator with polarization corrections. Although the wave functions are constructed as linear combinations of these analytic basis functions, all matrix element evaluations were done using Gaussian quadratures. The matrix elements are accurate to close to machine precision. The cutoff parameter for the modified dipole operator has usually been chosen in our earlier work by reference to the equivalent cutoff parameters of the ℓ-dependent polarization potential. This choice has resulted in oscillator strengths of high accuracy [34,38,40].

The present model-potential configuration interaction (CI) calculations of the alkaline-earth atoms are very similar to those reported in Refs. [18] and [19] apart from some minor changes in the cutoff parameters and the use of an orbital basis of larger dimension. The polarization potentials were initially defined by tuning the potential to reproduce the ns, np, nd, and nf binding energies of the respective singly ionized atom. The Hamiltonian was then diagonalized in a basis consisting of all the two-electron basis states that could be formed from a set of >120 single particle orbitals. The basis set contained orbitals up to and including $\ell\leqslant 8$. Typically the two-electron basis dimensions were about 900 for the $^1S^e$ symmetry, about 1700 for the $^1P^o$ symmetry, about 2400 for the $^1D^e$ symmetry, and about 3200 for the $^1F^o$ symmetry. For all practical purposes the basis for the two-valence electrons can be regarded as saturated. The binding energies obtained by this procedure were not in perfect

TABLE II. The resonant oscillator strength f_{res}, static and nonadiabatic multipole polarizabilities, $\alpha^{(1)}$, $\beta^{(1)}$, $\alpha^{(2)}$, $\beta^{(2)}$, $\alpha^{(3)}$, and $\beta^{(3)}$ for the lighter alkali atoms. In the row labeled Present: Valence, all terms in the *f*-value sums involving core-excitations were omitted. The resonant excitation energy ϵ_{res} is the statistically averaged excitation energy and f_{res} is the sum of the transitions to the $np_{1/2}$ and $np_{3/2}$ doublet. Two $\alpha^{(1)}$ values are given for the MBPT calculations. The first is obtained directly from the *ab initio* calculation. In the second, the energy and oscillator strength for the resonant transition are replaced by experimental values in the oscillator strength sum-rules. The number in brackets are the uncertainties in the last digits. All values are in atomic units.

Method	ϵ_{res}	f_{res}	$\alpha^{(1)}$	$\beta^{(1)}$	$10^{-3}\ \alpha^{(2)}$	$10^{-3}\ \beta^{(2)}$	$10^{-3}\ \alpha^{(3)}$	$10^{-3}\ \beta^{(3)}$
Li								
Present: Valence			164.0	1198	1.4242	4.7042	3.9680	10.238
Present	0.067 902	0.7475	164.21	1198	1.4243	4.7042	3.9680	10.238
MBPT [13]					1.424(4)		3.957	
MSSD [14]			164.0		1.424		3.969	
PT [42]			164.5		1.403		3.986	
MK Pseudopot [43]			164.3		1.383		3.680	
Variational [25,44]	0.067 904	0.7470	164.11		1.423 27		3.9650	
Na								
Present: Valence			161.8	1043	1.880	6.731	5.742	15.91
Present	0.077 310	0.9615	162.8	1044	1.881	6.731	5.743	15.91
MBPT [10,13,45]	0.077 297	0.9638	163.0/162.6(3)		1.885(26)		5.54	
MSSD [14]			159.2		1.878		5.552	
PT [42]			160.6		1.807		5.430	
MK Pseudopot [43]			162.6		1.799		5.117	
Experiment [46,47]	0.077 310	0.9602(14)	162.5(8)					
K								
Present: Valence			284.5	2393	5.002	25.01	18.07	63.88
Present	0.059 335	0.9986	290.0	2396	5.018	25.01	18.08	63.88
MBPT [45,10,13]	0.059 128	0.9926	289.1/290.2(8)		5.000(45)		17.7	
MSSD [14]			292.8		5.000		17.69	
PT [42]			290.9		4.760		16.30	
MK Pseudopot [43]			298.0		4.597		15.02	
Experiment [46,47]	0.059 340	0.9982(28)	292.9(59)					
Rb								
Present: Valence			306.6	2632	6.444	35.63	23.75	88.40
Present	0.058 101	1.030	315.7	2637	6.480	35.64	23.78	88.42
MBPT [45,10,13]	0.057 846	1.028	317.4/318.6(6)		6.520(80)		23.7	
MSSD [14]			319.2		6.495		23.69	
PT [42]			321.5		6.163		20.97	
MK Pseudopot [43]			333.0		5.979		21.27	
Experiment [46,47]	0.058 033	1.0374(13)	319.2(64)					

agreement with experiment with discrepancies for the ground and excited state energies of the order of 0.1–2.0% (refer to Refs. [18] and [19] to get an indication of the accuracy). Some further tuning of the cutoff parameters was done to improve the accuracy of the energy differences which directly impact on the accuracy of Eqs. (3)– (10).

III. DIPOLE, QUADRUPOLE, AND OCTUPOLE POLARIZABILITIES

A. Alkali-metal atoms

Table II gives the resonant oscillator strength, and the adiabatic and nonadiabatic multipole polarizabilities for the alkali-metal atoms and compares them with estimates from a variety of experimental and theoretical sources. It should be noted that there have been a large number of calculations of the polarizabilities of the alkali atoms. The data presented have generally been chosen to include only those calculations that give dispersion coefficients as well as polarizabilities.

The lithium atom has a relatively small core polarizability with $\alpha^{(1)}_{\mathrm{core}} = 0.1925$ a.u. [31] and it would be expected that the error associated with using a semiempirical core polarization potential would be small. This expectation is confirmed by the comparisons with the close to exact variational calculations [25,44]. The biggest difference is not much

TABLE III. The resonant oscillator strength f_{res}, static and nonadiabatic multipole polarizabilities, $\alpha^{(1)}$, $\beta^{(1)}$, $\alpha^{(2)}$, $\beta^{(2)}$, $\alpha^{(3)}$, and $\beta^{(3)}$ for the lighter alkaline-earth-metal atoms. In the row labeled Present: Valence, all terms in the *f*-value sums involving core-excitations were omitted. The numbers in brackets are the uncertainties in the last digits. All values are in atomic units.

Method	ϵ_{res}	f_{res}	$\alpha^{(1)}$	$\beta^{(1)}$	$10^{-3}\ \alpha^{(2)}$	$10^{-3}\ \beta^{(2)}$	$10^{-3}\ \alpha^{(3)}$	$10^{-3}\ \beta^{(3)}$
Be								
Present: Valence			37.64	95.27	0.3007	0.5101	3.955	5.081
Present	0.193 922	1.372	37.69	95.28	0.3007	0.5101	3.955	5.081
Variational [51,52]		1.375(7)	37.76		0.3010			
CI+MBPT [12]	0.194 291	1.374(4)						
4th order MP4 [53]			37.3(7)		0.2988(26)			
MK: CI+pseudopot [43]			36.7		0.3026		4.126	
Patil [54]			37.9		0.271		3.488	
Experiment	0.193 942							
Mg								
Present: Valence			70.87	218.6	0.8134	1.813	14.02	23.42
Present	0.159 742	1.732	71.35	218.7	0.8139	1.813	14.02	23.42
CI+MBPT [55]	0.159 173	1.729(17)						
4th order MP4 [56]			71.7		0.8093			
MK: CI+pseudopot [43]			70.5		0.828		14.74	
Patil [54]			72.0		0.709		11.7	
Experimental [57,47]	0.159 705	1.75(9)	71.5(31)					
Ca								
Present: Valence			156.2	712.0	3.056	12.14	65.12	150.8
Present	0.107 777	1.751	159.4	713.0	3.063	12.14	65.12	150.8
CI+MBPT [55]	0.107 776	1.732(50)	160					
4th order MP4 [56]			157		3.016			
MK: CI+pseudopot [43]			153.7		2.717		61.51	
Patil [54]			152.7		2.248		50.8	
Experimental [47,58]	0.107 768	1.727(15)	168.7(135)					
Sr								
Present: Valence			195.3	971.9	4.560	20.69	107.2	276.4
Present	0.098 866	1.850	201.2	974.3	4.577	20.70	107.2	276.4
CI+MBPT [55]	0.098 508	1.838(68)	199					
Patil [54]			193.2		3.237		80.7	
Experimental [47,59]	0.098 866	1.92(6)	186(15)					

larger than 0.1%.

Close to exact variational calculations of the type performed for lithium are just not feasible for heavier alkali-metal atoms. Fortunately, some high accuracy measurements of the resonant oscillator strengths for the alkali-metal atom have been made. It can be seen from Table II that the present measurements are in agreement with the oscillator strengths of Volz and Schmoranzer [46]. Agreement at the 0.1% level exists for Na and K, and at the 1% level for Rb. The experimental values of the polarizabilities are taken from the compilation of Miller [47]. The agreement with the experimental polarizabilities is very good, but estimates of $\alpha^{(1)}$ derived from the relativistic MBPT calculations [45] are probably more precise.

Table II gives two values of $\alpha^{(1)}$ for the MBPT calculation [45]. One estimate is obtained directly from the MBPT calculation. In the other estimate, the energy and oscillator strength for the resonant transition are replaced by experimental values in the oscillator strength sum-rules. Agreement with the empirically corrected value of $\alpha^{(1)}$ could hardly be better for Na and K. The present $\alpha^{(1)}$ for Rb lies outside the theoretical error bar of Safronova *et al.* [45], but is still within 1%. The cause for the larger (although still gratifyingly small) difference is the spin-orbit splitting of the $5p_{1/2}$ and $5p_{3/2}$ levels. The excitation energies from the ground state to these two levels differ by 2%. This energy splitting makes it difficult to achieve perfect agreement for the total oscillator strength, and also for $\alpha^{(1)}$.

This high level of agreement for the dipole polarizability was expected since both the present and experimentally corrected MBPT calculation account most of the dynamical factors that will have an impact on the polarizability. Both these calculations have been validated by comparisons with high accuracy oscillator strength data for the resonance dipole excitation [10]; both of the calculations have been tuned to correctly predict the binding energies of the ground and low lying excited states; both include dressing of the transition operator, and both take into explicitly include core excitations in the evaluation of the polarizabilities.

The largest differences with the MBPT calculation of Porsev and Derevianko [13] occur for $\alpha^{(3)}$. The MBPT values of $\alpha^{(3)}$ are slightly smaller than the present calculation for all systems, with the biggest differences of about 4% occurring for Na and K. Given that excitations to $\ell=3$ states should be less sensitive to short-range electron-electron correlations than excitations to $\ell=2$ and $\ell=1$ states it is surprising that the biggest differences occur for the $\ell=3$ excitations. There are two possible causes for the differences, physical and computational. We suspect that at least part of the discrepancy is computational in origin since Porsev and Derevianko make specific mention of the exacting nature of the calculation for the octupole polarizability. Within the confines of the present method, the octupole polarizability was no harder to compute than the dipole or quadrupole polarizability, although the $\ell=3$ orbital basis dimension was increased to 45 for sodium in a futile attempt to reduce the discrepancy.

Three other calculations that use a model potential for the core have values listed in Table II. Firstly, Marinescu and a number of co-workers in a series of works have determined polarizabilities and various dispersion parameters [14,24,26] using a model potential method. These calculations are collectively abbreviated as MSSD after the various individuals (Sadeghpour, Starace, and Dalgarno) who have been coauthors on some of the papers. The MSSD model potential was tuned to give the correct binding energies, but did not have a polarizable core. They did use a dressed transition operator, but the method used to tuned the operator is questionable. As will be seen later, it seems to be have been tuned so that the dipole polarizability of the active electron was exactly equal to dipole polarizability of the entire atom (the atomic polarizabilities were taken from Ref. [48]). The calculations of Patil and Tang [42] used simple parametrized wave functions with asymptotic forms based on binding energies to evaluate the $f^{(\ell)}$-value sums rules. The Patil and Tang (PT) calculation did not include any dressing of the multipole transition operators and also omitted the influence of the core in the calculations of the polarizabilities and dispersion parameters. The pseudo-potential calculation of Maeder and Kutzelnigg (MK) [43] also omitted the core from the polarizability and dispersion parameter computations. The pseudopotential Hamiltonian in the MK calculation was diagonalized with 5 d orbitals and 5 f orbitals and there was no dressing of the transition operator. All of these calculations omit some aspect of the physics that are included in the present calculation and the MBPT calculation. This results in all of these calculations having dipole polarizabilities that tend to fluctuate by 1–4% about the present values.

For the heavier alkali atoms there is almost no experimental information about quadrupole or octupole transitions since it is very difficult to measure the oscillator strengths. About the only information that is available are the inferred quadrupole and octupole core-polarizabilities of Patil [49,50]. The polarizabilities for the alkali ions Na^+, K^+, and Rb^+ were deduced from an analysis of the high angular momentum Rydberg levels of the neutral atoms. However, even here part of the analysis relies crucially on the values of the nonadiabatic dipole polarizability which are deduced using a method similar in style to that outlined in Sec. II.A. So the purely theoretical relativistic random phase approximation estimates of Johnson *et al.* [33] give the core polarizabilities with a smaller degree of uncertainty.

One feature noticed during the calculations was the diminishing importance of using a dressed transition importance as the polarity of the transition increased. For the potassium atom, the impact of using a dressed operator results in the resonance oscillator strength reducing from 1.0868 to 0.9986 [34]. The reduction in the potassium $4s\rightarrow 4d$ oscillator strength was 1% while the correction to the octupole transition operator for the $4s\rightarrow 4f$ transition was less than 1 part in 10^4.

The MSSD model potential calculations are also in reasonable agreement with the present results for all the entries in Table II. This is expected since MSSD tuned their transition operator to give the experimental dipole polarizability. As mentioned above, the effects of a modified transition operator decrease as the polarity of the transition increases so if two different approaches are tuned to give the correct binding energies then it is likely that the radial matrix elements between the upper and lower states will be very similar for polarity transitions. Also, the impact of the core on $\alpha^{(\ell)}$ decreases in importance as ℓ increase.

The parametrized wave functions of PT generally show much larger differences with the present calculations. The PT calculations give results that are smaller than the present calculations for almost all the entries in Table II. The tendency for PT to underestimate the polarizabilities is generally more pronounced for the higher order multipoles. One concludes that the accuracy of the PT approach is not likely to be better than 10% and it has a systematic tendency to underestimate the polarizabilities.

The MK pseudopotential calculations also shows a tendency to underestimate the higher polarity polarizabilities. The relative short orbital expansions with only five basis states for the d and f symmetries, respectively, are responsible for this since the MK basis sets are simply not large enough or not sufficiently well tuned to exhaustively recover all of the polarizability.

B. Alkaline-earth-metal atoms

The results of the present calculations for the Be, Mg, Ca, and Sr alkaline-earth-metal atoms are listed in Table III. The contribution from the core for octupole excitations was omitted from the calculation since no estimates of $\alpha^{(3)}$ exist for the alkaline-earth-metal cores. The calculations on the alkali atoms suggest that the omission of these terms has less than a 0.1% effect on the values of $\alpha^{(3)}$.

Atomic beryllium has a small core polarizability. Therefore since a large CI basis is used to describe the valence states one expects to make predictions that have better than 1% accuracy. This is confirmed by the comparison with the two *ab initio* calculations [51,52]. The variational calculation of Komasa [52] used a large basis of explicitly correlated gaussians (ECGs) and the resulting $\alpha^{(1)}$ of 37.76 a.u. and $\alpha^{(2)}$ of 301.0 a.u. are close to exact. The present dipole and quadrupole polarizabilities are only $0.1-0.2\%$ smaller. Further, the oscillator strength also agrees to better than 0.2% with the best CI calculation [51]. The fourth order Moller-Plesset (MP4) perturbation theory calculation gives polarizabilities that are 1% larger than the ECG calculation.

The CI+MBPT values of Porsev and Derevianko and Porsev *et al.* reported in Refs. [12] and [55] were the result of an *ab initio* calculation. In this calculation, the correlations between the two valence electrons are handled by the configuration interaction (CI) method while the interactions with the core are handled by MBPT. The CI+MBPT calculations were also fully relativistic. The oscillator strengths given for the CI+MBPT calculation in Table III were computed using by combining the dipole matrix element with experimental energy differences. The present dipole polarizabilities are in good agreement with the CI+MBPT calculations [12]. This is expected since the present and CI+MBPT resonant oscillator strengths for two of the systems, Be and Mg are within 0.5% of each other. For the Ca and Sr atoms, the present f_{res} are slightly larger than the CI+MBPT values.

Given the importance of the resonant oscillator strength in determining C_6 it is unfortunate that there has only been a single attempt to determine a high precision value of f_{res} for the alkaline-earth-metal atoms. This was from some photoassociation experiments for Ca [4,58]. The decay rate from the initial photoassociation experiment was slightly larger than the rate from a later experiment by the same group. The initial experiment gave $f_{\mathrm{res}}=1.753(8)$ [4] while the later experiment gave $f_{\mathrm{res}}=1.727(15)$ [58].

Large basis calculations using fourth-order Moller-Plesset perturbation theory (MP4) have also been done for Mg and Ca [56]. For magnesium, the present $\alpha^{(1)}$ of 71.35 a.u. is within 0.5% of the MP4 value of 71.7 a.u. The present $\alpha^{(2)}$ of 813.9 a.u. is 0.5% larger than MP4 value of 809.3 a.u. The present values are probably more reliable than the MP4 values since the present method did slightly better than a similar MP4 calculation at reproducing the precise dipole and quadrupole polarizabilities of Be. For calcium, the present $\alpha^{(1)}$ of 159.4 a.u. is 1.5% larger than the MP4 value of 157 a.u. The present $\alpha^{(2)}$ of 3063 a.u. is again 1.5% larger than the MP4 of 3016 a.u. The major uncertainty in the present calculation is in the definition of the core-polarization potential while the main uncertainty in the MP4 calculation is whether the CI basis was sufficiently large enough to recover all of the polarizability.

The results from two other approaches are listed in Table III. There are the pseudo-potential calculations of Maeder and Kutzelnigg (MK) [43]. The MK calculation was essentially a moderately sized CI (by moderately sized we are referring to todays standards) calculation with the core electrons replaced by the pseudopotential. For calcium, the MK calculation gives an $\alpha^{(2)}$ of 2.717×10^3 a.u. which is more than 10% smaller than the present calculation. The MK octupole polarizability of 61.51×10^3 a.u. is also almost 10% smaller than present $\alpha^{(3)}$ of 65.12×10^3 a.u. The CI basis used in the MK calculation is probably not large enough to give absolutely converged estimates of the polarizabilities.

A model potential description of the alkaline-earth-metals using a very simple wave function has also been presented by Patil [54]. However, the Patil polarizabilities differ from the present estimates by amounts up to 30%.

As far was we know the only other calculation of the higher polarity polarizabilities for strontium are the rather primitive calculations of Patil [54]. The present results in Table III stand as the recommended values for strontium since there is literally no other calculation that attempts to describe the higher-order polarization response of the strontium atom with any degree of realism.

IV. DISPERSION PARAMETERS FOR THE ALKALI-EARTH ATOMS

The results of the present calculations for the Li, Na, K, and Rb homonuclear alkali atom pairs are listed in Table IV. The dispersion parameters, C_6, C_8, and C_{10} for all possible pairs are listed in Tables V and VI. Also shown in Tables IV, V, and VI are the results from numerous other calculations. All the dispersion parameters in this paper are given in atomic units (a.u.). Besides, the PT, MK, and MSSD calculations, Table V also lists data from an all-electron coupled cluster (CC) calculations by Stanton [60]. Finally, there is the compendium of upper and lower bounds to the dispersion parameters compiled by Standard and Certain [27]. The Standard and Certain (SC) compilation used oscillator strength and polarizability data from a variety of theoretical and experimental sources to establish these bounds.

The dispersion parameter data for Li in Table IV reveals that the present data agree almost perfectly with the values from the close to exact variational calculations of Yan and co-workers [25] and Yan and Drake [44]. The biggest difference with any of the parameters is not much larger than 0.1%.

For the other homonuclear dimers, Table IV once again reveals that the present method gives dispersion parameters in very good agreement with the relativistic MBPT calculations with the exception being the atom-wall C_3 parameter. The largest discrepancy of 2% (comparing with the experimentally corrected MBPT value of 4691(23) a.u. [10]) for C_6 occurs for the Rb_2 dimer. As mentioned earlier, a nonrelativistic model which does not account for the spin-orbit splitting cannot be realistically expected to be accurate to 1%.

For the higher-order parameters, the present calculations give C_{10} values that are about 2% larger than the MBPT values for sodium and potassium. Since octupole transitions contribute to C_{10} this is consistent with the earlier comparisons for the octupole polarizability which revealed that the present approach yielded slightly larger $\alpha^{(3)}$ than the MBPT calculation. The largest difference for C_8 is only 1.5% and occurs for the Rb system. This difference could be due to the fact that rubidium with its nuclear charge of 37 is probably being influenced by relativistic effects.

The only parameter for which the present calculations gives results significantly different from the MBPT calculation is the atom-wall C_3 coefficient. The present calculation gives a C_3 that is 5% larger for K, and 7% larger for Rb. The tendency for the present calculation to give a value of

TABLE IV. The dispersion coefficients for homonuclear combinations of the lighter alkali-metal atoms. In the row labeled Present: Valence, all terms in the *f*-value sums involving core-excitations were omitted. Two C_6 values are given for the MBPT calculations. The first result is obtained directly from the *ab initio* calculation. In the second, the frequency dependent dipole polarizability is computed by replacing the energy and oscillator strength for the resonant transition by the experimental values. The uncertainty of the last digits of a number of the theoretical and experimental values are in the brackets. All values are in atomic units.

Method	C_3	C_6	10^{-5} D_8	10^{-5} C_9	10^{-4} C_8	10^{-6} C_{10}
			Li			
Present: Valence	1.446	1388.3	1.5017	1.7012	8.3219	7.3612
Present	1.521	1394.6	1.5019	1.7087	8.3515	7.3811
MBPT [11,13]		-/1390(2)			8.34(4)	7.35
MSSD [14,24,26]		1388	1.501	1.701	8.324	7.365
PT [42]		1388			8.183	7.289
MK Pseudopot [43]		1389			8.089	6.901
Variational [25,44]	1.518	1393.4		1.7060	8.3426	7.3721
			Na			
Present: Valence	1.577	1523	1.460	1.846	11.40	11.42
Present	1.931	1561	1.472	1.892	11.60	11.58
MBPT [10,13]	1.886	1564/1556(4)			11.60(18)	11.3
MSSD [14,24,26]		1472	1.427	1.758	11.19	11.07
PT [42]		1500			10.90	10.68
MK pseudopot [43]		1540			10.98	10.36
			K			
Present: Valence	2.128	3613	4.548	7.704	39.90	52.27
Present	3.017	3905	4.582	8.318	42.07	54.35
MBPT [10,13]	2.860	3867/3897(15)			42.0(5)	53.7
MSSD [14,24,26]		3813	4.834	8.374	40.96	52.48
PT [42]		3796			38.92	47.89
MK pseudopot [43]		3945			38.34	45.22
			Rb			
Present: Valence	2.248	4112	5.279	9.447	52.70	74.75
Present	3.633	4635	5.351	10.63	57.01	79.16
MBPT [10,13]	3.362	4628/4691(23)			57.7(8)	79.6
MSSD [14,24,26]		4426	5.743	10.60	55.06	76.65
PT [42]		4531			52.58	68.33
MK pseudopot [43]		4765			52.44	68.36
Experiment [7,8]		4707(9)			57.3(49)	

C_3 that is slightly larger is mainly the result of the contribution from the core. For example, the core contributes 1.385 to the total C_3 of Rb for the present calculation while contributing about 1.18 to C_3 in the MBPT calculation [10]. Of all the parameters given in Table IV C_3 is the most sensitive to the core *f*-value distribution since its sum rule has terms that are inversely proportional to the first power of the excitation energy.

The good agreement with the MBPT C_6 values for all combinations of the alkali-metal atoms is immediately apparent from Table V. The C_6 values agree to within 0.5% with the single exception of the Rb-Rb case. The comparison with the CC calculations of Stanton reveals the short-comings of the CC calculation which overestimate the present values of C_6 in every case. The description of core-valence correlation by a purely *ab initio* calculation is quite exacting and so it may not have been possible to drive the CC calculation to convergence. The amount by which the CC calculation overestimates C_6, namely 3% for the Li-Li is quite large for such a small system. The data of the SC compilation [27] are generally within a couple of percent of the modern calculations even for those instances where the present C_6 values lie outside the band of recommended values.

Even a brief inspection of Table VI shows that the present and MBPT C_8 values are in close agreement for all the heteronuclear alkali-atom combinations. The biggest relative differences between the present and MBPT values for C_{10} occur for systems containing either Na or K. The tendency for the present model to give a larger $\alpha^{(3)}$ than MBPT for these two atoms also manifested itself in the C_{10} parameter.

The MSSD model potential calculations are also in reasonable agreement with the present results for all the entries in Table IV. There is a tendency for the MSSD values of C_6, C_8, and C_{10} to be slightly smaller than the present and

TABLE V. The dispersion coefficient, C_6 for all the possible alkali-atom dimers. The MBPT values are not the result of pure *ab initio* calculations, the *ab initio* resonant oscillator strengths and excitation energies are replaced by the most accurate experimental data [46]. Two entries for the SC column are given; these are the estimated lower and upper bounds on C_6. The estimated theoretical uncertainty in the last digits of the MBPT C_6 are in brackets. All values are in atomic units.

Systems	Present	MBPT [11]	CC [60]	MSSD [14]	SC [27]
Li-Li	1394.6	1390(2)	1440	1388	1380–1390
Li-Na	1472	1467(2)	1532	1427	
Li-K	2328	2322(5)	2441	2293	2340–2360
Li-Rb	2533	2545(7)	2791	2469	2530–2550
Na-Na	1561	1556(4)	1639	1472	
Na-K	2454	2447(6)	2595	2348	
Na-Rb	2672	2683(7)	2966	2526	
K-K	3905	3897(15)	4158	3813	3970–4030
K-Rb	4253	4274(13)	4761	4108	4290–4370
Rb-Rb	4635	4691(23)	5456	4426	4640–4740

MBPT values. This is probably due to their omission of the core contribution to the dispersion parameters. The actual results listed in the MSSD column in Table VI come from two sources. The data for the homonuclear pairs are taken from Ref. [14] while the data for the heteronuclear pairs are taken from a later work [61]. The C_8 and C_{10} parameters for the heteronuclear pairs from Ref. [14] are consistently larger than those of the present work by about 25% (e.g., for the Na-K combination Ref. [14] gave $C_8 = 21.7\times 10^4$ a.u. and $C_{10} = 21.7\times 10^6$ a.u.). However, a later publication [61] gave smaller values of C_8 and C_{10}, which are in much closer agreement with the present values, and it is these data which are listed in Table VI. The tendency for the MSSD C_8 and C_{10} to be smaller for homonuclear pairs is also present for the heteronuclear pairs.

The parametrized wave functions of PT generally show much larger differences with the present calculations. The PT calculations give results that are smaller than the present calculations for practically all the entries in Table IV and the effect is enhanced for the higher-order multipoles. One concludes that the accuracy of the PT approach is not likely to be better than 10% and it has a systematic tendency to underestimate the dispersion parameters and polarizabilities. The higher-order dispersion parameters of the PT approach are without exception the smallest of any of the entries in Table VI.

The MK pseudopotential calculations also show a tendency to underestimate the present values of C_8 and C_{10}. The relatively short orbital expansions with only five basis states for the *d* and *f* symmetries, respectively, are responsible for this since the MK basis sets was not large enough to exhaustively recover all of the *f*-value distribution.

A recent experiment has given estimates of the dispersion coefficients for Rb_2 [7,8]. The values give in Table IVare those of Ref. [8] with indicative errors taken from Ref. [7]. (Note, van Kempen *et al.* [7] did give an estimate of C_{10} with a more ambitious fit. This fit did rely on an estimate of $C_{12} = 1.19\times 10^{10}$ a.u. as computed by Patil and Tang [42]. This PT estimate is too small and applying the present method gives $C_{12} = 1.427\times 10^{10}$ a.u. So the data from this other fit are not listed here.) The present calculations agree with the experimental data to an accuracy of 2%.

A. Accuracy of the Koopman approximation

It can be seen from Table IV that the relative size of the core correction rises as the atom gets larger. The core contribution is 0.2–0.5% for Li and about 7–12% for Rb. The relative correction for C_6 is slightly larger than the relative correction for C_8 which in turn is slightly larger than the correction for C_{10}.

1. Core correction for C_6

The tendency for the Koopman approximation to the core *f*-value distribution to overestimate C_3 does suggest that it might lead to some overestimation in the core contribution to C_6. However, Table IV does not show any overt signs of such an effect. This is best explained by examining the individual contributions, C_6^{c} and C_6^{cv} in detail.

TABLE VI. The dispersion coefficients, C_8 and C_{10} for all the possible alkali-metal-atom dimers that can be formed from Li, Na, K, and Rb. The estimated theoretical uncertainty in the last digits of the MBPT C_8 are contained in the brackets. All values are in atomic units.

	$10^{-4}\ C_8$				$10^{-6}\ C_{10}$			
Systems	Present	MBPT [13]	MSSD [14,61]	PT [42]	Present	MBPT [13]	MSSD [14,61]	PT [42]
Li-Li	8.351	8.34(4)	8.324	8.183	7.381	7.35	7.365	7.289
Li-Na	9.892	9.88(11)	9.806	9.49	9.297	9.16	9.13	8.859
Li-K	19.58	19.5(2)	19.25	18.52	21.18	21.0	20.73	19.49
Li-Rb	23.29	23.4(3)	22.83	21.90	26.08	26.1	25.65	23.56
Na-Na	11.60	11.60(18)	11.19	10.90	11.58	11.3	11.07	10.68
Na-K	22.44	22.4(3)	21.95	20.82	25.69	25.3	24.87	23.03
Na-Rb	26.49	26.6(4)	25.81	24.44	31.43	31.3	30.57	27.73
K-K	42.07	42.0(5)	40.96	38.92	54.35	53.7	52.48	47.89
K-Rb	49.09	49.3(6)	47.60	45.31	65.70	66	63.52	57.24
Rb-Rb	57.01	57.7(8)	55.06	52.58	79.16	79.6	76.65	68.33

For the potassium atom one finds that $C_6^{\rm c}=26.8$ a.u. and $C_6^{\rm cv}=265.3$ a.u. As expected, it is the core-valence contribution that is by far the most important. The core-valence contribution will be dominated by the resonant excitation and Eq. (17) can be rewritten for a homonuclear pair as

$$C_6^{\rm cv}=3\sum_{i\in\text{core-a},j}\frac{N_i f_{0j}}{(\epsilon_i+\Delta_a^{(1)})\epsilon_{0j}(\epsilon_i+\Delta_a^{(1)}+\epsilon_{0j})}$$

$$\approx\frac{3f_{\rm res}}{\epsilon_{\rm res}}\sum_{i\in\text{core-a}}\frac{N_i}{(\epsilon_i+\Delta_a^{(1)})(\epsilon_i+\Delta_a^{(1)}+\epsilon_{\rm res})}$$

$$\approx\frac{3f_{\rm res}}{\epsilon_{\rm res}}\sum_{i\in\text{core-a}}\frac{N_i}{(\epsilon_i+\Delta_a^{(1)})^2}=\frac{3f_{\rm res}}{\epsilon_{\rm res}}\alpha_{\rm core}, \qquad (19)$$

since $|\epsilon_i+\Delta_a^{(1)}|\gg|\epsilon_{\rm res}|$. The equation for $C_6^{\rm cv}$ collapses to include the expression that was used to fix $\Delta^{(1)}$ in the first place. Therefore, the error inherent in using the Koopman approximation is minimized.

Given that the core *f*-value distribution results in the core contribution to C_3 being overestimated by about 15–20%, one can reasonably assert the overestimation for C_6 will be smaller than this. Calculations of C_6 for H or Ps interacting with the noble gases showed that the Koopmans approximation resulted in C_6 being overestimated by about 5% [62]. Making the assumption that the core related error in C_6 is about this size, one then arrives at an estimate of 5% for the error in $C_6^{\rm c}+C_6^{\rm cv}$. These translate to overestimates of 15 and 25 in C_6 for K and Rb, respectively. The overall impact upon the final value of C_6 would be less than 0.5%. Comparisons of the $C_6^{\rm v}/C_6$ ratio with MBPT estimates [45] are compatible with this analysis. The present calculation for K gives $C_6^{\rm v}/C_6=0.926$ while the MBPT calculation gives $C_6^{\rm v}/C_6=0.93$. For rubidium, the present calculation gives $C_6^{\rm v}/C_6=0.887$ while the MBPT calculation gives $C_6^{\rm v}/C_6=0.89$.

One fine point of detail should be mentioned; the total sum over the core and valence electrons adds up to a number slightly different from the number of electrons. While the *f*-sum for the core is equal to the number of core electrons, the valence *f*-value sum is usually slightly larger than the number of valence electrons. This problem could easily be corrected by changing the shell occupancy of the most weakly bound core orbital to compensate for the excess contribution from the valence *f*-value sum. One could then redetermine $\Delta^{(1)}$ from Eq. (13) with this revised N_i for the most weakly bound orbital. However, the gain in theoretical purity is simply not worth the additional complexity. When this more complicated procedure was applied to the system with the largest core polarizability, namely rubidium the dispersion coefficient changed from 4635 to 4634 a.u.

2. Core correction for C_8 and C_{10}

The accuracy of the core $f^{(\ell)}$-value distribution can be determined from the difference of the full calculation with the valence only calculation. For potassium, this is 2.17×10^4 a.u. for C_8. The relativistic MBPT calculation gave 2.0×10^4 a.u. for the same core correction. Hence the present semiempirical calculation overestimates the correction of the core by just less than 10%. This means that usage of the semiemprical core $f^{(\ell)}$-value distribution could result in C_8 being overestimated by about 0.5%. A similar result holds for the C_{10} parameter of potassium. The core correction for C_8 is also overestimated for rubidium and the present calculation gives 4.31×10^4 au while the relativistic MBPT calculation gives a correction of 4.0×10^4 a.u. Once again the overestimation is just less than 10%. Even though the size of the correction for Rb is larger, the net error due to the use of the semiempirical $f^{(\ell)}$-value would still be less than 1%.

A cursory examination of Table II shows that the core corrections to the higher-order polarizabilities are not very large. For rubidium, the core contribution to $\alpha^{(2)}$ is 0.6% while the correction for $\alpha^{(3)}$ is 0.15%. However, for the dipole polarizability the correction is 3%. This suggests that the core-contribution to the C_n parameters largely comes from $f^{(1)}$ core-dipole terms. This has been verified by a calculation of C_8 with core terms included in the $f^{(1)}$ distribution but omitted from the $f^{(2)}$ and $f^{(3)}$ distributions. This gave 56.43×10^4 a.u. for C_8. Roughly 85% of the core correction to C_8 for Rb arises from the core terms in the $f^{(1)}$ distribution function. One concludes that omission of the core contribution to the $f^{(2)}$ distribution will affect the derived C_8 by an amount that is no larger than 1.0%. The impact of the core part of the $f^{(3)}$ distribution is even smaller, and its complete omission would impact C_{10} by an amount of order 0.1%.

B. Comparison with the calculations of Marinescu *et al.*

One notable feature of Tables IV and V is the variance with the model potential values of MSSD [14]. It has previously been noted [10] that the Marinescu C_6 underestimate the recommended values for the larger alkalis. It was suggested [10] that this occurred because MSSD *et al* did not include core contributions in their determinations of C_6.

However, since the MSSD calculations omit the core from their analysis they should therefore be in quite close agreement the *valence only* estimates of C_6, and D_8 listed in Table IV. As seen in Table IV, their C_6 for Na is too small by 4% and too large by about 7–8% for K and Rb. Similarly their values of D_8 are 6–10% too large for K and Rb. The likely cause of this problem are the choices they made for the cutoff parameters in the modified dipole operator

$$\mathbf{r}\rightarrow\mathbf{r}\left(1-\frac{\alpha_{\rm core}}{r^3}[1-\exp(-r^3/r_c^3)]\right). \qquad (20)$$

They tuned the r_c parameter to give the experimental dipole polarizability. While the experimental dipole polarizabilities adopted [48] are slightly different from the present calculations, this cannot explain the discrepancy. One possibility is that MSSD did not take the core polarizability into consideration when tuning r_c to the experimental dipole polarizability. We have tested this hypothesis for potassium by doing a valence only calculation and adjusting the cutoff in the modified dipole operator so that the valence polarizability

TABLE VII. The three-body dispersion coefficient, 10^{-4} C_9 for all the possible alkali-metal-atom trimers. The Midzuno-Kihara approximation was evaluated using the data of the present calculation reported in Table IV. All values are in atomic units.

Systems	Present	Midzuno-Kihara	MSSD [26]	SC [27]	Systems	Present	Midzuno-Kihara	SC [27]
Li-Li-Li	17.087	17.175	17.01	17.0	Be-Be-Be	0.5973	0.6023	0.612
Li-Li-Na	17.64	17.74	17.16		Be-Be-Mg	1.054	1.064	
Li-Li-K	28.90	29.19	28.84		Be-Be-Ca	2.003	2.035	
Li-Li-Rb	31.36	31.77	31.16		Be-Be-Sr	2.435	2.485	
Na-Na-Li	18.25	18.36	17.35		Mg-Mg-Be	1.872	1.888	
Na-Na-Na	18.92	19.06	17.58		Mg-Mg-Mg	3.338	3.369	3.36
Na-Na-K	30.74	31.13	29.28		Mg-Mg-Ca	6.463	6.561	
Na-Na-Rb	33.35	33.90	31.61		Mg-Mg-Sr	7.885	8.036	
K-K-Li	48.99	49.74	49.08		Ca-Ca-Be	7.029	7.172	
K-K-Na	50.37	51.24	49.29		Ca-Ca-Mg	12.75	13.00	
K-K-K	83.18	84.93	83.75	86.1	Ca-Ca-Ca	25.57	26.16	32.4
K-K-Rb	90.26	92.48	90.57		Ca-Ca-Sr	31.41	32.23	
Rb-Rb-Li	57.66	58.96	57.35		Sr-Sr-Be	10.52	10.81	
Rb-Rb-Na	59.30	60.77	57.56		Sr-Sr-Mg	19.14	19.64	
Rb-Rb-K	97.94	100.7	97.96		Sr-Sr-Ca	38.63	39.74	
Rb-Rb-Rb	106.3	109.7	106.0	110	Sr-Sr-Sr	47.53	49.03	
Li-Na-K	29.78	30.11	29.04		Be-Mg-Ca	3.590	3.646	
Li-Na-Rb	32.30	32.78	31.36		Be-Mg-Sr	43.73	44.60	
Li-K-Rb	53.15	54.15	53.05		Be-Ca-Sr	8.596	8.801	
Na-K-Rb	54.65	55.80	53.27		Mg-Ca-Sr	15.62	15.98	

was 292.8 a.u. Use of the resulting valence only f-value distribution in Eq. (5) increases the valence only estimate of C_6 from 3613 to 3824. This is only 11 different from the value of 3813 reported by MSSD [14]. Assuming our hypothesis is correct, the sodium $f_{\rm res}$ of Marinescu *et al.* is too small by about 3%, while their $f_{\rm res}$ for K and Rb are too large by about 3% (mainly because of the influence of $\alpha_{\rm core}$ in setting the cutoff parameters).

With this in mind it is now possible to reconcile the present values of D_8 with those of MSSD [24]. Firstly, the D_8 parameter has an energy denominator roughly proportional to $\epsilon^3_{\rm res}$. Therefore, this parameter is completely dominated by the resonant oscillator strength $f_{\rm res}$. For example, even for rubidium, the core makes a total contribution of less that 2%. The differences with MSSD arise directly from the details of the model used to describe the spectrum of the alkali-metal atoms. Their value of D_8 for Na is too small since their Na $f_{\rm res}$ is too small, while their D_8 for K and Rb are too large since their $f_{\rm res}$ are too large.

C. Three-body dispersion coefficients

The leading nonadditive interaction between 3 atoms (a,b,c) is written as

$$V_{abc} \sim \frac{C_9 f(\theta_{ab},\theta_{bc},\theta_{ca})}{R^3_{ab}R^3_{bc}R^3_{ac}}. \tag{21}$$

Estimates of the dispersion parameter, C_9 for the alkali atoms have been made by Langhoff and Karplus [63], MSSD [26], and the SC compilation [27]. This parameter has recently been computed to very high precision for all combinations of the very light atoms H, He, and Li [25]. Tabulations of C_9 for all possible combinations of the alkali atoms are given in Tables IV and VII.

For lithium there is only a very small (0.15%) difference between the present C_9 value of 1.7087 a.u. and the close to exact variational calculation giving 1.7060 a.u. [25]. For the heavier atoms, the C_9 parameters are in close agreement with those of MSSD for K and Rb but there is a disagreement for Na. The disagreement was expected for Na since MSSD also underestimated C_6. The apparently close agreement for K and Rb is most likely an accident. The omission of the core contributions to Eq. (10) by MSSD is compensated by their slightly too large resonant oscillator strengths.

The present calculations can be used to assess the accuracy of the Midzuno-Kihara approximation [64,65]. For a trimer consisting of three identical atoms, they get

$$C_9 = \frac{3}{4}\alpha_d C_6. \tag{22}$$

Other more complicated identities exist for the case of heteronuclear trimers [64,65]. For the homonuclear trimers, MSSD [26] report an agreement between their explicit calculation and the Midzuno-Kihara approximation that is better than one part in a thousand for all the alkalis except Li. Indeed, for three atoms, Na, Rb, and Cs the results of the Midzuno-Kihara approximation agree with their calculated values for all quoted digits. Such a close level of agreement is not seen in the values in Table VII and the Midzuno-Kihara approximation consistently overestimates the explic-

TABLE VIII. The dispersion coefficients for the lighter alkaline-earth atoms. In the valence only calculations, all terms in the *f*-value sums involving core-excitations are omitted. Two C_6 values are tabulated for the CI+MBPT calculation of Ca [12]. The first comes from a pure *ab initio* calculation. In the second frequency dependent polarizability is computed using the experimental oscillator strength of Zinner *et al* [4]. The experimental dispersion parameters for Ca are the average of two values that arise from different functional forms used to fit the Ca_2 rovibrational spectrum [9]. All values are in atomic units.

Method	C_3	C_6	$10^{-5}\ D_8$	$10^{-5}\ C_9$	$10^{-4}\ C_8$	$10^{-6}\ C_{10}$
			Be			
Present: Valence	0.972	211.87	0.7862	0.5940	1.0184	0.5154
Present	1.012	213.06	0.7865	0.5973	1.0220	0.5165
CI+MBPT [12]		214(3)				
MCSCF [67]		213.6				
MK: CI+pseudopot [43]		208.0			1.0127	0.5319
Patil [54]		248			1.06	0.501
			Mg			
Present: Valence	1.455	612.6	2.812	3.249	4.095	2.787
Present	1.704	629.5	2.818	3.338	4.164	2.817
CI+MBPT [12]		627(12)				
MK: CI+pseudopot [43]		618.4			4.233	2.992
Patil [54]		648			3.85	2.43
Experiment [68,69]		683(35)			3.8(8)	
			Ca			
Present: Valence	2.196	2022	13.61	23.59	21,56	21.35
Present	2.881	2188	13.75	25.57	22.60	22.00
CI+MBPT [12]		2168/2221(15)				
MK: CI+pseudopot [43]		2005			20.0	19.50
Patil [54]		2002			17.9	16.3
Experiment [9]		2080(7)			28.5(50)	13.0(100)
			Sr			
Present: Valence	2.507	2890	21.27	42.15	35.99	40.68
Present	3.643	3250	21.66	47.53	38.54	42.50
CI+MBPT [12]		3170(196)				
Patil [54]		2849			29.0	29.6

itly calculated C_9 by between 0.5 and 3%. This level of accuracy is more in keeping with the observations made by Chan and Dalgarno for three hydrogen atoms [66]. They found the Midzuno-Kihara formulas overestimated the C_9 parameter by 1.2%. The almost perfect level of agreement obtained by MSSD derives from the fact that they do not include any contribution from the core in their calculation, i.e., it is an artifact of their particular model. We can generate C_9 values computed by Eqs. (10) and (22) in agreement at the 0.1% level by the simple of expedient of omitting the *f*-value distribution due to the core from the summations.

The present values for C_9 for all these three-body systems should be regarded as superseding all the previous estimates (with the exception of the Li-Li-Li case). The earlier SC compilation [27] gives C_9 parameters that are within 5% of the present with one exception, namely calcium.

D. Relative importance of D_8 and C_8

According to Marinescu and Dalgarno [24] the adiabatic correction for the dispersion coefficient is

$$C_n \rightarrow C_n + \frac{1}{M}[(n-1)C_n - D_n] \tag{23}$$

with the proviso that there is no D_6 correction for C_6.

For the ^{7}Li dimer, the correction to C_8 is an increase of 34 au with the $(n-1)C_8$ term being about 5 times larger than D_8. As a percentage increase, the value of C_8 would increase by 0.04%. For Na^{22}, the percentage increase in C_8 would be 0.014%. The correction to C_8 would be even smaller for K and Rb.

V. DISPERSION PARAMETERS FOR THE ALKALINE-EARTH-METAL ATOMS

The results of the present calculations for the homonuclear combinations of the Be, Mg, Ca, and Sr alkaline-earth-metal atoms are listed in Table VIII. Heteronuclear combinations are listed in Table IX. The contribution from the core for octupole excitations was omitted from the calculation since no estimates of $\alpha^{(3)}$ exist for the alkaline-earth-metal cores. The calculations upon the alkali-metal at-

TABLE IX. The dispersion coefficients, C_6, C_8, and C_{10} for all the possible alkaline-earth-metal pairs. All values are in atomic units.

Systems	C_6				10^{-4} C_8		10^{-6} C_{10}	
	Present	CI+MBPT [12]	CC [60]	SC [27]	Present	SC [27]	Present	SC [27]
Be-Be	213.1	214(3)	207.4	219–222	1.022	1.04–1.09	0.5165	0.508–0.563
Be-Mg	364.6		365.2	369–374	2.082	2.08–2.19	1.232	1.20–1.34
Be-Ca	661.0		636.1	762–777	5.007	4.33–5.35	3.713	3.15–3.84
Be-Sr	800.0		790.5		6.645		5.354	
Mg-Mg	629.5	627(12)	647.8	630–638	4.164	4.11–4.35	2.817	2.73–3.04
Mg-Ca	1158		1140	1300–1330	9.807	8.74–10.5	8.088	6.90–8.44
Mg-Sr	1404		1421		12.94		11.49	
Ca-Ca	2188	2221(15)	2042	2740–2830	22.60	19.0–24.9	22.00	17.7–22.8
Ca-Sr	2665		2559		29.56		30.68	
Sr-Sr	3249	3170(196)	3212		38.54		42.50	

oms suggest that the omission of these terms has less than a 0.1% effect on the values of $\alpha^{(3)}$ and C_{10} for the neutral atom.

The CI+MBPT [12] value of C_6 for the Be_2 dimer was 214(3) a.u. This is only 0.5% larger than the present value of 213.1 a.u. The only other large scale *ab initio* calculation of C_6 for the Be_2 dimer was a multiconfiguration self-consistent field (MCSCF) calculation by Fowler *et al.* [67] which gave $C_6 = 213.6$ a.u. This is 0.3% larger than the present value. On the basis of these comparisons, and on the good agreement of the polarizabilities with the best variational calculations, one could comfortably assert the present values of C_8 and C_{10} have an accuracy of 0.5% or better.

The agreement with the CI+MBPT calculations [12] of C_6 is uniformly good for the heavier alkaline-earth-metals. For Mg, the level of agreement is better than 0.5%. For Ca and Sr, differences of a couple of percent occur, but it must be noted that the theoretical uncertainties that Porsev and Derevianko ascribe to their recommended values are somewhat larger. For calcium, Porsev and Derevianko performed a hybrid calculation of C_6. They replaced their *ab initio* estimate of the radial matrix element of the resonant transition by an experimental value deduced from the photoassociation experiment of Zinner *et al.* [4]. This estimate of C_6 is probably too large given that a later photoassociation experiment by the same group [58] gave a resonant transition that was slightly smaller.

Experimental values of C_6 and C_8 have been extracted from a Rydberg-Klein-Rees potential derived from the rovibrational levels of the Mg_2 ground state [68,69]. The derived value of $C_6 = 683(35)$ a.u. was almost 10% larger than the present value of 629.5 a.u., while the experimental $C_8 = 3800(800)$ a.u. was about 8% smaller than the present value of 4164 a.u. However, it has been shown by Allard *et al.* [9] that the C_n dispersion parameters obtained from a spectrum analysis are very strongly correlated. Hence, the fact that experiment is larger than theory for C_6 but smaller than theory for C_8 does suggest indicates that the overall difference between theory and experiment is smaller than indicated by a direct comparison of individual values.

The situation for Ca_2 is particularly interesting since a recently completed analysis of the rovibrational spectrum of this dimer gave estimates $C_6 = 2080(7)$ a.u., $C_8 = 28.5(50) \times 10^4$ a.u., and $C_{10} = 13.0(100) \times 10^6$ a.u. [9]. The experimental value of C_6 is 5% smaller than the present value and 7% smaller than the MBPT value computed with the Zinner *et al.* oscillator strength [4]. It is quite possible that further refinements of the theory and experiment could see the differences decrease. First, on the experimental side. A Monte Carlo analysis of the uncertainties in the potential fit showed that the dispersion parameters would be quite strongly correlated in any least-squares analysis of the spectrum [9]. So a least-squares fit that yields too large a value of C_6 will by way of compensation give too small a value of C_8. The value of C_8 obtained from the spectrum analysis is about 25% larger than the present value of C_8. While there are some uncertainties in the present calculation of C_8, the level of agreement achieved with the MBPT calculations of Porsev and Derevianko for $\alpha^{(1)}$ and C_6 [12] and the MP4 calculation for $\alpha^{(1)}$ and $\alpha^{(2)}$ suggests that it is very unlikely that the present estimates of C_8 and C_{10} could be in error by more than 10%. It is possible that using the present estimates of C_8 and C_{10} with suitable error limits as constraints in the least-squares fit to the potential will give a slightly larger value of C_6. On the theoretical side, the *f*-value corrected MBPT C_6 of 2221(15) could easily be decreased. The photoassociation experiment originally used to determine the decay rate of the Ca $4s4p\ ^1P^o$ excited state has recently been repeated [58] yielding a decay rate that was a couple of percent smaller than the original Zinner *et al.* determination. If the MBPT calculation was repeated by tuning the resonant oscillator strength to the newer decay rate it is likely that C_6 would decrease to a value of about 2150 a.u., which is closer to the recent experimental determination.

The strontium atom has the most polarizable core so it can be used to test whether the omission of the core part of the $f^{(3)}$-value distribution has a significant impact upon the calculation. The comparison with the valence only calculations in Table VIII reveals that the core contribution to C_8 is 8% while the core makes a 5% contribution to C_{10}. Most of this comes from the dipole contributions. For example, omitting the core-quadrupole terms and retaining dipole terms in Eqs. (6) and (7) gave $C_8 = 38.25 \times 10^4$ a.u. and C_{10}

TABLE X. The dispersion coefficients, C_6, C_8, and C_{10} for all possible pairs formed from one alkali-metal atom and one alkaline-earth-metal atom. Standard and Certain [27] did give bounds for dimers containing the Na atom, but their bounds are so far apart that they are of little practical value. All values are in atomic units.

Systems	C_6			10^{-4} C_8		10^{-6} C_{10}	
	Present	CC [60]	SC [27]	Present	SC [27]	Present	SC [27]
Li-Be	477.9	478.3	478−482	2.788	2.68−2.82	2.066	1.87−2.07
Li-Mg	856.6	878.6	852−857	5.683	5.48−5.74	4.541	4.15−4.58
Li-Ca	1688	1636	1830−1850	14.13	12.7−14.4	12.61	10.6−12.6
Li-Sr	2070	2075		18.95		17.79	
Na-Be	521.6	527.0		3.351		2.697	
Na-Mg	929.8	963.0		6.739		5.823	
Na-Ca	1814	1778		16.36		15.76	
Na-Sr	2220	2250		21.72		22.02	
K-Be	791.0	806.4	801−818	6.524	6.06−6.41	6.442	5.37−5.95
K-Mg	1417	1481	1430−1450	12.85	12.0−12.7	13.46	11.4−12.6
K-Ca	2803	2763	3080−3160	30.27	27.4−30.6	34.84	28.1−33.0
K-Sr	3443	3510		3.910		47.11	
Rb-Be	868.7	919.9	860−886	7.741	7.08−7.59	8.011	6.92−7.59
Rb-Mg	1553	1689	1530−1570	15.15	13.9−14.9	16.62	14.7−15.9
Rb-Ca	3063	3153	3320−3430	35.29	31.8−35.6	42.61	35.3−41.1
Rb-Sr	3762	4007		46.23		58.22	

$=42.19\times10^6$ a.u. The core-quadrupole distributions make a contribution of less than 1% to both C_8 and C_{10}. Contributions from the core-octupole distribution will be much smaller and their omission will not cause a significant error.

The other calculations with data reported in Tables VIII and IX are the MK CI+pseudo-potential calculation [43] and Patil estimates using a very simple wave function [54]. The MK estimates of C_6 for Be, Mg, and Ca are $2.5-9\%$ smaller than the present and CI+MBPT values. The MK C_8 and C_{10} values differ from the present estimates by similar amounts. As mentioned earlier, the two-electron basis used to diagonalize the model Hamiltonian is much smaller than that used for the present calculations. Limitations of the Patil calculation are most apparent for the Be_2 dimer where their C_6 estimate of 248 a.u. is some 15% larger than the present value of 213.6 a.u. Dispersion parameters computed with the Patil method cannot reliably expected to have an accuracy of much better than 25%.

Given the good agreement between the CI+MBPT and present calculations of C_6 for the homonuclear systems one can reasonably infer that the present values are to be preferred over previous published estimates for heteronuclear combinations of alkaline-earth-metal atoms listed in Table IX. The all-electron CC calculations of Stanton [60] differ from the present values by amounts of order 5%. One feature of the comparison with the bounds of the SC compilation is that all of the C_6 estimates lie outside the SC bounds suggesting that SC were a bit overoptimistic when estimating the reliability of the primary data used to determine the bounds. It was somewhat surprising that the SC bounds for even a small system like Be_2 were not compatible with the present estimate of C_6. It is noticeable that C_6 values of SC for systems containing Ca are much too large. It has previously been noted that the C_6 SC bounds for systems containing calcium were of questionable reliability [60] since the accuracy of the underlying theoretical calculations [70] used in the determination of the SC bounds have been criticized.

Table IX gives C_8 and C_{10} for all the possible combinations of the alkaline-earth-metal atoms and compares them with the SC compilation [27]. When there is a discrepancy between the present values of C_8 and C_{10} and the SC bounds the present data should be preferred since one of the primary inputs to the SC bounds were the data from the MK CI-pseudopotential calculation.

VI. MIXED ALKALI-METAL AND ALKALINE-EARTH-METAL SYSTEMS

Table X gives the dispersion coefficient for atom pairs consisting of one-alkali-metal and one alkaline-earth-metal atom. For reasons advanced earlier, the present parameters should be regarded as being more reliable than the previously published SC data set.

Once again, the C_6 parameters from the SC compilation [27] generally lie within a couple of percent of the present values, with systems containing Ca being the notable exception. The all-electron CC calculations give C_6 parameters that fluctuate from the present data by amounts of up to 5%.

The higher-order SC estimates are in reasonable agreement with the present calculations with the exception of systems containing K and Ca. The SC data for K are largely derived from the MK calculation [43] and it can be seen from Tables II and IV that the MK calculation overestimates all the dipole polarizabilities and the C_6 dispersion parameters of the K_2 dimer. For reasons outlined earlier, the SC bounds for systems with Ca are not expected to be particularly accurate.

VII. CONCLUSIONS

The three lowest order dispersion parameters, C_6, C_8, and C_{10} have been computed for a number of alkali-metal and alkaline-earth-metal combinations. For certain subsets of the possible combinations, accurate estimates from relativistic MBPT calculations already exist. However, there have been no calculations of comparable sophistication for other classes of atoms, notably the alkali-alkaline combinations. One of striking features of the present nonrelativistic model potential analysis is the amazingly good agreement with the sophisticated relativistic MBPT calculations. Notwithstanding the results obtained by earlier model potential or pseudopotential calculations [14,43], it is worth pondering why this should be the case.

For one-electron atoms, the $f^{(1)}$-value sums for $\alpha^{(1)}$ and C_6 are very strongly influenced by a single transition. So if $f_{\rm res}$ is predicted accurately, then one is already assured of a dispersion parameter that cannot be too inaccurate. In the second instance the model potential method is almost guaranteed to give an accurate transition matrix element. The model potentials have been tuned to give the correct binding energies for the resonant transition. Since the bulk of the dipole length matrix element comes from large values of r, and the radial forms of the wave function automatically have the correct form at asymptotic distances, it is to be expected that the semiempirical model gives accurate matrix elements. Additional uncertainties exist for two-electron atoms, but tuning the binding energy to the experimental energy does help to give a wave function with the correct asymptotics. Although the sum-rules for the higher-order dispersion parameters, C_8 and C_{10} are not dominated by a single transition, one can expect these parameters to be similarly accurate. The contribution from the core to the summations diminishes in importance and furthermore the nd and nf excited states are less influenced by short-range correlations with the core electrons.

One aspect of the calculations worth specific mention was the use of the constrained sum-rules to determine the $f^{(\ell)}$-value distributions for the core electrons. Other attempts to compute the dispersion parameters using model potential methods have simply ignored the contribution from the core electrons. Although the present approach may overestimate the core contribution to dispersion parameters, the excess contribution is hardly large enough to be noticed.

It should be that the actual calculations of the dispersion parameters were very easy once the $f^{(\ell)}$ distributions had been generated. Indeed it would be relatively easy to determine dispersion parameters for other combinations of atoms. The calculations take almost no time to do even for atoms with $f^{(\ell)}$-distributions with a couple of thousand elements. Since $f^{(\ell)}$-distribution functions have already been generated for H, it would literally take about 15 minutes to generate the dispersion coefficients between H and the alkali-metal and alkaline-earth-metal atoms.

The present methodology is not necessarily restricted to the systems or states that have already been treated. It really would not be a major effort to determine dispersion parameters between different combinations of excited states since the necessary formalism has already been developed [61]. Similarly, it would be possible to determine the dispersion parameters for other diatomic combinations involving H and the rare gases since the $f^{(\ell)}$-value distribution functions are easy to compute (for H and He) or empirically determined oscillator strength distributions already exist [71]. Given the ability to write an expression involving oscillator strength sums, the coefficient of the $O(R^{-7})$ retardation interaction can also be determined.

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