Relativistic configuration-interaction calculation of the polarizabilities of heliumlike ions

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Polarizabilities of ions of the helium isoelectronic sequence with nuclear charges in the range $2 \leqslant Z \leqslant 30$ are evaluated starting from the relativistic no-pair Hamiltonian and including both the Coulomb and Breit interactions. The ground state and perturbed wave functions are expanded in two-electron basis functions constructed from B splines. For each ion, the ground-state wave function is determined by a configuration interaction calculation; the perturbed wave function is then found by solving an inhomogeneous algebraic equation. Nonrelativistic calculations are carried out in parallel with the relativistic calculations, permitting relativistic corrections to be isolated. The present nonrelativistic calculations are found to be in good agreement with other precise calculations. For the experimentally interesting case of heliumlike lithium, we obtain the value $\Delta\alpha_{\rm Rel} = -(4.50 \pm 0.05) \times 10^{-5}$ a.u. for the relativistic correction to the ground-state polarizability.

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I. INTRODUCTION

Recent measurements of the Rydberg levels of lithium [1] are of such high accuracy that relativistic corrections to the polarizability of the Li^+ ion becomes an issue in predicting the level structure theoretically [2]. Motivated by these measurements, we undertake calculations of the polarizabilities of heliumlike ions with nuclear charges ranging from $Z=2$ to 30 within the framework of the relativistic no-pair theory [3].

The ground-state wave function for each ion considered is determined from a relativistic configuration-interaction (CI) calculation essentially identical to that described in Ref. [4]. The calculation is based on the no-pair Hamiltonian [3] and uses two-electron configuration-state basis functions constructed from B-spline orbitals constrained to a cavity of finite radius [5]. The perturbed wave function is also expanded in a basis of configuration-state functions and the expansion coefficients are determined by solving a set of linear inhomogeneous equations. In the calculation, only positive-energy orbitals are used in the construction of configuration-state functions to accommodate the positive-energy projection operators in the no-pair Hamiltonian.

A nonrelativistic CI calculation of the polarizability α is carried out in parallel with the relativistic one. The nonrelativistic values of α are in good agreement with previous high-precision nonrelativistic calculations. The relativistic correction for heliumlike lithium, obtained from the difference between the relativistic and nonrelativistic values, is found to be $\Delta\alpha_{\rm Rel} = -(4.50 \pm 0.05) \times 10^{-5}$ a.u. Moreover, the relativistic correction takes the limiting form

$$\Delta\alpha_{\rm Rel} \rightarrow -\frac{4.86 \times 10^{-4}}{Z^2} \text{ a.u.}$$

for large Z.

II. METHOD

The polarizability of an atom is given by

$$\alpha = 2\sum_n \frac{\langle\Psi_0|\mathscr{Z}|\Psi_n\rangle\langle\Psi_n|\mathscr{Z}|\Psi_0\rangle}{E_n - E_0}, \tag{1}$$

where $\mathscr{Z} = \Sigma_i z_i$ is the coordinate operator. This equation can be reformulated as

$$\alpha = -2\langle\Psi|\mathscr{Z}|\Psi_0\rangle, \tag{2}$$

where the perturbed wave function Ψ satisfies the inhomogeneous equation

$$(H - E_0)\Psi = -\mathscr{Z}\Psi_0. \tag{3}$$

The symbol H designates the Schrödinger Hamiltonian in the nonrelativistic case or the no-pair Hamiltonian (including the instantaneous Breit interaction) in the relativistic case. We expand the ground-state wave function as

$$\Psi_0 = \sum_{l \geqslant k} c_{kl}\Phi_{kl}(00), \tag{4}$$

where, in the relativistic case, $\Phi_{kl}(JM)$ is a jj-coupled configuration-state function given by

$$\Phi_{kl}(JM) = \eta_{kl}\sum_{m_k m_l} \langle j_k m_k, j_l m_l | JM\rangle |kl\rangle. \tag{5}$$

Here, $|kl\rangle$ is a two-electron Slater determinant, η_{kl} is a symmetry factor defined by

$$\eta_{kl} = \begin{cases} 1/\sqrt{2} & \text{for } k = l, \\ 1 & \text{for } k \neq l, \end{cases}$$

and $\langle j_k m_k, j_l m_l | JM\rangle$ is a Clebsch-Gordan coefficient. The wave-function normalization condition is

TABLE I. Partial-wave contributions to the polarizability α_ℓ and electric-dipole shielding factor σ_ℓ of heliumlike neon ($Z=10$). Units of α: 10^{-3} a.u.

Ψ_0	Ψ	α_ℓ	$\alpha_\ell-\alpha_{\ell-1}$	σ_ℓ	$\sigma_\ell-\sigma_{\ell-1}$
(s,s)	(s,p)	1.0564619		0.2037619	
(p,p)	(p,d)	1.0446033	−0.0118586	0.1999394	−0.0038225
(d,d)	(d,f)	1.0447408	0.0001375	0.1999824	0.0000430
(f,f)	(f,g)	1.0447696	0.0000288	0.1999923	0.0000099
(g,g)	(g,h)	1.0447799	0.0000103	0.1999959	0.0000036
(h,h)	(h,i)	1.0447845	0.0000046	0.1999976	0.0000016
Extrapolated	$(\ell\geqslant 6)$	1.0447909	0.0000064	0.1999998	0.0000023

$$\sum_{l\geqslant k} c_{kl}^2=1. \tag{6}$$

The expansion coefficients c_{kl} are the components of the lowest-energy solution to the eigenvalue problem

$$\sum_{l\geqslant k} H_{ij,kl}(0)c_{kl}=E_0 c_{ij}. \tag{7}$$

We use the notation

$$H_{ij,kl}(J)=(\epsilon_i+\epsilon_j)\,\delta_{ik}\delta_{jl}+V_{ij,kl}(J), \tag{8}$$

where $V_{ij,kl}(J)$ is the matrix element of the potential V taken between two configuration-state functions with angular momentum J,

$$V_{ij,kl}(J)=\langle\Phi_{ij}(JM)|V|\Phi_{kl}(JM)\rangle.$$

A discussion of solutions to the ground- and excited-state eigenvalue problems in the relativistic case, together with extensive experimental comparisons, are given in Ref. [4].

The perturbed wave function Ψ is an odd parity $J=1$ state that can be represented by the expansion

$$\Psi=\sum_{n>m} d_{mn}\Phi_{mn}(10),$$

where $\Phi_{mn}(10)$ is the configuration-state functions given in Eq. (5) with $(JM)=(10)$, and where the expansion coefficients d_{mn} are to be determined from Eq. (3). The latter equation, when expressed in terms of the expansion coefficients d_{nm}, becomes

$$\sum_{n>m}[H_{st,mn}(1)-E_0\delta_{sm}\delta_{tn}]d_{mn}=B_{st}, \tag{9}$$

where $H_{st,mn}(J)$ is defined in Eq. (8) above and where

$$B_{st}=-\sum_{l\geqslant k}\eta_{kl}\frac{\delta_{\kappa_k\kappa_l}}{\sqrt{3[j_k]}}[\langle s\|z\|k\rangle\delta_{tl}+\langle s\|z\|l\rangle\delta_{tk}-\langle k\|z\|t\rangle\delta_{sl} -\langle l\|z\|t\rangle\delta_{sk}]c_{kl}. \tag{10}$$

Here $[j]=2j+1$, $\kappa=\mp(j+1/2)$ for $j=\ell\pm 1/2$, and $\langle a\|z\|b\rangle$ are reduced matrix elements of the coordinate operator. With this notation, the polarizability is given by

$$\alpha=2\sum_{n>m} B_{mn}d_{mn}. \tag{11}$$

The nonrelativistic expression for the polarizability can be obtained from the above formalism by simply replacing the jj-coupled configuration-state functions by their LS-coupled counterparts and by using nonrelativistic

TABLE II. Summary of nonrelativistic polarizabilities with estimated extrapolation errors. Numbers in brackets are multiplicative factors in powers of 10. Units: a.u.

Z	$\alpha_{\rm NR}$	Extrap. error
2	1.3831992	0.0000078
3	1.9245363[−1]	0.0000029[−1]
4	5.2268814[−2]	0.0000051[−2]
6	8.9639358[−3]	0.0000087[−3]
8	2.6525078[−3]	0.0000022[−3]
10	1.0447909[−3]	0.0000006[−3]
14	2.6031928[−4]	0.0000008[−4]
18	9.3013338[−5]	0.0000020[−5]
22	4.1058333[−5]	0.0000006[−5]
26	2.0830394[−5]	0.0000002[−5]
30	1.1663255[−5]	0.0000001[−5]

TABLE III. Comparison of nonrelativistic "input" energies, E_0(in), from Drake [8] with extrapolated "output" energies, E_0(out), obtained using partial waves with $\ell\leqslant 5$ from the present calculation. Units: a.u.

Z	E_0(in)	E_0(out)	Extrap. error
2	−2.90372437	−2.90372	0.000002
3	−7.27991339	−7.27991	0.000001
4	−13.65556619	−13.65556	0.000002
6	−32.40624656	−32.40622	0.000004
8	−59.15659512	−59.15654	0.000006
10	−93.90680651	−93.90672	0.000008
14	−187.4070500	−187.40691	0.000011
18	−312.9071861	−312.90718	0.000003
22	−470.4072729	−470.40726	0.000003
26	−659.9073332	−659.90732	0.000002
30	−881.4073775	−881.40736	0.000001

TABLE IV. Differences between partial-wave contributions to relativistic and nonrelativistic polarizabilities for heliumlike neon ($Z=10$). Here, α_{NR} represents nonrelativistic values, α_{Coul} represents relativistic values including only the Coulomb interaction, and α_{Rel} represents relativistic values including both Coulomb and Breit interactions. Units: 10^{-3} a.u.

ℓ	α_{NR}	α_{Coul}	$\Delta\alpha_{\mathrm{Coul}}$	α_{Rel}	$\Delta\alpha_{\mathrm{Rel}}$
0	1.056462	1.051281	−0.005181	1.051805	−0.004657
1	1.044603	1.039503	−0.005100	1.039879	−0.004724
2	1.044741	1.039640	−0.005101	1.040014	−0.004727
3	1.044770	1.039668	−0.005101	1.040042	−0.004728
4	1.044780	1.039679	−0.005101	1.040051	−0.004729

B-spline basis orbitals. Comparing our nonrelativistic calculation with other precise nonrelativistic calculations serves to calibrate the accuracy of our subsequent relativistic calculation.

As a first step in our calculations, only s orbitals are included in the ground-state wave function. The resulting two-particle configurations are designated by (ms,ns) where m and n are different principal quantum numbers. Correspondingly, the perturbed wave function is made up of all possible (ms,np) configurations. As a second step, (mp,np) configurations are included in the ground state and (mp,nd) configurations are added to the perturbed wave function. We continue these steps, adding one angular momentum value at a time to the wave function until all configurations up to (mh,nh) are included in the ground state and the corresponding (mh,ni) configurations are included in the perturbed wave function. At each step, we determine the partial contribution to the polarizability from the added angular-momentum state, and, at the final step, we estimate the remainder from those angular-momentum states not included in the wave function by extrapolation. Incremental partial-wave contributions from high-ℓ states are found to decrease with increasing ℓ as $1/(\ell+1/2)^4$.

III. RESULTS AND DISCUSSIONS

To illustrate our method of calculation, we give in Table I the successive contributions to the polarizability α and the electric-dipole shielding factor σ for the case of heliumlike neon ($Z=10$). The shielding factor is evaluated using exactly the same ground state wave function and solving the same inhomogeneous equation for the perturbed wave functions but replacing z by z/r^2 in Eq. (10). The nonrelativistic value of the shielding factor for a two-electron ion with nuclear charge Z is exactly $\sigma=2/Z$. As seen from the table, the two quantities σ and α exhibit similar convergence patterns: both fall off as $1/(\ell+1/2)^4$ asymptotically. Moreover, the extrapolated value of σ is within 0.0001% of the exact value.

Since $\sigma=2/Z$, the extrapolation error in σ can be determined exactly. This error ranges from 0.4% of the extrapolated remainder for $Z=2$ to about 10% of the remainder for $Z\geqslant 10$. Given the similarity in convergence patterns of α and σ, one expects the extrapolation error for α to be approximately the same fraction of the remainder in α. We use this rule to obtain a first estimate of the extrapolation error. For the case of heliumlike neon, this estimate leads to the value $\alpha=1.044\,790\,9(6)\times10^{-3}$ a.u. for the polarizability. The absolute value of the difference obtained on extrapolating α from $\ell=5$ and from $\ell=4$ gives a second measure of the extrapolation error.

We take a conservative approach and quote the larger of the two estimates described above as the extrapolation error in Table II, where we present the extrapolated nonrelativistic values of α, together with estimated extrapolation errors. For $Z=2$, the present value $\alpha=1.383\,199(8)$ can be compared

TABLE V. Relativistic corrections, $\Delta\alpha_{\mathrm{Rel}}$, to the polarizability given by differences of $\alpha_{\mathrm{NR}}(\ell=4)$, and $\alpha_{\mathrm{Rel}}(\ell=4)$, which are calculated with the first five partial waves only. Full relativistic polarizabilities, α_{Rel}, are obtained by adding $\Delta\alpha_{\mathrm{Rel}}$ to the nonrelativistic polarizabilities, α_{NR}, shown in Table II. Numbers in brackets are multiplicative factors in powers of 10. Units: a.u.

Z	$\alpha_{\mathrm{NR}}(\ell=4)$	$\alpha_{\mathrm{Rel}}(\ell=4)$	$\Delta\alpha_{\mathrm{Rel}}$	α_{Rel}
2	1.383226	1.383149	−7.650[−5]	1.383123
3	1.924457[−1]	1.924008[−1]	−4.485[−5]	1.924088[−1]
4	5.226683[−2]	5.223981[−2]	−2.702[−5]	5.224179[−2]
6	8.963723[−3]	8.951057[−3]	−1.267[−5]	8.951270[−3]
8	2.652467[−3]	2.645174[−3]	−7.293[−6]	2.645215[−3]
10	1.044780[−3]	1.040051[−3]	−4.729[−6]	1.040062[−3]
14	2.603178[−4]	2.578710[−4]	−2.447[−6]	2.578725[−4]
18	9.301300[−5]	9.152248[−5]	−1.491[−6]	9.152282[−5]
22	4.105823[−5]	4.005668[−5]	−1.002[−6]	4.005678[−5]
26	2.083036[−5]	2.011188[−5]	−7.185[−7]	2.011192[−5]
30	1.166324[−5]	1.112320[−5]	−5.400[−7]	1.112322[−5]

with a recent, more precise value $\alpha = 1.383\,192\,179$ given by Bhatia and Drachman [6], and to an older, less precise value $\alpha = 1.3830$ given by Grasso, Chung, and Hurst [7]. Similarly, the present nonrelativistic value $\alpha = 0.192\,453\,6(3)$ for Li^+ can be compared with the high-precision value $\alpha = 0.192\,453\,204$ of Drachman and Bhatia [2] and the older value $\alpha = 0.192\,45$ from Ref. [7]. For both ions, the present values are larger than the high-precision values by approximately the estimated extrapolation error.

In our nonrelativistic calculations, we fix the "input" value of E_0 at the value given by by Drake [8]. As we successively increase the number of angular-momentum states included in our basis, the "output" value of E_0 obtained by solving the eigenvalue problem in Eq. (7) gradually approaches the input value. This is illustrated in Table III, where the input E_0 value is compared with the value inferred by extrapolation of the sequence of output E_0 values obtained from Eq. (7). The sequence of incremental energies is found to converge as $1/(\ell + 1/2)^4$. In all cases, the extrapolated energies agree with the input values to the level of the estimated extrapolation errors. The relativistic calculations are carried out in a similar way, except that the input energies from Ref. [8] include relativistic corrections.

In Table IV, we compare the partial-wave contributions from our nonrelativistic and relativistic calculations for heliumlike neon. In the second column, we list the successive approximations to the nonrelativistic polarizability and, in the third column, we list the corresponding relativistic values evaluated using only the Coulomb interaction in the no-pair Hamiltonian. The differences between the relativistic and nonrelativistic values, $\Delta\alpha_{\rm Coul}$, are tabulated in the fourth column. For $\ell \geqslant 1$, these differences are seen to be stable as ℓ increases. In the fifth and sixth columns, we give the partial-wave approximations to the relativistic polarizability, $\sigma_{\rm Rel}$, including both Coulomb and unretarded Breit interactions in the Hamiltonian, and the differences with the nonrelativistic values, $\Delta\alpha_{\rm Rel}$, respectively. The difference $\Delta\alpha_{\rm Coul}$ accounts for the dominant part of the total relativistic correction. However, including the Breit interaction reduces the relativistic Coulomb correction by about 20%.

In Table V, we list the nonrelativistic and relativistic (Coulomb + Breit) values of the polarizabilities calculated up to $\ell = 4$ for the ions considered, together with the relativistic corrections. As the relativistic corrections are nearly independent of ℓ, they are combined with the nonrelativistic polarizability results shown in Table II to get the full relativistic polarizabilities. Results are shown as $\alpha_{\rm Rel}$ in Table V. The corrections $\Delta\alpha_{\rm Rel}$ are plotted in Fig. 1, where they are seen to decrease as $1/Z^2$ with increasing Z. Indeed, from this figure, one infers that $\Delta\alpha_{\rm Rel} \to -4.86\times10^{-4}/Z^2$ a.u. for large values of the nuclear charge Z.

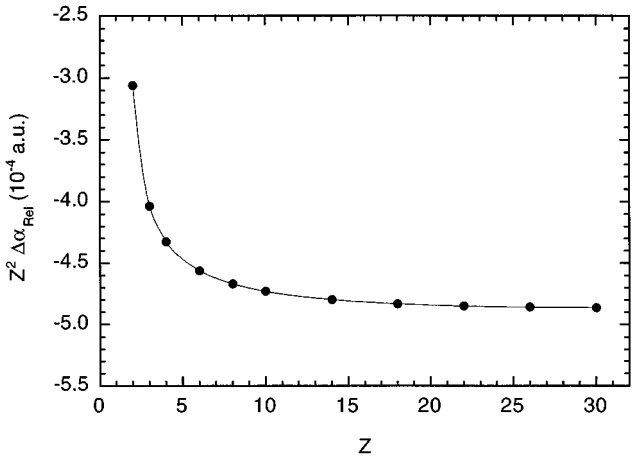

FIG. 1. Relativistic corrections to the polarizability of heliumlike ions (including the Breit interaction) plotted against nuclear charge Z.

Applying the present analysis to the high-Rydberg states of Li^+ mentioned in the introduction, we found that relativistic corrections reduce the value of α for Li^+ by 0.0232%. The theoretically predicted $10h - 10i$ interval for $^7_3Li^+$, which is dominated by the dipole polarizability, is 109.2466(11) MHz [2]. This value was calculated using $\alpha = 0.192\,485\,410$, which includes reduced mass corrections. Reducing this value by 0.0232% (which ignores relativistic corrections to the $10h$ and $10i$ wave functions) changes the predicted interval to 109.2213(11) MHz. This relativistically corrected interval may be compared with the measured interval 109.2140(47) MHz. We find that relativistic corrections to the dipole polarizability account for more than 75% of the difference between the observed and predicted intervals in this case.

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