Many-body calculations of the static atom-wall interaction potential for alkali-metal atoms

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We present third-order many-body perturbation theory calculations of the Lennard-Jones C_3 coefficient for the alkali-metal atoms lithium, sodium, potassium, rubidium, cesium, and francium. All-order singles-doubles calculations of C_3 are also presented for lithium, sodium, and potassium. For lithium and sodium the present values of C_3 are compared with other theoretical and semiempirical values. [S1050-2947(98)04404-7]

I. INTRODUCTION

The long-range interaction between an atom and a perfect conducting wall is dominated by a static image potential, first considered by Lennard-Jones [1] more than 60 years ago. At distances from the wall Z, large compared to the atomic size, the Lennard-Jones potential is given by the dipole-dipole interaction between the atom and its image:

$$V(Z) = -\frac{e^2 C_3}{Z^3}. \tag{1}$$

The coefficient C_3 in Eq. (1) is the expectation value of the operator[1]

$$\frac{1}{16} \sum_{i,j} (x_i x_j + y_i y_j + 2 z_i z_j),$$

in the atomic ground state. Here, $\boldsymbol{r}_i = (x_i, y_i, z_i)$ is the coordinate of the ith atomic electron with respect to the nucleus. For an atom with a spherically symmetric ground state, one can replace C_3 by the equivalent expression

$$C_3 = \frac{1}{12} \langle 0 | R^2 | 0 \rangle,$$

where $\boldsymbol{R} = \Sigma_i \boldsymbol{r}_i$. It is worth noting that the Lennard-Jones interaction constant is an integral part of models accounting for the finite conductivity of the wall material by Bardeen [2] and by Mavroyannis [3]. In addition, the wall-atom-wall interaction constant for small wall separation distances is also proportional to C_3, as discussed in Refs. [4,5].

Precise values of C_3 for lithium were obtained by Yan and Drake [6] from an elaborate configuration interaction (CI) calculation and confirmed by an independent calculation by Yan et al. [4]. The CI value of C_3 for lithium is in close agreement with the value inferred from a variational calculation by King [7]. These accurate values of C_3 for lithium

are about 2% smaller than the corresponding value obtained from a Hartree-Fock (HF) calculation.

An accurate semiempirical value of C_3 for sodium was also obtained by Kharchenko et al. [5] from an analysis of the S_{-1} sum rule:

$$S_{-1} = \frac{2}{3} \langle R^2 \rangle = \sum_n \frac{f_n}{E_0 - E_n},$$

where f_n is the oscillator strength of the transition from the ground state to an excited state n. The quantities E_0 and E_n are energies of the ground state and excited state, respectively. This value differs from the HF value of C_3 by about 10%. While more elaborate calculations [8] improve the agreement between theoretical and semiempirical values for sodium somewhat, all calculations known to the authors disagree with the semiempirical value by more than 2%.

In the paragraphs below, we carry out third-order many-body perturbation theory (MBPT) calculations of C_3 for all alkali-metal atoms. For lithium, these calculations differ from the CI value by about 0.2%, while for sodium, they differ from the semiempirical value by 0.6%. Comparisons of third-order MBPT calculations of dipole transition amplitudes with precise experimental values [9] lead us to believe that the present MBPT calculations are accurate to better than 5% for all alkali-metal atoms.

For lithium, sodium, and potassium, we also carry out all-order many-body calculations using the relativistic singles-doubles (SD) approach [10]. The values of C_3 obtained from these all-order calculations are in very close agreement with the CI value for lithium and the semiempirical value for sodium. The SD value of C_3 for potassium is 0.8% smaller than the MBPT value. The aim of this paper is twofold: first, to provide accurate third-order MBPT values of C_3 for all alkali-metal atoms; and second, to confirm the semiempirical value of C_3 for sodium using an all-order SD calculation.

II. MBPT

The present calculations of C_3 are based on the relativistic *no-pair* Hamiltonian [11], $H = H_0 + V$, which in second quantization is given by

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[1]There is a factor of 2 error in the expression for this operator given in Ref. [1].

TABLE I. Contributions to $S^{(1)}$ and $2T^{(1)}$.

Term	Li	Na	K	Rb	Cs	Fr
$S_v^{(1)}$	17.7393	20.7148	31.5133	35.4253	42.4514	40.5414
$S_c^{(1)}$	0.8904	6.4050	19.4792	31.4361	51.2239	65.6445
$S^{(1)}$	18.6297	27.1198	50.9924	66.8614	93.6753	106.1860
$2T_v^{(1)}$	0.0000	−0.1046	−0.3894	−0.6746	−1.0407	−1.8341
$2T_c^{(1)}$	0.0000	−2.4128	−7.6073	−13.2647	−22.9727	−30.0423
$2T^{(1)}$	0.0000	−2.5174	−7.9967	−13.9393	−24.0134	−31.8764
$\langle R^2 \rangle^{(1)}$	18.6297	24.6024	42.9957	52.9221	69.6618	74.3096

$$H_0 = \sum_i \epsilon_i a_i^\dagger a_i, \quad V = \frac{1}{2} \sum_{i,j,k,l} v_{ijkl} a_i^\dagger a_j^\dagger a_k a_l - \sum_{i,j} U_{ij} a_i^\dagger a_j. \tag{2}$$

Here, ϵ_i is an eigenvalue of the one-electron Dirac equation that defines the single-electron orbitals, and U designates the central potential used to approximate the effect of the atomic cloud in the one-electron Dirac equation. For alkali-metal atoms, we choose $U = V_{HF}$; the ''frozen-core'' Hartree-Fock potential of the $(N-1)$-electron closed-shell ionic core.

The quantities a_i and $a_i^\dagger$ are electron destruction and creation operators, respectively. In Eq. (2), the summation indices i, j, k, and l are restricted to range over positive-energy states only. The quantity v_{ijkl} in Eq. (2) is the Coulomb interaction:

$$v_{ijkl} = \left\langle ij \left| \frac{1}{r_{12}} \right| kl \right\rangle.$$

Later, we use the notation $\widetilde{v}_{ijkl} = v_{ijkl} - v_{ijlk}$ to designate antisymmetrized Coulomb matrix elements.

A. Decomposition of R^2

The operator R^2 is decomposed into the sum of a single-particle operator S and a two-particle operator T, $R^2 = S + 2T$, where

$$S = \sum_{i,j} s_{ij} a_i^\dagger a_j, \tag{3}$$

$$T = \frac{1}{2} \sum_{i,j,k,l} t_{ijkl} a_i^\dagger a_j^\dagger a_l a_k. \tag{4}$$

Here, $s_{ij} = \langle i | r^2 | j \rangle$ and $t_{ijkl} = \langle i | \mathbf{r} | k \rangle \cdot \langle j | \mathbf{r} | l \rangle$.

In Eqs. (3) and (4), and in subsequent equations, we use the following conventions for the summation indices: the subscript v designates the valence orbital; subscripts a, b, c, at the beginning of the alphabet designate occupied core orbitals; subscripts n, m, o, near the middle of the alphabet designate virtual orbitals; and the subscripts i, j, k, and l designate arbitrary orbitals, either occupied or virtual. We also use the notation $\widetilde{t}_{ijkl} = t_{ijkl} - t_{ijlk}$ for the antisymmetrized matrix element.

It should be mentioned that the diamagnetic susceptibility of an atom can be expressed in terms of S by

$$\chi = -\frac{e^2}{6mc^2} \langle S \rangle.$$

Indeed, in Ref. [1], Lennard-Jones used this relation to obtain approximate values of C_3 from measured susceptibilities. It is also interesting to note that the ground-state atomic form factor for elastic scattering of fast electrons $F(q)$, in the limit of small momentum transfer q, is given in terms of $\langle S \rangle$ by

$$F(q) = 1 - \frac{q^2}{6Z} \langle S \rangle,$$

where Z is the nuclear charge of the atom. Since we determine the expectation values of the operators S and T separately, the results below can also be applied to calculations of susceptibilities and elastic scattering form factors.

B. First-order MBPT

First-, second-, and third-order matrix elements of single-particle operators such as S were worked out in [12] and later applied to transition amplitudes in alkali-metal atoms in [9]. The first-order matrix elements of the operators S and T can be conveniently divided into valence and core contributions $S^{(1)} = S_v^{(1)} + S_c^{(1)}$ and $T^{(1)} = T_v^{(1)} + T_c^{(1)}$, with

$$S_v^{(1)} = s_{vv}, \tag{5}$$

$$S_c^{(1)} = \sum_b s_{bb}, \tag{6}$$

$$T_v^{(1)} = \sum_a \widetilde{t}_{vava}, \tag{7}$$

$$T_c^{(1)} = \frac{1}{2} \sum_{ab} \widetilde{t}_{abab}. \tag{8}$$

The first-order contributions to S are given for alkali-metal atoms in the upper two rows of Table I. As might be expected, the core contribution to S is larger than the valence contribution for cesium and francium. The matrix elements of T are given in the fourth, fifth, and sixth rows of the table and the first-order value of $\langle R^2 \rangle$ is given in the last row. Since we use HF orbitals as our basis, the first-order matrix element is just the HF matrix element. For lighter alkali-metal atoms, the approximation suggested by Lennard-Jones

TABLE II. Contributions to $S^{(2)}$ and $2T^{(2)}$.

Term	Li	Na	K	Rb	Cs	Fr
$S^{(2)}$	0.0019	0.0386	0.1344	0.2197	0.3382	0.5450
$2T_c^{(2)}$	-0.0319	-0.3484	-2.4737	-4.2103	-8.5791	-11.7083
$2T_s^{(2)}$	0.0000	-0.0006	0.0010	0.0123	0.0203	0.1106
$2T_d^{(2)}$	-0.0868	-0.4363	-2.1891	-3.3702	-5.4432	-6.6505
$2T_e^{(2)}$	0.0000	-0.0052	-0.0128	-0.0135	-0.0152	0.0063
$2T^{(2)}$	-0.1188	-0.7905	-4.6746	-7.5817	-14.0172	-18.2419
$\langle R^2 \rangle^{(2)}$	-0.1168	-0.7519	-4.5402	-7.3620	-13.6789	-17.6969

of neglecting contributions from T is seen to be well justified; however, for the heavier alkali-metal atoms these contributions are seen to be substantial. The present relativistic HF values are smaller than previously published nonrelativistic HF values [13], presumably because of the relativistic contraction of inner orbitals. As mentioned in the Introduction, the HF value of $\langle R^2 \rangle$ differs from the accurate semiempirical value for sodium by 10%. This difference, which is from second- and higher-order corrections, grows rapidly along the alkali-metal sequence from lithium to francium.

C. Second-order MBPT

There is a single second-order contribution to S, which is the leading term in a perturbation expansion of the random-phase approximation (RPA):

$$S^{(2)} = \sum_{n,b} \frac{s_{bn} \widetilde{v}_{vnvb}}{\epsilon_b - \epsilon_n} + \sum_{n,b} \frac{\widetilde{v}_{vbvn} s_{nb}}{\epsilon_b - \epsilon_n}. \qquad (9)$$

The more complicated second-order matrix element of T is the sum of four terms, $T^{(2)} = T_c^{(2)} + T_s^{(2)} + T_d^{(2)} + T_e^{(2)}$, where

$$T_c^{(2)} = \sum_{a,b,m,n} \frac{\widetilde{t}_{abmn} v_{mnab}}{\epsilon_{ab} - \epsilon_{mn}},$$

$$T_s^{(2)} = \sum_{a,b,m} \frac{\widetilde{t}_{abvm} v_{mvab}}{\epsilon_{ab} - \epsilon_{mv}} + \sum_{a,b,m} \frac{\widetilde{t}_{vmab} v_{abmv}}{\epsilon_{ab} - \epsilon_{mv}},$$

$$T_d^{(2)} = \sum_{m,n,b} \frac{\widetilde{t}_{vbmn} v_{mnvb}}{\epsilon_{vb} - \epsilon_{mn}} + \sum_{m,n,b} \frac{\widetilde{t}_{mnvb} v_{vbmn}}{\epsilon_{vb} - \epsilon_{mn}},$$

$$T_e^{(2)} = \sum_{n,b} \frac{\widetilde{t}_{bn} \widetilde{v}_{vnvb}}{\epsilon_b - \epsilon_n} + \sum_{n,b} \frac{\widetilde{v}_{vbvn} \widetilde{t}_{nb}}{\epsilon_b - \epsilon_n}. \qquad (10)$$

In the above equations, we have introduced $\widetilde{t}_{ij} = \Sigma_b \widetilde{t}_{ibjb}$ and used the notation $\epsilon_{xy} = \epsilon_x + \epsilon_y$.

The sums over intermediate states in the above expressions are carried out using B-spline basis functions, as discussed in Ref [14]. The contribution of $S^{(2)}$ is given in the top row of Table II, and a breakdown of contributions to $T^{(2)}$ together with the entire second-order value of $\langle R^2 \rangle$ is given in the following rows.

D. Third-order MBPT

The third-order correction $S^{(3)}$ consists of five parts: $S_{RPA}^{(3)}$, the second term in an expansion of RPA; $S_{BO}^{(3)}$, the Brueckner-orbital contribution; $S_{SR}^{(3)}$, the structural radiation correction; $S_{no}^{(3)}$, the wave-function normalization correction, and $S_{diag}^{(3)}$, a diagonal third-order contribution that contributes only for scalar operators such as S. These terms are written out in detail in Refs. [9,12] and will not be repeated here. We do not evaluate third-order corrections to T for reasons explained below in our discussion of the SD approximation. A detailed breakdown of $S^{(3)}$ is given in Table III. These corrections are dominated by the Brueckner-orbital contribution, which accounts for the contraction of the valence electron wave function caused by the interaction of the valence electron with the dipole moment that it induces in the atomic core. In Table III, as in Ref. [9], we include third-order and all higher-order RPA corrections in the term $S_{RPA}^{(3)}$.

Finally, a summary of the first-, second-, and third-order corrections to $\langle R^2 \rangle$ is given in Table IV. It is far from clear, examining this table, that the fourth- and higher-order contributions to the matrix element are negligible. To assess the role of these higher-order terms, we now turn to all-order MBPT techniques.

III. SD APPROXIMATION

To go beyond the third-order MBPT calculations for atoms with one valence electron, we make use of the singles-

TABLE III. Contributions to $S^{(3)}$.

Term	Li	Na	K	Rb	Cs	Fr
$S_{RPA}^{(3)}$	0.0002	-0.0028	0.0024	0.0094	0.0210	0.0415
$S_{BO}^{(3)}$	-0.2533	-1.1042	-4.1836	-5.8553	-8.8675	-9.4181
$S_{SR}^{(3)}$	0.0033	0.0251	0.1484	0.2414	0.4101	0.5264
$S_{no}^{(3)}$	-0.0079	-0.0404	-0.2305	-0.3447	-0.5636	-0.6761
$S_{diag}^{(3)}$	0.0008	0.0655	-0.1421	-0.2422	-0.6281	-0.6514
$\langle R^2 \rangle^{(3)}$	-0.2570	-1.0568	-4.4054	-6.1914	-9.6281	-10.1776

TABLE IV. Summary of perturbation theory for $\langle R^2 \rangle$.

Term	Li	Na	K	Rb	Cs	Fr
$\langle R^2 \rangle^{(1)}$	18.6297	24.6024	42.9957	52.9221	69.6618	74.3096
$\langle R^2 \rangle^{(2)}$	-0.1168	-0.7519	-4.5402	-7.3620	-13.6789	-17.6969
$\langle R^2 \rangle^{(3)}$	-0.2570	-1.0568	-4.4054	-6.1914	-9.6281	-10.1776
$\langle R^2 \rangle_{\mathrm{pert}}$	18.2559	22.7936	34.0501	39.3687	46.3548	46.4351

doubles approach described and developed in Ref. [10]. In this approach, the wave function Ψ_v of the atomic system is represented as

$$|\Psi_v\rangle = \left(1 + \sum_{m,a} \rho_{ma} a_m^\dagger a_a + \frac{1}{2} \sum_{m,n,a,b} \rho_{mnab} a_m^\dagger a_n^\dagger a_a a_b \right.$$
$$\left. + \sum_{m \neq v} \rho_{mv} a_m^\dagger a_v + \sum_{m,n,a} \rho_{mnva} a_m^\dagger a_n^\dagger a_a a_v \right) |\Phi_v\rangle,$$
(11)

where Φ_v is the unperturbed wave function. The SD wave function accounts for single and double excitation from the core, single excitations of the valence electron, and simultaneous excitations of the valence electron and a single core electron. Later we will use the antisymmetrized combinations of the doubles coefficients: $\widetilde{\rho}_{mnab} = \rho_{mnab} - \rho_{nmab}$, and $\widetilde{\rho}_{mnva} = \rho_{mnva} - \rho_{nmva}$.

Substituting the wave function from Eq. (11) into the no-pair Hamiltonian, one obtains a set of coupled algebraic equations given in Ref. [10] for the singles and doubles excitation coefficients. Iteration of these equations corresponds to the order-by-order hierarchy of MBPT, with a major set of diagrams iterated to all orders. After the ρ coefficients are determined, one is in a position to calculate matrix elements of operators corresponding to physical observables. The diagonal matrix element of a one-particle operator $Z = \sum_{i,j} z_{ij} a_i^\dagger a_j$ is represented as

$$Z_{vv} = Z_{\mathrm{core}} + \frac{Z_{\mathrm{val}}}{1 + \delta N_v}.$$
(12)

Here, δN_v is the valence electron contribution to normalization of $|\Psi_v\rangle$. Z_{val} is represented as a sum of 21 terms given in Ref. [10]. The expression for Z_{core} was not given in [10], since it vanishes for nonscalar operators. However, S is a scalar operator, so we must include these additional terms. They are given by $Z_{\mathrm{core}} = Z^{(0)} + Z^{(1)} + \cdots + Z^{(6)}$, with

$$Z^{(0)} = \sum_a z_{aa}, \quad Z^{(1)} = 2 \sum_{a,m} \rho_{ma} z_{am},$$

$$Z^{(2)} = -\sum_{a,b,m} \rho_{ma} \rho_{mb} z_{ab}, \quad Z^{(3)} = \sum_{a,m,n} \rho_{ma} \rho_{na} z_{mn},$$

$$Z^{(4)} = 2 \sum_{a,b,m,n} \rho_{nb} \widetilde{\rho}_{mnab} z_{am},$$

$$Z^{(5)} = \sum_{a,b,m,n,r} \rho_{mnab} \widetilde{\rho}_{mrab} z_{nr},$$

$$Z^{(6)} = -\sum_{a,b,c,m,n} \widetilde{\rho}_{mnca} \rho_{mncb} z_{ab}.$$

We now turn to a discussion of the diagonal matrix element of T. It is convenient to separate this operator into a sum of zero-body T_0, one-body T_1, and two-body T_2 parts:

$$T_0 = -\frac{1}{2} \sum_{a,b} \widetilde{t}_{abab},$$
(13)

$$T_1 = \sum_{i,j} \widetilde{t}_{ij} a_i^\dagger a_j,$$
(14)

$$T_2 = \frac{1}{2} \sum_{i,j,k,l} t_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k : .$$
(15)

Here :: denotes the normal form of operator products. The effective one-body matrix element $\widetilde{t}_{ij}$ was defined previously. Matrix elements of the one-body operator T_1 can be calculated in precisely the same way as the matrix elements of the operator S, discussed earlier.

At this point, we derive matrix elements of the two-body part T_2. The resulting expression consists of 36 terms, which will not be written out in detail. Fortunately, there is a significant reduction in the number of terms for the lithium ground state due to angular selection rules. We obtain only 14 nonvanishing terms for the case of lithium. Below we separate these terms into groups corresponding to the effective MBPT order of contribution. Such a separation is based on the fact that the all-order doubles coefficients ρ_{mnab} and ρ_{mnva} appear initially in the first-order MBPT wave function, while the singles coefficients ρ_{ma} and ρ_{mv} appear starting from the second order. We find effective second order:

$$T_2^{(a)} = \sum_{a,b,m,n} t_{mnab} \widetilde{\rho}_{mnab}, \quad T_2^{(b)} = 2 \sum_{a,m,n} t_{mnva} \widetilde{\rho}_{mnva},$$

effective third order

$$T_2^{(c)} = \frac{1}{2} \sum_{a,m,n,r,s} t_{mnrs} \widetilde{\rho}_{mnva} \widetilde{\rho}_{rsva},$$

$$T_2^{(d)} = \sum_{a,b,m,n,r} \widetilde{t}_{bnar} \widetilde{\rho}_{nmva} \widetilde{\rho}_{mrvb},$$

$$T_2^{(e)} = \sum_{a,b,m,n,r} \widetilde{t}_{bmnr} \widetilde{\rho}_{mvva} \widetilde{\rho}_{nrab},$$

$$T_2^{(f)} = \sum_{a,b,m,n,r} \widetilde{t}_{bnrv} \widetilde{\rho}_{mnva} \widetilde{\rho}_{rmab},$$

TABLE V. Effective order-by-order contributions to $2T_2$ for lithium in the SD approach.

MBPT order	$2T_2$
$(2T_2)^{(2)}$	-0.140772
$(2T_2)^{(3)}$	0.003022
$(2T_2)^{(4)}$	-0.000232
$(2T_2)_{\text{norm}}$	0.000056
$2T_2$	-0.137926

$$T_2^{(g)} = \sum_{a,b,c,m,n,r} \widetilde{t}_{ncbr}\widetilde{\rho}_{mnab}\widetilde{\rho}_{mrac},$$

$$T_2^{(h)} = \frac{1}{4}\sum_{a,b,m,n,r,s} t_{mnrs}\widetilde{\rho}_{mnab}\widetilde{\rho}_{rsab},$$

$$T_2^{(i)} = \frac{1}{2}\sum_{a,b,m,n,r} \widetilde{t}_{nvrv}\widetilde{\rho}_{mrab}\widetilde{\rho}_{mnab},$$

$$T_2^{(j)} = -2\sum_{a,b,m,n,r} t_{mnrv}\widetilde{\rho}_{rvab}\widetilde{\rho}_{mnab},$$

effective fourth order

$$T_2^{(k)} = 2\sum_{a,m,n,r} t_{arnm}\rho_{rv}\widetilde{\rho}_{mnva},$$

$$T_2^{(l)} = 2\sum_{a,b,m,n,r} t_{mnrb}\rho_{ra}\widetilde{\rho}_{mnab},$$

$$T_2^{(m)} = 2\sum_{a,b,m,n} t_{bvmn}\rho_{va}\widetilde{\rho}_{mnab},$$

$$T_2^{(n)} = 2\sum_{a,m,n,r} t_{mnrv}\rho_{ra}\widetilde{\rho}_{nmva}.$$

The normalized matrix element of the two-body operator is given by an expression similar to Eq. (12):

$$(T_2)_{vv} = (T_2)_{\text{core}} + \frac{(T_2)_{\text{val}}}{1 + \delta N_v}, \tag{16}$$

where $(T_2)_{\text{core}}$ includes all terms of $\langle \Psi_v | T_2 | \Psi_v \rangle$ that are independent of v, such as $T_2^{(a)}$ and $T_2^{(g)}$, and $(T_2)_{\text{val}}$ includes

TABLE VI. Contributions to $\langle R^2 \rangle$ in the SD approach.

Term	Li	Na	K
S_{HF}	18.6287	27.1198	50.9924
S_{corr}	-0.2778	-1.0896	-3.7853
S_{tot}	18.3519	26.0302	47.2071
$(2T)_{\text{HF}}$	0.0000	-2.5174	-7.9967
$(2T)_{\text{corr}}$	-0.1389	-0.8836	-4.8868
$(2T)_{\text{tot}}$	-0.1389	-3.4010	-12.8835
$\langle R^2 \rangle_{\text{tot}}$	18.2130	22.6293	34.3236

TABLE VII. Comparison of many-body calculations for lithium.

	S	$2T$	$\langle R^2 \rangle$	C_3
Yan and Drake [6]	18.354614	-0.138610	18.216004	1.518000
King [7]	18.35474	-0.13861	18.21613	1.51801
SD	18.3519	-0.1389	18.2130	1.5178
CC	18.3460			
Third-order MBPT	18.3746	-0.1188	18.2558	1.5213

all other terms. The derivation of such a size-consistent normalization expression can be found in Ref. [10].

The present SD calculations for lithium include all non-vanishing terms in the expression for T_2. An order-by-order analysis of the contributions to the matrix element of T_2 for lithium, which is presented in Table V , shows that there is a strong suppression of contributions to T_2 with increasing effective order of MBPT.

Calculations of T_2 for sodium and other more complex atoms ideally require the evaluation of all 36 terms. Since the leading contribution to $\langle R^2 \rangle$ arises mainly from the operator S, and the contributions to T_2 become smaller with increasing effective order, we approximate the matrix element of T_2 for sodium by the effective second-order terms only. There is an additional effective second-order term, that vanishes for lithium, but remains finite for the other alkali-metal atoms:

$$(T_2)^{(o)} = 2\sum_{a,b,m} t_{mvab}\widetilde{\rho}_{vmab}. \tag{17}$$

In general, we expect the all-order SD results to be more reliable than the corresponding MBPT calculations. For example, in a particular case of one-particle operator, the SD approximation reproduces third-order MBPT contributions and, in addition, includes higher-order corrections.

Numerical results

We solve the SD equations numerically using a B-spline basis [14]. The basis set for lithium consists of partial waves with maximum angular momentum $l_{\max} = 4$. We use 25 out of 30 splines for each value of l. A breakdown of the contributions to the value of $\langle R^2 \rangle$ for lithium is given in Table VI.

The resulting value of $\langle R^2 \rangle$ for lithium, 18.213, is in close agreement with the value 18.216 from the calculations by Yan and Drake [6] and King [7]. The difference between the present value and the earlier ones is affected by two factors. First, the present calculations omitted triple excitations from the wave function. Including triple excitations would change

TABLE VIII. Comparison of values of C_3.

Term	Li	Na	K	Rb	Cs	Fr
Third-order MBPT	1.5213	1.8895	2.838	3.281	3.863	3.870
SD	1.5178	1.8858	2.860			
CI [6,7]	1.5180					
Ref. [4]	1.518(2)					
Ref. [5]		1.888				

the SD approach into an exact CI calculation. Second, the present calculations start from a Dirac-Hartree-Fock basis, thus relativistic effects are included in an *ab initio* fashion. We estimate relativistic corrections to be of order $(\alpha Z)^2$, which could explain a major part of the difference.

The singles-doubles calculations for sodium were performed using a basis set consisting of 27 out of 30 splines with $l_{max}=6$, while the results for potassium were obtained with a basis of 27 out of 30 splines with $l_{max}=5$. A breakdown of the contributions to $\langle R^2 \rangle$ for Na and K is also given in Table VI. In this table we explicitly separated contributions arising from the Hartree-Fock approximation (first-order matrix elements discussed in the MBPT section) and the correlation contributions beyond the Hartree-Fock approximation. The correlation effects tend to decrease the size of the atom, consistent with the MBPT results.

For heavier systems, in contrast to the case of lithium, we performed the calculations of the two-body part of two-particle operator T in effective second order only, as discussed earlier. The resulting value of $\langle R^2 \rangle$ for sodium, 22.63, is in good agreement with the semiempirical value of Kharchenko *et al.* [5], 22.65.

In addition to the SD approximation, we also performed relativistic coupled-cluster (CC) calculations, including one- and two-particle cluster operators. Only matrix elements of the one-particle operator S were calculated in this approach. A discussion of the CC method can be found in Ref. [15]. To solve the CC equations in intermediate normalization, we used the relativistic pair program by Salomonson and Öster [16]. To calculate the expectation value of the operator S, we adapted the program described in Ref. [17].

The CC calculations for lithium gave the value of $S=18.3460$ which is close to the value 18.3519 calculated in SD approximation. For the case of sodium, the CC value $S=25.8812$ agrees within 0.6% with the SD value. The coupled-cluster method treats triple excitations from the core partially, to the extent of including terms nonlinear in singles and doubles coefficients. On the other hand, the SD approximation omits such terms completely. Thus, numerical issues aside, the difference between these two approaches gives an indication of the importance of a full treatment of triple excitations.

IV. SUMMARY

In Table VII, we compare the present MBPT and all-order calculations of $\langle R^2 \rangle$ for lithium with the precise variational values from Refs. [6,7]. We see that the more elaborate calculations agree to better than 0.1%, and that MBPT overestimates C_3 by 0.2%.

For sodium, the comparisons of the all-order calculations of C_3 with the MBPT and with the precise values obtained in Refs. [4] and [5] are given in Table VIII. All of the values are in close agreement. In particular, the 3% difference between the theoretical and semiempirical values of C_3 noted in Ref. [5] has been reduced by an order of magnitude. For potassium, the MBPT and SD values agree to within 0.8%. Also in Table VIII, we present our MBPT predictions of C_3 for the heavier alkali-metal ions. As mentioned in the Introduction, we expect the MBPT calculations to be accurate to better than 5%.

ACKNOWLEDGMENTS

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