Higher-order C_n dispersion coefficients for the alkali-metal atoms

J. Mitroy[*] and M. W. J. Bromley[†]

Faculty of Technology, Charles Darwin University, Darwin, Northern Territory 0909, Australia

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The van der Waals coefficients, from C_{11} through to C_{16} resulting from second-, third-, and fourth-order perturbation theory are estimated for the alkali-metal (Li, Na, K, and Rb) atoms. The dispersion coefficients are also computed for all possible combinations of the alkali-metal atoms and hydrogen. The parameters are determined from sum rules after diagonalizing a semiempirical fixed core Hamiltonian in a large basis. Comparisons of the radial dependence of the C_n/r^n potentials give guidance as to the radial regions in which the various higher-order terms can be neglected. It is seen that including terms up to C_{10}/r^{10} results in a dispersion interaction that is accurate to better than 1% whenever the inter-nuclear spacing is larger than $20a_0$. This level of accuracy is mainly achieved due to the fortuitous cancellation between the repulsive (C_{11}, C_{13}, C_{15}) and attractive (C_{12}, C_{14}, C_{16}) dispersion forces.

I. INTRODUCTION

The experimental realization of Bose-Einstein condensation (BEC) for the alkali-metal atoms Li, Na, Rb and atomic hydrogen [1,2] has resulted in an upsurge of interest in the area of cold atom physics. One consequence of this is the increased importance in determining the interaction potentials between alkali-metal and alkaline-earth atoms. For example, the stability and structure of BECs depends on the sign (and magnitude) of the scattering length, and the scattering length depends sensitively on the fine details of the interaction potential [3,4].

One can try and determine the interaction potential by either explicit calculation [5–7], or by analysis of high-precision spectroscopic experiments of the dimer [8–10]. These approaches are most suited to determining the potential at small to intermediate values of internuclear distance (e.g., $r < 25a_0$). At large distances, one relies on the approach pioneered by Dalgarno and collaborators [11–13], namely, using oscillator strength sum rules to determine the so-called dispersion coefficients.

The long-range interaction between two spherically symmetric atoms can be written in the general form

$$V(r \rightarrow \infty) = -V_6(r) - V_8(r) - V_{10}(r) - V_{11}(r) - V_{12}(r) - \cdots, \tag{1}$$

where the dispersion potential $V_n(r)$ of order n is written

$$V_n(r) = \frac{C_n}{r^n}. \tag{2}$$

The C_n parameters are the van der Waals dispersion coefficients. The even ($n = 6, 8, \ldots$) dispersion coefficients are calculated using oscillator-strength sum rules derived from second-order perturbation theory and provide an attractive interaction. The odd ($n = 11, 13, \ldots$) terms come from third-

order perturbation theory, and are repulsive [14]. Contributions from fourth-order perturbation theory start at $n = 12$ [14,15]. The calculations were stopped at $n = 16$ since the contributions from fifth- and sixth order perturbation theory start at $n = 17$ and $n = 18$, respectively.

It has been customary in previous systematic studies of dispersion coefficients to restrict the calculations to just the C_6, C_8, and C_{10} terms [16]. With the recent interest in determining the scattering lengths of A-A systems to high precision [4,9,17–20], it is now worthwhile to evaluate the higher n dispersion coefficients with a view to determining whether these make a significant contribution to the interatomic potential for those radial separations at which the long-range form of the potential is first applied.

The recent spectrum analyses have typically an internuclear distance of about $20a_0$ as the boundary point used to join the explicitly determined potential with the asymptotic form given in terms of the dispersion forces [8–10]. Taking the Rb-Rb potential as a specific example, explicit calculations have shown that $C_6 = 4.635 \times 10^3$ a.u., $C_8 = 5.701 \times 10^5$ a.u., $C_{10} = 7.916 \times 10^7$ a.u., and $C_{12} = 1.427 \times 10^{10}$ a.u. [21]. At a radius of $20a_0$ the ratios of the contributions from the various terms are 1:0.308:0.1068:0.0481. The contribution of the highest multipole potential is about 5% of the dipole-dipole C_6 term.

In this article, the C_{11} to C_{16} dispersion coefficients and related parameters are computed using a semiempirical approach for the alkali atoms. The method adopted utilizes oscillator strengths calculated within a semiempirical framework [21]. Comparisons with previous high accuracy *ab initio* calculations [21–26] of the C_6, C_8, and C_{10} dispersion coefficients suggests the methodology is able to generate coefficients that are accurate to about 1–2 % for the lighter alkali-metal atoms.

II. CALCULATION OF THE DISPERSION PARAMETERS

All the dispersion coefficients computed in this paper were computed by first diagonalizing the semiempirical Hamiltonian [21] in a large mixed Laguerre-type orbital or

*Electronic address: jxm107@rsphysse.anu.edu.au
†Electronic address: mbromley@cdu.edu.au

Slater-type orbital basis set. Next various sum rules involving oscillator strengths or reduced matrix elements were summed over the set of physical and pseudostates.

The respective formulae for the various coefficients are now given. The notation C_n is used to denote the total dispersion coefficient for a given n. So for $n \geq 12$, C_n is the sum of $C_n^{(2)}$ and $C_n^{(4)}$, where $C_n^{(2)}$ arises from second-order perturbation theory and $C_n^{(4)}$ arises from fourth-order perturbation theory.

A. The second-order contributions to C_{12} and C_{14}

While the higher n dispersion coefficients for the H-H system have been determined to high precision [27–29], only a few calculations of C_{12} and C_{14} have been done for the alkali-metal atoms [14,30]. The calculations of Ovsiannikov, Guilyarovski, and Lopatko (OGL) [14,27] used an approximate expression for the Greens function and can only be expected to be accurate at the 20% level. Explicit comparisons with the C_8 and C_{10} values of Patil and Tang (PT) [30] in Refs. 21 and 25 reveal discrepancies of order 10% for Na_2, K_2, and Rb_2. Recursion rules exist for estimating C_n at high n from data tabulations of C_n for lower values of n [28].

The polarization and dispersion parameters can be computed from their respective oscillator strength sum rules which are well known. The oscillator strength, $f_{0i}^{(l)}$ from the ground state (with orbital and spin angular momentum equal zero) to the ith excited state is defined as

$$f_{0i}^{(l)} = \frac{2|\langle \psi_0 \| r^l \mathbf{C}^l(\hat{\mathbf{r}}) \| \psi_i \rangle|^2 \epsilon_{0i}}{(2l+1)}. \qquad (3)$$

In this expression $\mathbf{C}^l$ is the spherical tensor of rank l, the Wigner-Eckart theorem is defined according to Ref. 31, and ϵ_{0i} is the excitation energy of the transition. The sum rule for the adiabatic multipole polarizability, $\alpha^{(l)}$ is

$$\alpha^{(l)} = \sum_i \frac{f_{0i}^{(l)}}{\epsilon_{0i}^2} = S^{(l)}(-2). \qquad (4)$$

The second-order contributions to C_{12} and C_{14} are defined

$$C_{2n}^{(2)} = \sum_{l_i l_j} \frac{(2n-2)!}{2l_i! 2l_j!} \sum_{ij} \frac{f_{0i}^{(l_i)} f_{0j}^{(l_j)}}{\epsilon_{0i} \epsilon_{0j}(\epsilon_{0j} + \epsilon_{0i})}, \qquad (5)$$

with $l_i + l_j + 1 = n$. 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.

The sum rules involve contributions from both core and valence excitations. The valence contributions were evaluated by diagonalizing the model Hamiltonian in a very large basis. Determination of the f-value distribution for the core was handled by using the properties of f-value sum rules and an approach that gives a reasonable estimate of the f-value distribution with a minimum of computation [21]. We use the sum rule for the polarizability, Eq. (4) and

$$lN\langle r^{2l-2} \rangle = \sum_i f_i^{(l)} = S^{(l)}(0), \qquad (6)$$

[21,32] to estimate an $f^{(l)}$-value distribution function of reasonable accuracy. This expression reduces to the well-known Thomas-Reiche-Kuhn sum rule for $l=1$, viz.

$$N = \sum_i f_i^{(1)} = S^{(1)}(0). \qquad (7)$$

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

The core $f^{(l)}$-value distribution was determined by assuming each closed subshell made a contribution of $N_i r_i^{2l-2}$ to the sum rules, where N_i the number of electrons in the subshell and r_i^{2l-2} is the $\langle r^{2l-2} \rangle$ Hartree-Fock (HF) expectation value. Next, the excitation energy for each subshell is set to the HF single particle, ϵ_i plus an energy shift. The energy shift, $\Delta^{(l)}$ was set by using the core multipole polarizability, $\alpha_{\text{core}}^{(l)}$ and the relation

$$\alpha_{\text{core}}^{(l)} = \sum_i \frac{lN_i r_i^{2l-2}}{(\epsilon_i + \Delta^{(l)})^2}. \qquad (8)$$

A full description of the details and core polarizabilities used to fix $\Delta^{(l)}$ for $l=1$, 2, and 3 has been published [21]. The contribution from the core was omitted for $l=4$ and 5 since there are no reliable estimates of these core polarizabilities and, in addition, the $lr_i^{(2l-2)}$ weighting factors lead to the core becoming less important for larger l. The core contribution to $\alpha^{(3)}$ was less than 0.2% for Rb and most of the core contribution to $C_{2n}^{(2)}$ comes from the $f^{(1)}$ distribution.

B. The third- and fourth-order potentials

The dispersion coefficients C_{11} and C_{13} arise from third-order perturbation theory [13–15,27,29,33]. The standard expressions are given in terms of sums of products of reduced matrix elements. The expressions derived by OGL [14,27] are used. Given the complexity of the expressions, it is not surprising there have been relatively few calculations of these coefficients for any atoms. Accurate values for $C_{11}^{(3)}$ through to $C_{31}^{(3)}$ for the H-H system have recently been published [27,29].

For the alkali-metal atoms, the only estimates of C_{11} have been obtained from the relatively small calculations of OGL [14] and Patil and Tang [30]. There have been some C_{11} and C_{12} estimates for Cs [34], but that atom is deemed too heavy to accurately describe with the present nonrelativistic method and is not discussed any further here.

The dispersion coefficients C_{12} and C_{14} both have contributions that arise from fourth-order perturbation theory. However, there have been very few calculations of the fourth-order term for any systems. Bukta and Meath [15] made an explicit calculation $C_{12}^{(4)}$ for the H-H dimer. In addition to deriving a general expression, OGL [14,27] also made some estimates of $C_{12}^{(4)}$ for combinations of hydrogen and the alkali atoms. Finally, the present authors made a comprehensive calculation of $C_n^{(4)}$ up to $n=32$ for the H-H interaction [27] using the OGL formalism.

TABLE I. The higher multipole polarizabilities for the lighter alkali atoms. All values are in atomic units.

Method	$10^{-6}\alpha^{(4)}$		$10^{-9}\alpha^{(5)}$	$10^{-9}\alpha^{(6)}$
	Present	PT [30]	Present	Present
Li	1.999	1.947	0.1551	17.04
Na	2.973	2.828	0.2450	28.53
K	11.82	10.69	1.204	172.4
Rb	16.57	14.49	1.762	259.6

Although the core has not been taken explicitly into account in the evaluation of the third- and higher-order dispersion parameters their impact is expected to be smaller than second order due the third- and fourth-order sum rules have an energy denominator involving the square or cube of the excitation energy.

III. RESULTS OF THE CALCULATION

A. Sensitivity of calculations to the ground-state wave function

One aspect of the calculations that warrants particular mention was the sensitivity of the higher-l polarizabilities (listed in Table I) and thus $C_{12}^{(2)}$, $C_{14}^{(2)}$, and $C_{16}^{(2)}$ to the representation of the ground-state wave function. While there are many advantages to representing the wave function with a linear combination of convenient basis functions, there are some negative features. One of those negative features relates to the behavior at large distances from the nucleus. Unlike a grid based calculation, the correct asymptotics are not imposed and so the large-r part of the wave function, which has a weak influence on the total binding energy can be inaccurate.

This is best illustrated by a specific calculation. Our initial calculations for the $\alpha^{(4)}$ and $\alpha^{(5)}$ polarizibilities Na used a $3s$ wave function written as a linear combination of 12 Slater type orbitals (STOs). This wave function had a binding energy against ionization of 0.1888532 Hartree. The resulting polarizabilities were $\alpha^{(4)}=3.46\times10^6$ a.u. and $\alpha^{(5)}=6.42\times10^8$ a.u.. When the STO basis was replaced by a large Laguerre type orbital (LTO) basis (this was necessary for the evaluation of C_{11}) and the energy driven to convergence the resulting binding energy was 0.1888549 Hartree. However there were dramatic changes in the polarizabilities, with the new values being $\alpha^{(4)}=2.97\times10^6$ a.u. and $\alpha^{(5)}=2.45\times10^8$ a.u. (refer to Table I). The polarizability $\alpha^{(5)}$ decreased by a factor of about 2.5 when the binding energy changed by 1.7×10^{-6} Hartree. The dispersion parameters $C_{12}^{(2)}$ and $C_{12}^{(4)}$ were also sensitive to the representation of the ground-state wave function. The initial $C_{14}^{(2)}$ of 4.04×10^{11} a.u. was decreased to 2.602×10^{11} a.u. when the ground-state basis was made exhaustively large. The impact of the basis set on the dispersion coefficients was was not so extreme as for the polarizability but was still substantial.

The $f^{(2)}$ and $f^{(3)}$ distributions used in earlier calculations of the Na and K polarizabilities and dispersion coefficients [21,35] were affected to a smaller extent by this problem [26]. The octupole polarizabilities were 3–4 % too large for these atoms, while the effect upon C_{10} was to make them about 1–2 % too large. The impact upon $\alpha^{(2)}$ and C_8 was an order of magnitude smaller but it was still discernible [27]. Where values of C_8 and C_{10} are required in the present work, the revised values [26] are used.

B. The homonuclear alkali-metal–alkali-metal systems

The results of the present calculations for the Li, Na, K and Rb homonuclear alkali atom pairs are listed in Tables I and II, and compared with the calculations of Ovsiannikov *et al.* [14] and Patil and Tang [30]. All of the present values of $C_{12}^{(2)}$ are larger than the PT and OGL estimates by amounts ranging from 10–50 %. This is not a concern since the OGL and PT estimates of C_6, C_8, and C_{10} are also smaller than the latest data for these parameters [21,24,25]. The present estimates of C_{11} and C_{13} are also 10–50 % larger than the PT and OGL estimates.

In Table II, $C_n^{(2)}$ and $C_n^{(4)}$ are given as separate entries. The total dispersion parameter C_n is given in Table IV which tabulates the dispersion parameters for all possible atom-atom combinations. The fourth-order terms $C_{12}^{(4)}$ are about 4–5 % the size of $C_{12}^{(2)}$. The fourth-order correction to C_{12} is about the same size as the correction due to the core. The size of the fourth-order correction to C_{14} is larger, with about 25% of the final value of C_{14} coming from $C_{14}^{(4)}$. For C_{16}, the fourth-order terms are almost as large as the 2nd-order terms, with $C_{16}^{(4)}$ being 80% the size of $C_{16}^{(2)}$ for K_2 and Rb_2.

The contribution of the core to $C_{12}^{(2)}$, $C_{14}^{(2)}$, and $C_{16}^{(2)}$ is relatively small. The contribution is largest for the Rb_2 dimer, but even here the effect is 4.2% for $C_{12}^{(2)}$, 3.2% for $C_{14}^{(2)}$, and 2.5% for $C_{16}^{(2)}$.

C. Critical radius for dispersion formula

The LeRoy radius is often used as an estimate of the critical radius beyond which the interaction can be described by the use of a dispersion formula [36,37]. It is defined for two atoms A and B as

$$R_{LR} = 2(\sqrt{\langle r^2\rangle_A} + \sqrt{\langle r^2\rangle_B}), \qquad (9)$$

where $\langle r^2\rangle_A$ is evaluated for the ground state. The LeRoy radius for the homonuclear dimers are given in Table III.

We introduce some parameters so that the range of validity of the dispersion formula can be discussed in a quantitative manner. First, the partial sum of the dispersion energy up to the nth term is defined as

$$W_n(r) = \sum_{m=6}^{m=n} V_m(r). \qquad (10)$$

One would then consider the relative size of $W_n(r)$ to $W_\infty(r)$ as a measure of the accuracy of the truncated dispersion potential to the exact potential. There are of course problems associated with the evaluation of W_∞, and so we identify $W_\infty(r)$ with $W_{16}(r)$. It is natural to stop the analysis at n

TABLE II. The dispersion coefficients for homonuclear combinations of the lighter alkali atoms. The $C_n^{(2)}$ terms have core contributions. All values are in atomic units.

Method	$10^{-6}C_{11}$	$10^{-9}C_{12}^{(2)}$	$10^{-9}C_{12}^{(4)}$	$10^{-9}C_{13}$	$10^{-12}C_{14}^{(2)}$	$10^{-12}C_{14}^{(4)}$	$10^{-12}C_{15}$	$10^{-15}C_{16}^{(2)}$	$10^{-15}C_{16}^{(4)}$
				Li					
Present	−40.44	0.9015	0.0401	−11.05	0.1455	0.04251	−2.873	0.02997	0.01908
PT [30]	−37.36	0.8648		−10.11					
OGL [14]	−36.0	0.648	0.0433	−8.85					
				Na					
Present	−61.01	1.500	0.06699	−18.90	0.2602	0.0720	−5.368	0.05736	0.03637
PT [30]	−53.32	1.375		−16.46					
OGL [14]	−39.5	0.917	0.0396	−11.3					
				K					
Present	−364.9	9.102	0.4640	−147.2	2.000	0.6807	−53.02	0.5544	0.4480
PT [30]	−312.3	7.749		−122.8					
OGL [14]	−250	5.430	0.361	−89.3					
				Rb					
Present	−536.2	14.26	0.6986	−236.5	3.314	1.098	−91.20	0.9656	0.7897
PT [30]	−464.4	11.56		−195.1					
OGL [14]	−376	8.370	0.556	−145.0					

=16 since the contributions from fifth and sixth-order perturbation theory start at $n=17$ and $n=18$, respectively.

Figure 1 shows the ratio $|W_{10}(r)-W_{16}(r)|/|W_{16}(r)|$ as a function of r for the Li, Na, K, and Rb dimers. This ratio is seen to be smaller than 1% for all values of r greater than $20a_0$. The curves for Li_2 and Na_2 are very similar, as are the curves for K_2 and Rb_2. The existence of two sets of two very similar curves is probably related to the fact that the lowest lying d excitations for Li and Na involve a change in principal quantum number whereas those for K and Rb do not.

There is a sign change in $[W_{10}(r)-W_{16}(r)]$ near $20a_0$ for all four dimers. The magnitude of $W_{10}(r)$ is generally smaller than $W_{16}(r)$ for small separations, but for large separations $W_{10}(r)$ is generally larger in magnitude than $W_{16}(r)$. This is caused by the repulsive $V_{11}(r)$, $V_{13}(r)$, and $V_{15}(r)$ interactions.

A useful way to parameterize this information is to define R_n such that it gives the smallest radius for which the partial dispersion energy $W_n(r)$ is accurate to 1%. In effect, R_n is the largest r solution of the equation

$$|W_n(r) - W_{16}(r)| = 0.010 W_{16}(r), \quad n \leqslant 16. \quad (11)$$

Table III gives R_n for the hydrogen and alkali-metal homonuclear dimers. The values of R_n get larger as the atom gets heavier. A dispersion potential only involving C_6 would not be accurate to 1% until the separation distance increased to more than $100a_0$ in the case of Rb_2. This distance shrinks dramatically with the inclusion of the V_8 and V_{10} potentials. The size of R_8 indicates that a dispersion interaction with only V_6 and V_8 is not good enough to describe these alkali-metal dimers. The R_{10} parameter is smaller than the LeRoy radius for all systems, and so the use of $W_{10}(r)$ will be accurate to better than 1% as long as the internuclear separation is greater than R_{LR}.

Figures 2, 3, 4, and 5 show the ratio $|V_n(r)|/|W_{16}(r)|$ as a function of r for all the alkali dimers. One of the most noticeable features of these curves is the existence of a nexus

TABLE III. Various radial distances (in a_0) related to the accuracy of different order expansions of the dispersion parameters for the homonuclear alkali-metal atom dimer.

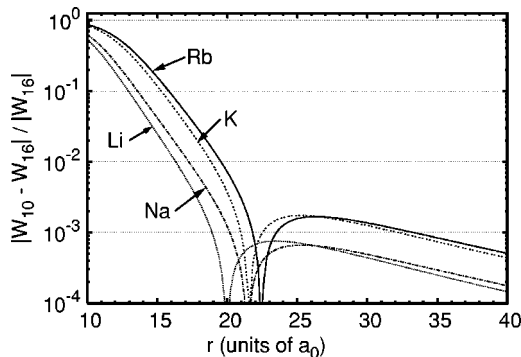| Atom	$\langle r^2 \rangle$	R_{LR}	R_6	R_8	R_{10}
Li	17.47	16.72	77.53	25.92	16.30
Na	19.51	17.67	86.24	28.07	17.24
K	27.97	21.16	103.8	32.61	18.82
Rb	30.76	22.18	111.0	34.44	19.54

FIG. 1. The ratio of $|W_{10}(r)-W_{16}(r)|/|W_{16}(r)|$ as a function of r (units of a_0) for all the possible homonuclear pairs.
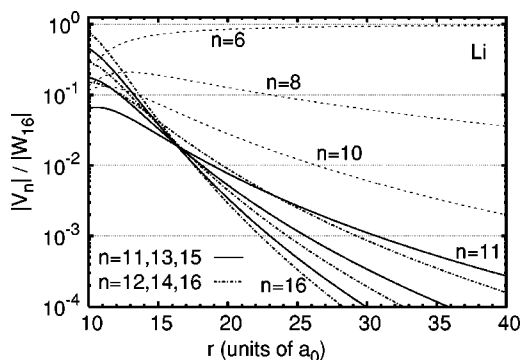
FIG. 2. The ratio of $|V_n(r)|/|W_{16}(r)|$ as a function of r (units of a_0) for the lithium dimer. The decay of the ratio at large r is fastest for large n.

FIG. 4. The ratio of $|V_n(r)|/|W_{16}(r)|$ as a function of r (units of a_0) for the potassium dimer. The decay of the ratio at large r is fastest for large n.

point for the V_{11}, V_{13}, V_{14}, V_{15}, and V_{16} potentials between $(16-21)a_0$ for all alkali dimers. This suggests that a recursion relation of the type $C_{n+m} = A^m C_n$ exists between the respective dispersion coefficients.

The biggest correction to $W_{10}(r)$ for sufficiently large r should be $V_{11}(r)$. The $C_{12}:C_{11}$ ratios for Li_2, Na_2, K_2, and Rb_2 from Table IV are 23.3, 25.7, 26.2, and 27.9, respectively, and for r less than these values it is actually $V_{12}(r)$ which is the largest correction to $W_{10}(r)$ (note, at sufficiently small r, V_{13}, $V_{14}, \ldots$, will also be larger than V_{11}).

The extent to which mutual cancellations act to minimize the error can be gauged by adding the magnitudes of $V_n(r)$ at $r=20a_0$. For Na, the $\Sigma_{n=11}^{16}|V_n(r)|$ is equal to $0.047 \times W_{16}(r)$ at $r=20a_0$. But, the partial sum $|W_{10}(r) - W_{16}(r)|$ is equal to $0.0012 \times W_{16}(r)$ at this radius. The alternating signs reduce the impact of the higher order terms by a factor of about 40. For Rb, the $\Sigma_{n=11}^{16}|V_n(r)|$ sum gives $0.168 \times W_{16}(r)$ at $r=20a_0$. The magnitudes of $|V_n(r)|/|W_{10}(r)|$ are greater than 0.025 for all n between 11 and 16. The partial sum $|W_{10}(r) - W_{16}(r)|$ is equal to $0.0071 \times W_{16}(r)$ at this radius. In this case, the alternating signs have reduced the impact of the higher order terms by a factor of more than 20.

Figures 6 and 7 better illustrate the extent to which mutual cancellations result in W_{10} being a very good approximation to the total dispersion potential for Na and Rb. The combination $[V_{11}(r)+V_{12}(r)]$ is much smaller than either V_{11} or
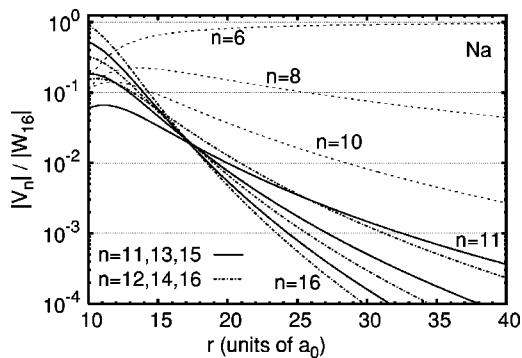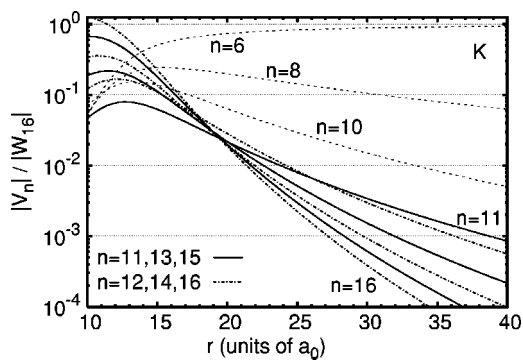
V_{12}, and similarly $[V_{13}(r)+V_{14}(r)]$ is smaller than V_{13} or V_{14} while $[V_{15}(r)+V_{16}(r)]$ is smaller than $V_{15}(r)$ or $V_{16}(r)$. The combination of $V_{2n-1}(r)+V_{2n}(r)$ falls to 1% of $W_{16}(r)$ about $(5-10)a_0$ closer to the origin than either $V_{2n-1}(r)$ or $V_{2n}(r)$.

The rubidium dimer. A recent analysis of three complementary experiments by van Kempen *et al.* [9] for the Rb_2 dimer resulted in experimental estimates of the dispersion parameters C_6, C_8, C_{10}, and C_{11} and gave estimates of the scattering length to a precision of about 1% for Rb^{87}.

The present work suggests that their estimates of C_6, C_8, and C_{10} may be well founded and our previous calculations agreed with the experimental values to an accuracy of 2% [21]. However, it is probable that their attempt to determine C_{11} was overly ambitious. The present calculation gave $C_{11} = -5.362 \times 10^9$ a.u. which lies outside the van Kempen estimate of $C_{11} = (-8.6 \pm 0.17) \times 10^9$ a.u.. We believe this difference is a consequence of the assumptions made by van Kempen *et al.* when they performed the fit to extract the dispersion coefficient.

First, their least squares fit relied on a value of C_{12} of 1.19×10^{10} a.u. computed by Patil and Tang [38]. This estimate of C_{12} is about 25% smaller than the present second-plus fourth-order C_{12} of 1.496×10^{10} a.u. Second, their estimate is derived from the energies of bound states that have an outer turning radius of about $20a_0$. At this radius, V_{12} is actually larger than V_{11}. Furthermore, the higher order terms
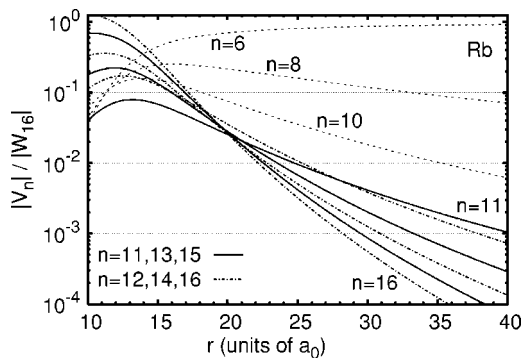

FIG. 3. The ratio of $|V_n(r)|/|W_{16}(r)|$ as a function of r (units of a_0) for the sodium dimer. The decay of the ratio at large r is fastest for large n.

FIG. 5. The ratio of $|V_n(r)|/|W_{16}(r)|$ as a function of r (units of a_0) for the rubidium dimer. The decay of the ratio at large r is fastest for large n.

TABLE IV. The dispersion coefficients $C_{11} \rightarrow C_{16}$ for all the possible interacting pairs formed by hydrogen and the alkali-metal atoms. The C_{12}, C_{14}, and C_{16} coefficients have contributions from both second- and fourth-order perturbation theory. All values are in atomic units.

System	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
H-H [27]	−3474.9	1.2273×10^5	-3.2699×10^5	6.3617×10^6	-2.8396×10^7	4.4121×10^8
	$10^{-6}C_{11}$	$10^{-6}C_{12}$	$10^{-9}C_{13}$	$10^{-9}C_{14}$	$10^{-9}C_{15}$	$10^{-12}C_{16}$
H-Li	−0.2251	21.17	−0.04752	2.735	−9.438	0.4593
H-Na	−0.2760	29.43	−0.06269	4.030	−13.25	0.7160
H-K	−0.5636	92.69	−0.1635	15.68	−43.10	3.409
H-Rb	−0.6619	12.34	−0.2064	21.86	−57.57	4.936
	$10^{-6}C_{11}$	$10^{-9}C_{12}$	$10^{-9}C_{13}$	$10^{-12}C_{14}$	$10^{-12}C_{15}$	$10^{-13}C_{16}$
Li-Li	−40.44	0.9417	−11.05	0.1880	−2.873	4.906
Li-Na	−49.63	1.221	−14.48	0.2512	−3.937	6.819
Li-K	−119.4	3.216	−40.67	0.7685	−12.68	24.08
Li-Rb	−143.9	4.134	−51.84	1.018	−16.84	32.90
Na-Na	−61.01	1.567	−18.90	0.3323	−5.368	9.373
Na-K	−146.5	4.015	−52.60	0.9834	−17.04	31.97
Na-Rb	−176.5	5.125	−66.85	1.292	−22.54	43.32
K-K	−364.9	9.567	−147.2	2.681	−53.02	100.24
K-Rb	−442.1	11.99	−186.7	3.449	−69.63	133.0
Rb-Rb	−536.2	14.96	−236.5	4.412	−91.20	175.5

V_{13}, V_{14}, V_{15}, and V_{16} were all slightly larger than V_{11} at a radius of $20a_0$. However, as has been noted, the alternating signs of the successive terms results in a considerable degree of cancellation. Nevertheless, one can conclude that the van Kempen estimate of C_{11} is sensitive to the accuracy and presence of the high n terms in the dispersion interaction.

D. The heteronuclear systems including H

The $n > 10$ dispersion parameters for all possible combinations of H, Li, Na, K, and Rb are given in Table IV. The radial matrix elements for hydrogen were those of the $N = 15$ calculation used in an earlier calculation of the H-H dispersion parameters [27]. The C_{11} and C_{12} parameters re-

ported by OGL [14] and PT [30] are not listed since the present calculations are more sophisticated.

IV. CONCLUSIONS

The complete set of dispersion parameters up to $n = 16$ has been computed for all combinations of hydrogen and the alkali atoms up to rubidium. The relative importance of the dispersion potentials $V_n(r)$ increases as the atoms get heavier. It was found that the dispersion energy given by the first three terms of Eq. (1) is accurate to 1% whenever $R > 20a_0$. This degree of accuracy at relatively small internuclear separations comes from a fortuitous cancellation between the terms with $n > 10$ in the dispersion energy. The third-order
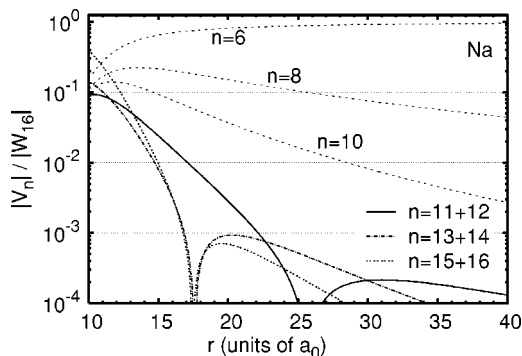

FIG. 6. The ratio of $|V_n(r)|/|W_{16}(r)|$ for $n = 6$, 8 and 10 as a function of r (units of a_0) for the sodium dimer. The other curves show the ratio of $|V_{2n-1}(r) + V_{2n}(r)|/|W_{16}(r)|$ for $2n = 12, 14, 16$.
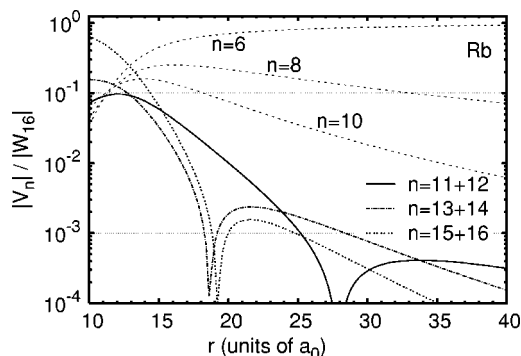

FIG. 7. The ratio of $|V_n(r)|/|W_{16}(r)|$ for $n = 6$, 8, and 10 as a function of r (units of a_0) for the rubidium dimer. The other curves show the ratio of $|V_{2n-1}(r) + V_{2n}(r)|/|W_{16}(r)|$ for $2n = 12, 14, 16$.

potentials V_{11}, V_{13}, and V_{15} are repulsive, while the even terms V_{12}, V_{14}, and V_{16} are attractive. The fourth-order contribution to C_{16} was almost as large as the second-order contribution to C_{16}. It is worth noting that Dalgarno and Lewis showed that the second-order multipole expansion of the dispersion series was actually divergent [39]. However, the cancellations that occur between the terms of different polarities are consistent with their statement that truncating the dispersion series to a finite number of terms can lead to an accurate interaction potential despite the formal properties of the multipole expansion.

Whether terms in the dispersion interaction with $n > 10$ are important in the description of alkali dimers is essentially a question about whether the dispersion interaction has to be known to a precision of 1.0% or 0.1%. It is clear that additional terms going beyond C_{10} should be introduced in pairs. There is no point in including the V_{11} potential without also including the V_{12} potential. Indeed, inclusion of just one member of the (V_{11}, V_{12}) would most likely degrade rather than improve the accuracy of the dispersion potential. Given that the C_6 parameter has been calculated to a precision of better than 1% for most alkali systems [21,24,25], usage of a dispersion interaction involving the (V_{11}, V_{12}) potentials may be warranted.

There have been a couple of experimental investigations of alkali-dimer potentials that have included dispersion forces with $n > 10$. The value of C_{11} for the Rb dimer has been given by van Kempen *et al.* [9]. However, this value of C_{11} is most likely model dependent for reasons discussed earlier. Consideration of the $V_{12}(r)$ potential has also occurred in analyses of the spectrum of the Cs dimer [40,41]. In this case, the $V_{11}(r)$ potential was omitted so it is doubtful whether the inclusion of $V_{12}(r)$ was justified in this case.

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