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

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Abstract

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 $C_{10}$. A 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$_2$.

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I. INTRODUCTION

We carry out accurate relativistic many-body atomic-structure calculations of van der Waals interactions \(^1\) between alkali-metal atoms in their respective ground states. These long-range interactions may be parameterized using dispersion (van der Waals) coefficients \(C_n\)

\[
V(R) \approx -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} + \cdots ,
\]

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 \textit{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 per cent \(^3, 4, 5\). 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 \(^7, 8\) and Cs \(^9\). This latest progress and discrepancies between previous determinations \(^10, 11, 12, 13, 14\) 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 heteronuclear Li, Na, K, Rb, and Cs dimers is presented in Tables VI–IX. The rest of the paper is organized as follows. In Section II we present the formalism. Numerical evaluation is discussed in Section III. A detailed analysis of underlying multipole dynamic and static polarizabilities is presented in Section IV. Finally, in Section V we compile dispersion coefficients and estimate theoretical uncertainties. Atomic units (\(|e|=m_e=\hbar=1\)) 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 as \(^1\)

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

where \(R\) is the distance between atoms. For ground-state atoms van der Waals coefficients are given by \(^15\)

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

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

\[ \alpha_l(i\omega) = 2 \text{Re} \sum_k \frac{\langle \Psi_0 | T_0^{(l)} | \Psi_k \rangle \langle \Psi_k | T_0^{(l)} | \Psi_0 \rangle}{(E_k - E_0) + i\omega}. \]  

(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.

Previously many-body calculations of dispersion coefficients \( C_6 \) were carried out in Refs. [6, 17], 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 \( \alpha_1 \), quadrupole \( \alpha_2 \), and octupole \( \alpha_3 \) dynamic polarizabilities. In this work we employ dynamic dipole polarizabilities calculated previously in Ref. [6] and determine higher-multipole polarizabilities \( \alpha_2 \) and \( \alpha_3 \).

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

\[ \alpha_l(i\omega) = \alpha^v_l(i\omega) + \alpha^c_l(i\omega) + \alpha^{cv}_l(i\omega), \]  

(6)

where \( \alpha^v_l(i\omega) \) is a traditional term encapsulating excitations of the valence electron. Contributions of electric-multipole excitations of core electrons are denoted by \( \alpha^c_l(i\omega) \). Finally, a small counter term \( \alpha^{cv}_l(i\omega) \) 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. [18] for more details). We will discuss calculations of the \( \alpha^v_l(i\omega) \) and \( \alpha^c_l(i\omega) \) terms later on. Here we just briefly comment on the counter term \( \alpha^{cv}_l(i\omega) \). For octupole polarizabilities \( \alpha^{cv}_3(i\omega) \) 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 \( \alpha^v_1 \) 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 has been employed to refine the dipole polarizabilities. In the following we focus on the quadrupole and octupole polarizabilities.

To find the quadrupole \( \alpha^v_2 \) and octupole \( \alpha^v_3 \) valence contributions we applied a relativistic many-body method initially suggested in Refs. [13, 20] and subsequently developed in [21, 22, 23, 24]. In this method one determines wave functions from solution of the effective many-body Shrödinger equation

\[ H_{\text{eff}}(E_n) | \Psi_n \rangle = E_n | \Psi_n \rangle, \]  

(7)
with the effective Hamiltonian defined as

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

Here $H_{\text{FC}}$ is the frozen-core Dirac-Hartree-Fock Hamiltonian and self-energy operator $\Sigma$ is the energy-dependent correction, involving core excitations. Qualitatively $\Sigma$ operator corresponds to core polarization term in model potentials employed in Refs. [13, 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 $H_{\text{eff}}$ may be extended to other operators. We introduce effective (or dressed) electric-multipole operators $T_{\text{eff}}^l$ acting in the model space of valence electrons. These operators were obtained within the relativistic random-phase approximation (RRPA) [21, 25, 26]. 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 wavefunctions are obtained from Eq. (7), the dynamic valence polarizabilities $\alpha_v^l(i\omega)$ are computed with the Sternheimer [27] or Dalgarno-Lewis [28] method implemented in the DHF+\Sigma+RRPA framework. (In the following we denote $\Sigma$+RRPA corrections as the many-body perturbation theory (MBPT) corrections.) Given ground-state wave-function $\Psi_0$ and energy $E_0$, we find an intermediate-state wave function $\Psi_f$ from an inhomogeneous equation

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

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

With such introduced $\Psi_f$ Eq. (4) becomes simply

$$\alpha_v^l(i\omega) = 2 \langle \Psi_0| (T_{\text{eff}}^l)|\Psi_f\rangle, \quad (10)$$

where subscript $v$ emphasized that only excitations of the valence electron to higher virtual orbitals are included in the intermediate-state wave function $\Psi_f$ due to a presence of $H_{\text{eff}}$ in Eq. (9). As to additional contribution $\alpha_c^l$ of core-excited states, we employ the relativistic random-phase approximation method described in Refs. [25, 26].

### 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 [29]. The virtual orbitals were determined with the help of a recurrent procedure [30]. One-electron basis sets of the following sizes were used on the stage DHF+\Sigma calculations:

- Li: $1 - 17s, 2 - 17p, 3 - 16d, 4 - 16f, 5 - 10g$;
- Na: $1 - 18s, 2 - 18p, 3 - 17d, 4 - 17f, 5 - 11g$;
- K: $1 - 19s, 2 - 19p, 3 - 18d, 4 - 19f, 5 - 12g$;
TABLE I: Comparison of DHF and many-body one-electron removal energies $E_{\text{val}}$ for Cs with experimental values. $E_{\text{val}}$ are given in atomic units. $\Delta$ 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 | Experiment $^{[33]}$ |
|---------|-----|----------|---------------------|
| $6s_{1/2}$ | 0.127368 | 0.143085 | 0.143099$^{a}$ |
| $6p_{1/2}$ | 0.085616 | 0.092173 | 0.092167 |
| $6p_{3/2}$ | 0.083785 | 0.089609 | 0.089642 |
| $5d_{3/2}$ | 0.064419 | 0.076995 | 0.077035 |
| $5d_{5/2}$ | 0.064529 | 0.076459 | 0.076590 |
| $7s_{1/2}$ | 0.055187 | 0.058475 | 0.058645 |
| $7p_{1/2}$ | 0.042021 | 0.043868 | 0.043928 |
| $7p_{3/2}$ | 0.041368 | 0.043041 | 0.043103 |

$^{a}$For the ground state $E_{\text{val}} = \text{IP (Cs)} = 31406.71$ cm$^{-1}$$^{[33]}$.

Rb : 1 – 20s, 2 – 20p, 3 – 19d, 4 – 19f, 5 – 13g;
Cs : 1 – 23s, 2 – 23p, 3 – 23d, 4 – 26f, 5 – 14g.

Using these basis sets we solved the multi-particle Shr"odinger equation $^7$ and found the wave functions of low-lying states. As discussed in $^{[31]}$ and demonstrated in $^{[30, 32]}$ 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 $\delta$ and replace $\Sigma(E) \rightarrow \Sigma(E - \delta)$ in the effective Hamiltonian, Eq. $^8$. We have determined $\delta$ from a fit of theoretical energy levels to experimental spectrum. Using only one fitting parameter $\delta$ 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 $\delta$ 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 $\delta$ 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 Section $^1$ we determined ground state wave functions from the effective many-body Shr"odinger equation $^7$, calculated dressed electric multipole operators $T_{\text{eff}}$, solved inhomogeneous equation $^9$ and computed valence parts $\alpha_v^l$ of dynamic polarizability with Eq. $^{10}$. Additional contributions $\alpha_c^l$ of core-exited states were calculated using RRPA method.

Calculation of dynamic polarizabilities with $\omega = 0$ gives us the static polarizabilities. We provide these data in Tables $^1$ and $^{II}$ 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
TABLE II: Static quadrupole polarizabilities $\alpha_2$ 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 $\alpha_2^v$ (DHF+MBPT) and $\alpha_2^c$.

|         | Li     | Na    | K     | Rb    | Cs     |
|---------|--------|-------|-------|-------|--------|
| $\alpha_2^v$ (DHF) | 1485.5 | 2230.3| 7049  | 9790  | 16613  |
| $\alpha_2^v$ (DHF+MBPT) | 1424.5 | 1883.6| 4983  | 6488  | 10388  |
| $\alpha_2^c$ (RRPA) | 0.1    | 1.5   | 16    | 35    | 86     |
| Final   | 1424(4)| 1885(26)| 5000(45)| 6520(80)| 10470(390) |

Other works

Patil and Tang [35] | 1393 | 1796 | 4703 | 6068 | 10260 |
Patil and Tang [14] | 1403 | 1807 | 4760 | 6163 | 10400 |
Yan et al. [34] | 1423.266(5) |
Marinescu et al. [13] | 1424 | 1878 | 5000 | 6495 | 10462 |
Spelsberg et al. [36] | 1423 | 1879 | 5001 | —    | —     |
Maeder and Kutzelnigg [10] | 1383 | 1799 | 4597 | 5979 | 9478 |

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 $\alpha_2^v$ for Li is only 4%, while for Cs it attains 38%. For static octupole polarizabilities $\alpha_3^v$, 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 $\delta$. As mentioned in Section 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 $\delta$. Further an overwhelming contribution to static $2l$-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

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

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) from benchmark high-accuracy variational non-relativistic calculations by Yan et al. [34]. 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 Kutzelnigg [10] 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
TABLE III: Static octupole polarizabilities $\alpha_3$ 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 $\alpha^v_3$ (DHF+MBPT) and $\alpha^c_3$.

|           | Li    | Na    | K     | Rb    | Cs     |
|-----------|-------|-------|-------|-------|--------|
| $\alpha^v_3$ (DHF) | 4.185 | 6.888 | 28.10 | 41.50 | 76.49  |
| $\alpha^v_3$ (DHF+MBPT) | 3.957 | 5.536 | 17.73 | 23.66 | 39.43  |
| $\alpha^c_3$ (RRPA) | 0.000 | 0.001 | 0.01  | 0.03  | 0.10   |
| Final     | 3.957 | 5.54  | 17.7  | 23.7  | 39.5   |

Other works

| Patil and Tang [35] | 3.871 | 5.287 | 16.07 | 20.73 | 33.12  |
| Patil and Tang [14] | 3.986 | 5.430 | 16.30 | 20.97 | 33.33  |
| Yan et al. [34]    | 3.965049(8) |
| Marinescu et al. [13] | 3.969 | 5.552 | 17.69 | 23.69 | 39.53  |
| Spelsberg et al. [36] | 3.927 | 5.486 | 19.14 |
| Maeder and Kutzelnigg [10] | 3.680 | 5.117 | 15.02 | 21.27 | 33.99  |

pseudo-potential and they also included effects of shielding (or field dressing) in the multipole operators. Patil and Tang [14] also used effective potential in their calculations to obtain the wave functions of excited states, but they used one-parametric potential and did not shielding in the multipole operators. Generally, our results are in a good agreement with all results except for values by Maeder and Kutzelnigg [10]. One of possible reasons for this discrepancy is that these authors used very small number of basis functions (e.g. only 5 basis orbitals for $p$, $d$, and $f$ partial waves) while $\alpha_2$ and $\alpha_3$ polarizabilities are very sensitive to details of construction and saturation of basis sets.

Also shown in Tables II and III are the corrections $\alpha^c_l$ due to core-excited states. These quantities are essentially polarizabilities of singly-charged ions of alkali-metal atoms. Only disregarding distortion of the core by the valence electrons, one may identify corrections $\alpha^c_l$ 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 $\alpha^c_l$ 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 $\omega$. 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 paper [6] 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 $\alpha^c_l(i\omega)$ 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. [26] and incorporated frequency dependence into the calculations. Compared to Ref. [26] we also employed a different numerical technique using B-spline basis sets. With our newly developed code we recover the previous results [26] for static dipole and quadrupole polarizabilities. We found that unusually large basis sets of 100 B-splines were required to achieve a numerical
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. [26]. All values are in atomic units.

|         | Li$^+$ | Na$^+$ | K$^+$   | Rb$^+$ | Cs$^+$ |
|---------|--------|--------|---------|--------|--------|
| RRPA    | 0.11   | 1.52   | 16.3    | 35.4   | 86.4   |
| Patil [37, 38] | 1.64(15) | 18.2(3.0) | 42(3) | 128(40) |
| Freeman and Kleppner [39] | 1.91(15) |

TABLE V: Static octupole polarizabilities $\alpha_3^c(0)$ 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 [37] | 95(10) | 280(40) | 1220(200) |        |

convergence, especially for octupole polarizabilities of heavy atoms. Finally, we present a comparison of the computed RRPA static quadrupole and octupole core polarizabilities with other works in Tables IV and V. Patil [37, 38] 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

$$C_{6}^{ab} = C_{ab}(1, 1),$$

$$C_{8}^{ab} = C_{ab}(1, 2) + C_{ab}(2, 1),$$

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

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

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

$$C_{ab}(1, 2) = \frac{15}{2\pi} \int_0^\infty \alpha_a^a(i\omega)\alpha_b^b(i\omega)d\omega,$$

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

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

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, 17]. 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 Section IV and Ref. [6]. The error induced in $C_{ab}$ is

$$\delta C_{ab} = \left\{ (\delta C_{ab}(1, 2))^2 + (\delta C_{ab}(2, 1))^2 \right\}^{1/2}.$$ 

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 $\alpha_c(i\omega)$ to dynamic polarizabilities and thus to $C_n$ coefficients. Such corrections are omitted in the model potential calculations such as Ref. [13, 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

$$\alpha_l(i\omega) \rightarrow \alpha_v^l(i\omega).$$

Such calculated dispersion coefficients are marked as $C_v^8$ and $C_v^{10}$ 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 $\alpha_c^l(i\omega)$ 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 Ref. [13, 14] disregard contribution of core-excited states. This corresponds to the valence term denoted as $C_v^n$ 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 $C_v^n$ values.

Only very 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, 4, 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$_2$ [7, 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
TABLE VI: van der Waals $C_8$ coefficients in $10^5$ a.u. for homonuclear dimers. $C_8$ 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   |
|--------|------|------|------|------|------|
| $C_8^v$ |      |      |      |      |      |
| Final  | 0.832| 1.15 | 4.00 | 5.37 | 9.16 |
| Patil and Tang [14] | 0.8183 | 1.090 | 3.892 | 5.258 | 9.546 |
| Yan et al. [34] | 0.834258(4) |      |      |      |      |
| Marinescu et al. [13] | 0.8324 | 1.119 | 4.096 | 5.506 | 9.630 |
| Spelsberg et al. [36] | 0.8303 | 1.141 | 4.011 |      |      |
| Maeder and Kutzelnigg [10] | 0.8089 | 1.098 | 3.834 | 5.244 | 9.025 |
| Other theoretical works |      |      |      |      |      |
| Experiment |      |      |      |      |      |
| van Kempen et al. [7] | 5.79(49) |      |      |      |      |
| Marte et al. [8] |      | 5.73 |      |      |      |
| Leo et al. [9] |      |      |      | 8.4(4) |      |

$C_8 = 5.73$ by Marte et al. [8]. However, we disagree with 1%-accurate result [7] 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$_2$ the inferred value by Leo et al. [9] is $C_8 = 8.4(4)$, it disagrees with our prediction, 10.2(4) 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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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 |
| Patil and Tang [14] | 0.7289 | 1.068 | 4.789 | 6.833 | 13.58 |
| Yan et al. [34] | 0.7372(1) | | | | |
| Marinescu et al. [13] | 0.7365 | 1.107 | 5.248 | 7.665 | 15.20 |
| Spelsberg et al. [36] | 0.7306 | 1.113 | 5.431 | | |
| Maeder and Kutzelnigg [10] | 0.6901 | 1.036 | 4.522 | 6.836 | 13.01 |

Other works

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) |
| Patil and Tang [14] | 0.949 | 1.852 | 2.190 | 3.049 | 2.082 | 2.444 | 3.355 | 4.531 | 6.162 | 7.111 |
| Yan et al. [34] | 1.068 | 2.517 | 3.137 | 4.586 | 2.614 | 3.250 | 4.727 | 5.123 | 7.547 | 8.120 |
| Spelsberg et al. [36] | 0.978 | 1.911 | 2.174 | | | | | | | |

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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  |
| Patil and Tang [14] | 0.8859 | 1.949 | 2.356 | 3.379 | 2.303 | 2.773 | 3.948 | 5.724 | 8.077 | 9.629 |
| Yan et al. [34] | 0.982 | 2.651 | 3.413 | 5.303 | 2.949 | 3.784 | 5.844 | 6.726 | 10.37 | 11.79 |
| Maeder and Kutzelnigg [10] | 0.9058 | 2.139 | 2.553 | | | | | | | |
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