I. INTRODUCTION

The long-range interaction between an atom and a perfectly conducting wall is governed by the Lennard-Jones static image potential

\[ V(z) = -\frac{\epsilon^2 C_3}{z^3} , \]

where \( z \) is the distance between the atom and the wall. The coefficient \( C_3 \) in Eq. (1) is the expectation value of the operator

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

in the atomic ground state. Here, \( \mathbf{r}_i = (x_i, y_i, z_i) \) is the coordinate of the \( i \)-th 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 \( \mathbf{R} = \sum_i \mathbf{r}_i \). The Lennard-Jones interaction constant is important in models accounting for the finite conductivity of the wall material by Bardeen [2] and Mavroyannis [3]. Additionally, the wall-atom-wall interaction constant is important in models accounting for the finite conductivity of the wall material by Bardeen [2] and Mavroyannis [3].

Precise values of \( C_3 \) for lithium were obtained 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 value obtained from a Hartree-Fock (HF) calculation.

An accurate semi-empirical 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%. The more elaborate calculations by Per Jönsson et al. [6] improve the agreement between theoretical and semi-empirical values for sodium somewhat.

Third-order many-body perturbation theory calculations of \( C_3 \) for all alkali-metal atoms and all-order singles-doubles calculations of \( C_3 \) for Li, Na, and K were given by Derevianko et al. [9]. The all-order calculations for Li and Na were in close agreement with other precise values. More recently, Derevianko et al. [8] deduced accurate theoretical and semi-empirical values of \( C_3 \) for all alkali-metal atoms from oscillator-strength sum rules.

In the present work, we use finite-field many-body methods to obtain values of \( \langle R^2 \rangle \) and make comparisons with previous work. One advantage of the finite field-method is that all-order random-phase approximation (RPA) corrections are included from the start. A second advantage is that \( n \)-th order corrections to the energy give many-body perturbation theory (MBPT) corrections to matrix elements of \( R^2 \) normally associated with order \( (n+1) \). A third advantage is that matrix elements of one- and two-particle operators are essentially trivial to obtain, in contrast to the lengthy calculations
ordinary required.

II. METHOD

The method used here to evaluate the expectation value of the operator

\[ R^2 = \left( \sum_{i=1}^{N} r_i \right)^2 = \sum_i r_i^2 + 2 \sum_{i \neq j} r_i \cdot r_j \]  

(2)

is known as the “finite-field” method and widely used in quantum chemistry. We evaluate the ground-state expectation value of the operator by adding the scalar operator \( \lambda R^2 \) to the many-electron Hamiltonian and calculating the resulting energy \( E(\lambda) \). The desired expectation value is then given by

\[ \langle R^2 \rangle = \lim_{\lambda \to 0} \frac{dE}{d\lambda}. \]

To evaluate the energy, we use standard many-body methods.

The modified many-electron Hamiltonian may be written

\[ H = \sum_i h_0(i) + \frac{1}{2} \sum_{i \neq j} \left[ \frac{1}{r_{ij}} + 2 \lambda \mathbf{r}_i \cdot \mathbf{r}_j \right] - \sum_i U(r_i), \]

where,

\[ h_0 = c \mathbf{\alpha} \cdot \mathbf{p} + \beta mc^2 + V_{\text{ion}}(r) + \lambda r^2 + U(r). \]

Expressing the Hamiltonian in second-quantized form and normally ordering with respect to the closed core, we find

\[ H = E_0 + \sum_i \epsilon_i :a_i^\dagger a_i: + \frac{1}{2} \sum_{ijkl} v_{ijkl} :a_i^\dagger a_j^\dagger a_l a_k:\]

\[ + \sum_{ij} (V_{\text{HF}} - U)_{ij} :a_i^\dagger a_j,: \]

(3)

where

\[ E_0 = \sum_a \epsilon_a + \sum_a \left( \frac{1}{2} V_{\text{HF}} - U \right)_{aa}. \]

In the above, equations,

\[ (V_{\text{HF}})_{ij} = \sum_a [v_{iaja} - v_{iaaj}], \]

with

\[ v_{ijkl} = \langle ij | \frac{1}{r_{12}} + 2 \lambda \mathbf{r}_i \cdot \mathbf{r}_j | kl \rangle. \]

The lowest approximation to the wave function for a closed-shell atom is

\[ \Psi_0 = a^\dagger_1 a^\dagger_2 \cdots a^\dagger_n |0\rangle. \]

The expectation of the Hamiltonian in this state, which gives the first approximation to the ground-state energy, is

\[ \langle \Psi_0 | H | \Psi_0 \rangle = E_0 = \sum_a \epsilon_a + \sum_a \left( \frac{1}{2} V_{\text{HF}} - U \right)_{aa}. \]

In particular, if we choose \( U = V_{\text{HF}} \), then the corresponding value of the closed-shell energy is

\[ E_{\text{HF}} = \sum_a [\epsilon_a - \frac{1}{2} (V_{\text{HF}})_{aa}]. \]

III. RESULTS

A. HF-level

We consider an atom with one electron beyond closed shells. The core and valence energies are given at the HF level of approximation by

\[ E^{(\text{HF})}_c = \sum_a [\epsilon_a - \frac{1}{2} (V_{\text{HF}})_{aa}] \]

(4)

\[ E^{(\text{HF})}_v = \epsilon_v \]

(5)

where the summation index \( a \) ranges over closed shells, and where \( \epsilon_v \) is the eigenvalue of the valence “frozen core” (Dirac)-Hartree-Fock equation.

In setting up the HF equations, we add \( \lambda r^2 \) to the nuclear potential and add \( 2 \lambda \mathbf{r}_i \cdot \mathbf{r}_j \) to the two-particle interaction that defines the HF potential. The modified electron-electron interaction becomes

\[ \frac{1}{r_{12}} + 2 \lambda \mathbf{r}_1 \cdot \mathbf{r}_2 = \sum_{L=0}^{\infty} \sum_{r_{12} > r_{ij}} r_{12}^L P_L (\cos \theta) + 2 \lambda r_1 r_2 P_1 (\cos \theta). \]

It follows that only the \( L = 1 \) term in the HF potential is modified and this term becomes

\[ v_1(ab,r) \rightarrow v_1(ab,r) \]

\[ + 2 \lambda r \int_0^\infty r' [P_a(r') P_b(r') + Q_a(r') Q_b(r')] \, dr', \]

where \( P_a(r) \) and \( Q_a(r) \) are large and small component radial Dirac wave functions, respectively. As a practical matter, we choose \( \lambda \ll 1 \) for neutral atoms to maintain some resemblance to the usual HF picture. The HF energy includes first-order MBPT corrections, together with all second- and higher-order RPA corrections. In columns 2 and 3 of Table II we list HF valence energies \( E_v^{(\text{HF})}(\lambda) \) and the HF core energies \( E_c^{(\text{HF})}(\lambda) \) as functions of \( \lambda \) for the alkali-metal atoms from Li to Fr.

B. 2nd-order MBPT

We can easily go beyond the HF approximation and include the second-order MBPT corrections to the core
energy $E_c^{(2)}$ and to the valence energy $E_v^{(2)}$

$$E_c^{(2)} = -\frac{1}{2} \sum_{abmn} v_{mnab} \frac{dE}{d\lambda}$$

$$E_v^{(2)} = -\sum_{bnm} v_{bnab} \frac{dE}{d\lambda}$$

$$+ \sum_{abm} v_{anab} \frac{dE}{d\lambda}.$$  

(6)

(7)

In the above equations, indices $a$ and $b$ refer to core orbitals, indices $m$ and $n$ refer to virtual orbitals, and $\lambda$ refers to the valence orbital. The second-order energies include those corrections to the matrix element of $R^2$ usually associated with third-order MBPT – one interaction with $R^2$ and two Coulomb interactions. In columns 4 and 5 of Table I, we list $E_c^{(2)}(\lambda)$ and $E_v^{(2)}(\lambda)$ for various values of $\lambda$.

C. Differentiation Formulas

The energies are given on the grid

$$\lambda_n = (-3h, -2h, -h, 0, h, 2h, 3h)$$

with spacing $h = 0.00002$. To evaluate $\langle R^2 \rangle$, we make use of an hierarchy of successively more accurate Lagrangian differentiation formulas

$$\frac{dE}{d\lambda}^{(3)} = \frac{1}{2h} \left( E[1] + E[-1] \right)$$

$$\frac{dE}{d\lambda}^{(5)} = \frac{1}{24h} \left( 16E[1] - E[-1] \right)$$

$$-2(E[2] - E[-2])$$

$$\frac{dE}{d\lambda}^{(7)} = \frac{1}{720h} \left( 540(E[1] - E[-1]) \right)$$

$$-108(E[2] - E[-2]) + 12(E[3] - E[-3])$$

to obtain $dE/d\lambda$ at $\lambda = 0$. In the above, we designate $E(\lambda_n)$ by $E[n]$. The k-th approximation to the derivative $(dE/d\lambda)^{(k)}$ has an error proportional to $h^k$. The first two of these formulas are given in Abramowitz and Stegun [11, Chap. 25].

In Table I, we show results of applying the differentiation formulas to the data in Table II. The resulting values of $\langle R^2 \rangle$ are numerically stable to about 4 digits for the cases considered. These values are compared with values from third-order MBPT and other accurate values in Table III.

D. Third-Order MBPT

Expressions for third-order correlation corrections to core and valence energies of atoms with a single valence electron were given in [12] and applied to study ground-state removal energies of Cs and Tl in [13]. In the present applications, these formulas are used to evaluate, effectively, fourth-order corrections to matrix elements of $R^2$. Although we do not expect the third-order calculations presented in this section to be as accurate as the singles-doubles (SD) calculations given in the following section, it is in any case necessary to carry out third-order energy calculations to determine $E_v^{(3)}$, the correction to the SD energies that accounts approximately for omitted triple excitations in the SD equations.

Third-order corrections for lithium are $dE_v^{(3)}/d\lambda = ...
method of including important correlation corrections to the atomic wave function to all-orders in perturbation theory. One solves a set of coupled equations for single excitation

coefficients $\rho_{ma}$, $\rho_{m}$, and double excitation coefficients $\rho_{mnab}$, $\rho_{mnva}$ of the HF ground state [see (12) for example]. Once these expansion coefficients have been determined, the correlation correction to the core energy $\Delta E_c$ is given by

$$\Delta E_c = \frac{1}{2} \sum_{mnab} v_{abmn} \tilde{\rho}_{mnab},$$

and the correction correlation to the valence energy is given by

$$\Delta E_v = \sum_{ma} \tilde{\rho}_{va} \rho_{ma} + \sum_{mab} v_{abcm} \tilde{\rho}_{mva} + \sum_{mna} v_{mnab} \tilde{\rho}_{mna}.$$  

The core energy is exact through third order in MBPT and contains important fourth- and higher-order corrections. The valence energy also includes important fourth- and higher-order corrections but is missing small third-order corrections [written out explicitly in (12) referred to as $E^{(3)}_{\text{extra}}$. These missing terms have their origin in omitted triple excitations (single-valence – double-core excitations) of the HF ground state. Numerical values of $E^{(3)}_{\text{extra}}$ for the alkali-metal atoms are given at the end of Section III D.

a. Lithium: Calculations for Li include all partial waves with $l \leq 6$. To estimate higher $l$ contributions we use Aitken’s $\delta^2$ method. Table IV shows contributions to $\langle R^2 \rangle$ evaluated with $l_{\text{max}}$ ranging from 2 to 5. The final extrapolated value $\langle R^2 \rangle = 18.213$ from Table IV differs from the “exact” nonrelativistic value (18.216004) for lithium given by Yan and Drake [9], but is in precise agreement with an earlier SD result by Derevianko et al. [10]. The small difference with the exact nonrelativistic value is dominated by the contribution from $E^{(3)}_{\text{extra}}$, evaluated in the previous subsection, which has the value $dE^{(3)}_{\text{extra}}/d\lambda = 0.0025$. When this correction is added to the SD result 18.2130 for lithium, we obtain the value 18.2155, differing from the exact nonrelativistic result by only -0.0005. The residual difference has the sign and order of magnitude expected for a relativistic correction to $R^2$.

b. Other alkalis In Table V we show the derivatives of valence and core energies of alkali atoms from Li to Fr calculated in the SD approximation with $l_{\text{max}} = 6$ as the order of the differentiation is increased. We also include the contribution from the missing third-order energy $E^{(3)}_{\text{extra}}$ evaluated in the previous section.

The SD result for sodium $\langle R^2 \rangle = 22.6425(3)$ agrees well with the earlier SD result 22.6293 from Derevianko et al. [9] and with the semi-empirical value 22.65 from Kharchenko et al. [10]. Note however, that present results for all alkali atoms other than lithium are substantially

## Table II: Values of $(dE/d\lambda)_{\lambda=0} = \langle R^2 \rangle$ for alkali-metal atoms as order of differentiation formula is increased. Step size: $h = 0.00002.$

| Element | HF(2) | MBPT | SE |
|---------|-------|------|----|
| Li      | 18.26 | 18.26 | 18.27 |
| Na      | 22.80 | 22.79 | 22.45 |
| K       | 34.13 | 34.05 | 34.52 |
| Rb      | 39.46 | 39.37 | 40.92 |
| Cs      | 46.59 | 46.35 | 50.96 |

$-0.0297$ and $dE^{(3)}_{\text{extra}}/d\lambda = -0.0011$. Adding these values to the earlier second-order result, leads to $\langle R^2 \rangle = 18.2250$ for lithium. This slightly improves the agreement of MBPT with the exact nonrelativistic value. However, better agreement can be achieved in the SD approximation. Therefore, here we only calculate $dE^{(3)}_{\text{extra}}/d\lambda$. These contributions are 0.00252 for Li, 0.00201 for Na, 0.72532 for K, 1.10114 for Rb, 2.32450 for Cs, and 2.59698 for Fr.

## E. All-Order Singles-Doubles

The singles-doubles (SD) equations, also referred to as all-order pair equations [14, Chap. 15], provide a
TABLE IV: Calculated values of $\langle R^2 \rangle$ for Li as the number of partial waves $l_{\text{max}}$ included in the SD equations is increased are tabulated along with extrapolated values obtained by applying Aitken’s $\delta^2$ method to $l_{\text{max}} = (2, 3, 4)$ and $(3, 4, 5)$.

| $l_{\text{max}}$ | $d\Delta E_v/d\lambda$ | $d\Delta E_c/d\lambda$ | $\langle R^2 \rangle$ |
|------------------|-------------------------|-------------------------|----------------------|
| 2                | -0.37905                | -0.03284                | 18.2200              |
| 3                | -0.38362                | -0.03279                | 18.2155              |
| 4                | -0.38509                | -0.03279                | 18.2140              |
| 5                | -0.38570                | -0.03279                | 18.2134              |
| 2-3              | -0.38579                | -0.03279                | 18.2133              |
| 3-4              | -0.38612                | -0.03279                | 18.2130              |

TABLE V: Values of $(dE/d\lambda)_{\lambda=0}$ in the SD+$E^{(3)}_{\text{extra}}$ approximation as the order of differentiation formula is increased. Step size: $h = 0.00002$. The SD equations included all partial waves with $l \leq 6$ for Li, Na, K, Rb, Cs and with $l \leq 5$ for Fr.

| Order | $dE^{(HF)}(dE^{(HF)})_{Li} / d\lambda$ | $dE^{(HF)}(dE^{(HF)})_{Na} / d\lambda$ | $dE^{(HF)}(dE^{(HF)})_{K} / d\lambda$ | $dE^{(HF)}(dE^{(HF)})_{Rb} / d\lambda$ | $dE^{(HF)}(dE^{(HF)})_{Cs} / d\lambda$ | $dE^{(HF)}(dE^{(HF)})_{Fr} / d\lambda$ | $\langle R^2 \rangle$ |
|-------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------|
| 3     | 17.7418                                | 0.8904                                 | -0.38900                               | -0.0328                                | 18.216                                 | 18.216                                 | 18.216               |
| 5     | 17.7415                                | 0.8904                                 | -0.38900                               | -0.0328                                | 18.216                                 | 18.216                                 | 18.216               |
| 7     | 17.7415                                | 0.8904                                 | -0.38900                               | -0.0328                                | 18.216                                 | 18.216                                 | 18.216               |
| 3     | 20.6437                                | 3.9922                                 | -1.7038                                | -0.2922                                | 22.642                                 | 22.642                                 | 22.642               |
| 5     | 20.6427                                | 3.9922                                 | -1.7037                                | -0.2922                                | 22.641                                 | 22.641                                 | 22.641               |
| 7     | 20.6427                                | 3.9922                                 | -1.7037                                | -0.2922                                | 22.641                                 | 22.641                                 | 22.641               |
| 3     | 31.2556                                | 11.8719                                | -5.9711                                | -2.2868                                | 35.594                                 | 35.594                                 | 35.594               |
| 5     | 31.2532                                | 11.8718                                | -5.9703                                | -2.2866                                | 35.592                                 | 35.592                                 | 35.592               |
| 7     | 31.2532                                | 11.8718                                | -5.9703                                | -2.2866                                | 35.592                                 | 35.592                                 | 35.592               |
| 3     | 34.9792                                | 18.1725                                | -8.2136                                | -3.6888                                | 42.351                                 | 42.351                                 | 42.351               |
| 5     | 34.9755                                | 18.1729                                | -8.2119                                | -3.6888                                | 42.349                                 | 42.349                                 | 42.349               |
| 7     | 34.9755                                | 18.1730                                | -8.2117                                | -3.6888                                | 42.349                                 | 42.349                                 | 42.349               |
| 3     | 41.7773                                | 28.2500                                | -11.6972                               | -6.6590                                | 56.536                                 | 56.536                                 | 56.536               |
| 5     | 41.7703                                | 28.2499                                | -11.6942                               | -6.6590                                | 53.991                                 | 53.991                                 | 53.991               |
| 7     | 41.7704                                | 28.2498                                | -11.6943                               | -6.6590                                | 53.991                                 | 53.991                                 | 53.991               |
| 3     | 39.3401                                | 35.6056                                | -12.4105                               | -8.5968                                | 56.536                                 | 56.536                                 | 56.536               |

larger than semi-empirical values obtained in Ref. [10] (see Table III).

The resulting values $\langle R^2 \rangle$ from the SD calculation, which are our most accurate predictions, are summarized in Table VI.

TABLE VI: Final results for $\langle R^2 \rangle$ for alkali atoms.

|       | Li | Na | K  | Rb | Cs | Fr |
|-------|----|----|----|----|----|----|
| $\langle R^2 \rangle$ | 18.216 | 22.641 | 35.593 | 42.349 | 53.994 | 56.536 |

Conclusion

In this paper we present the most complete fully ab initio all-order calculations of the Lennard-Jones interaction constant $C_3$ for alkali-metal atoms. Incorporating of the rescaled $R^2$ operator into original Hartree-Fock Hamiltonian allows us to stay within standard SD technique while also including important subclasses of higher-order contributions. Results for Li agree precisely with the “exact” CI results of Yan and Drake [6], while results for other alkali atoms are probably the most accurate available to date.

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