PHYSICAL REVIEW A **69**, 022508 (2004)

Finite-field evaluation of the Lennard-Jones atom-wall interaction constant C_3 for alkali-metal atoms

W. R. Johnson,* V. A. Dzuba,† and U. I. Safronova‡
Department of Physics, 225 Nieuwland Science Hall, University of Notre Dame, Notre Dame, Indiana 46566, USA

M. S. Safronova
Department of Physics and Astronomy, 223 Sharp Lab, University of Delaware, Newark, Delaware 19716, USA

(Received 28 October 2003; published 23 February 2004)

A finite-field scaling method is applied to evaluate the Lennard-Jones interaction constant C_3 for alkali-metal atoms. The calculations are based on the relativistic single-double approximation in which single and double excitations of Dirac-Hartree-Fock wave functions are included to all orders in perturbation theory.

DOI: 10.1103/PhysRevA.69.022508 PACS number(s): 31.15.Ar, 34.50.Dy, 31.25.Eb

I. INTRODUCTION

The long-range interaction between an atom and a perfectly conducting wall is governed by the Lennard-Jones [1] static image potential

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

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

$$\frac{1}{16}\sum_{i,j}(x_ix_j+y_iy_j+2z_iz_j),$$

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

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

where $\boldsymbol{R}=\Sigma_i\boldsymbol{r}_i$. 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 for small wall separation distances is proportional to C_3 [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 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%. The more elaborate calculations by Jönsson *et al.* [8] improve the agreement between theoretical and semiempirical values for sodium somewhat.

Third-order many-body perturbation-theory calculations of C_3 for all alkali-metal atoms and all-order single-double 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.* [10] deduced accurate theoretical and semiempirical 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 nth 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 ordinarily required.

II. METHOD

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

---

*Electronic address: johnson@nd.edu; URL: www.nd.edu/johnson

†Permanent address: School of Physics, University of New South Wales, Sydney 2052, Australia; Electronic address: V.Dzuba@unsw.edu.au

‡Electronic address: usafrono@nd.edu

$$R^2=\left[\sum_{i=1}^{N}\boldsymbol{r}_i\right]^2=\sum_i r_i^2+2\sum_{i\neq j}\boldsymbol{r}_i\cdot\boldsymbol{r}_j \tag{2}$$

is known as the "finite-field" method and is widely used in quantum chemistry. We evaluate the ground-state expectation value of the operator by adding the scalar operator λR^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

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

where

$$h_0=c\boldsymbol{\alpha}\cdot\boldsymbol{p}+\beta mc^2+V_{\text{nuc}}(r)+\lambda r^2+U(r).$$

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

$$H=E_0+\sum_i \epsilon_i:a_i^\dagger a_i:+\frac{1}{2}\sum_{ijkl}v_{ijkl}:a_i^\dagger a_j^\dagger a_l a_k:$$
$$+\sum_{ij}(V_{\text{HF}}-U)_{ij}:a_i^\dagger a_j:, \tag{3}$$

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

$$v_{ijkl}=\left\langle ij\left|\frac{1}{r_{12}}+2\lambda\boldsymbol{r}_i\cdot\boldsymbol{r}_j\right|kl\right\rangle.$$

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

$$\Psi_0=a_a^\dagger a_b^\dagger\cdots a_n^\dagger|0\rangle.$$

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

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

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

$$E_c^{(\text{HF})}=\sum_a\left[\epsilon_a-\frac{1}{2}(V_{\text{HF}})_{aa}\right], \tag{4}$$

$$E_v^{(\text{HF})}=\epsilon_v, \tag{5}$$

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

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

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

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

$$v_1(ab,r)\to v_1(ab,r)+2\lambda r\int_0^\infty r'[P_a(r')P_b(r')$$
$$+Q_a(r')Q_b(r')]dr',$$

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 I, we list HF valence energies $E_v^{(\text{HF})}(\lambda)$ and the HF core energies $E_c^{(\text{HF})}(\lambda)$ as functions of λ for the alkali-metal atoms from Li to Fr.

B. Second-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 $E_v^{(2)}$:

TABLE I. Variation of MBPT contributions to energies of alkali-metal atoms with the scaling parameter λ, where $H(\lambda)=H+\lambda R^2$.

λ	$E_v^{(\mathrm{HF})}(\lambda)$	$E_c^{(\mathrm{HF})}(\lambda)$	$E_v^{(2)}(\lambda)$	$E_c^{(2)}(\lambda)$
		Li		
−0.00006	−0.1973918	−7.2372588	−0.0016257	−0.0400988
−0.00004	−0.1970331	−7.2372410	−0.0016327	−0.0400995
−0.00002	−0.1966760	−7.2372232	−0.0016397	−0.0401001
0.00002	−0.1959663	−7.2371876	−0.0016535	−0.0401014
0.00004	−0.1956137	−7.2371698	−0.0016603	−0.0401020
0.00006	−0.1952625	−7.2371520	−0.0016671	−0.0401026
		Na		
−0.00006	−0.1832811	−161.8961446	−0.0057754	−0.3836680
−0.00004	−0.1828627	−161.8960647	−0.0058073	−0.3836734
−0.00002	−0.1824466	−161.8959849	−0.0058389	−0.3836788
0.00002	−0.1816209	−161.8958252	−0.0059014	−0.3836896
0.00004	−0.1812111	−161.8957454	−0.0059323	−0.3836950
0.00006	−0.1808033	−161.8956655	−0.0059630	−0.3837004
		K		
−0.00006	−0.1493919	−601.3789128	−0.0120214	−0.7237274
−0.00004	−0.1487522	−601.3786754	−0.0121561	−0.7237770
−0.00002	−0.1481185	−601.3784379	−0.0122889	−0.7238267
0.00002	−0.1468683	−601.3779630	−0.0125494	−0.7239262
0.00004	−0.1462511	−601.3777256	−0.0126774	−0.7239760
0.00006	−0.1456389	−601.3774882	−0.0128041	−0.7240257
		Rb		
−0.00006	−0.1414238	−2979.6664077	−0.0144304	−1.8931869
−0.00004	−0.1407050	−2979.6660442	−0.0146265	−1.8932719
−0.00002	−0.1399943	−2979.6656808	−0.0148194	−1.8933569
0.00002	−0.1385951	−2979.6649539	−0.0151967	−1.8935271
0.00004	−0.1379058	−2979.6645905	−0.0153817	−1.8936122
0.00006	−0.1372228	−2979.6642272	−0.0155647	−1.8936974
		Cs		
−0.00006	−0.1299267	−7786.6477893	−0.0168211	−3.1079015
−0.00004	−0.1290615	−7786.6472240	−0.0171307	−3.1080755
−0.00002	−0.1282090	−7786.6466589	−0.0174334	−3.1082495
0.00002	−0.1265379	−7786.6455289	−0.0180225	−3.1085978
0.00004	−0.1257176	−7786.6449640	−0.0183103	−3.1087722
0.00006	−0.1249066	−7786.6443992	−0.0185943	−3.1089466
		Fr		
−0.00006	−0.1334806	−24307.9714413	−0.0206103	−5.8273192
−0.00004	−0.1326676	−24307.9707289	−0.0209570	−5.8275533
−0.00002	−0.1318658	−24307.9700168	−0.0212968	−5.8277875
0.00002	−0.1302922	−24307.9685926	−0.0219595	−5.8282563
0.00004	−0.1295191	−24307.9678807	−0.0222839	−5.8284909
0.00006	−0.1287542	−24307.9671690	−0.0226043	−5.8287257

$$E_c^{(2)}=-\frac{1}{2}\sum_{abmn}\frac{v_{mnab}\tilde{v}_{abmn}}{\epsilon_m+\epsilon_n-\epsilon_a-\epsilon_b}, \tag{6}$$

$$E_v^{(2)}=-\sum_{bmn}\frac{v_{mnvb}\tilde{v}_{vbmn}}{\epsilon_m+\epsilon_n-\epsilon_v-\epsilon_b}+\sum_{abm}\frac{v_{mvab}\tilde{v}_{abmv}}{\epsilon_m+\epsilon_v-\epsilon_a-\epsilon_b}. \tag{7}$$

In the above equations, indices a and b refer to core orbitals, indices m and n refer to virtual orbitals, and v 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 $E_v^{(2)}(\lambda)$ and $E_c^{(2)}(\lambda)$ for various values of λ.

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, $h=0.000\,02$.

Order	$dE_v^{(\mathrm{HF})}/d\lambda$	$dE_c^{(\mathrm{HF})}/d\lambda$	$dE_v^{(2)}/d\lambda$	$dE_c^{(2)}/d\lambda$	$\langle R^2\rangle$
			Li		
3	17.7418	0.8904	−0.3445	−0.0315	18.256
5	17.7415	0.8904	−0.3445	−0.0315	18.256
7	17.7415	0.8904	−0.3445	−0.0315	18.256
			Na		
3	20.6433	3.9922	−1.5631	−0.2694	22.803
5	20.6427	3.9922	−1.5629	−0.2694	22.803
7	20.6427	3.9922	−1.5629	−0.2694	22.803
			K		
3	31.2556	11.8718	−6.5118	−2.4864	34.129
5	31.2531	11.8718	−6.5105	−2.4864	34.128
7	31.2532	11.8718	−6.5105	−2.4864	34.128
			Rb		
3	34.9792	18.1725	−9.4361	−4.2549	39.461
5	34.9755	18.1729	−9.4336	−4.2549	39.460
7	34.9755	18.1730	−9.4337	−4.2549	39.460
			Cs		
3	41.7773	28.2500	−14.7337	−8.7108	46.583
5	41.7703	28.2499	−14.7276	−8.7108	46.582
7	41.7704	28.2498	−14.7278	−8.7108	46.582
			Fr		
3	39.3401	35.6056	−16.5691	−11.7207	46.656
5	39.3343	35.6068	−16.5634	−11.7207	46.657
7	39.3344	35.6073	−16.5635	−11.7207	46.658

C. Differentiation formulas

The energies are given on the grid

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

with spacing $h=0.000\,02$. To evaluate $\langle R^2\rangle$, we make use of a hierarchy of successively more accurate Lagrangian differentiation formulas:

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

$$\left(\frac{dE}{d\lambda}\right)^{(5)}=\frac{1}{24h}\{16(E[1]-E[-1])-2(E[2]-E[-2])\},$$

$$\left(\frac{dE}{d\lambda}\right)^{(7)}=\frac{1}{720h}\{540(E[1]-E[-1])-108(E[2]-E[-2])+12(E[3]-E[-3])\}$$

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

TABLE III. Comparison of the present second-order finite-field (FF$^{(2)}$) values of R^2 with third-order MBPT values from Ref. [9] and with semiempirical (SE) values from Ref. [10]. The value for Li reported under SE is obtained by rounding the "exact" value 18.216 . . . given in Refs. [6,7].

Element	FF$^{(2)}$	MBPT	SE
Li	18.26	18.26	18.22
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

In Table II, we show results of applying the differentiation formulas to the data in Table I. The resulting values of $\langle R^2\rangle$ are numerically stable to about four 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 Ref. [12] and applied to study ground-state removal energies of Cs and Tl in Ref. [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 single-double (SD) calculations given in the following section, it is in any case necessary to carry out third-order energy calculations to determine $E_{\mathrm{extra}}^{(3)}$, the correction to the SD energies that accounts approximately for omitted triple excitations in the SD equations.

Third-order corrections for lithium are $dE_v^{(3)}/d\lambda=-0.0297$ and $dE_c^{(3)}/d\lambda=-0.0011$. 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 $dE_{\mathrm{extra}}^{(3)}/d\lambda$. 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.

TABLE IV. Calculated values of $\langle R^2\rangle$ for Li as the number of partial waves $l_{\max}$ included in the SD equations is increased are tabulated along with extrapolated values obtained by applying Aitken's δ^2 method to $l_{\max}$=(2,3,4) and (3,4,5).

$l_{\max}$	$d\Delta E_v/d\lambda$	$d\Delta E_c/d\lambda$	$\langle R^2\rangle$
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
2-3-4	−0.38579	−0.03279	18.2133
3-4-5	−0.38612	−0.03279	18.2130

TABLE V. Values of $(dE/d\lambda)_{\lambda=0}$ in the SD$+E^{(3)}_{\rm extra}$ approximation as the order of differentiation formula is increased. Step size, $h=0.000\,02$. The SD equations included all partial waves with $l \leqslant 6$ for Li, Na, K, Rb, Cs and with $l \leqslant 5$ for Fr.

Order	$\frac{dE^{(\rm HF)}_v}{d\lambda}$	$\frac{dE^{(\rm HF)}_c}{d\lambda}$	$\frac{d\Delta E_v}{d\lambda}$	$\frac{d\Delta E_c}{d\lambda}$	$\frac{dE^{(3)}_{\rm extra}}{d\lambda}$	$\langle R^2\rangle$
			Li			
3	17.7418	0.8904	−0.3860	−0.0328	0.0025	18.216
5	17.7415	0.8904	−0.3859	−0.0328	0.0025	18.216
7	17.7415	0.8904	−0.3859	−0.0328	0.0025	18.216
			Na			
3	20.6433	3.9922	−1.7038	−0.2922	0.0020	22.642
5	20.6427	3.9922	−1.7037	−0.2922	0.0020	22.641
7	20.6427	3.9922	−1.7037	−0.2922	0.0020	22.641
			K			
3	31.2556	11.8719	−5.9711	−2.2866	0.7255	35.595
5	31.2531	11.8718	−5.9703	−2.2866	0.7253	35.593
7	31.2532	11.8718	−5.9703	−2.2866	0.7253	35.593
			Rb			
3	34.9792	18.1725	−8.2136	−3.6888	1.1014	42.351
5	34.9755	18.1729	−8.2119	−3.6888	1.1011	42.349
7	34.9755	18.1730	−8.2117	−3.6888	1.1011	42.349
			Cs			
3	41.7773	28.2500	−11.6972	−6.6590	2.3254	53.997
5	41.7703	28.2499	−11.6942	−6.6590	2.3245	53.991
7	41.7704	28.2498	−11.6943	−6.6590	2.3245	53.991
			Fr			
3	39.3401	35.6056	−12.4105	−8.5968	2.5970	56.536

E. All-order single-double calculations

The SD equations, also referred to as all-order pair equations (see Chap. 15 of Ref. [14]), provide a 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 ρ_{ma}, ρ_{mv} and double excitation coefficients ρ_{mnab}, ρ_{mnva} of the HF ground state, see Ref. [15], for example. Once these expansion coefficients have been determined, the correlation correction to the core energy ΔE_c is given by

$$\Delta E_c = \frac{1}{2}\sum_{mnab} v_{abmn}\tilde{\rho}_{mnab} \tag{8}$$

and the correlation correction to the valence energy is given by

$$\Delta E_v = \sum_{ma}\tilde{v}_{vavm}\rho_{ma} + \sum_{mab} v_{abvm}\tilde{\rho}_{mvab} + \sum_{mna} v_{vbmn}\tilde{\rho}_{mnvb}. \tag{9}$$

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 Ref. [15]) referred to as $E^{(3)}_{\rm extra}$. These missing terms have their origin in omitted triple excitations (single-valence—double-core excitations) of the HF ground state. Numerical values of $E^{(3)}_{\rm extra}$ for the alkali-metal atoms are given at the end of Sec. III D.

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

Li	Na	K	Rb	Cs	Fr
18.216	22.641	35.593	42.349	53.991	56.536

a. Lithium. Calculations for Li include all partial waves with $l \leqslant 6$. To estimate higher l contributions we use Aitken's δ^2 method. Table IV shows contributions to $\langle R^2\rangle$ evaluated with $l_{\rm max}$ ranging from 2 to 5. The final extrapolated value $\langle R^2\rangle = 18.213$ from Table IV differs from the "exact" nonrelativistic value (18.216 004) for lithium given by Yan and Drake [6], but is in precise agreement with an earlier SD result by Derevianko *et al.* [9]. The small difference with the exact nonrelativistic value is dominated by the contribution from $E^{(3)}_{\rm extra}$, evaluated in the preceding subsection, which has the value $dE^{(3)}_{\rm extra}/d\lambda = 0.0025$. 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 $l_{\rm max}=6$ as the order of the differentiation is increased. We also include the contribution from the missing third-order energy $E^{(3)}_{\rm extra}$ evaluated in the preceding 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 semiempirical value 22.65 from Kharchenko *et al.* [5]. Note, however, that present results for all alkali atoms other than lithium are substantially larger than semiempirical 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.

IV. 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.

ACKNOWLEDGMENTS

The work of W.R.J. and U.I.S was supported in part by National Science Foundation, Grant No. PHY-01-39928.

[1] J.E. Lennard-Jones, Trans. Faraday Soc. **28**, 333 (1932).
[2] J. Bardeen, Phys. Rev. **58**, 727 (1940).
[3] C. Mavroyannis, Mol. Phys. **6**, 593 (1963).
[4] Z.-C. Yan, A. Dalgarno, and J.F. Babb, Phys. Rev. A **55**, 2882 (1997).
[5] P. Kharchenko, J.F. Babb, and A. Dalgarno, Phys. Rev. A **55**, 3566 (1997).
[6] Z.-C. Yan and G.W.F. Drake, Phys. Rev. A **52**, 3711 (1995).
[7] F.W. King, Phys. Rev. A **40**, 1735 (1989).
[8] Per Jönsson, A. Ynnerman, Charlotte Froese Fischer, Michel R. Godefroid, and J. Olsen, Phys. Rev. A **53**, 4021 (1996).
[9] A. Derevianko, W.R. Johnson, and S. Fritzsche, Phys. Rev. A **57**, 2629 (1998).
[10] A. Derevianko, W.R. Johnson, M.S. Safronova, and J.F. Babb, Phys. Rev. Lett. **82**, 3589 (1999).
[11] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (U. S. Government Printing Office, Washington, D.C., 1968).
[12] S.A. Blundell, D.S. Guo, W.R. Johnson, and J. Sapirstein, At. Data Nucl. Data Tables **37**, 103 (1987).
[13] S.A. Blundell, W.R. Johnson, and J. Sapirstein, Phys. Rev. A **42**, 3751 (1990).
[14] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1986).
[15] M.S. Safronova, A. Derevianko, and W.R. Johnson, Phys. Rev. A **58**, 1016 (1998).