Dispersion coefficients for alkali-metal dimers

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(Received 23 August 1993)

Knowledge of the long-range interaction between atoms and molecules is of fundamental importance for low-energy and low-temperature collisions. The electronic interaction between the charge distributions of two ground-state alkali-metal atoms can be expanded in inverse powers of \( R \), the internuclear distance. The coefficients \( C_6, C_8, \) and \( C_{10} \) of, respectively, the \( R^{-6}, R^{-8}, \) and \( R^{-10} \) terms are calculated by integrating the products of the dynamic electric multipoles polarizabilities of the individual atoms at imaginary frequencies, which are in turn obtained by solving two coupled inhomogeneous differential equations. Precise one-electron model potentials are developed to represent the motion of the valence electron in the field of the closed alkali-metal positive-ion core. The numerical results for the static multipole polarizabilities for the alkali-metal atoms and the coefficients \( C_6, C_8, \) and \( C_{10} \) for homonuclear and heteronuclear alkali-metal diatoms are compared with other calculations.

PACS number(s): 34.20.\,-b, 34.40.+n, 82.20.Kh

I. INTRODUCTION

Advances in laser cooling and trapping technology have rekindled interest in the knowledge of the long-range forces between atoms and molecules. Confinement of alkali-metal atoms at sub-Kelvin temperatures depends on their determination of the asymptotic long-range properties [1–3]. At large separations, the atomic charge distributions hardly overlap and the internuclear potential \( V_{ab}(R) \) between two atoms \( a \) and \( b \) can be represented as a sum of electronic potentials. This interaction between the charge distributions of two atoms or molecules can be expanded in a power of \( R^{-1} \), where \( R \) is the separation distance between the charge centers. Each term in this series corresponds to a particular multipole moment of the charge-charge interaction [4–9].

In this work, we concentrate on the multipole moments which arise in the second order of perturbation expansion, and determine the coefficients for the dipole-dipole interaction \( C_6 \), the dipole-quadrupole interaction \( C_8 \), and the dipole-octupole and quadrupole-quadrupole interaction \( C_{10} \) in the expansion

\[
V_{ab}(R) = C_6 \frac{C_8}{R^6} \frac{C_{10}}{R^8} \ldots \quad (1)
\]

The calculation of the long-range interactions between atoms can be reduced to the evaluation of electric dynamic multipole polarizabilities at imaginary frequencies [10–12]. Many theoretical studies have been reported using a variety of methods on the evaluation of the multipole polarizabilities of the alkali-metal atoms [13–26], and it has been demonstrated that model potential methods are capable of achieving high accuracy [18].

In this paper we present a method for computing dynamic multipole polarizabilities at imaginary frequencies that is exact given the assumption of a model potential for the motion of a valence electron in the presence of a frozen core. The infinite second-order sums are transformed into integrals over the solutions of two coupled inhomogeneous differential equations. Section II contains a brief derivation of the expression for the multipole coefficients and a detailed discussion of the numerical procedure for solving the coupled inhomogeneous equations. The numerical results including values for the electric multipole polarizabilities, and the dispersion coefficients for the homonuclear and heteronuclear cases, are presented in Sec. III, followed by a discussion. A detailed comparison with other theoretical values is included.

II. FORMULATION OF THE PROBLEM

A. Theory

The coefficients of expansion in Eq. (1) are conveniently represented in the compact form [12]

\[
C_{2n+2} = -\frac{1}{2\pi} \sum_{k=1}^{n} \left[ \sum_{j=\text{min}(k,n)}^{n} \left[ \frac{n}{k+j} \right] \left[ \frac{n}{k-j} \right] \right] \int_{0}^{\infty} \alpha_{(n-k)}(i\omega)\alpha_{k}(i\omega) d\omega \quad \text{for } n \geq 2 \quad (2)
\]

where \( \alpha_{l}(i\omega) \) are the dynamic \( 2l \) polarizabilities at imaginary frequencies:

\[
\alpha_{l}(i\omega) = \frac{4\pi}{2l+1} \sum_{s} \left| \langle 0|\gamma_{l}^{(s)}|s \rangle \right|^2 \sum_{s} \frac{\left| \langle 0|\gamma_{l}^{(s)}|s \rangle \right|^2}{E_{s}-E_{0}+i\omega} + \sum_{s} \frac{\left| \langle 0|\gamma_{l}^{(s)}|s \rangle \right|^2}{E_{s}-E_{0}-\omega} \quad (3)
\]

The initial state is represented by the eigenstate \( |0 \rangle \) and eigenenergy \( E_0 \). The sum in Eq. (3) is over all possible discrete and continuum states. \( \gamma_{l}^{(s)} \) represents a tensor of rank \( l \) and zero magnetic quantum number. Its alternative definition is \( \gamma_{l}^{(s)} = r_{l}^{(s)} Y_{lm}(\hat{r}) \), where \( Y_{lm} \) are the usual spherical harmonics.

The sums in Eq. (3) can be evaluated exactly by trans-
forming into a differential equation form as
\[ \alpha_l(i\omega) = \frac{8\pi}{2l+1} \text{Re}\langle 0| r^{(l+1)}(E_0 - i\omega) r^{(l)}|0 \rangle, \]
(4)
where \( G(E_0 - i\omega) \) is the Green's function evaluated at complex energies, and \( \text{Re} \) represents the real part of the matrix element. Upon carrying out the angular integration of the matrix element we obtain
\[ \alpha_l(i\omega) = \frac{2}{2l+1} \text{Re} \int_0^\infty R_0(r) \mathcal{F}_l(E_0 - i\omega; r) r^{l+1} dr, \]
(5)
where
\[ \mathcal{F}_l(E_0 - i\omega; r) = \frac{1}{r} \int_0^\infty g_1(E_0 - i\omega; r, r') R_0(r') r'^{l+1} dr', \]
(6)
and \( R_0 \) is the radial wave function for the ground state and \( g_1 \) is the radial Green's function for the multipole order of \( l \). Equation (6) can be written as an inhomogeneous differential equation [27]
\[ \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] \chi_l^{(R)}(r) + 2[E_0 - i\omega - V_l(r)] \chi_l^{(D)}(r) = 2r R_0(r), \]
(7)
where the central field potential \( V_l(r) \) is in general an \( l \)-dependent function of the radial coordinate. The boundary conditions on the solution of Eq. (7) can be extracted from the integral expression for \( \mathcal{F}_l \) in Eq. (6). In the small-\( r \) region \( \mathcal{F}_l \to \text{const} \) and for the large-\( r \) region \( \mathcal{F}_l \to 0 \). Because the energy in Eq. (7) is complex, solutions of Eq. (7) take on the complex form
\[ \mathcal{F}_l = \frac{1}{r} \left( \chi_l^{(R)} - i \chi_l^{(D)} \right). \]
(8)
Substituting Eq. (8) into Eq. (7), we find the following coupled system of second-order inhomogeneous differential equations:
\[ \begin{align*}
\frac{d^2}{dr^2} &+ \frac{l(l+1)}{r^2} + 2[E_0 - V_l(r)] \chi_l^{(R)}(r) \\
-2\omega \chi_l^{(D)}(r) &= 2r R_0(r), \tag{9}
\end{align*} \]
From Eq. (8), it can be seen that \( \chi_l^{(R)} \) should satisfy the same boundary conditions as for \( \mathcal{F}_l \). Upon determining the solutions of Eqs. (9), the evaluation of the multipole polarizability reduces to a one-dimensional integral:
\[ \alpha_l(i\omega) = \frac{2}{2l+1} \int_0^\infty R_0(r) \chi_l^{(R)}(r) r^{l+1} dr. \]
(10)

The multipole expansion coefficients are obtained from Eq. (2) by substituting for the polarizabilities from Eq. (10) and performing the integration over \( \omega \). At \( \omega = 0 \), the system of differential equations in (9) becomes decoupled and the imaginary part of \( \mathcal{F}_l \) becomes identically zero as the second differential equation does not possess a solution for \( l \neq 0 \) at energy \( E_0 \).

B. Numerical method for solving coupled inhomogeneous differential equations

We opted to use the Numerov method to solve the set of coupled inhomogeneous equations
\[ \frac{d^2}{dr^2} y = F y + g, \]
(11)
where \( y \) is the solution vector and \( g \) contains the inhomogeneity. For the problem at hand, \( y, F, \) and \( g \) have the following explicit expressions:
\[ \begin{bmatrix}
\chi_l^{(R)}(r) \\
\chi_l^{(D)}(r)
\end{bmatrix}
\begin{bmatrix}
2r R_0(r) \\
0
\end{bmatrix},
\]
\[ F(r) = \begin{bmatrix}
\frac{l(l+1)}{r^2} -2[E_0 - V_l(r)] & 2\omega \\
-2\omega & \frac{l(l+1)}{r^2} -2[E_0 - V_l(r)]
\end{bmatrix}, \]
(12)
where \( h \) is the step size and \( F_m, g_m, \) and \( y_m \) are the functional values of the matrix \( F \) and vectors \( g \) and \( y \), evaluated at the \( m \)th point on the radial scale. Equation (13) can be rewritten as a tridiagonal system of linear inhomogeneous equations where all the coefficients are matrices. Upon applying the boundary conditions on \( y \), the solutions at the \( k \)th radial point, \( y_k \), are obtained.

Due to the chaotic sensitivity of the inhomogeneous solutions to the initial conditions (i.e., near the origin), special care must be taken to ensure that the numerical
solutions are stable. This task is made more difficult by the singular nature of the potentials arising in atomic
physics. We therefore exercise care in choosing the grid
scheme for numerical integration. The commonly used
square root and arctangent mesh schemes, though quite
useful for solving homogeneous equations, do not provide
sufficient grid-point density near the origin for the solu-
tion of inhomogeneous equations. We chose the loga-

\begin{align}
\mathcal{Y}(x) & \equiv \begin{pmatrix} \chi_1^{(R)}(x) \\ \chi_1^{(I)}(x) \end{pmatrix}, \quad \mathcal{G}(x) \equiv \begin{pmatrix} 2e^{il+1/2+ix}R_0(e^{ix}) \\ 0 \end{pmatrix}, \\
\mathcal{F}(x) & \equiv \begin{pmatrix} (l+1)^2 - 2e^{2ix}[E_0 - V(e^{ix})] \\ 2e^{2ix} \omega \\ -2e^{2ix} \omega \\ (l+1)^2 - 2e^{2ix}[E_0 - V(e^{ix})] \end{pmatrix}
\end{align}

such that the relation between \( y(r) \) and \( \mathcal{Y}(x) \) is

\[ y(r) = \exp(x/2)\mathcal{Y}(x). \] (16)

The accuracy of the numerical scheme was tested for
the following case. Let \( V(r) = -1/r \) in Eqs. (9). \( E_0 \)
and \( R_0(r) \) are then the ground-state energy and wave
function for the hydrogen atom. Defining \( u_0 = \pi R_0 \) and \( u_1 \) as
the reduced wave functions for the 1s and 2p states of hydro-
gen, we premultiply Eqs. (9) once by \( u_0 \) and again by \( u_1 \)
and integrate over \( r \) to obtain the following four identi-
ties:

\begin{align}
\int_0^\infty u_0(r)\chi_1^{(R)}(r)dr + \omega \int_0^\infty u_0(r)\chi_1^{(I)}(r)dr & = 0, \\
\int_0^\infty u_0(r)\chi_1^{(I)}(r)dr & = 0, \\
(E_1 - E_0) \int_0^\infty u_1(r)\chi_1^{(R)}(r)dr & = \omega \int_0^\infty u_1(r)\chi_1^{(I)}(r)dr + \int_0^\infty u_1(r)u_0(r)rdr = 0, \\
(E_1 - E_0) \int_0^\infty u_1(r)\chi_1^{(I)}(r)dr & = 0.
\end{align}

Although \( u_0 \) and \( u_1 \) are known analytically, in order
to test our numerical efficiency we continue to compute \( E_0, \)
\( E_1, u_0, \) and \( u_1. \) We find that these identify are satisfied
to within one part in 10^9. A more stringent test is how-
ever provided by the static dipole, quadrupole, and octu-
pole polarizabilities arising in hydrogen-hydrogen in-
teraction, for which analytic results are available. Our
numerical values for the multipole polarizabilities of hy-
drogen \( \alpha_1 = 4.500, \alpha_2 = 15.000, \) and \( \alpha_3 = 131.250 \)
agree with the analytical results of Chan and Dalgarno [29].
The corresponding values for the dispersion coefficients \( C_6, C_8, \)
and \( C_{10} \) in hydrogen are 6.499, 124.399, and 3285.833, in
agreement with Chan and Dalgarno who give 6.499, 124.400,
and 3285.500 [29].

C. Parametric model potential

To describe the motion of the valence electron for
the alkali-metal atoms we developed a model potential
along the lines of Laughlin and Victor [30] and Greene and
Aymar [31]. These potentials which are parametrically
fitted to one-electron energy levels have been successful in
predicting many observed phenomena such as the two-
electron resonances in the spectra of alkali-metal cations
[31] and alkaline-earth atoms [32].

The form of this potential which can depend also on
the orbital angular momentum of the valence electron, \( l, \)
is

\begin{align}
V_l(r) = & -\frac{Z_l(r)}{r} - \frac{\alpha_c}{2r^2}\left[1 - e^{-r/r_c}\right], \\
Z_l(r) = 1 + (z - 1)e^{-a_1r} - r(a_3 + a_4r)e^{-a_2r},
\end{align}

(18a, b)

where \( z \) is the nuclear charge of the neutral atom and \( r_c \)
is the cutoff radius introduced to truncate the unphysical
short-range contribution of the polarization potential
near the origin. The potential in (18) is \( l \) dependent, but
this does not introduce any practical difficulties.

The five-parameter nonlinear fit of Eqs. (18), with \( \alpha_c \)
kept fixed, to the alkali-metal-atom Rydberg energies
were carried out. The optimized parameters in (18) are
listed in Table I. For each value of angular momentum \( l, \)
TABLE I. Optimized parameters for the l-dependent model potential.

<table>
<thead>
<tr>
<th>l</th>
<th>α</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>α_1</td>
<td>2.47718079</td>
<td>4.82223117</td>
<td>3.56079437</td>
<td>3.69628474</td>
<td>3.49546309</td>
</tr>
<tr>
<td></td>
<td>α_2</td>
<td>1.84150932</td>
<td>2.45449865</td>
<td>1.83909682</td>
<td>1.64915255</td>
<td>1.47533800</td>
</tr>
<tr>
<td></td>
<td>α_3</td>
<td>-0.02169712</td>
<td>-1.12255048</td>
<td>-1.74701102</td>
<td>-9.86069196</td>
<td>-9.72143084</td>
</tr>
<tr>
<td></td>
<td>α_4</td>
<td>-0.11983362</td>
<td>-1.42633133</td>
<td>-1.03273713</td>
<td>0.19579987</td>
<td>0.02629242</td>
</tr>
<tr>
<td></td>
<td>r_0</td>
<td>0.61340824</td>
<td>0.45489422</td>
<td>0.83167545</td>
<td>1.66242117</td>
<td>1.92046930</td>
</tr>
<tr>
<td>1</td>
<td>α_1</td>
<td>3.45414648</td>
<td>5.08382502</td>
<td>3.65670429</td>
<td>4.44088978</td>
<td>4.69366096</td>
</tr>
<tr>
<td></td>
<td>α_2</td>
<td>2.55151050</td>
<td>2.18226881</td>
<td>1.67520788</td>
<td>1.92828831</td>
<td>1.71398344</td>
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<tr>
<td></td>
<td>α_3</td>
<td>-0.21646561</td>
<td>-1.19534623</td>
<td>-2.07416615</td>
<td>-16.79579770</td>
<td>-24.65624280</td>
</tr>
<tr>
<td></td>
<td>α_4</td>
<td>-0.06990078</td>
<td>-1.03142811</td>
<td>-0.89030412</td>
<td>-0.81633314</td>
<td>-0.09545125</td>
</tr>
<tr>
<td></td>
<td>r_0</td>
<td>0.61566441</td>
<td>0.45798739</td>
<td>0.85233581</td>
<td>1.50195124</td>
<td>2.13383095</td>
</tr>
<tr>
<td>2</td>
<td>α_1</td>
<td>2.51909839</td>
<td>3.53324121</td>
<td>4.12713694</td>
<td>3.78717363</td>
<td>4.32466196</td>
</tr>
<tr>
<td></td>
<td>α_2</td>
<td>2.43712450</td>
<td>2.48697936</td>
<td>1.79837462</td>
<td>1.57027864</td>
<td>1.61365288</td>
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<tr>
<td></td>
<td>α_3</td>
<td>0.32505524</td>
<td>-0.75688448</td>
<td>-1.69935174</td>
<td>-11.65588970</td>
<td>-6.70128850</td>
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<tr>
<td></td>
<td>α_4</td>
<td>0.10602430</td>
<td>-1.27852357</td>
<td>-0.98913582</td>
<td>0.52942835</td>
<td>0.74095193</td>
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<tr>
<td></td>
<td>r_0</td>
<td>2.34126273</td>
<td>0.71875312</td>
<td>0.83216907</td>
<td>4.86851938</td>
<td>0.93007296</td>
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<td>≥ 3</td>
<td>α_1</td>
<td>2.51909839</td>
<td>1.11056646</td>
<td>1.42310446</td>
<td>2.39848933</td>
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<td></td>
<td>α_2</td>
<td>2.43712450</td>
<td>1.05458759</td>
<td>1.27861156</td>
<td>1.76810544</td>
<td>1.40000001</td>
</tr>
<tr>
<td></td>
<td>α_3</td>
<td>0.32505524</td>
<td>1.73203428</td>
<td>4.77441476</td>
<td>-12.07106780</td>
<td>-3.20036138</td>
</tr>
<tr>
<td></td>
<td>α_4</td>
<td>0.10602430</td>
<td>-0.09265696</td>
<td>-0.94829262</td>
<td>0.77256589</td>
<td>0.00034538</td>
</tr>
<tr>
<td></td>
<td>r_0</td>
<td>2.34126273</td>
<td>28.6730595</td>
<td>6.50294371</td>
<td>4.79831327</td>
<td>1.99969677</td>
</tr>
</tbody>
</table>

D. Core polarizability

If the motion of the outer valence electron in the presence of the core is taken, in the spirit of Born-Oppenheimer approximation, to be adiabatic, then it can be shown [33] that the core perturbation due to the external electric field of the valence electron manifests itself in a correction to the multipole operator \( \bar{Q} \) as

\[
\bar{Q} \rightarrow \bar{Q} \left[ 1 - \frac{\alpha_{c}^{(n)}}{r_{0}^{2n+1}} \right] e^{-\left(\frac{r_{0}^{2n+1}}{r^{2n+1}}\right)},
\]

where \( \alpha_{c}^{(n)} \) is the core tensor polarizability and \( r_{0}^{2n} \) is a cutoff radius to be determined empirically. We have chosen it so that the corrected values of the neutral alkali-metal static dipole polarizabilities are in agreement with the experimental data [34]. The numerical values of \( r_{0}^{2n} \) are, respectively, 2.3542392, 0.3798660, 4.4395871, 4.3397730, and 4.9164157 for Li, Na, K, Rb, and Cs, producing substantial corrections to the electric dipole moments.

III. DISCUSSION OF RESULTS

The dipole polarizabilities calculated with and without the core polarization correction are listed in Table II. By construction, the corrected values are in agreement

TABLE II. Dipole polarizabilities \( \alpha_{c}(a_{0}^{2}) \).

<table>
<thead>
<tr>
<th>Source</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
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<tbody>
<tr>
<td>[13]</td>
<td>170.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>[18]</td>
<td>164.3</td>
<td>162.6</td>
<td>298.0</td>
<td>333.0</td>
<td>416.5</td>
</tr>
<tr>
<td>[21]</td>
<td>163.7</td>
<td>162.4</td>
<td>287.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[22]</td>
<td>165.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[24]</td>
<td>164.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[25]</td>
<td></td>
<td></td>
<td></td>
<td>343.3</td>
<td>440.6</td>
</tr>
<tr>
<td>[35]</td>
<td></td>
<td></td>
<td>295.6</td>
<td>334.0</td>
<td>413.7</td>
</tr>
<tr>
<td>[38]</td>
<td>165.0</td>
<td>151.0</td>
<td>292.0</td>
<td>328.0</td>
<td>405</td>
</tr>
<tr>
<td>experiment</td>
<td>164.0±3.4</td>
<td>159.2±3.4</td>
<td>292.8±6.1</td>
<td>319.2±6.1</td>
<td>402.2±8.1</td>
</tr>
<tr>
<td>a</td>
<td>164.9</td>
<td>165.8</td>
<td>306.8</td>
<td>344.2</td>
<td>443.6</td>
</tr>
<tr>
<td>b</td>
<td>164.0</td>
<td>159.2</td>
<td>292.8</td>
<td>319.2</td>
<td>402.2</td>
</tr>
</tbody>
</table>

*Present results without the core-polarization effect on the dipole operator.

**Present results with the core-polarization cutoff radius chosen to reproduce the experimental polarizabilities.
The correction is very small for Li, but amounts to 10% for Cs. The increasing magnitude of the correction as the core size grows has been noted previously [20, 21]. The experimental value of 164.0±3.4 [34] for Li has been reproduced by accurate many-electron calculations. The theoretical value of 164.1a_0^2 of Pipin and Bishop [24] is probably the most precise result. We include in Table II the values of Maeder and Kutzelnigg [18] and the calculations of Muller, Flesch, and Mayer [21] and Kello, Sadlej, and Faegri [35]. The close agreement suggests that the empirical correction procedure we have adopted adequately reflects the contribution from the core-electron transitions and should lead to reliable values of the van der Waals coefficients.

The quadrupole and octupole polarizabilities are given in Tables III and IV. For these the core corrections are small and may be neglected. There are no experimental data. For Li the most accurate value of the quadrupole polarizability is due to Pipin and Bishop [24] who, using correlated products of Hartree-type basis functions, obtained a value of 142a_0^2 in perfect agreement with our value of 142a_0^2. For the heavier alkali-metal atoms, the only useful comparison data are the results of Maeder and Kutzelnigg [18]. The values reported by Adelman and Szabo [36] are based on the method of Dalgarano and Pengelly [37], which is less accurate than the present procedure. Our values are considerably larger than those of Maeder and Kutzelnigg [18]. For Li, their value is certainly too small and we suspect it is a characteristic of their method.

A similar behavior occurs for octupole polarizabilities given in Table IV. Our values are again consistently larger than those of Maeder and Kutzelnigg [18]. For Li, there are useful comparison values of α_3 from Knowles and Meath [22], who used an R-dependent ab initio nonexpanded method for the calculation of dispersion energies. We have quoted the values from the basis-III column of their Table III. Their procedure overestimates α_3 and may also do so for α_3.

The coefficients C_6, C_8, and C_10 of the R^{-6}, R^{-8}, and R^{-10} terms in the long-range interaction between two Li atoms are presented in Table V, which also includes a selection of previous results. The agreement amongst the different values of C_6 is close except for value of Knowles and Meath [22], which is too large. Our value of 1388 a.u. lies very near to the value of 1391 a.u. obtained in the most refined ab initio many-electron calculation [13]. The self-consistent-field polarization potential method of [21] gives a value of 1386 a.u. For C_8 and C_10, our values lie between those of [22] which are likely to be overestimates and those of [18] and [38], which are likely to be underestimates, as suggested for [18] and [22] by the discussion of polarizabilities and for [38] by the low value of C_6. The large discrepancies with the results of Bussery and Aubert-Frecon [39] are unexpected.

Table VI is a compilation of values of C_6, C_8, and C_10 for the homonuclear cases Na-Na, K-K, Rb-Rb, and Cs-Cs. Our results for C_6 are consistently lower than those in [18] and are consistently larger for C_8 and C_10. Part of the difference can be attributed to the inclusion of the core-polarization potential and its contraction effect on the electric dipole operator. We have no explanation, however, for the occasional large differences with the results of Bussery and Aubert-Frecon [39]. With one exception, our results are consistent with the upper and lower bounds of Tang, Norbeck, and Certain [40] which however do not place rigorous bounds on the values.

None of the calculated values takes explicit account of contributions from core excitations. An uncertain cancellation of errors occurs in attempts to include core contributions [5], and it is probably more accurate to ignore

### Table III. Quadrupole polarizabilities α_2(a_0^2).

<table>
<thead>
<tr>
<th>Source</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>[15]</td>
<td>1428</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[18]</td>
<td>1383</td>
<td>1799</td>
<td>4587</td>
<td>5979</td>
<td>9742</td>
</tr>
<tr>
<td>[22]</td>
<td>1486</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[23]</td>
<td>1428</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[24]</td>
<td>1423</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present</td>
<td>1424</td>
<td>1878</td>
<td>5000</td>
<td>6495</td>
<td>10462</td>
</tr>
</tbody>
</table>

### Table IV. Octupole polarizabilities α_3(a_0^3).

<table>
<thead>
<tr>
<th>Source</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>[18]</td>
<td>36495</td>
<td>51167</td>
<td>150161</td>
<td>212657</td>
<td>339920</td>
</tr>
<tr>
<td>[22]</td>
<td>41675</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present</td>
<td>39688</td>
<td>55518</td>
<td>176940</td>
<td>236850</td>
<td>395343</td>
</tr>
</tbody>
</table>

### Table V. Values of C_6, C_8, and C_10 in a.u. for Li-Li.

<table>
<thead>
<tr>
<th>Source</th>
<th>10^{-3}C_6</th>
<th>10^{-3}C_8</th>
<th>10^{-3}C_10</th>
</tr>
</thead>
<tbody>
<tr>
<td>[18]</td>
<td>1.389</td>
<td>0.8089</td>
<td>0.6901</td>
</tr>
<tr>
<td>[21]</td>
<td>1.386</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[22]</td>
<td>1.445</td>
<td>0.8847</td>
<td>0.7902</td>
</tr>
<tr>
<td>[39]</td>
<td>1.383</td>
<td>0.7578</td>
<td>0.4817</td>
</tr>
<tr>
<td>[38]</td>
<td>1.360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present</td>
<td>1.388</td>
<td>0.8324</td>
<td>0.7365</td>
</tr>
</tbody>
</table>

### Table VI. Values of C_6, C_8, and C_10 in a.u. for alkali-metal atom pairs.

<table>
<thead>
<tr>
<th>Source</th>
<th>Na-Na</th>
<th>K-K</th>
<th>Rb-Rb</th>
<th>Cs-Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-3}C_6</td>
<td>[18]</td>
<td>1.540</td>
<td>3.945</td>
<td>4.768</td>
</tr>
<tr>
<td>[21]</td>
<td>1.518</td>
<td>3.574</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[38]</td>
<td>1.330</td>
<td>3.780</td>
<td>4.700</td>
<td>6.500</td>
</tr>
<tr>
<td>Present</td>
<td>1.472</td>
<td>3.813</td>
<td>4.426</td>
<td>6.331</td>
</tr>
</tbody>
</table>

| 10^{-3}C_8 | [18] | 1.098 | 3.834 | 5.244 | 9.025 |
| Present | 1.119 | 4.096 | 5.506 | 9.630 |

| 10^{-3}C_10 | [18] | 1.036 | 4.522 | 6.836 | 13.010 |
| [39] | 0.6939 | 4.069 | 6.316 | 14.510 |
| Present | 1.107 | 5.248 | 7.665 | 15.200 |
TABLE VII. Dispersion coefficients in a.u. for different alkali-metal-atom interactions.

<table>
<thead>
<tr>
<th></th>
<th>C₆ (units of 10⁶)</th>
<th>C₄ (units of 10⁶)</th>
<th>C₁₀ (units of 10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Na</td>
<td>1.460,¹ 1.427, 1.448b</td>
<td>1.068</td>
<td>0.982</td>
</tr>
<tr>
<td>Li-K</td>
<td>2.334,¹ 2.293, 2.219b</td>
<td>2.517</td>
<td>2.651</td>
</tr>
<tr>
<td>Li-Rb</td>
<td>2.469</td>
<td>3.137</td>
<td>3.413</td>
</tr>
<tr>
<td>Li-Cs</td>
<td>2.934</td>
<td>4.586</td>
<td>5.303</td>
</tr>
<tr>
<td>Na-K</td>
<td>2.443,¹ 2.348, 2.309b</td>
<td>2.614</td>
<td>2.949</td>
</tr>
<tr>
<td>Na-Rb</td>
<td>2.526</td>
<td>3.250</td>
<td>3.784</td>
</tr>
<tr>
<td>Na-Cs</td>
<td>2.993</td>
<td>4.727</td>
<td>5.844</td>
</tr>
<tr>
<td>K-Rb</td>
<td>4.108</td>
<td>5.123</td>
<td>6.726</td>
</tr>
<tr>
<td>K-Cs</td>
<td>4.903</td>
<td>7.547</td>
<td>10.369</td>
</tr>
<tr>
<td>Rb-Cs</td>
<td>5.286</td>
<td>8.120</td>
<td>11.793</td>
</tr>
</tbody>
</table>

¹References [18].
²Reference [21].

them [18], particularly since the core-polarization contribution to the dipole polarizability has been arranged so that the experimental values are reproduced. Probable upper limits to this error have been given by Dal g arno and Davison [5].

For the heteronuclear cases, we have listed the values for the dispersion coefficients in Table VII. The magnitudes of the dispersion coefficients lie between the values for the corresponding homonuclear cases. For instance, the C₆ coefficient for Na-K falls between the value of C₆ for Na-Na and the value of C₆ for K-K. Table VII also includes results from [18] and [21] for the C₆ coefficients. Once again, the values in [18] are larger than ours, mainly due to their neglect of the core-polarization effects.

It is often assumed that C₁₀ = 1.3(C₄² / C₆) [41]. For the cases in Tables V–VII, the ratio of C₁₀ to (C₄² / C₆) varies between 0.74 and 1.48.

IV. CONCLUSIONS

Using an efficient numerical algorithm originally developed for obtaining absorption line profiles, we calculate the dispersion coefficients in the long-range 1/r expansion of the electrostatic interaction between two ground-state alkali-metal atoms. First, we describe the motion of the valence electron in the presence of the closed-shell core by the well-established method of parametric model potential. This angular-momentum dependent central potential includes the effect of the core polarizability which is cut off at the core boundary to eliminate the unphysical nature of the polarization potential near the nucleus. We then evaluate the dispersion energy coefficients by integrating over the dynamic electric multipole polarizabilities of the product dimer at imaginary frequencies. The polarizabilities are obtained by solving two coupled inhomogeneous differential equations. We have extended the single-channel Numerov differential equation solver method to handle coupled inhomogeneous equations. In this vein, our calculations in the spirit of perturbation theory are “exact”, i.e., no approximation is made in solving the inhomogeneous equations.

We also investigate the effect of the core polarization on the electric dipole of the valence electron and show that this effect leads to a general lowering of the 1/R⁶ dispersion energies, as expected in view of the fact that the polarization of the core amounts to a contraction of the dipole moment. We present a comprehensive compilation of the multipole polarizabilities and dispersion energies for alkali-metal dimers.

ACKNOWLEDGMENTS

H.R.S. and A.D. were supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research. M.M. was supported by the Smithsonian Institution.

[16] G. D. Zeiss, W. J. Meath, J. C. F. MacDonald, and D. J.