

Accurate relativistic many-body calculations of van der Waals coefficients C_8 and C_{10} for alkali-metal dimers

Sergey G. Porsev^{a)} and Andrei Derevianko
Physics Department, University of Nevada, Reno, Nevada 89557-0058

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We consider long-range interactions between two alkali-metal atoms in their respective ground states. We extend the previous relativistic many-body calculations of C_6 dispersion coefficients [Phys. Rev. Lett. **82**, 3589 (1999)] to higher-multipole coefficients C_8 and C_{10} . Special attention is paid to usually omitted contribution of core-excited states. We calculate this contribution within relativistic random-phase approximation and demonstrate that for heavy atoms core excitations contribute as much as 10% to the dispersion coefficients. We tabulate results for both homonuclear and heteronuclear dimers and estimate theoretical uncertainties. The estimated uncertainties for C_8 coefficients range from 0.5% for Li_2 to 4% for Cs_2 . © 2003 American Institute of Physics. [DOI: 10.1063/1.1578052]

I. INTRODUCTION

We carry out accurate relativistic many-body atomic-structure calculations of van der Waals interactions¹ between alkali-metal atoms in their respective ground states. These long-range interactions may be parametrized using dispersion (van der Waals) coefficients C_n

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

where R is the internuclear separation. A renewed interest in high-accuracy interatomic potentials has been stimulated by advances in studies of ultracold collisions.² At low energies, collision properties are typically very sensitive to details of the potentials. Thus accurate potentials are essential for reliable *ab initio* description of ultracold collision properties and, conversely, a wealth of information about the potentials may be inferred from photoassociation and Feshbach-resonance spectroscopy with ultracold atomic samples. In particular, only recently interpretation of experiments with ultracold atoms allowed several groups to reduce uncertainties in the C_6 coefficients to a fraction of a percent.^{3–5} These inferred coefficients are in an excellent agreement with our values predicted using many-body perturbation theory.⁶ Even more refined understanding of details of ultracold collisions led very recently to constraints on higher-multipole coefficient C_8 for Rb (Refs. 7 and 8) and Cs.⁹ This latest progress and discrepancies between previous determinations^{10–14} of C_8 and C_{10} coefficients motivate us to calculate these coefficients using accurate relativistic many-body techniques of atomic structure. In particular, we demonstrate that usually omitted contribution of core-excited states increases C_n for heavy atoms by as much as 10%.

The main result of the paper—compilation of van der Waals coefficients C_8 and C_{10} for homonuclear and hetero-

nuclear Li, Na, K, Rb, and Cs dimers—is presented in Tables VI–IX. The rest of the paper is organized as follows. In Sec. II we present the formalism. Numerical evaluation is discussed in Sec. III. A detailed analysis of underlying multipole dynamic and static polarizabilities is presented in Sec. IV. Finally, in Sec. V we compile dispersion coefficients and estimate theoretical uncertainties. Atomic units ($|e| = m_e = \hbar \equiv 1$) are used throughout the paper.

II. GENERAL FORMALISM

The long-range part of electrostatic interaction between two atoms a and b in their respective spherically symmetric states may be represented as¹

$$V(R) = -\sum_{n=3} C_{2n}^{ab} / R^{2n}, \quad (2)$$

where R is the distance between atoms. For ground-state atoms van der Waals coefficients are given by¹⁴

$$C_{2n}^{ab} = \frac{(2n-2)!}{2\pi} \sum_{l=1}^{n-2} \frac{1}{(2l)!(2l')!} \int_0^\infty \alpha_l^a(i\omega) \alpha_{l'}^b(i\omega) d\omega, \quad (3)$$

where $l' = n - l - 1$; $\alpha_l^a(i\omega)$ and $\alpha_{l'}^b(i\omega)$ are, respectively, 2^l -pole dynamic polarizability of atom a and $2^{l'}$ -pole dynamic polarizability of atom b . The dynamic polarizabilities in Eq. (3) are defined as

$$\alpha_l(i\omega) = 2 \operatorname{Re} \sum_k \frac{\langle \Psi_0 | T_0^{(l)} | \Psi_k \rangle \langle \Psi_k | T_0^{(l)} | \Psi_0 \rangle}{(E_k - E_0) + i\omega}. \quad (4)$$

Here the summation extends over a complete set of atomic states and $T_0^{(l)}$ are the zeroth components of spherical tensors of electric-multipole operators,

$$T_m^{(l)} = \sum_{i=1}^N r_i^l C_m^{(l)}(\hat{\mathbf{r}}_i), \quad (5)$$

^{a)}Permanent address: Petersburg Nuclear Physics Institute, Gatchina, Leningrad district, 188300, Russia.

TABLE I. Comparison of DHF and many-body one-electron removal energies E_{val} for Cs with experimental values. E_{val} are given in atomic units. Δ are excitation energies from the ground $6s_{1/2}$ state in cm^{-1} . For s states the energies were calculated with $\delta = -0.20$ a.u., for d states with $\delta = 0.0$ a.u., and for p with $\delta = -0.09$ a.u.

| Config. | DHF | | DHF+MBPT | | Experimental (Ref. 34) | |
|------------|------------------|----------|------------------|----------|------------------------|----------|
| | E_{val} | Δ | E_{val} | Δ | E_{val} | Δ |
| $6s_{1/2}$ | 0.127368 | | 0.143085 | | 0.143099 ^a | |
| $6p_{1/2}$ | 0.085616 | 9163.6 | 0.092173 | 11172.2 | 0.092167 | 11178.2 |
| $6p_{3/2}$ | 0.083785 | 9565.3 | 0.089609 | 11734.9 | 0.089642 | 11732.4 |
| $5d_{3/2}$ | 0.064419 | 13815.7 | 0.076995 | 14503.3 | 0.077035 | 14499.5 |
| $5d_{5/2}$ | 0.064529 | 13791.5 | 0.076459 | 14621.0 | 0.076590 | 14597.1 |
| $7s_{1/2}$ | 0.055187 | 15841.8 | 0.058475 | 18568.0 | 0.058645 | 18535.5 |
| $7p_{1/2}$ | 0.042021 | 18731.4 | 0.043868 | 21773.9 | 0.043928 | 21765.7 |
| $7p_{3/2}$ | 0.041368 | 18874.8 | 0.043041 | 21955.4 | 0.043103 | 21946.7 |

^aFor the ground state E_{val} is equal to the ionization potential $\text{IP}(\text{Cs}) = 31\,406.71 \text{ cm}^{-1}$ (Ref. 34).

where $C_m^{(l)}$ are normalized spherical harmonics¹⁵ and the sum is over all N atomic electrons.

Previously many-body calculations of dispersion coefficients C_6 were carried out in Refs. 6 and 16, and here we focus on dispersion coefficients C_8 and C_{10} . As follows from an examination of Eq. (3), we need to compute dipole α_1 , quadrupole α_2 , and octupole α_3 dynamic polarizabilities. In this work we employ dynamic dipole polarizabilities calculated previously in Ref. 6 and determine higher-multipole polarizabilities α_2 and α_3 .

Following Ref. 6 we separate all intermediate states in the sum Eq. (4) into valence and core-excited states,

$$\alpha_l(i\omega) = \alpha_l^v(i\omega) + \alpha_l^c(i\omega) + \alpha_l^{cv}(i\omega). \quad (6)$$

Here $\alpha_l^v(i\omega)$ is a traditional term encapsulating excitations of the valence electron. Contributions of electric-multipole excitations of core electrons are denoted by $\alpha_l^c(i\omega)$. Finally, a small counter term $\alpha_l^{cv}(i\omega)$ is related to excitations of core electrons to occupied valence state. We include these exclusion-principle-forbidden excitations in the calculations of core polarizabilities and thus we have to introduce the counter term (see Ref. 17 for more details). We will discuss calculations of the $\alpha_l^v(i\omega)$ and $\alpha_l^c(i\omega)$ terms later on. Here we just briefly comment on the counterterm $\alpha_l^{cv}(i\omega)$. For octupole polarizabilities $\alpha_3^{cv}(i\omega)$ term simply vanishes in independent-particle approximation since $E3$ selection rules

would require an excitation from f shell to valence s state and none of the alkalis considered here (Li through Cs) has filled f shells. Since we employ dipole polarizabilities from Ref. 6, the counter term, calculated in Dirac-Hartree-Fock (DHF) approximation is included in $\alpha_1(i\omega)$. Finally we disregard this correction for quadrupole polarizabilities; it gives a negligible contribution due to required excitation of deeply bound d electrons from the core.

High-accuracy calculations of the *dipole* dynamic polarizabilities were carried out earlier in Ref. 6 and we employ these dipole polarizabilities in the present work. In those calculations a combination of several relativistic many-body techniques was employed. A dominant contribution to α_1^v has been calculated with all-order linearized coupled-cluster method truncated at single and double excitations. High-accuracy experimental values for energies and electric-dipole matrix elements for principle transitions have been employed to refine the dipole polarizabilities. In the following we focus on the quadrupole and octupole polarizabilities.

To find the quadrupole α_2^v and octupole α_3^v valence contributions we applied a relativistic many-body method initially suggested in Refs. 18 and 19 and subsequently developed in Refs. 20 and 21. In this method one determines wave functions from solution of the effective many-body Schrödinger equation,

TABLE II. Static quadrupole polarizabilities α_2 for ground states of alkali-metal atoms in a.u. We present valence contributions for the cases of pure DHF and DHF+MBPT, and core contributions. Final values were determined as sum of α_2^v (DHF+MBPT) and α_2^c .

| | Li | Na | K | Rb | Cs |
|-----------------------------------|-------------|----------|-------------|----------|------------|
| α_2^v (DHF) | 1485.5 | 2230.3 | 7049 | 9790 | 16613 |
| α_2^v (DHF+MBPT) | 1424.5 | 1883.6 | 4983 | 6488 | 10388 |
| α_2^c (RRPA) | 0.1 | 1.5 | 16 | 35 | 86 |
| Final | 1424(4) | 1885(26) | 5000(45) | 6520(80) | 10470(390) |
| | | | Other works | | |
| Patil and Tang (Ref. 35) | 1393 | 1796 | 4703 | 6068 | 10260 |
| Patil and Tang (Ref. 14) | 1403 | 1807 | 4760 | 6163 | 10400 |
| Yan <i>et al.</i> (Ref. 30) | 1423.266(5) | | | | |
| Marinescu <i>et al.</i> (Ref. 13) | 1424 | 1878 | 5000 | 6495 | 10462 |
| Spelsberg <i>et al.</i> (Ref. 36) | 1423 | 1879 | 5001 | | |
| Maeder and Kutzelnigg (Ref. 10) | 1383 | 1799 | 4597 | 5979 | 9478 |

TABLE III. Static octupole polarizabilities α_3 for ground states of alkali-metal atoms in 10^4 a.u. We present valence contributions for the cases of pure DHF and DHF+MBPT, and core contributions. Final values were determined as sum of α_3^v (DHF+MBPT) and α_3^c .

| | Li | Na | K | Rb | Cs |
|-----------------------------------|-------------|-------|-------|-------|-------|
| α_3^v (DHF) | 4.185 | 6.888 | 28.10 | 41.50 | 76.49 |
| α_3^v (DHF+MBPT) | 3.957 | 5.536 | 17.73 | 23.66 | 39.43 |
| α_3^c (RRPA) | 0 | 0.001 | 0.01 | 0.03 | 0.10 |
| Final | 3.957 | 5.54 | 17.7 | 23.7 | 39.5 |
| | Other works | | | | |
| Patil and Tang (Ref. 35) | 3.871 | 5.287 | 16.07 | 20.73 | 33.12 |
| Patil and Tang (Ref. 14) | 3.986 | 5.430 | 16.30 | 20.97 | 33.33 |
| Yan <i>et al.</i> (Ref. 30) | 3.965049(8) | | | | |
| Marinescu <i>et al.</i> (Ref. 13) | 3.969 | 5.552 | 17.69 | 23.69 | 39.53 |
| Spelsberg <i>et al.</i> (Ref. 36) | 3.927 | 5.486 | 19.14 | | |
| Maeder and Kutzelnigg (Ref. 10) | 3.680 | 5.117 | 15.02 | 21.27 | 33.99 |

$$H_{\text{eff}}(E_n)|\Psi_n\rangle = E_n|\Psi_n\rangle, \quad (7)$$

with the effective Hamiltonian defined as

$$H_{\text{eff}}(E) = H_{\text{FC}} + \Sigma(E). \quad (8)$$

Here H_{FC} is the frozen-core Dirac-Hartree-Fock Hamiltonian and self-energy operator Σ is the energy-dependent correction, involving core excitations. Qualitatively the Σ operator corresponds to the core polarization term in model potentials employed in Refs. 13 and 14. In the present calculation the self-energy operator recovers second order of perturbation theory in residual Coulomb interaction and additionally accounts for certain classes of many-body diagrams in all orders of perturbation theory.

The concept of effective Hamiltonian H_{eff} may be extended to other operators. We introduce effective (or dressed) electric-multipole operators T_{eff}^l acting in the model space of valence electrons. These operators were obtained within the relativistic random-phase approximation (RRPA).^{20,22,23} Qualitatively, the RRPA describes a shielding of the externally applied electric-multipole field by the core electrons. The RRPA sequence of diagrams was summed to all orders of the perturbation theory.

Once the ground-state wave functions are obtained from Eq. (7), the dynamic valence polarizabilities $\alpha_i^v(i\omega)$ are computed with the Sternheimer²⁴ or Dalgarno-Lewis²⁵ method implemented in the DHF+ Σ +RRPA framework. [In the following we denote Σ +RRPA corrections as the many-body perturbation theory (MBPT) corrections.] Given the ground-state wave function Ψ_0 and energy E_0 , we find an intermediate-state wave function Ψ_f from an inhomogeneous equation,

$$|\Psi_f\rangle = \text{Re} \left\{ \frac{1}{H_{\text{eff}} - E_0 + i\omega} \sum_i |\Psi_i\rangle \langle \Psi_i | (T_0^l)_{\text{eff}} | \Psi_0 \rangle \right\} \\ = \text{Re} \left\{ \frac{1}{H_{\text{eff}} - E_0 + i\omega} (T_0^l)_{\text{eff}} | \Psi_0 \rangle \right\}. \quad (9)$$

With such introduced Ψ_f Eq. (4) becomes simply

$$\alpha_i^v(i\omega) = 2 \langle \Psi_0 | (T_0^l)_{\text{eff}} | \Psi_f \rangle, \quad (10)$$

where subscript v emphasized that only excitations of the valence electron to higher virtual orbitals are included in the intermediate-state wave function Ψ_f due to the presence of H_{eff} in Eq. (9). As to additional contribution α_i^c of core-excited states, we employ the relativistic random-phase approximation method described in Refs. 22 and 23.

III. DETAILS OF NUMERICAL CALCULATION

At the first stage of calculations we determined core orbitals and valence orbitals for several low-lying states from the frozen-core Dirac-Hartree-Fock equations.²⁶ The virtual orbitals were determined with the help of a recurrent procedure.²⁷ One-electron basis sets of the following sizes were used on the stage DHF+ Σ calculations:

$$\begin{aligned} \text{Li: } & 1-17s, 2-17p, 3-16d, 4-16f, 5-10g; \\ \text{Na: } & 1-18s, 2-18p, 3-17d, 4-17f, 5-11g; \\ \text{K: } & 1-19s, 2-19p, 3-18d, 4-19f, 5-12g; \\ \text{Rb: } & 1-20s, 2-20p, 3-19d, 4-19f, 5-13g; \\ \text{Cs: } & 1-23s, 2-23p, 3-23d, 4-26f, 5-14g. \end{aligned}$$

TABLE IV. Static quadrupole polarizabilities $\alpha_2^c(0)$ of singly charged ions of alkali-metal atoms (core polarizabilities). Results marked RRPA are results of our calculations; these numerical values are identical to those by Johnson *et al.*²³ All values are in atomic units.

| | Li ⁺ | Na ⁺ | K ⁺ | Rb ⁺ | Cs ⁺ |
|--------------------------------|-----------------|-----------------|----------------|-----------------|-----------------|
| RRPA | 0.11 | 1.52 | 16.3 | 35.4 | 86.4 |
| Patil (Refs. 32 and 33) | | 1.64(15) | 18.2(3.0) | 42(3) | 128(40) |
| Freeman and Kleppner (Ref. 37) | | 1.91(15) | | | |

TABLE V. Static octupole polarizabilities $\alpha_3^s(0)$ of singly charged ions of alkali-metal atoms (core polarizabilities). All values are in atomic units.

| | Li ⁺ | Na ⁺ | K ⁺ | Rb ⁺ | Cs ⁺ |
|-----------------|-----------------|-----------------|----------------|-----------------|-----------------|
| This work | 0.17 | 7.5 | 110 | 314 | 1014 |
| Patil (Ref. 32) | | | 95(10) | 280(40) | 1220(200) |

Using these basis sets we solved the multiparticle Schrödinger equation (7) and found the wave functions of low-lying states. As discussed in Ref. 28 and demonstrated in Ref. 29 a proper approximation for the effective Hamiltonian can substantially improve an agreement between calculated and experimental spectra of multielectron atom. One can introduce an energy shift δ and replace $\Sigma(E) \rightarrow \Sigma(E - \delta)$ in the effective Hamiltonian, Eq. (8). We have determined δ from a fit of theoretical energy levels to experimental spectrum. Using only one fitting parameter δ we reproduced the experimental energies for 12 low-lying states for Li and for 10 low-lying states for Na and K with accuracy 0.1–0.2%. To reproduce the low-lying energy levels with the same 0.1–0.2% accuracy for heavier Rb and Cs we used three fitting parameters (different shifts δ for different partial waves). An illustrative comparison for the heaviest atom Cs (55 electrons) is presented in Table I. It is worth noting that an empirical introduction of shifts δ mimics higher-order many-body corrections in perturbation theory. We will estimate theoretical uncertainty based on sensitivity of our results to variation in these shifts.

IV. QUADRUPOLE AND OCTUPOLE POLARIZABILITIES

To reiterate major steps of the formalism described in Sec. II, we determined ground-state wave functions from the effective many-body Schrödinger equation (7), calculated dressed electric multipole operators T_{eff} , solved inhomogeneous equation (9), and computed valence parts α_i^v of dy-

namic polarizability with Eq. (10). Additional contributions α_i^c of core-excited states were calculated using the RRPA method.

Calculation of dynamic polarizabilities with $\omega = 0$ gives us the static polarizabilities. We provide these data in Tables II and III and compare them with other results. To estimate uncertainties we present in the tables results of pure DHF calculations and compare them with DHF+MBPT ones. The uncertainties of calculations are associated with higher orders of the MBPT which are taken into account only partially. The heavier the atom, the larger MBPT contribution is and we expect theoretical accuracy to become worse. For instance, the MBPT correction to the static quadrupole polarizability α_2^v for Li is only 4%, while for Cs it attains 38%. For static octupole polarizabilities α_3^v the MBPT corrections are larger and range from 5% for Li to 48% for Cs.

Let us turn to estimates of theoretical uncertainty of quadrupole polarizabilities. Essentially it is based on sensitivity of our results to semiempirically introduced shifts δ . As mentioned in Sec. III an introduction of these shifts mimics omitted higher orders of perturbation theory. We estimate the theoretical error bar as a half of the difference between *ab initio* ($\delta = 0$) value and result with semiempirically chosen δ . Further, an overwhelming contribution to static 2^l -pole polarizabilities Eq. (4) comes from the lowest-lying valence state of proper angular symmetry. Since we recover experimental energies almost exactly (see Table I), the theoretical uncertainty is determined by an accuracy of calculation for electric-multipole operators of principal transitions. We write

$$\frac{\delta\alpha_2(0)}{\alpha_2(0)} \sim \left| \frac{\langle ns | T_0^2 | n'd \rangle_{\delta} - \langle ns | T_0^2 | n'd \rangle_{\delta=0}}{\langle ns | T_0^2 | n'd \rangle_{\delta=0}} \right|,$$

where ns denotes the ground state and $n'd$ stands for lowest-lying valence d states. For example, following this procedure we obtain an error bar of 0.3% for Li. Our result of 1424(4) for Li is in excellent agreement with the value 1423.266(5)

TABLE VI. van der Waals C_8 coefficients in 10^5 a.u. for homonuclear dimers. C_8^v values include only valence contributions. The final values were determined as combination of DHF+MBPT method for valence contributions with RRPA calculations for core excitations.

| | Li | Na | K | Rb | Cs |
|-----------------------------------|-------------|-----------|---------|----------|----------|
| C_8^v | 0.832 | 1.15 | 4.00 | 5.37 | 9.16 |
| Final | 0.834(4) | 1.160(18) | 4.20(5) | 5.77(8) | 10.2(4) |
| Other theoretical works | | | | | |
| Patil and Tang (Ref. 14) | 0.8183 | 1.090 | 3.892 | 5.258 | 9.546 |
| Yan <i>et al.</i> (Ref. 30) | 0.834258(4) | | | | |
| Marinescu <i>et al.</i> (Ref. 13) | 0.8324 | 1.119 | 4.096 | 5.506 | 9.630 |
| Spelsberg <i>et al.</i> (Ref. 36) | 0.8303 | 1.141 | 4.011 | | |
| Maeder and Kutzelnigg (Ref. 10) | 0.8089 | 1.098 | 3.834 | 5.244 | 9.025 |
| Experiment | | | | | |
| van Kempen <i>et al.</i> (Ref. 7) | | | | 5.79(49) | |
| | | | | 6.09(7) | |
| Marte <i>et al.</i> (Ref. 8) | | | | 5.73 | |
| Amiot and Dulieu (Ref. 38) | | | | | 9.63(19) |
| Leo <i>et al.</i> (Ref. 9) | | | | | 8.4(4) |

TABLE VII. van der Waals C_{10} coefficients in 10^7 a.u. for homonuclear dimers. C_{10}^v values include only valence contributions.

| | Li | Na | K | Rb | Cs |
|-----------------------------------|------------|-------|-------|-------|-----------|
| C_{10}^v | 0.734 | 1.12 | 5.18 | 7.55 | 14.7 |
| Final | 0.735 | 1.13 | 5.37 | 7.96 | 15.9 |
| Other theoretical works | | | | | |
| Patil and Tang (Ref. 14) | 0.7289 | 1.068 | 4.789 | 6.833 | 13.58 |
| Yan <i>et al.</i> (Ref. 30) | 0.73721(1) | | | | |
| Marinescu <i>et al.</i> (Ref. 13) | 0.7365 | 1.107 | 5.248 | 7.665 | 15.20 |
| Spelsberg <i>et al.</i> (Ref. 36) | 0.7306 | 1.113 | 5.431 | | |
| Maeder and Kutzelnigg (Ref. 10) | 0.6901 | 1.036 | 4.522 | 6.836 | 13.01 |
| Experiment | | | | | |
| Amiot and Dulieu (Ref. 38) | | | | | 13.59(27) |

from benchmark high-accuracy variational nonrelativistic calculations by Yan *et al.*³⁰ We estimate theoretical uncertainties for octupole polarizabilities to be at 10% level for heavy atoms. Our results for static polarizabilities are listed in Tables II and III. In these tables we also compare our results with the predictions by other authors. We find that for light atoms there is a good agreement between different results except the values obtained by Maeder and Kutzelnigg¹⁰ are consistently smaller. As the number of atomic electrons increases, the correlation effects become more pronounced and discrepancies between results from different groups grow larger. Marinescu *et al.*¹³ used a model potential with five adjustment parameters obtained by fitting to experimental energy levels. Core polarization was included in the pseudopotential and they also included effects of shielding (or field dressing) in the multipole operators. Patil and Tang¹⁴ also used effective potential in their calculations to obtain the wave functions of excited states, but they used one-parametric potential and did not use shielding in the multipole operators. Generally, our results are in a good agreement with all results except for values by Maeder and Kutzelnigg.¹⁰ The latter were obtained more than 20 years ago. The core-polarization and relativistic effects were simulated by a pseudopotential, and the alkali-metal atoms were treated as one-electron systems. Besides that these authors used small number of basis functions (e.g., only five basis orbitals for p , d , and f partial waves) while α_2 and α_3 polarizabilities are very sensitive to details of construction and saturation of basis sets.

Also shown in Tables II and III are the corrections α_i^c due to core-excited states. These quantities are essentially polarizabilities of singly charged ions of alkali-metal atoms.

Only by disregarding distortion of the core by the valence electrons, may one identify corrections α_i^c as core polarizabilities. For static quadrupole polarizabilities their relative contribution to the total polarizabilities ranges from 0.01% for Li to 0.8% for Cs. The core corrections to static octupole polarizabilities are even smaller (just 0.25% for Cs). Relative smallness of α_i^c terms for *static* polarizabilities may lead one to a wrong assumption that the core excitations may be disregarded in calculations of van der Waals coefficients C_n . In fact the expression (3) for C_n contains integration over an infinite range of frequencies ω . While the region around $\omega = 0$ does provide the dominant contribution to C_n , the high-frequency tail of the polarizability is still important. As $\omega \rightarrow \infty$ the core polarizability overpowers valence contribution. In fact, one of the points of the paper⁶ was to explicitly demonstrate that for heavy atoms the core polarizability may contribute as much as 15% to C_6 dispersion coefficient. Here using RRPA calculations of $\alpha_i^c(i\omega)$ core polarizability we will arrive at a similar conclusion for higher-multipole coefficients C_8 and C_{10} .

We calculated the core polarizabilities in the framework of relativistic random-phase approximation method (RRPA). Essentially we extended approach of Johnson *et al.*²³ and incorporated frequency dependence into the calculations. Compared to Ref. 23 we also employed a different numerical technique using B -spline basis sets.³¹ With our newly developed code we recover the previous results²³ for static dipole and quadrupole polarizabilities. We found that unusually large basis sets of 100 B -splines were required to achieve a numerical convergence, especially for octupole polarizabilities of heavy atoms. Finally, we present a comparison of the

TABLE VIII. van der Waals C_8 coefficients in 10^5 a.u. for heteronuclear dimers. C_8^v values include only valence contributions.

| | Li–Na | Li–K | Li–Rb | Li–Cs | Na–K | Na–Rb | Na–Cs | K–Rb | K–Cs | Rb–Cs |
|-------------------------|-----------|---------|---------|----------|---------|---------|----------|---------|----------|----------|
| C_8^v | 0.982 | 1.91 | 2.26 | 3.07 | 2.18 | 2.56 | 3.43 | 4.64 | 6.13 | 7.04 |
| Final | 0.988(11) | 1.95(2) | 2.34(3) | 3.21(10) | 2.24(3) | 2.66(4) | 3.62(12) | 4.93(6) | 6.62(19) | 7.69(22) |
| Other theoretical works | | | | | | | | | | |
| Ref. 14 | 0.949 | 1.852 | 2.190 | 3.049 | 2.082 | 2.444 | 3.355 | 4.531 | 6.162 | 7.111 |
| Ref. 13 | 1.068 | 2.517 | 3.137 | 4.586 | 2.614 | 3.250 | 4.727 | 5.123 | 7.547 | 8.120 |
| Ref. 36 | 0.978 | 1.911 | | | 2.174 | | | | | |

TABLE IX. van der Waals C_{10} coefficients in 10^7 a.u. for heteronuclear dimers. C_{10}^v values include only valence contributions.

| | Li–Na | Li–K | Li–Rb | Li–Cs | Na–K | Na–Rb | Na–Cs | K–Rb | K–Cs | Rb–Cs |
|------------|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| C_{10}^v | 0.912 | 2.07 | 2.55 | 3.73 | 2.48 | 3.04 | 4.40 | 6.3 | 8.9 | 10.6 |
| Final | 0.916 | 2.10 | 2.61 | 3.84 | 2.53 | 3.13 | 4.55 | 6.6 | 9.4 | 11.3 |
| | Other theoretical works | | | | | | | | | |
| Ref. 14 | 0.8859 | 1.949 | 2.356 | 3.379 | 2.303 | 2.773 | 3.948 | 5.724 | 8.077 | 9.629 |
| Ref. 13 | 0.982 | 2.651 | 3.413 | 5.303 | 2.949 | 3.784 | 5.844 | 6.726 | 10.37 | 11.79 |
| Ref. 36 | 0.9058 | 2.139 | | | 2.553 | | | | | |

computed RRPAs static quadrupole and octupole core polarizabilities with other works in Tables IV and V. Patil^{32,33} has inferred these polarizabilities analyzing Rydberg spectra of alkalis. His results are in a uniform agreement with our *ab initio* values.

V. VAN DER WAALS COEFFICIENTS

From general formula (3) dispersion coefficients may be expressed as

$$C_6^{ab} = C_{ab}(1,1), \quad C_8^{ab} = C_{ab}(1,2) + C_{ab}(2,1),$$

$$C_{10}^{ab} = C_{ab}(2,2) + C_{ab}(1,3) + C_{ab}(3,1). \quad (11)$$

Here the coefficients $C_{ab}(l,l')$ are quadratures of atomic 2^l - and $2^{l'}$ -pole dynamic polarizabilities,

$$C_{ab}(1,1) = \frac{3}{\pi} \int_0^\infty \alpha_1^a(i\omega) \alpha_1^b(i\omega) d\omega, \quad (12)$$

$$C_{ab}(1,2) = \frac{15}{2\pi} \int_0^\infty \alpha_1^a(i\omega) \alpha_2^b(i\omega) d\omega, \quad (13)$$

$$C_{ab}(2,2) = \frac{35}{\pi} \int_0^\infty \alpha_2^a(i\omega) \alpha_2^b(i\omega) d\omega, \quad (14)$$

$$C_{ab}(1,3) = \frac{14}{\pi} \int_0^\infty \alpha_1^a(i\omega) \alpha_3^b(i\omega) d\omega. \quad (15)$$

Calculations of dynamic polarizabilities were discussed in the previous section and here we proceed to evaluation of the dispersion coefficients.

The computed C_8 and C_{10} coefficients for homonuclear and heteronuclear species are presented in Tables VI–IX. The dispersion coefficients C_6 were tabulated previously in Refs. 6 and 16. This completes the first application of relativistic many-body methods of atomic structure to calculations of leading long-range interactions between ground-state alkali-metal atoms.

To estimate uncertainties in our values we notice that the main value of the quadratures, Eqs. (12)–(15), is accumulated in the low-frequency region $\omega \approx 0$. Therefore the error may be expressed via uncertainties in the static multipole polarizabilities,

$$\frac{\delta C_{ab}(l,l')}{C_{ab}(l,l')} = \left\{ \left(\frac{\delta \alpha_l(0)}{\alpha_l(0)} \right)^2 + \left(\frac{\delta \alpha_{l'}(0)}{\alpha_{l'}(0)} \right)^2 \right\}^{1/2}.$$

The required uncertainties $\delta \alpha_l(0)$ were estimated in Sec. IV and Ref. 6. The error induced in C_8^{ab} is

$$\delta C_8^{ab} = \{ [\delta C_{ab}(1,2)]^2 + [\delta C_{ab}(2,1)]^2 \}^{1/2}.$$

Here we assumed that $a \neq b$. The formulas for homonuclear dimers may be derived in a similar manner. The resulting theoretical uncertainties for C_8 coefficients range from 0.5% for Li_2 to 4% for Cs dimer. We anticipate uncertainty in C_{10} coefficients to be better than 10%.

It is instructive to consider the effect of core excitation contribution $\alpha_l^c(i\omega)$ to dynamic polarizabilities and thus to C_n coefficients. Such corrections are omitted in the model potential calculations such as Ref. 13 and 14. To illuminate the relative contributions of core excitations we computed C_n coefficients by keeping only the valence contributions to the total dynamic polarizabilities,

$$\alpha_l(i\omega) \rightarrow \alpha_l^v(i\omega).$$

Such calculated dispersion coefficients are marked as C_8^v and C_{10}^v in Tables VI–IX, while values marked “final” were obtained with an additional inclusion of core excitations. Comparing these values, we observe that relative contribution of $\alpha_l^c(i\omega)$ term grows rapidly as the number of atomic electrons increases. For example, examining Table VI we see that core correction to C_8 for Li is only 0.2%, while for Cs it is 10%. For C_{10} coefficients the core contributions for all atoms are slightly smaller. Still for Cs core excitations contribute 8% to the C_{10} coefficient.

A comparison with results by other authors is presented in Tables VI–IX. There is good agreement for light Li and Na atoms. For heavier atoms, in particular for Cs, there is discrepancy at the level of 10% for C_8 and 20% for C_{10} coefficients. Such tendency may be attributed to two factors. First, correlations become enhanced for heavier atoms. Another cause is that model-potential calculations such as Refs. 13 and 14 disregard contribution of core-excited states. This corresponds to the valence term denoted as C_n^v in Tables VI–IX. As mentioned above the core-excited states contribute at the level of 10% for Cs. If we disregard this contribution, we see that the model-potential results are in a reasonable agreement with our C_n^v values.

Only recently interpretation of experiments with ultracold atoms allowed several groups to reduce uncertainties in the C_6 coefficients to a fraction of a percent.^{3–5} These inferred coefficients are in an excellent agreement with our values predicted using many-body perturbation theory.⁶ Even more refined understanding of details of ultracold collisions led very recently to constraints on higher-multipole coefficient C_8 for Rb_2 (Refs. 7 and 8) and Cs dimer.⁹ In Table VI we present a comparison with these inferred values. Our

computed value for Rb_2 5.77(8) agrees well with $C_8 = 5.79(49)$ by van Kempen *et al.*⁷ and $C_8 = 5.73$ by Marte *et al.*⁸ However, we disagree with 1%-accurate result⁷ of 6.09(7) by four standard deviations. This 1%-accurate result was obtained in Ref. 7 by setting additional constraints on the singlet potential of Rb dimer while including higher-multipole van der Waals coefficients C_{11} and C_{12} in the fit. For Cs_2 our value 10.2(4) is in reasonable agreement with the result of Amiot and Dulieu,³⁸ 9.63(19). The inferred value by Leo *et al.*⁹ is $C_8 = 8.4(4)$; it disagrees with our prediction by more than four standard deviations. It is worth noting that while for Rb the inferred value lies above our result, for Cs the situation is reversed and our value is larger.

To conclude, we calculated static and dynamic quadrupole and octupole polarizabilities for ground states of Li, Na, K, Rb, and Cs atoms. The calculations were carried out using accurate relativistic many-body methods of atomic structure. With the computed polarizabilities we evaluated C_8 and C_{10} van der Waals coefficients for homonuclear and heteronuclear dimers and estimated theoretical uncertainties. The estimated uncertainties for C_8 coefficients range from 0.5% for Li_2 to 4% for Cs_2 . We have highlighted the role of usually omitted core excitations in calculation of C_8 and C_{10} coefficients and found that their contribution is important for heavy atoms K, Rb, and Cs.

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