Dispersion coefficients of the excited states of lithium atoms

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The dispersion coefficients of a number of the low-lying states of Li are determined for the homonuclear case. The Li wave functions and energies were computed in a frozen core Hamiltonian with a semiempirical polarization potential. Besides computing the dispersion coefficients, the scalar and tensor polarizabilities and oscillator strengths are computed and generally seen to be in good agreement with other accurate calculations.

I. INTRODUCTION

The recent of upsurge of interest in cold atom physics means that it has become more important to precisely define the interaction potential between pairs of alkali-metal atoms [1–5]. For example, the stability and structure of Bose-Einstein condensates (BECs) depend on the sign (and magnitude) of the scattering length, and the scattering length depends on the precise values of the dispersion constants [1,3]. One part of the interaction potential is the long-range van der Waals interaction. For two spherically symmetric atoms in their respective ground states, this can be written in the general form

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

The C_n parameters are the van der Waals dispersion coefficients. In recent years there have been a number of studies aimed at determining the dispersion coefficients between various combinations of alkali-metal and alkaline-earth-metal atoms [6–14]. One approach evaluated the sum rules explicitly using states that were derived by diagonalizing a fixed core Hamiltonian [15,16] in a very large basis of square integrable functions [17–19].

The present paper reports the values of the C_n coefficients between different combinations of the low-lying states of a pair of homonuclear lithium atoms. In addition, the array of oscillator strengths between the low-lying states are computed and the polarizabilities of a number of low-lying states are given.

II. RESULTS OF THE CALCULATIONS

A. Methodology

All the dispersion coefficients computed in this paper were computed by first diagonalizing the semiempirical Hamiltonian for the valence electron [15–19] in a large Laguerre-type orbital (LTO) basis set [19]. The details are very similar to those reported in [17,19,20].

The initial step was to perform a Hartree-Fock calculation of the Li ground state. The core $1s^2$ wave function was then frozen, giving the working Hamiltonian for the valence electron:

$$H = -\frac{1}{2}\nabla^2 + V_{\text{dir}}(\mathbf{r}) + V_{\text{exc}}(\mathbf{r}) + V_p(\mathbf{r}) \tag{2}$$

The direct and exchange interactions of the valence electron with the core were calculated exactly. The ℓ-dependent polarization potential V_p was semiempirical in nature with the functional form

$$V_p(r) = -\sum_{\ell m} \frac{\alpha_d g_\ell^2(r)}{2r^4}|\ell m\rangle\langle\ell m|. \tag{3}$$

The factor $\alpha_d = 0.1925a_0^3$ [21,22] is the static dipole polarizability of the core, and $g_\ell^2(r) = 1 - \exp(-r^6/\rho_\ell^6)$ is a cutoff function designed to make the polarization potential finite at the origin. The cutoff parameters ρ_ℓ were tuned so that they reproduced the binding energies of the ns ground state and the np, nd, and nf excited states. The energies of the states with $\ell \geq 1$ were assigned to the statistical average of their respective spin-orbit doublets. The Hamiltonian was diagonalized in a very large orbital basis with 50 Laguerre-type orbitals for each ℓ value. Although the wave functions are constructed as linear combinations of LTOs, all matrix element evaluations were done using Gaussian quadratures and are accurate to close to machine precision. The cutoff parameters were different for each $\ell \leq 2$. The parameters for $\ell > 2$ were set to ρ_2. The oscillator strengths (and other multipole expectation values) were computed with operators that included polarization corrections [16,19,23,24].

The model potential is quite realistic since the direct and exchange interactions with the core were computed without approximation from a Hartree-Fock (HF) wave function, and only the core polarization potential is described with a model potential. The resulting oscillator strengths and polarizabilities, for small atoms like Li or Be, are generally within 1% of the best variational calculations [14,19,25].

Diagonalizing the Hamiltonian results in a set of states that describes the low-lying states and in addition gives a

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discretization of the infinity of states that make up the positive energy continuum. The polarizabilities and dispersion coefficients that are all evaluated by means of sum rules. The polarizabilities are evaluated using Eqs. (8), (13), and (14) using the real states and pseudostates arising from the diagonalization in the intermediate-state summation. Similarly, the van der Waals constants are also given by the sum rules, Eqs. (B14) and (B15). Finite-dimension sums over pseudostates provide a rapidly convergent expansion of the continuum of intermediate states provided all the pseudostates are retained [21,22,26].

B. Energy levels

The energy levels of the present calculations are given in Table I and compared with experiment. The agreement with experiment is excellent since the polarization cutoff parameters were tuned to reproduce the experimental binding energy of the lowest states of each symmetry.

The agreement between the theoretical and experimental energy levels is sufficiently close to discount the possibility that energy level considerations might make a significant contribution to the uncertainty in the radial matrix elements. Values of the mean-square distance of the valence electron from the nucleus, $\langle r^2 \rangle$, are given for each level in Table I since these are needed in the determination of the LeRoy radius which determines the smallest distance at which the dispersion interaction is accurate [29,30].

C. Oscillator strengths of low-lying transitions

The oscillator strengths for the transitions between the low energy states are given in Table II. The absorption oscillator strength from state ψ_0 is calculated according to the identity [14,19]

TABLE I. Theoretical and experimental energy levels (in hartree) of some of the low-lying states of the Li atom. The energies are given relative to the energy of the ionized core. The experimental energies for the doublet states are averages with the usual $(2J+1)$ weighting factors. The experimental data were derived from the energy levels of [27] and the ionization potential of [28].

Level	Theory	Experiment	$\langle r^2 \rangle$
2s	−0.198141	−0.198142	17.47
2p	−0.130239	−0.130235	27.06
3s	−0.074168	−0.074182	117.41
3p	−0.057228	−0.057236	168.69
3d	−0.055611	−0.055606	125.63
4s	−0.038610	−0.038615	426.31
4p	−0.031970	−0.031975	571.98
4d	−0.031277	−0.031274	502.95
4f	−0.031254	−0.031251	359.87

$$f_{0n}^k = \frac{2|\langle \psi_0; L_0 || r^k \mathbf{C}^k(\hat{\mathbf{r}}) || \psi_n; L_n \rangle|^2 \epsilon_{n0}}{(2k+1)(2L_0+1)}. \tag{4}$$

In this expression, $\epsilon_{n0} = (E_n - E_0)$ is energy difference between the initial state and final state, while k is the multipolarity of the transition, and $\mathbf{C}^k(\hat{\mathbf{r}})$ is a spherical tensor. The comparison with available high-accuracy *ab initio* data of Yan and Drake [32] and Fischer *et al.* [33] is uniformly good. In no instance is there a difference exceeding 0.8% with these calculations. This level of agreement attests to the accuracy of the underlying model potential and in addition the numerical integrity of the computations.

The comparison with the fixed core model potential data of Qu *et al.* [34–36] cannot verify the accuracy of the model

TABLE II. Absorption oscillator strengths for various dipole transition lines of Li.

Transition	Present work	HF [31]	Other
$f(2s\text{-}2p)$	0.7475	0.7655	0.74695 [32], 0.74706 [33]
$f(2s\text{-}3p)$	0.00469	0.0337	0.00471 [33], 0.00482 [34]
$f(2s\text{-}4p)$	0.00424	0.0350	0.00428 [34]
$f(2p\text{-}3s)$	0.1106	0.1129	0.11053 [33]
$f(2p\text{-}4s)$	0.01284	0.0129	0.01283 [33]
$f(2p\text{-}3d)$	0.6388	0.6534	0.63857 [32], 0.63850 [33], 0.6385 [35]
$f(2p\text{-}4d)$	0.1227	0.1228	0.1232 [35]
$f(3s\text{-}3p)$	1.2153	1.231	1.21523 [33]
$f(3s\text{-}4p)$	4.24×10^{-5}	8.8×10^{-6}	
$f(3p\text{-}3d)$	0.07378	0.0552	0.0741 [33]
$f(3p\text{-}4s)$	0.2232	0.2275	0.22315 [33]
$f(3p\text{-}4d)$	0.5227	0.5452	
$f(3d\text{-}4p)$	0.01807	0.0162	
$f(3d\text{-}4f)$	1.0153	1.017	1.0153 [36]
$f(4s\text{-}4p)$	1.6410	1.659	
$f(4p\text{-}4d)$	0.1343	0.1021	
$f(4d\text{-}4f)$	0.00234		

potential, since the underlying assumptions of the work of Qu *et al.* are almost identical to the present calculation. However, the 1% level of agreement does indicate that the present results are reliable within the confines of the underlying model potentials.

D. Scalar and tensor polarizabilities

This analysis is done under the premise that spin-orbit effects are small and the radial parts of the wave functions are the same for the states with different J. The Stark energy shifts for the different L_0 levels in an electric field F are written as [37]

$$\Delta E = -\frac{1}{2}\alpha_{L_0 M_0}F^2. \quad (5)$$

The Stark shifts for the different M_0 states of the $^2P^o$ level are different, and the polarizability is written as

$$\alpha_{L_0 M_0} = \alpha_0 + \frac{3M_0^2 - L_0(L_0+1)}{L_0(2L_0-1)}\alpha_2, \quad (6)$$

where α_2 is taken from the state with $M_0 = L_0$. The total polarizability is written in terms of both a scalar and tensor polarizability. The scalar polarizability represents the average shift of the different M levels while the tensor polarizability gives the differential shift.

In terms of second-order perturbation theory, the energy shift from an electric field F pointing in the z direction is

$$\Delta E = -\frac{1}{2}\sum_n \frac{2\langle\psi_0;L_0 M_0|rC_0^1(\hat{\mathbf{r}})|\psi_n;L_n M_0\rangle}{(E_n - E_0)}$$

$$\times \langle\psi_n;L_n M_0|rC_0^1(\hat{\mathbf{r}})|\psi_0;L_0 M_0\rangle F^2. \quad (7)$$

The polarizability can therefore be written

$$\alpha_{L_0 M_0} = \sum_n \begin{pmatrix} L_0 & 1 & L_n \\ -M_0 & 0 & M_0 \end{pmatrix}^2 \frac{2|\langle\psi_0;L_0\|rC^1(\hat{\mathbf{r}})\|\psi_n;L_n\rangle|^2}{\epsilon_{n0}}, \quad (8)$$

where the Wigner-Eckart theorem has been used to isolate the M-dependent terms. Using the definition of the oscillator strength, Eq. (4), and taking the average of the energy shifts leads to the usual definition as a sum rule over the oscillator strengths. It is

$$\alpha_0 = \sum_{M_0=-L_0}^{L_0} \alpha_{L_0 M_0}/(2L_0+1) = \sum_n \frac{f_{0n}}{\epsilon_{n0}^2}, \quad (9)$$

where the sum includes both valence and core excitations. The energy distribution of the oscillator strengths originating from core excitations was estimated using a semiempirical technique [19]. In this approach, we utilize the fact that the f-value distribution for the core can be written

$$\alpha_{core} = \sum_{i \in core} \frac{N_i}{(\epsilon_i + \Delta)^2}, \quad (10)$$

where N_i is the number of electrons in a core orbital, ϵ_i is the Koopman energy, and Δ is an energy shift parameter. The

energy shift parameter Δ was chosen so that Eq. (10) reproduces accurate estimates of the core polarizabilities determined by close to exact calculations [19,21,22].

Since the M-dependent part of the polarizability is a tensor of rank 2, it is easiest to define it in terms of $\alpha_{2,L_0 L_0}$:

$$\alpha_{2,L_0 M_0} = \alpha_{2,L_0 L_0}(-1)^{L_0-M_0}\frac{\begin{pmatrix} L_0 & 2 & L_0 \\ -M_0 & 0 & M_0 \end{pmatrix}}{\begin{pmatrix} L_0 & 2 & L_0 \\ -L_0 & 0 & L_0 \end{pmatrix}}$$

$$= \alpha_{2,L_0 L_0}\frac{3M_0^2 - L_0(L_0+1)}{L_0(2L_0-1)}, \quad (11)$$

where $\alpha_{2,L_0 L_0}$ is

$$\alpha_{2,L_0 L_0} = \sum_n \left[\begin{pmatrix} L_0 & 1 & L_n \\ -L_0 & 0 & L_0 \end{pmatrix}^2 - \frac{1}{3(2L_0+1)}\right]$$

$$\times \frac{2|\langle\psi_0;L_0\|rC^1(\hat{\mathbf{r}})\|\psi_n;L_n\rangle|^2}{(E_0 - E_n)}. \quad (12)$$

This equation can be expressed in terms of an f-value sum, for an $L_0=1$ initial state, as

$$\alpha_{2,L_0 L_0} = -\left(\sum_{n,L_n=0}\frac{f_{0n}}{\epsilon_{n0}^2} + \frac{1}{10}\sum_{n,L_n=2}\frac{f_{0n}}{\epsilon_{n0}^2}\right). \quad (13)$$

If the initial state is a d state, the f-value sum is

$$\alpha_{2,L_0 L_0} = -\left(\sum_{n,L_n=1}\frac{f_{0n}}{\epsilon_{n0}^2} + \frac{2}{7}\sum_{n,L_n=3}\frac{f_{0n}}{\epsilon_{n0}^2}\right). \quad (14)$$

The core does not make a contribution to the tensor polarizability since it has an equal impact on all the different M levels.

The development above is for LS coupled states, but it is common to give the tensor polarizability for LSJ states. These can be related to the LS states by geometric factors arising from the application of Racah algebra. The polarizability can be expanded:

$$\alpha_{J_0 M_0} = \alpha_0 + \frac{3M_0^2 - J_0(J_0+1)}{J_0(J_0-1)}\alpha_{2,J_0 J_0}, \quad (15)$$

where $\alpha_{2,J_0 J_0}$ is the tensor polarizability of the state with $M_0=J_0$. The scalar polarizabilities for the different J levels are the same (if spin-orbit splitting is neglected) and equal to the scalar polarizability in the L representation. The tensor polarizabilities between the L and J representations can be related by

$$\alpha_{2,J_0 J_0} = \alpha_{2,L_0 L_0}(2J_0+1)(-1)^{S+L_0+J_0+2}\begin{Bmatrix} S & L_0 & J_0 \\ 2 & J_0 & L_0 \end{Bmatrix}$$

$$\times \begin{pmatrix} J_0 & 2 & J_0 \\ -J_0 & 0 & J_0 \end{pmatrix}\Big/\begin{pmatrix} L_0 & 2 & L_0 \\ -L_0 & 0 & L_0 \end{pmatrix}. \quad (16)$$

When $L_0=1$ and $J_0=3/2$ this reduces to $\alpha_{2,J_0 J_0}=\alpha_{2,L_0 L_0}$. When $L_0=2$ the $J_0=3/2$ case gives $\alpha_{2,J_0 J_0}=7\times\alpha_{2,L_0 L_0}/10$ while the $J_0=5/2$ case gives $\alpha_{2,J_0 J_0}=\alpha_{2,L_0 L_0}$.

TABLE III. The scaler and tensor polarizabilities of the low-lying states of the alkali-metal atoms. The core polarizabilities from [19] are also listed. All polarizabilities are in atomic units. The numbers in the square brackets denote powers of 10.

Method	α_1	α_2	α_3	α_{2,L_0L_0}
		$1s^2$ core		
	0.193	0.114	0.168	
		$2s$		
Present	164.21	1424.4	3.9680[4]	
Exact [14]	164.11	1423.4	3.9650[4]	
MSD [6]	164.0	1.424[3]	3.969[4]	
RKR [38]	164.14	1423.3		
Model pot. [39]	164			
Expt. [40]	164.2(11)			
		$2p$		
Present	126.95	4104.9	3.2135[5]	1.6627
RKR [38]	126.4			1.73
Model pot. [39]	126.4			1.5
Expt. [41]	126.88(50)			1.64(4)
		$3s$		
Present	4134.5	3.5642[5]	3.1594[7]	
Model pot. [39]	4098			
CA [42]	4133			
		$3p$		
Present	2.8454[4]	4.6692[5]	4.2217[8]	−2188.0
Model pot. [39]	2.6637[4]			−2016
CA [42]	2.835[4]			−2173
		$3d$		
Present	−1.5044[4]	1.5786[5]	−1.3548[8]	1.6414[4]
Model pot. [39]	−1.395[4]			1.5324[4]
CA [42]	−1.51[4]			1.645[4]
Expt. [43]	−1.513(4)[4]			1.643(6)[4]
		$4s$		
Present	3.5303[4]	1.1587[7]	4.5133[9]	
Model pot. [39]	3.504[4]			
CA [42]	3.526[4]			
		$4p$		
Present	2.7617[5]	5.3492[7]	4.3264[10]	−2.1000[4]
Model pot. [39]	2.540[5]			1.88[4]
CA [42]	2.735[5]			−2.07[4]
		$4d$		
Present	4.1926[6]	6.6239[6]	2.8113[11]	−1.0781[6]
Model pot. [39]	4.680[5]			−1.65[5]
CA [42]	3.10[6]			−6.749[5]

Results of calculations

Table III gives the polarizabilities of the lowest eight states of Li and reports polarizabilities from a variety of other sources. For the ground $2s$ state, the comparison with the close to exact Hylleraas calculation of Yan *et al.* [14] could hardly be better. The level of agreement is at the 0.1% level of accuracy.

The most stringent test of the $2p$ state is with the experiment of Windholz *et al.* [41] which gave polarizabilities for both the ^{7}Li and ^{6}Li [41] isotopes. The numbers reported in Table III are the average of the two polarizabilities. The present α_1 and α_{2,L_0L_0} agree with the experiment to within experimental error.

The experiment of Ashby *et al.* [43] gives a stringent test of our calculations for the $3d$ level. Ashby *et al.* give polarizabilities for the *LSJ* coupling scheme. These were converted into *LS* coupling by making a weighted sum of the $3d_{3/2}$ and $3d_{5/2}$ polarizabilities with a $(2J+1)$ weighting factor. The agreement with the experimental polarizabilities is better than 1%.

The comparisons with the model potential results of Magnier and Aubrey-Frecon [39] and the Coulomb approximation (CA) of Ashby and van Wijngaarden [42] do not provide particularly stringent tests of our calculations since the approximations made in these two calculations render them less accurate than the present calculations. These calculations are mainly useful in determining whether there are any gross errors in the present results, and this is not the case. The largest differences occur for the $4d$ state. However, it can be seen from Table I that the $4d$-$4f$ energy difference is very small, so even a minor error in the energy of these levels can lead to a major error in the polarizability. While the present $4d$-$4f$ energy difference is accurate to 1.4%, it is not clear whether a similar degree of accuracy has been achieved in Refs. [39,42] since they do not give an energy tabulation.

III. van der WAALS COEFFICIENTS

This section reports the van der Waals coefficients for the different configurations and compares them with other data where available. Most of the dispersion coefficients presented here involved pairs of atoms with at least one of the electrons in the $2s$ or $2p$ states. This was done to reduce the amount of numerical data in the tables.

The theoretical work leading to the expressions for the van der Waals coefficients followed the formalism developed by one of the authors (J. Y. Z.) for helium [44–47]. A summary of the theoretical development leading to the determination of the molecular representations and a tabulation of the formulas for C_3 and C_5 are given in Appendices A and B. Another completely independent calculation was undertaken as part of the verification process. This other calculation used expressions for the C_n coefficients based on those developed by Marinescu and coworkers [7–9]. These expressions are tabulated in Appendix B. The two independent calculations of the dispersion coefficients agreed to all significant digits. Some errors were identified in the published formulas of Marinesu and Dalgarno [7,8]. In the first case, the A_9^{+1} coefficient in Table I of [7] was listed as −6/15 when it should have been listed as −6/25. It is most likely that this error was purely typographical in nature and did not affect any of the C_8 results for the $2s$-np states listed in [7]. A second discrepancy for the C_8 coefficient of the $2p$-$2p$ configuration was traced back to errors in Eqs. (5.15) and (5.18) of [8]. The coefficient in front of S_9 should be 0 in Eq. (5.15) and $\frac{192}{175}$ in Eq. (5.18). [The same error was also present in [9] which

TABLE IV. The dispersion coefficients C_6, C_8, and C_{10} for Li(ns)-Li($n's$) combinations. The numbers in the square bracket denote powers of 10. Data by other groups are identified by the citation in the first column.

Molecule	β	C_6	C_8	C_{10}
2s-2s	0	1394.6	8.3515[4]	7.3811[6]
Exact [14]	0	1393.4	8.3426[4]	7.3721[6]
MSD [6]	0	1388	8.324[4]	7.365[6]
2s-3s	−1	1.3850[4]	3.5489[6]	1.0672[9]
MSD [7]	−1	1.381[4]	3.539[6]	1.064[9]
	+1	3.1160[4]	4.5232[6]	1.2528[9]
MSD [7]	+1	3.110[4]	4.514[6]	1.250[9]
2s-4s	−1	6.7694[4]	5.7126[7]	5.2444[10]
MSD [7]	−1	6.575[4]	5.700[7]	5.231[10]
	+1	6.7243[4]	5.7038[7]	5.2413[10]
MSD [7]	+1	6.712[4]	5.691[7]	5.228[10]
3s-3s	0	1.9591[5]	8.8534[7]	3.7180[10]
4s-4s	0	4.6129[6]	−9.6796[10]	−1.3152[15]
3s-4s	−1	1.0762[6]	4.3114[8]	1.0768[12]
	+1	−3.5233[6]	−5.9915[10]	2.0824[12]

dealt with heteronuclear case. The coefficient for $(S_{14}+S_{16})$ should be zero in Eq. (5.15) and $\frac{96}{175}$ for Eq. (5.18)].

The most accurate calculations for lithium so far are the close to exact calculations of Yan *et al.* [14]. However, they only report dispersion coefficients for the 2s-2s and 2s-2p cases. The most comprehensive set of calculations were those carried out by Marienscu Sadeghpour, and Dalgarno (MSD) [6–9]. The MSD calculations use a model potential, and they do not do a sum over radial matrix elements; instead, they use the Dalgarno-Lewis technique [49]. An older compilation by Bussery and co-workers exists [50–53], but the results are not presented here since their description of the radial wave functions is more primitive than that used for the MSD compilation and the present work. For example, their estimates of C_6 and C_8 for two Li atoms in their grounds states underestimate the close to exact values of Yan *et al.* [14] by 10% and 30%, respectively [14].

The comparison with the exact values of Yan *et al.* in Table IV for the 2s-2s case show agreement at the 0.1% level of accuracy. The dispersion coefficients for the other *ns-ms*-type cases are reasonably close to the MSD results.

For the other possible combinations of states given in Tables V–VII, there is some agreement with the model potential calculations of MSD but there are a number of discrepancies which are too large to be ascribed to differences of detail. As a general rule, agreement with MSD is best for the lower states and the dispersion coefficients of smaller polarity. Detailed comparisons have revealed that in some instances the specific sum rules used by MSD are incorrect, and further there is a lack of accuracy in the numerical evaluations of the sums and integrals that make up the dispersion coefficient.

The numerical inaccuracies present in the MSD calculations can be demonstrated most clearly in the C_6 coefficients

for the 2s-4d molecule listed in Table VI. The present values of C_6 are all about 40% larger than the MSD values. For this case it is possible to extract the underlying radial matrix element sums

$$T_1 = \sum_{mn} \frac{|\langle 2s|r|mp\rangle|^2 |\langle 4d|r|np\rangle|^2}{E_{mp} - E_{2s} + E_{np} - E_{4d}},$$

$$T_2 = \sum_{mn} \frac{|\langle 2s|r|mp\rangle|^2 |\langle 4d|r|nf\rangle|^2}{E_{mp} - E_{2s} + E_{nf} - E_{4d}}, \quad (17)$$

from the published dispersion coefficients of MSD. We get $T_1 = 1.26 \times 10^5$ and $T_2 = 5.77 \times 10^4$ from the MSD data. The values obtained from our sum rules are $T_1 = 1.288 \times 10^5$ and $T_2 = 1.136 \times 10^5$. The source of the discrepancy lies in the dipole matrix elements for the $4d \rightarrow nf$ transitions. The $|\langle 4d|r|nf\rangle|^2$ matrix elements should be close to the hydrogenic values for lithium. We get $|\langle 4d|r|4f\rangle|^2 = 252.2\, a_0^2$ which agrees with the hydrogenic value of 252.0 [54]. We also get $|\langle 4d|r|5f\rangle|^2 = 196.5\, a_0^2$ which also agrees with the hydrogenic value of 197.8 [54]. As another check, the oscillator strength sum rule $S_0 = \sum_n f(4d \rightarrow n\ell)$ has been evaluated, yielding a value of $S_0 = 0.999\,998\,89$. The available information suggests that the present calculations are correct and it is the results of Marinescu and Dalgarno [7] that should be discounted.

Table V gives the C_n coefficients for the 2s-2p, 2s-np, and 2p-ns cases. The agreement with the close to exact C_6 calculation of Yan *et al.* for the 2s-2p case is at the level of 0.1%. The core corrections were small, but did improve the agreement with the C_6 of Yan *et al.*. For example, the core correction increased the C_6 for the Σ state from 2066.4 to 2076.3, which is closer to the C_6 of Yan *et al.* of 2075.1.

The very high level of agreement with MSD does not carry over to the 2s-3p configuration. While the values of C_6 are in agreement with the MSD results, this is not the case for C_8 where there are large differences with all the MSD values with one exception (which we suspect is an accident). It is not possible to isolate the reason for the differences since there are too many sum rules that contribute to the different C_8.

The situation for the 2s-nd array of the dispersion coefficients is easily summarized. The agreement with the MSD compilation is almost perfect for the 2s-3d array. The agreement with the MSD compilation is uniformly poor for the 2s-4d array. The MSD sum rules involving excitations to the 4f level are believed to be inaccurate for reasons outlined earlier.

The comparison with MSD for the 2p-2p case listed in Table VII gives very good agreement for all values of C_6 with the exception of the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetries with $C_5 \neq 0$ and $(\beta, \gamma) = (+1, +1)$. The present results are completely different. This symmetry involves both intermediate excitations in the sum rule occupying $\ell = 0$ orbitals. This sum rule contributes −16,383 to the value of C_6. The negative contribution arises since the largest terms involve at least one of the intermediate states in the sum rule occupying the 2s level. These terms make a large negative contribution to C_6

TABLE V. The dispersion coefficients C_3, C_6, C_8, and C_{10} for the interactions between the $2s$-np and $2p$-ns states of Li. The numbers in the square brackets denote powers of 10. Data by other groups are identified by the citation in the first column.

Molecule	β	C_3	C_6	C_8	C_{10}
$\Sigma(2s\text{-}2p)$	−1	−11.008	2.0763[3]	9.9202[5]	1.2113[8]
MSD [7]	−1	−11.01	2.066[3]	9.880[5]	
YD [48]	−1	−11.000	2.0751[3]		
	+1	11.008	2.0763[3]	2.7431[5]	3.0096[7]
MSD [7]	+1	11.01	2.066[3]	2.705[5]	
YD [48]	+1	−11.000	2.0751[3]		
$\Pi(2s\text{-}2p)$	−1	5.5041	1.4074[3]	4.8629[4]	9.1839[5]
MSD [7]	−1	5.503	1.401[3]	4.756[4]	
YD [48]	−1	−5.500	1.4061[3]		
	+1	−5.5041	1.4074[3]	1.0316[5]	8.9295[6]
MSD [7]	+1	−5.5041	1.401[3]	1.021[5]	
YD [48]	+1	−5.500	1.4061[3]		
$\Sigma(2s\text{-}3p)$	−1	−3.3314[−2]	3.8236[4]	2.3183[7]	1.1180[10]
MSD [7]	−1	−3.364[−2]	3.814[4]	2.702[7]	
	+1	3.3314[−2]	3.8236[4]	2.4870[7]	1.0769[10]
MSD [7]	+1	3.364[−2]	3.814[4]	2.533[7]	
$\Pi(2s\text{-}3p)$	−1	1.6657[−2]	2.0282[4]	−3.7222[5]	1.3252[8]
MSD [7]	−1	1.682[−2]	2.022[4]	3.714[5]	
	+1	−1.6657[−2]	2.0282[4]	7.8976[5]	1.5536[8]
MSD [7]	+1	−1.682[−2]	2.002[4]	1.535[6]	
$\Sigma(2s\text{-}4p)$	−1	−2.5533[−2]	1.2982[5]	2.9926[8]	3.8300[11]
	+1	2.5533[−2]	1.2982[5]	2.9918[8]	3.8302[11]
$\Pi(2s\text{-}4p)$	−1	1.2766[−2]	7.2669[4]	8.2886[6]	4.7487[9]
	+1	−1.2766[−2]	7.2669[4]	8.3348[6]	4.7521[9]
$\Sigma(3s\text{-}2p)$	−1	−5.91546	9.5385[3]	1.6420[7]	4.7116[9]
	+1	5.91546	9.5385[3]	−1.2272[6]	8.1476[7]
$\Pi(3s\text{-}2p)$	−1	2.95773	1.4098[4]	3.3706[5]	3.3236[8]
	+1	−2.95773	1.4098[4]	3.8905[6]	6.3272[8]
$\Sigma(4s\text{-}2p)$	−1	−0.42050	4.7234[4]	8.3742[7]	9.0090[10]
	+1	0.42050	4.7234[4]	7.0882[7]	9.0968[10]
$\Pi(4s\text{-}2p)$	−1	0.21025	5.1569[4]	4.5252[7]	4.7677[10]
	+1	−0.21025	5.1569[4]	4.9604[7]	4.6483[10]

since the energy of the $2s$ level lies below that of the $2p$ level. However, this sum rule seems to be making a contribution of about +12 000 in the MSD calculation. Since the present calculation reproduces the experimental dipole and tensor polarizabilities of the $2p$ level (see Table III), it is most likely that the value in [8] is incorrect due to a calculation mistake. One interesting aspect of the $2p$-$2p$ case is the large size of the C_6 coefficients; the $2p$ polarizability is smaller than that of the $2s$ level, yet the dispersion coefficients for some of the symmetries are an order of magnitude larger. The reason for this is a fortuitous cancellation of the $2p$-$2s$ and $2p$-$3d$ energy differences in the sum over intermediate states.

The C_8 values for the $2p$-$2p$ configuration in Table VII are in reasonable agreement with those of MSD with the exception of $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetries where there is a 10%

discrepancy for the $C_5 = 0$ case. This is not surprising since these are the cases where there are errors in the formula of MSD. The difference with MSD can be largely removed if the incorrect MSD expressions are used to evaluate these dispersion coefficients.

The dispersion coefficients for the $2p$-$3p$ configuration are also given in Table VII. The C_6 values might seem to be rather small when compared with the $2p$-$2p$ values. However, as explained earlier, it is the $2p$-$2p$ system that has anomalously large dispersion coefficients.

IV. CONCLUSIONS

A systematic study of the dispersion parameters of the low-lying states of Li is presented. The present results reproduce all known high-accuracy data from experiment or close

TABLE VI. The dispersion coefficients C_5, C_6, C_8, and C_{10} for the interactions between the 2s and nd states of Li. The numbers in the square brackets denote powers of 10.

Molecule	β	C_5	C_6	C_8	C_{10}
$\Sigma(2s\text{-}3d)$	−1	451.43	2.0396[4]	1.6282[7]	8.6460[9]
MSD [7]	−1	449.8	2.039[4]		
	+1	−451.43	−1.6635[4]	1.2269[7]	8.7395[9]
MSD [7]	+1	−449.8	−1.663[4]		
$\Pi(2s\text{-}3d)$	−1	−300.95	−9.7192[3]	5.8684[6]	5.3251[8]
MSD [7]	−1	−299.9	−9.718[3]		
	+1	300.95	1.4968[4]	7.0630[6]	9.1099[7]
MSD [7]	+1	299.9	1.496[4]		
$\Delta(2s\text{-}3d)$	−1	75.238	1.1027[4]	−7.0083[5]	−1.8995[7]
MSD [7]	−1	74.97	1.102[4]		
	+1	−75.238	−1.3170[3]	3.7950[5]	−3.1047[7]
MSD [7]	+1	−74.97	−1.323[3]		
$\Sigma(2s\text{-}4d)$	−1	79.581	1.0408[5]	2.6590[8]	4.4512[11]
MSD [7]	−1	79.19	7.733[4]		
	+1	−79.581	1.0302[5]	2.6583[8]	4.4505[11]
MSD [7]	+1	−79.19	7.626[4]		
$\Pi(2s\text{-}4d)$	−1	−53.054	9.1358[4]	9.1477[7]	2.0677[10]
MSD [7]	−1	−52.79	6.641[4]		
	+1	53.054	9.2063[4]	9.1512[7]	2.0700[10]
MSD [7]	+1	52.79	6.712[4]		
$\Delta(2s\text{-}4d)$	−1	13.264	5.6359[4]	−1.4539[7]	−7.7159[8]
MSD [7]	−1	13.20	3.668[4]		
	+1	−13.264	5.6006[4]	−1.4563[7]	−7.6738[8]
MSD [7]	+1	−13.20	3.650[4]		

to exact calculations using correlated basis sets. However, the comparison with the extensive MSD compilation which used a model potential formalism [6–8] is mixed. There is agreement at the 1% level for about 80% of the distinct C_6 and C_8 coefficients. However, for about 20% of the cases there are differences exceeding 10%. These discrepancies are simply too large to be ascribed to the differences in the underlying model Hamiltonian or in the construction of the wave functions. The most likely explanation is that some of the dispersion coefficients presented in the MSD compilation [6–8] are contaminated by a calculation error. Although we do not discuss the heavier alkalis metals here, it should be noted that we have also performed calculations on these systems as well. We also find serious discrepancies with the MSD compilation for the heavier alkali-metal atoms for more or less the same configurations that are problematic in Li. Despite all these problems, it should be noted that the overall level of agreement is better with the MSD compilation than with the earlier compilation by Bussery and co-workers [51–53].

One novel aspect of the present work is that a prescription for including the core into the calculation of dispersion parameters is presented. For lithium, the impact of the core never exceeds 0.6%. However, it is likely to be more important for the heavier alkali-metal atoms [11,19].

One general aspect about the calculation of van der Waals coefficients must be noted. The expressions for the different symmetries were essentially derived individually by reduction of the matrix elements of electron-electron operator—namely, Eq. (B2) [e.g., Eq. (7) of [55]]. The nature of this expression is such that it is not a convenient form for a reduction in the general case. The net result is a process that is susceptible to human error and it is not surprising that the accuracy of the MSD compilation was marred by the occasional error. We tried to minimize human error in the present work by essentially having two independent calculations of most of the dispersion coefficients. This proved valuable since there were a number of instances where this helped us to catch programming mistakes that otherwise would have gone undetected. It also highlights the need to develop an algorithm that can be used to mechanically churn out dispersion coefficients regardless of the angular momentum symmetries of the two atoms. The recent work by Santra, Christ, and Greene [56,57] obviously represents a step toward this goal.

TABLE VII. The dispersion coefficients C_5, C_6, C_8, and C_{10} for the interactions between $2p$ and np states for Li. The numbers in the square brackets denote powers of 10.

Molecule	β	γ	C_5	C_6	C_8	C_{10}
			$2p$-$2p$			
Σ_1^+	+1	+1	0	2.8463[4]	8.7799[5]	1.3019[8]
MSD [8]	+1	+1	0	2.8451[4]	7.8764[5]	
Σ_2^+	+1	+1	−1.0546[3]	−4.0780[2]	8.6071[6]	9.0917[8]
MSD [8]	+1	+1	−1.0478[3]	2.4263[4]	8.4351[6]	
Σ^-	+1	−1	0	1.3522[3]	−1.0297[4]	−1.7416[6]
MSD [8]	+1	−1	0	1.3447[3]	−1.0569[4]	
Π	+1	−1	0	3.1979[4]	1.0097[6]	1.1162[8]
MSD [8]	+1	−1	0	3.1965[4]	1.0069[6]	
Π	+1	+1	7.0305[2]	5.2059[3]	−4.3753[5]	2.0893[8]
MSD [8]	+1	+1	6.9855[2]	5.195[3]	−4.3598[5]	
Δ	+1		−1.7576[2]	1.4739[4]	−6.2969[5]	7.7614[6]
MSD [8]	+1		−1.7463[2]	1.4730[4]	−6.3043[5]	
			$2p$-$3p$			
Σ_1^+	−1	+1	0	6.8307[3]	1.3017[7]	1.5639[9]
Σ_1^+	+1	+1	0	2.6877[4]	5.1316[7]	4.7984[9]
Σ_2^+	−1	+1	−5.7690[3]	3.2794[3]	6.0005[6]	1.5758[10]
Σ_2^+	+1	+1	−7.3785[3]	4.7820[4]	3.1740[7]	4.0435[10]
Σ^-	−1	−1	0	1.9168[4]	5.7425[6]	−2.9571[7]
Σ^-	+1	−1	0	1.1218[4]	1.4093[6]	9.6763[6]
Π	−1	−1	0	2.9638[4]	5.8203[7]	4.5886[9]
Π	−1	+1	3.8460[3]	1.4526[4]	1.1276[7]	−7.2649[7]
Π	+1	−1	0	7.3344[3]	1.6543[7]	2.0616[9]
Π	+1	+1	4.9190[3]	2.6721[4]	2.2359[7]	−3.9251[9]
Δ	−1		−9.6151[2]	7.6231[3]	3.9224[6]	−2.4591[9]
Δ	+1		−1.2298[3]	2.0627[4]	1.8111[7]	−6.0144[9]

APPENDIX A: THE MOLECULAR WAVE FUNCTIONS

1. *S-L* case

For two identical atoms a and b, where one is in an S state and the other in a state with orbital angular momentum L_b and magnetic quantum number M_b, the zeroth-order wave function for the combined system $a-b$ can be written in the form

$$\Psi^{(0)}(M_b,\beta) = \frac{C}{\sqrt{2}}[\Psi_{n_a}(\sigma)\Psi_{n_b}(L_bM_b;\rho)$$

$$+ \beta\Psi_{n_a}(\rho)\Psi_{n_b}(L_bM_b;\sigma)], \quad (A1)$$

where Ψ_{n_a} is the S-state wave function with the energy eigenvalue E_{n_a}, Ψ_{n_b} is the L_b-state wave function with the energy eigenvalue E_{n_b}, σ and ρ represent the coordinates of the two atoms, C is the normalization factor, and β describes the symmetry due to the exchange of two atoms. The parameter β is related to the total spin S and the individual orbital angular momentum of the two atoms by $\beta=(-1)^{S+L_a+L_b}P$, where $P=+1$ for gerade states and $P=-1$ for ungerade states [8,58]. If two atoms in the same S state, C is $\sqrt{2}$ and β is zero. If they are in different states, C is 1 and β is ±1. The

complete specification of the wave functions is give in Table VIII. The complete specifications of the wave functions are given in Table IX.

2. *P-P* case

The zeroth-order wave function for two identical atoms in P state and with the $a-b$ combined system in a Δ state can be written in the form

$$\Psi^{(0)}(\Delta,\beta) = \frac{C}{\sqrt{2}}[\Psi_{n_a}(11;\sigma)\Psi_{n_b}(11;\rho)$$

$$+ \beta\Psi_{n_a}(11;\rho)\Psi_{n_b}(11;\sigma)], \quad (A2)$$

If two atoms are in the same P state, then C is equal to $\sqrt{2}$ and $\beta=0$. If they are in different P states, then C is 1 and $\beta=\pm1$.

For the Π state, the zeroth-order wave function is

TABLE VIII. The electronic wave functions for Li_2 molecules in an ns-$m\ell$ configuration. The notation $|n_m^\ell\rangle$ indicates the radial quantum number n, the orbital angular momentum ℓ, and its projection m.

Asymptote	M	$\beta=1$	$\beta=-1$	Representation
ns-ms	0	$^1\Sigma_g^+$-$^3\Sigma_u^+$	$^1\Sigma_u^+$-$^3\Sigma_g^+$	$\dfrac{(|n_0^0 m_0^0\rangle+\beta|m_0^0 n_0^0\rangle)}{\sqrt{2(1+\delta_{nm})}}$
ns-mp	1	$^1\Pi_u$-$^3\Pi_g$	$^1\Pi_g$-$^3\Pi_u$	$\dfrac{1}{\sqrt{2}}(|n_0^0 m_1^1\rangle+\beta|m_1^1 n_0^0\rangle)$
ns-mp	0	$^1\Sigma_u^+$-$^3\Sigma_g^+$	$^1\Sigma_g^+$-$^3\Sigma_u^+$	$\dfrac{1}{\sqrt{2}}(|n_0^0 m_0^1\rangle+\beta|m_0^1 n_0^0\rangle)$
ns-md	2	$^1\Delta_g$-$^3\Delta_u$	$^1\Delta_u$-$^3\Delta_g$	$\dfrac{1}{\sqrt{2}}(|n_0^0 m_2^2\rangle+\beta|m_2^2 n_0^0\rangle)$
ns-md	1	$^1\Pi_g$-$^3\Pi_u$	$^1\Pi_u$-$^3\Pi_g$	$\dfrac{1}{\sqrt{2}}(|n_0^0 m_1^2\rangle+\beta|m_1^2 n_0^0\rangle)$
ns-md	0	$^1\Sigma_g^+$-$^3\Sigma_u^+$	$^1\Sigma_u^+$-$^3\Sigma_g^+$	$\dfrac{1}{\sqrt{2}}(|n_0^0 m_0^2\rangle+\beta|m_0^2 n_0^0\rangle)$

$$\Psi^{(0)}(\Pi,\beta,\gamma) = \frac{C}{2}\Psi_{n_a}(1M_a;\sigma)\Psi_{n_b}(1M_b;\rho)$$

$$+\frac{C\gamma}{2}\Psi_{n_a}(1M_b;\sigma)\Psi_{n_b}(1M_a;\rho)$$

$$+\frac{C\beta}{2}\Psi_{n_a}(1M_a;\rho)\Psi_{n_b}(1M_b;\sigma)$$

$$+\frac{C\beta\gamma}{2}\Psi_{n_a}(1M_b;\rho)\Psi_{n_b}(1M_a;\sigma), \quad (A3)$$

where $M_a=0$, $M_b=1$, and $\gamma=\pm 1$. In the above, β reflects the exchange symmetry of two atoms and $\gamma=\pm 1$ is related to the exchange symmetry of the projected components of atomic angular momenta M_a and M_b. If $n_a=n_b$, C is equal to $\sqrt{2}$ and β is zero. If $n_a\neq n_b$, then $C=1$ and β is equal to ± 1. The states are identified as $\Pi(\beta,\gamma)$.

The zeroth-order wave functions for the Σ states are written in two kinds of form:

$$\Psi^{(0)}(\Sigma,\beta) = \frac{C}{\sqrt{2}}\Psi_{n_a}(10;\sigma)\Psi_{n_b}(10;\rho)$$

$$+\frac{C\beta}{\sqrt{2}}\Psi_{n_a}(10;\rho)\Psi_{n_b}(10;\sigma) \quad (A4)$$

and

$$\Psi^{(0)}(\Sigma,\beta,\gamma) = \frac{C}{2}\Psi_{n_a}(1M_a;\sigma)\Psi_{n_b}(1M_b;\rho)$$

$$+\frac{C\gamma}{2}\Psi_{n_a}(1M_b;\sigma)\Psi_{n_b}(1M_a;\rho)$$

$$+\frac{C\beta}{2}\Psi_{n_a}(1M_a;\rho)\Psi_{n_b}(1M_b;\sigma)$$

TABLE IX. The electronic wave functions for Li_2 molecules in a np-mp configuration. The notation $|n_m^\ell\rangle$ indicates the radial quantum number n, the orbital angular momentum ℓ, and its projection m. Only states with $\beta=+1$ survive for the np-np configuration. The two Σ^+ combinations are distinguished by an additional row entry.

Asymptote	M	$\beta=1$	$\beta=-1$	Representation
np-mp	2	$^1\Delta_g$-$^3\Delta_u$	$^1\Delta_u$-$^3\Delta_g$	$\dfrac{1}{\sqrt{2(1+\delta_{nm})}}(|n_1^1 m_1^1\rangle+\beta|m_1^1 n_1^1\rangle)$
np-mp	1	$^1\Pi_g$-$^3\Pi_u$	$^1\Pi_u$-$^3\Pi_g$	$\dfrac{\sqrt{1+\delta_{nm}}}{2}(|n_0^1 m_1^1\rangle+\beta|m_1^1 n_0^1\rangle+\gamma(1-\delta_{nm})[|n_1^1 m_0^1\rangle+\beta|m_0^1 n_1^1\rangle])$
np-$mp\Sigma_1^+$	0	$^1\Sigma_g^+$-$^3\Sigma_u^+$	$^1\Sigma_u^+$-$^3\Sigma_g^+$	$\dfrac{1}{\sqrt{3(1+\delta_{nm})}}[|n_0^1 m_0^1\rangle+\beta|m_0^1 n_0^1\rangle]+\dfrac{1}{\sqrt{12(1+\delta_{nm})}}[|n_1^1 m_{-1}^1\rangle +\beta|m_{-1}^1 n_1^1\rangle+|n_{-1}^1 m_1^1\rangle+\beta|m_1^1 n_{-1}^1\rangle]$
np-$mp\Sigma_2^+$	0	$^1\Sigma_g^+$-$^3\Sigma_u^+$	$^1\Sigma_u^+$-$^3\Sigma_g^+$	$\dfrac{-1}{\sqrt{6(1+\delta_{nm})}}[|n_0^1 m_0^1\rangle+\beta|m_0^1 n_0^1\rangle]+\dfrac{1}{\sqrt{6(1+\delta_{nm})}}[|n_1^1 m_{-1}^1\rangle +\beta|m_{-1}^1 n_1^1\rangle+|n_{-1}^1 m_1^1\rangle+\beta|m_1^1 n_{-1}^1\rangle]$
np-mp	0	$^1\Sigma_g^-$-$^3\Sigma_u^-$	$^1\Sigma_u^-$-$^3\Sigma_g^-$	$\dfrac{1}{2\sqrt{(1+\delta_{nm})}}[|n_{-1}^1 m_1^1\rangle+\beta|m_1^1 n_{-1}^1\rangle-|n_1^1 m_{-1}^1\rangle-\beta|m_{-1}^1 n_1^1\rangle]$

$$+ \frac{C\beta\gamma}{2}\Psi_{n_a}(1M_b;\rho)\Psi_{n_b}(1M_a;\sigma), \quad \text{(A5)}$$

where $M_a = -M_b = 1$ and $\gamma = \pm 1$. In the first case, the magnetic quantum numbers of both atomic states are zero. In the second case, their magnetic quantum numbers are nonzero and equal and opposite. For $\Psi^{(0)}(\Sigma, \beta)$ and $\Psi^{(0)}(\Sigma, \beta, \gamma)$, β is equal to zero and C is equal to $\sqrt{2}$ when $n_a = n_b$. However, the condition $n_a \neq n_b$ leads to $\beta = \pm 1$ and $C = 1$.

For $\Psi^{(0)}(\Sigma, \beta, \gamma)$, γ indicates the reflection of the wave functions on a plane containing the molecular axis [8]. If $\hat{Q}$ is the reflection operator, then

$$\hat{Q}\Psi_{n_a}(1M_a;\sigma) = (-1)^{M_a}\Psi_{n_a}(1-M_a;\sigma), \quad \text{(A6)}$$

leading to

$$\hat{Q}\Psi^{(0)}(\Sigma, \beta) = \Psi^{(0)}(\Sigma, \beta) \quad \text{(A7)}$$

and

$$\hat{Q}\Psi^{(0)}(\Sigma, \beta, \gamma) = \gamma\Psi^{(0)}(\Sigma, \beta, \gamma). \quad \text{(A8)}$$

The degeneracy between the state $\Psi^{(0)}(\Sigma, \beta, -1)$ and other two states can be removed by the reflection symmetry, and this state is identified as the Σ^- state. However, the degeneracy between $\Psi^{(0)}(\Sigma, \beta)$ and $\Psi^{(0)}(\Sigma, \beta, 1)$ states with positive reflection symmetry still remains. This is removed by diagonalizing the first-order interaction in a basis containing these two states. The (normalized) eigenvectors are

$$\Psi^{(0)}(\Sigma, \beta, \lambda_1) = \frac{-1}{\sqrt{3}}\Psi^{(0)}(\Sigma, \beta) + \sqrt{\frac{2}{3}}\Psi^{(0)}(\Sigma, \beta, 1)$$

$$\text{(A9)}$$

and

$$\Psi^{(0)}(\Sigma, \beta, \lambda_2) = \sqrt{\frac{2}{3}}\Psi^{(0)}(\Sigma, \beta) + \frac{1}{\sqrt{3}}\Psi^{(0)}(\Sigma, \beta, 1).$$

$$\text{(A10)}$$

The first state—e.g., Eq. (A9)—is labeled as the Σ_1^+ state. The second state, Eq. (A10), is labeled as the Σ_2^+ state.

APPENDIX B: THE van der WAALS INTERACTION

The interaction between two nonoverlapping charge distributions a and b, V, can be expanded as an infinite series in powers of $1/R$ [55]:

$$V = \sum_{\ell=0}^{\infty}\sum_{L=0}^{\infty}\frac{V_{\ell L}}{R^{\ell+L+1}}, \quad \text{(B1)}$$

where

$$V_{\ell L} = 4\pi(-1)^L(\ell,L)^{-1/2}\sum_{\mu}K_{\ell L}^{\mu}T_{\mu}^{(\ell)}(\sigma)T_{-\mu}^{(L)}(\rho). \quad \text{(B2)}$$

The position vector σ points from the origin of atom a (O_1) to the active electron. Similarly, ρ points from the origin of atom b (O_2) to the second active electron. The vector $\mathbf{R}$ points from O_1 to O_2. In the above, $T_{\mu}^{(\ell)}(\sigma)$ and $T_{-\mu}^{(L)}(\rho)$ are the multipole tensor operators of two charge distributions. In atomic units ($e = 1$) these can be written

$$T_{\mu}^{(\ell)}(\sigma) = \sigma^{\ell}Y_{\ell\mu}(\hat{\sigma}) \quad \text{(B3)}$$

and

$$T_{-\mu}^{(L)}(\rho) = \rho^L Y_{L-\mu}(\hat{\rho}). \quad \text{(B4)}$$

The coefficient $K_{\ell L}^{\mu}$ is

$$K_{\ell L}^{\mu} = \left[\binom{\ell+L}{\ell+\mu}\binom{\ell+L}{L+\mu}\right]^{1/2} \quad \text{(B5)}$$

and $(\ell, L, \ldots) = (2\ell+1)(2L+1)\cdots$.

1. First-order energy correction for the *S-L* case

The first-order energy is given by

$$V^{(1)} = \langle\Psi^{(0)}|V|\Psi^{(0)}\rangle = -\frac{C_{2L_b+1}(M_b,\beta)}{R^{2L_b+1}}, \quad \text{(B6)}$$

where $C_{2L_b+1}(M_b,\beta)$ is the long-range interaction coefficient:

$$C_{2L_b+1}(M_b,\beta) = \beta(-1)^{1+L_b-M_b}\frac{4\pi}{(2L_b+1)^2}\binom{2L_b}{L_b+M_b}$$

$$\times |\langle\Psi_{n_a}(\sigma)\|\sigma^{L_b}Y_{L_b}(\hat{\sigma})\|\Psi_{n_b}(L_b;\sigma)\rangle|^2.$$

$$\text{(B7)}$$

2. First-order energy correction for the *P-P* case

For $\Psi^{(0)}(\Delta, \beta)$, the first-order energy is given by

$$V^{(1)}(\Delta, \beta) = \langle\Psi^{(0)}(\Delta)|V|\Psi^{(0)}(\Delta)\rangle = -\frac{C_5(\Delta, \beta)}{R^5}, \quad \text{(B8)}$$

where

$$C_5(\Delta, \beta) = -(\mathcal{A}_1 + \beta\mathcal{A}_2). \quad \text{(B9)}$$

In Eq. (B9), $\mathcal{A}_1$ and $\mathcal{A}_2$ are

$$\mathcal{A}_1 = \frac{4\pi}{25}\langle\Psi_{n_a}(1;\sigma)\|\sigma^2 Y_2(\hat{\sigma})\|\Psi_{n_a}(1;\sigma)\rangle$$

$$\times\langle\Psi_{n_b}(1;\rho)\|\rho^2 Y_2(\hat{\rho})\|\Psi_{n_b}(1;\rho)\rangle \quad \text{(B10)}$$

and

$$\mathcal{A}_2 = \frac{4\pi}{25}|\langle\Psi_{n_a}(1;\sigma)\|\sigma^2 Y_2(\hat{\sigma})\|\Psi_{n_b}(1;\sigma)\rangle|^2. \quad \text{(B11)}$$

The first-order energy correction $V^{(1)}(\Pi, \beta, \gamma)$ gives

$$C_5(\Pi, \beta, \gamma) = -C^2(1 + 2\gamma + \gamma^2)C_5(\Delta, \beta). \quad \text{(B12)}$$

The dispersion coefficient, C_5 is zero for both the Σ_1^+ and Σ^- states. For the Σ_2^+, C_5 is

$$C_5(\Sigma_2^+, \beta) = 6C_5(\Delta, \beta). \quad \text{(B13)}$$

3. Second-order energy correction

The second-order energy is

$$V^{(2)} = -\sum_{n_s n_t}{}' \sum_{\substack{L_s M_s \\ L_t M_t}} \frac{|\langle \Psi^{(0)}|V|\chi_{n_s}(L_s M_s;\sigma)\omega_{n_t}(L_t M_t;\rho)\rangle|^2}{E_{n_s n_t} - E_{n_a n_b}^{(0)}},$$

(B14)

where $\chi_{n_s}(L_s M_s;\sigma)\omega_{n_t}(L_t M_t;\rho)$ is one of the intermediate states with the energy eigenvalue $E_{n_s n_t} = E_{n_s} + E_{n_t}$ and the prime in the summation indicates that the terms with $E_{n_s n_t} = E_{n_a n_b}^{(0)}$ should be excluded. It should be noted that the molecular states in Eq. (B14) do allow for the exchange of the two atomic states Ψ_{n_a} and Ψ_{n_b} making up $\Psi^{(0)}$. Expressions for van der Waals matrix elements for various states of helium expressed in terms of reduced matrix elements have been given by Zhang and co-workers [44–47]. These expressions can be adapted to single-electron atoms, but they are not reproduced here due to their complexity.

Instead expressions are presented for the second-order matrix elements written in terms of sums over products of radial matrix elements multiplied by an angular factor A_i and also by an energy denominator—viz.,

$$V_i^{(2)} = -A_i \sum_{n_s n_t}{}' \sum_{k_1 k_2 k_3 k_4} \frac{\langle n_a l_a | r^{k_1} | n_s l_s \rangle \langle n_s l_s | r^{k_2} | n_a l_a \rangle}{E_{n_s n_t} - E_{n_a n_b}^{(0)}}$$
$$\times \frac{\langle n_b l_b | r^{k_3} | n_t l_t \rangle \langle n_t l_t | r^{k_4} | n_b l_b \rangle}{R^{k_1+k_2+k_3+k_4+2}}.$$

(B15)

The A_i are coefficients that result from the angular integrations and sums over magnetic quantum numbers. The dispersion coefficients are obtained by multiplying Eq. (B15) by -1 and omitting the $R^{k_1+k_2+k_3+k_4+2}$ factor. These A_i coefficients were determined by using the formalism presented in [44–46]. With one or two exceptions the coefficients reproduced those listed in the MSD compilations [7,9].

Expressions for C_6, C_8, and C_{10} for the case $\ell_a = \ell_b = 0$ have been given in [7]. That article also gave C_6 and C_8 for the $\ell_a = 0$, $\ell_b = 1$ configuration and C_6 for the $\ell_a = 0$, $\ell_b = 2$ case. We note that the coefficient A_9^{+1} in Table I of [7] that contributes to C_8 for the $(\ell_a = 0, \ell_b = 1)$ configuration was listed as $-6/15$ when it should have been listed as $-6/25$. As noted earlier, some of the coefficients presented in [8,9] for the np-np configuration were incorrect.

The approach adopted here is to mainly present the angular coefficients and expressions for those cases which have not been given previously. Table X gives the expressions used to determine C_6 and C_8 for the ns-md case. Table XI gives the expressions used to determine C_6 and C_8 for the np-mp case. When $n = m$, one can set $\beta = 1$ and divide by 2 (setting $\beta = 0$ also works). If $n \neq m$, then β is ± 1. Explicit expressions are not given for C_{10} since they are somewhat unwieldy.

Care must be taken in evaluating Eq. (B15) in cases where both atoms are in excited states. It is possible that the energy spectrum of the pseudostate continuum could result in an energy denominator that was accidentally very close to zero. However, the adverse consequences of this can be largely eliminated by using LTO basis sets of different di-

TABLE X. The angular coefficients multiplying the radial sums for the C_6 and C_8 dispersion coefficient for the ns-md case. The contribution of each term is obtained by multiplying the radial sum with the angular coefficient. For reasons of compactness the energy denominator is omitted.

$\Sigma(\beta)$	$\Pi(\beta)$	$\Delta(\beta)$	Radial sum rule
			C_6
$\frac{2}{5}$	$\frac{1}{3}$	$\frac{2}{15}$	$(n_a0\|r\|n_s1)^2(n_b2\|r\|n_t1)^2$
$\frac{16}{35}$	$\frac{3}{7}$	$\frac{12}{35}$	$(n_a0\|r\|n_s1)^2(n_b2\|r\|n_t3)^2$
$\frac{2}{5}\beta$	$-\frac{4}{15}\beta$	$\frac{2}{15}\beta$	$(n_a0\|r\|n_s1)(n_s1\|r\|n_b2)(n_a0\|r\|n_t1)(n_t1\|r\|n_b2)$
			C_8
$\frac{3}{5}$	$\frac{1}{5}$	0	$(n_a0\|r\|n_s1)^2(n_b2\|r^2\|n_t0)^2$
$\frac{2}{7}$	$\frac{10}{49}$	$\frac{18}{49}$	$(n_a0\|r\|n_s1)^2(n_b2\|r^2\|n_t2)^2$
$\frac{14}{25}$	$\frac{12}{25}$	$\frac{6}{25}$	$(n_a0\|r^2\|n_s2)^2(n_b2\|r\|n_t1)^2$
$\frac{24}{35}$	$\frac{146}{245}$	$\frac{17}{49}$	$(n_a0\|r\|n_s1)^2(n_b2\|r^2\|n_t4)^2$
$\frac{117}{175}$	$\frac{111}{175}$	$\frac{93}{175}$	$(n_a0\|r^2\|n_s2)^2(n_b2\|r^1\|n_t3)^2$
$\frac{24}{35}$	$-\frac{8}{35}$	$-\frac{4}{35}$	$(n_a0\|r\|n_s1)^2(n_b2\|r\|n_t1)(n_t1\|r^3\|n_b2)$
$\frac{88}{105}$	$\frac{16}{45}$	$-\frac{244}{315}$	$(n_a0\|r\|n_s1)^2(n_b2\|r\|n_t3)(n_t3\|r^3\|n_b2)$
$\frac{24}{35}\beta$	$-\frac{8}{35}\beta$	$-\frac{4}{35}\beta$	$(n_a0\|r\|n_s1)(n_s1\|r\|n_b2)(n_a0\|r\|n_t1)(n_t1\|r^3\|n_b2)$
$\frac{4}{7}\beta$	$-\frac{12}{35}\beta$	$\frac{12}{35}\beta$	$(n_a0\|r\|n_s1)(n_s1\|r\|n_b2)(n_a0\|r^2\|n_t2)(n_t2\|r^2\|n_b2)$
$\frac{24}{35}\beta$	$-\frac{8}{35}\beta$	$-\frac{4}{35}\beta$	$(n_a0\|r\|n_s1)(n_s1\|r\|n_b2)(n_a0\|r^3\|n_t3)(n_t3\|r\|n_b2)$

mension to evaluate the dispersion coefficients and checking whether this leads to large changes in the coefficients.

4. Treatment of the core

It is desirable to add the contribution of the core into the van der Waals coefficients. Although the effect is small for Li, for the heavier alkali-metal atoms the core can contribute more than 5% to the dispersion coefficients for the ground state.

The key to including the core is to examine how the core will affect the oscillator strength sum rules. The initial state of the alkali-metal atom can be regarded as a simple product of the core ($|00\rangle$) multiplied by the state of the valence electron ($|LM\rangle$):

$$\Psi_{\text{init}} = |00{:}LM\rangle.$$

(B16)

Now consider an excitation out of the core with the valence electron remaining a spectator; the wave function for this final state is

$$\Psi_{\text{fin}} = |\ell m{:}LM\rangle.$$

(B17)

This state is an uncoupled state, but it can be written in a coupled representation as

$$|\ell m{:}LM\rangle = \sum_{L_T M_T} \langle \ell m L M | L_T M_T \rangle |\ell L{:}L_T M_T \rangle.$$

(B18)

TABLE XI. The angular coefficients multiplying the radial sums for dispersion coefficients C_6 and C_8 for the n_ap-n_bp case. The angular coefficients when $n_a=n_b$ are easily obtained by setting $\beta=1$ and dividing by 2. For reasons of compactness the energy denominator is omitted.

$\Sigma_1^+(\beta)$	$\Sigma_2^+(\beta)$	$\Sigma^-(\beta)$	$\Pi(\beta,+1)$	$\Pi(\beta,-1)$	$\Delta(\beta)$	Radial sum rule
			C_6			
0	$\frac{2}{3}$	0	0	0	0	$(n_a1|r|n_s0)^2(n_b1|r|n_t0)^2$
$\frac{4}{15}$	$\frac{2}{15}$	0	$\frac{1}{30}$	$\frac{3}{10}$	$\frac{2}{15}$	$(n_a1|r|n_s0)^2(n_b1|r|n_t2)^2$
$\frac{4}{15}$	$\frac{2}{15}$	0	$\frac{1}{30}$	$\frac{3}{10}$	$\frac{2}{15}$	$(n_a1|r|n_s2)^2(n_b1|r|n_t0)^2$
$\frac{14}{75}$	$\frac{38}{75}$	$\frac{8}{25}$	$\frac{31}{75}$	$\frac{1}{5}$	$\frac{16}{75}$	$(n_a1|r|n_s2)^2(n_b1|r|n_t2)^2$
0	$\frac{2}{3}\beta$	0	0	0	0	$(n_a1|r|n_s0)(n_s0|r|n_b1)(n_a1|r|n_t0)(n_t0|r|n_b1)$
$\frac{8}{15}\beta$	$\frac{4}{15}\beta$	0	$\frac{1}{15}\beta$	$-\frac{3}{5}\beta$	$\frac{4}{15}\beta$	$(n_a1|r|n_s0)(n_s0|r|n_b1)(n_a1|r|n_t2)(n_t2|r|n_b1)$
$\frac{14}{75}\beta$	$\frac{38}{75}\beta$	$-\frac{8}{25}\beta$	$\frac{31}{75}\beta$	$-\frac{1}{5}\beta$	$\frac{16}{75}\beta$	$(n_a1|r|n_s2)(n_s2|r|n_b1)(n_a1|r|n_t2)(n_t2|r|n_b1)$
			C_8			
0	$\frac{18}{25}$	0	$\frac{6}{25}$	0	0	$(n_a1|r|n_s0)^2(n_b1|r^2|n_t1)^2$
0	$\frac{18}{25}$	0	$\frac{6}{25}$	0	0	$(n_a1|r^2|n_s1)^2(n_b1|r|n_t0)^2$
$\frac{12}{25}$	$\frac{21}{125}$	$\frac{9}{125}$	$\frac{3}{25}$	$\frac{63}{125}$	$\frac{27}{125}$	$(n_a1|r^2|n_s1)^2(n_b1|r|n_t2)^2$
$\frac{12}{25}$	$\frac{21}{125}$	$\frac{9}{125}$	$\frac{3}{25}$	$\frac{63}{125}$	$\frac{27}{125}$	$(n_a1|r|n_s2)^2(n_b1|r^2|n_t1)^2$
$\frac{3}{7}$	$\frac{24}{175}$	0	$\frac{3}{175}$	$\frac{3}{7}$	$\frac{6}{35}$	$(n_a1|r^2|n_s3)^2(n_b1|r|n_t0)^2$
$\frac{3}{7}$	$\frac{24}{175}$	0	$\frac{3}{175}$	$\frac{3}{7}$	$\frac{6}{35}$	$(n_a1|r|n_s0)^2(n_b1|r^2|n_t3)^2$
$\frac{36}{175}$	$\frac{648}{875}$	$\frac{342}{875}$	$\frac{3}{5}$	$\frac{219}{875}$	$\frac{246}{875}$	$(n_a1|r|n_s2)^2(n_b1|r^2|n_t3)^2$
$\frac{36}{175}$	$\frac{648}{875}$	$\frac{342}{875}$	$\frac{3}{5}$	$\frac{219}{875}$	$\frac{246}{875}$	$(n_a1|r^2|n_s3)^2(n_b1|r|n_t2)^2$
0	$\frac{24}{35}$	0	$-\frac{8}{35}$	0	$-\frac{4}{35}$	$(n_a1|r|n_s0)^2(n_b1|r|n_t2)(n_t2|r^3|n_b1)$
0	$\frac{24}{35}$	0	$-\frac{8}{35}$	0	$-\frac{4}{35}$	$(n_a1|r|n_s2)(n_s2|r^3|n_a1)(n_b1|r|n_t0)^2$
0	$\frac{96}{175}$	$-\frac{72}{175}$	$\frac{4}{25}$	$\frac{36}{175}$	$-\frac{76}{175}$	$(n_a1|r|n_s2)(n_s2|r^3|n_a1)(n_b1|r|n_t2)^2$
0	$\frac{96}{175}$	$-\frac{72}{175}$	$\frac{4}{25}$	$\frac{36}{175}$	$-\frac{76}{175}$	$(n_a1|r|n_s2)^2(n_b1|r|n_t2)(n_t2|r^3|n_b1)$
0	$\frac{24}{35}\beta$	0	$-\frac{8}{35}\beta$	0	$-\frac{4}{35}\beta$	$(n_a1|r|n_s0)(n_s0|r|n_b1)(n_a1|r^3|n_t2)(n_t2|r|n_b1)$
0	$\frac{24}{35}\beta$	0	$-\frac{8}{35}\beta$	0	$-\frac{4}{35}\beta$	$(n_a1|r|n_s0)(n_s0|r|n_b1)(n_a1|r|n_t2)(n_t2|r^3|n_b1)$
0	$\frac{96}{175}\beta$	$\frac{72}{175}\beta$	$\frac{4}{25}\beta$	$-\frac{36}{175}\beta$	$-\frac{76}{175}\beta$	$(n_a1|r|n_s2)(n_s2|r|n_b1)(n_a1|r|n_t2)(n_t2|r^3|n_b1)$
0	$\frac{96}{175}\beta$	$\frac{72}{175}\beta$	$\frac{4}{25}\beta$	$-\frac{36}{175}\beta$	$-\frac{76}{175}\beta$	$(n_a1|r|n_s2)(n_s2|r|n_b1)(n_a1|r^3|n_t2)(n_t2|r|n_b1)$
$\frac{24}{25}\beta$	$\frac{42}{125}\beta$	$-\frac{18}{125}\beta$	$\frac{6}{25}\beta$	$-\frac{126}{125}\beta$	$\frac{54}{125}\beta$	$(n_a1|r^2|n_s1)(n_s1|r^2|n_b1)(n_a1|r|n_t2)(n_t2|r|n_b1)$
$\frac{6}{7}\beta$	$\frac{48}{175}\beta$	0	$\frac{6}{175}\beta$	$-\frac{6}{7}\beta$	$\frac{12}{35}\beta$	$(n_a1|r|n_s0)(n_s0|r|n_b1)(n_a1|r^2|n_t3)(n_t3|r^2|n_b1)$
$\frac{72}{175}\beta$	$\frac{1296}{875}\beta$	$-\frac{684}{875}\beta$	$\frac{6}{5}\beta$	$-\frac{438}{875}\beta$	$\frac{492}{875}\beta$	$(n_a1|r|n_s2)(n_s2|r|n_b1)(n_a1|r^2|n_t3)(n_t3|r^2|n_b1)$
0	$\frac{36}{25}\beta$	0	$\frac{12}{25}\beta$	0	0	$(n_a1|r|n_s0)(n_s0|r|n_b1)(n_a1|r^2|n_t1)(n_t1|r^2|n_b1)$

The oscillator strength for a transition to $|\ell m:LM\rangle$ can be decomposed in terms of transitions to the $|\ell L:L_TM_T\rangle$ coupled states as

$$f^\ell(00LM \to \ell mLM) = \sum_{L_TM_T} |\langle \ell mLM|L_TM_T\rangle|^2$$
$$\times f^\ell(0L:LM \to \ell L:L_TM_T). \quad (B19)$$

Similarly, the oscillator strength in the coupled representation can be decomposed:

$$f^\ell(0L:LM \to \ell L:L_TM_T) = \sum_{m'M'} f^\ell(00:LM' \to \ell m':LM')$$
$$\times |\langle \ell m'LM'|L_TM_T\rangle|^2. \quad (B20)$$

We are interested in the contribution that the core oscillator strength $f^\ell(00:LM'=M \to \ell m':LM'=M)$ makes to $f^\ell(0L:LM \to \ell L:L_TM_T)$. The excitations from the core occur independently of the valence spectator state $|00:LM\rangle$, so $f^\ell(00LM \to \ell mLM)$ does not depend on M (or L)—e.g.,

$$f^\ell(\ell L:LM \to \ell L:L_TM_T) = \sum_{m'M'} |\langle \ell m'LM'|L_TM_T\rangle|^2$$
$$\times f^\ell(00 \to \ell m'). \quad (B21)$$

So the oscillator strength we are interested in can be written

$$f^\ell(\ell LM:LM \to \ell LM:L_TM_T) = \frac{1}{2L+1}\sum_{m'M'} f^\ell(00 \to \ell m')$$
$$\times |\langle \ell m'LM'|L_TM_T\rangle|^2. \quad (B22)$$

Further, the value of $f^\ell(00LM \to \ell mLM)$ does not depend on m since the angular momentum of the core is zero and summing over the m' magnetic sublevels gives the usual absorption oscillator strength $f^\ell(0 \to \ell)$:

$$f^\ell(\ell LM{:}LM \to \ell L{:}L_T M_T) = \frac{1}{2L+1} \sum_{m'M'} \frac{f^\ell(0 \to \ell)}{2\ell+1}$$

$$\times |\langle \ell m'LM'|L_T M_T\rangle|^2$$

$$= \frac{f^\ell(0 \to \ell)}{(2L+1)(2\ell+1)}. \quad \text{(B23)}$$

The absorption oscillator strength for the $(0 \to \ell)$ core excitation with an $|LM\rangle$ spectator is just

$$f^\ell(\ell L{:}L \to \ell L{:}L_T) = \frac{(2L_T+1)}{(2L+1)(2\ell+1)} f^\ell(0 \to \ell). \quad \text{(B24)}$$

The oscillator strength is distributed into L_T final states according to the $(2L_T+1)$ degeneracy factor.

Inclusion of the core into the dispersion sum rules is done quite easily. Any term in a sum rule with a $|\langle nl|r^k|n'l'\rangle|^2$-type structure can be replaced by the corresponding oscillator strength. The core terms are including by simply adding them to the arrays storing oscillator strengths and squares of radial matrix elements. For example, the $f^1(2p \to nd)$ array is augmented by an additional f value of 10/9 (the core f value is taken as the number of core electrons) and an excitation energy of 0.745 hartree [19]. The core was included in the calculation of all the C_n dispersion coefficients.

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