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Polarizability of the Si^{2+} ion

J. Mitroy
School of Engineering, Charles Darwin University, Darwin NT 0909, Australia

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The dipole polarizability of the Si^{2+} ground state has been determined by a large-scale configuration-interaction (CI) calculation using the sum-over-states approach. The CI calculation was used to describe the valence electron dynamics with respect to the Hamiltonian which treats core-valence correlations with a semiempirical approach. Various higher-order polarizabilities were computed, and this permitted a more refined analysis of the energy intervals measured by resonant excitation Stark ionization spectroscopy (RESIS). The polarizability derived from the revised analysis of the RESIS data was 11.669(9) a.u., only 0.03% larger than that reported in Komara *et al.* [J. Phys. B **38**, 87 (2005)]. The CI value of the polarizability, 11.688 a.u., was only 0.2% larger than experiment, while the quadrupole polarizability of 35.75 a.u. was also consistent with experiment. A resonant oscillator strength of 1.621(3) was derived from the experimental dipole polarizability.

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I. INTRODUCTION

Recently, the dipole polarizability of Mg-like silicon—i.e. Si^{2+}—has been measured by resonant excitation Stark ionization spectroscopy (RESIS) [1]. This technique has given polarizabilities for Mg^+ [2], Si^{3+} [3,4], Ba^+ [5,6], and Si^{2+} [7]. The precision in the dipole polarizabilities deduced from these experiments is about 0.1%.

While these experiments are interesting in themselves, they are relevant to the new generation of single atomic ion clocks currently under investigation [8–12]. These clocks have the potential the exceed the precision of the existing cesium microwave standard [13,14].

For many of these clocks the single largest systematic source of uncertainty is the blackbody radiation (BBR) shift [12,15–20]. The lowest-order expression for the BBR shift is proportional to the difference in polarizabilities of the two states involved in the clock transition. Accordingly, the determination of atomic polarizabilities for atomic (ionic) states involved in clock transitions has become a topic of high priority.

One of these clocks is based upon the Al^+ $^3P^o_0 \rightarrow {}^1S^e$ transition. Indeed, a recent experiment measured the frequency ratio for the Al^+ and Hg^+ clock transitions to a precision of 4.3×10^{-17} [12]. While the polarizability of Al^+ has not been measured in a RESIS experiment, the isoelectronic ion Si^{2+} has had its dipole polarizability measured [7]. Therefore, a calculation of the Si^{2+} polarizability and comparison with the RESIS polarizability can be used to benchmark the accuracy of calculations upon Al^+ provided the same basic calculational technique is used. These comparisons can be used to assign realistic error limits on any theoretical techniques and thus ultimately help constrain the uncertainties associated with the BBR shift.

A calculation of the dipole polarizability of the ground state of Si^{2+} using a configuration-interaction (CI) approach is presented. The basis used to describe the two valence electrons was large, and consequently the error associated with this part of the calculation is small enough to be ignored. The underlying Hamiltonian is based upon a fixed-core Hartree-Fock wave function with core-valence correlations represented by semiempirical polarization potentials. The importance of terms in the polarization expansion beyond the leading-order dipole polarization potential was also studied. This permitted a more refined analysis of the RESIS data and gives increased confidence in the RESIS determination of the dipole polarizability.

II. DESCRIPTION OF THE GROUND AND EXCITED STATES

A. CI calculations

The CI calculations used to generate the physical and L^2 pseudostates were very similar in style to those used previously to determine the dispersion parameters of a number of two-electron systems [22,21,23]. The Hamiltonian for the two active electrons is written

$$H = \sum_{i=1}^{2} \left(-\frac{1}{2}\nabla_i^2 + V_{\mathrm{dir}}(\mathbf{r}_i) + V_{\mathrm{exc}}(\mathbf{r}_i) + V_{\mathbf{p}1}(\mathbf{r}_i) \right) + V_{\mathbf{p}2}(\mathbf{r}_1,\mathbf{r}_2) + \frac{1}{r_{12}}. \tag{1}$$

The direct and exchange interactions of the valence electrons with the Hartree-Fock (HF) core were calculated exactly. The $1s^2 2s^2 2p^6$ core wave function was taken from a HF calculation [24] of the Si^{3+} ground state using an $(8s,5p)$ Slater-type orbital (STO) basis. The ℓ-dependent polarization potential V_{p1} was semiempirical in nature with the functional form

$$V_{\mathbf{p}1}(r) = -\sum_{\ell m} \frac{\alpha_d g_\ell^2(r)}{2r^4} |\ell m\rangle\langle \ell m|. \tag{2}$$

The coefficient α_d 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 to reproduce the binding energies of the Si^{3+} ns ground state and the np, nd, and nf excited states. The core polarizability of $\alpha_d = 0.1624$ a.u. was computed with the random phase approximation [25]. The

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TABLE I. Theoretical and experimental energy levels (in hartree) of some of the low-lying singlet states of the Si^{2+} ion. The energies are given relative to the energy of the Si^{4+} core. The experimental energies are taken from the National Institute of Standards database [26,27].

State	Energy (a.u.) Theory	Energy (a.u.) Experiment
$3s^2\ {}^1S^e$	−2.889727	−2.889775
$3s3p\ {}^1P^o$	−2.512090	−2.512126
$3p^2\ {}^1D^e$	−2.331706	−2.332925
$3p^2\ {}^1S^e$	−2.189308	−2.190632
$3s4s\ {}^1S^e$	−2.165268	−2.165001
$3s3d\ {}^1D^e$	−2.134707	−2.134494
$3s4p\ {}^1P^o$	−2.085718	−2.085640
$3s4d\ {}^1D^e$	−1.958978	−1.958775
$3s4f\ {}^1F^o$	−1.956832	−1.956510

cutoff parameters for $\ell=0\rightarrow 3$ were $0.7473a_0$, $0.8200a_0$, $1.022a_0$, and $0.900a_0$, respectively. The cutoff was set to $0.90a_0$ for $\ell>3$.

The two-body polarization potential V_{p2} is defined as

$$V_{p2}(\mathbf{r}_i,\mathbf{r}_j) = -\frac{\alpha_d}{r_i^3 r_j^3}(\mathbf{r}_i\cdot\mathbf{r}_j)g_{p2}(r_i)g_{p2}(r_j), \tag{3}$$

where g_{p2} has the same functional form as $g_\ell(r)$. The cutoff for g_{p2} was $0.869a_0$—i.e., the average of ρ_0, ρ_1, ρ_2, and ρ_3

There were a total of 187 valence orbitals with a maximum orbital angular momentum of $\ell=6$. The radial dependence of the orbitals was described by a mixture of STOs and Laguerre-type orbitals (LTOs) [21,22]. The number of active orbitals for $\ell=0\rightarrow 6$ was 32, 30, 30, 30, 25, 20, and 20, respectively. Some $\ell=0$ and $\ell=1$ valence orbitals were generated from the STOs used for the core. All the other orbitals were written as LTOs due to the superior linear dependence properties of LTOs when compared with STO basis sets. The use of the large orbital basis resulted in wave functions and energies for the low-lying states that were close to convergence. The length of the CI expansions for the different states ranged from 2000 to 7000. There were some minor changes made to the ρ_ℓ values tuned to the Si^{3+} spectrum to improve the agreement of the Si^{2+} energies with experiment. The current CI calculations with a semiempirical core potential are termed the CICP model.

The oscillator strengths were computed with operators that included polarization corrections [21,28–30]. The cutoff parameter in the operator correction was $0.869a_0$. The quadrupole core polarizability was chosen as $0.1021a_0^5$ [25], while the octupole polarizability was set to zero.

B. Energy levels

The binding energies of some low-lying states of the Si^{2+} ion are tabulated and compared with experiment in Table I. The agreement between the CICP energies and the experimental energies is generally of the order of $10^{-4}-10^{-3}$ hartree.

C. Oscillator strengths

Table II lists the oscillator strengths for a number of Si^{2+} transitions involving low-lying states. The absorption oscillator strength for a multipole transition from $g\rightarrow n$, with an energy difference of $\Delta E_{ng}=E_g-E_n$, is defined as

$$f_{gn}^{(k)} = \frac{2|\langle\psi_g;L_g\|r^k\mathbf{C}^k(\hat{\mathbf{r}})\|\psi_n;L_n\rangle|^2\Delta E_{ng}}{(2k+1)(2L_g+1)}. \tag{4}$$

In this expression, L_g is the orbital angular momentum of the initial state, while k is the polarity of the transition. This definition of the oscillator strength is convenient for theoretical analysis. However, there are other definitions of the oscillator strength that give different numerical values for $k\geqslant 2$ [39].

Values from the extensive tabulation of dipole line strengths using a *B*-spline nonorthogonal configuration interaction with the Briet interaction (BSR-CI) [31] are listed in Table II. Oscillator strengths from an older CI calculation [32] based on a semiempirical model potential (MPCI) are also listed in Table II.

TABLE II. Theoretical and experimental values of the oscillator strengths for selected transitions of the Si^{2+} ion. Oscillator strengths from other sources are identified by citation. The uncertainties in the last digits are given in parentheses.

Transition	CICP	BSR-CI [31]	MPCI [32]	Other
$3s^2\ {}^1S^e\rightarrow 3s3p\ {}^1P^o$	1.623	1.609	1.62	1.694 CI [33], 1.59 MBPT [34], 1.60(24) Expt. [35], 1.64(41) Expt. [36]
$3s^2\ {}^1S^e\rightarrow 3s4p\ {}^1P^o$	0.0215	0.0225	0.031	0.0147 CI [33]
$3s^2\ {}^1S^e\rightarrow 3p^2\ {}^1D^e$	6.020			
$3s^2\ {}^1S^e\rightarrow 3s3d\ {}^1D^e$	8.758			
$3s3p\ {}^1P^o\rightarrow 3p^2\ {}^1S^e$	0.2211	0.2246	0.279	0.173(12) Expt. [37]
$3s3p\ {}^1P^o\rightarrow 3s4s\ {}^1S^e$	0.0806	0.0767	0.0175	
$3s3p\ {}^1P^o\rightarrow 3p^2\ {}^1D^e$	0.0458	0.0480	0.0482	0.062(4) Expt. [38]
$3s3p\ {}^1P^o\rightarrow 3s3d\ {}^1D^e$	1.661	1.655	1.66	

The present CICP and BSR-CI oscillator strengths are within 1% of each other for the strong transitions and 4% for the weaker transitions. The oscillator strengths for the stronger transitions from the older MPCI calculation agree well with the more modern calculations. A relativistic many-body perturbation theory (MBPT) calculation [34] gave 1.59 for the resonance oscillator strength. The MBPT calculation is not expected to be as accurate as either the CICP or BSR-CI calculation. The correlations between the two valence electrons were treated perturbatively, while more modern MBPT-type calculations used CI to treat the interactions between valence electrons while using MBPT to treat core-valence correlations [40].

A number of experimental oscillator strengths are listed in Table II. However the data do not have sufficient precision to discriminate between the BSR-CI and CICP oscillator strengths.

III. POLARIZATION EXPANSION

A. Definitions

The polarization interactions between the core and a single Rydberg electron leads to the effective potential [1,41,42]

$$V_{\text{pol}} = -\frac{C_4}{r^4} - \frac{C_6}{r^6} - \frac{C_7}{r^7} - \frac{C_8}{r^8} - \frac{C_{8L}L(L+1)}{r^8} + \cdots . \quad (5)$$

This functional form has been applied to the analysis of the fine-structure spectrum of the Rydberg states of neutral Mg and Si^{2+}, resulting in precise estimates of the dipole polarizabilities of the sodiumlike Mg^+ and Si^{3+} ground states [2–4].

The leading coefficient C_4 is half the size of the static dipole polarizability:

$$C_4 = \frac{\alpha_1}{2}. \quad (6)$$

The dipole polarizability is defined as

$$\alpha_1 = \sum_n \frac{f_{gn}^{(1)}}{(\Delta E_{gn})^2}, \quad (7)$$

where $f_{gn}^{(k)}$ is the absorption oscillator strength for a dipole transition from state g to state n. The sum is over all excited states of the system.

The next term C_6 is composed of two separate terms:

$$C_6 = \frac{\alpha_2 - 6\beta_1}{2}. \quad (8)$$

The quadrupole polarizability, α_2 is computed as

$$\alpha_2 = \sum_n \frac{f_{gn}^{(2)}}{(\Delta E_{gn})^2}. \quad (9)$$

The second term in Eq. (8) is the nonadiabatic dipole polarizability. It is defined as

$$\beta_1 = \sum_n \frac{f_{gn}^{(1)}}{2(\Delta E_{gn})^3}. \quad (10)$$

The r^{-7} term C_7 also comes in two parts: namely,

TABLE III. The final polarizabilities and C_n parameters used in the analysis of the RESIS spectrum for Si^{2+}.

Property	Value	Property	Value
α_1	11.688	C_4	5.8440
α_2	35.754	C_6	−27.558
α_3	171.85	C_7	−124.89
β_1	15.145	C_8	595.23
β_2	27.904	C_{8L}	71.957
γ_1	19.988		
α_{112}	121.86		
α_{1111}	175.05		

$$C_7 = -\frac{(\alpha_{112} + 3.2q\gamma_1)}{2}. \quad (11)$$

The γ_1 is a higher-order nonadiabatic term; it is defined as

$$\gamma_1 = \sum_n \frac{f_{gn}^{(1)}}{4(\Delta E_{gn})^4}, \quad (12)$$

where q is the charge on the core. The dipole-dipole-quadrupole polarizability α_{112} arises from third order in perturbation theory [41] and cannot be expressed as an oscillator strength sum. Explicit expressions have been given by Snow and Lundeen [4]. Quite a few terms contribute to C_8:

$$C_8 = \frac{\alpha_3 - \beta_2 - \alpha_1\beta_1 + \alpha_{1111} + 72\gamma_1}{2}. \quad (13)$$

The octupole polarizability α_3 is computed as.

$$\alpha_3 = \sum_n \frac{f_{gn}^{(3)}}{(\Delta E_{gn})^2}. \quad (14)$$

The β_2 comes from the nonadiabatic part of the quadrupole polarizability; it is

$$\beta_2 = \sum_n \frac{f_{gn}^{(2)}}{2(\Delta E_{gn})^3}. \quad (15)$$

The fourth-order term α_{1111} is part of the hyperpolarizability [41,41,43], and explicit expressions have been given by Robb and co-workers [43]. The final term C_{8L} is nonadiabatic in origin and defined as

$$C_{8L} = \frac{18\gamma_1}{5}. \quad (16)$$

B. Computed polarizabilities

The values of all polarizabilities for the $3s^2$ ground state are listed in Table III. The static and nonadiabatic dipole polarizabilities are dominated by the term arising from the resonant transition. One finds that 97.4% of α_1 arises from the $f_{3s^2 \to 3s3p}$ transition. The weighting of the resonant transition is even larger for the nonadiabatic polarizabilities with 99.5% of β_1 and 99.85% of γ_1 coming from this transition.

The actual breakdown of the different contributions to the polarizability is 11.3859 a.u. from the resonant transition, 0.1396 a.u. from the rest of the valence transitions, and 0.1624 a.u. from the core.

The dipole polarizability of the $3s3p\ ^1P^0$ excited state was also computed. It was found to be 12.707 a.u.

The actual calculations of the α_{112} and α_{1111} polarizabilities were performed in an excitation space restricted to the $3s3p\ ^1P^0$ state and the two lowest $^1S^e$ and three lowest $^1D^e$ excited states. The core was also omitted from the calculation.

One aspect of Table III that is relevant to the interpretation of experiments is the importance of the nonadiabatic dipole polarizabilities for the higher-order terms. The respective contributions to C_6 are 17.877 from α_2 and -45.44 from $-6\beta_2$. Similarly, one finds that the γ_1 term of -3.2×19.988 makes up 50% of the C_7 value of -124.9 a.u. Finally, the C_8 value of 595.2 a.u. is largely due to the $36\gamma_1$ contribution of 719.6 a.u.

The procedures used to determine the α_{112} and α_{1111} polarizabilities were validated on the He^+ system. A calculation of the He^+ excitation spectrum was performed, and the resulting lists of reduced matrix were entered into the polarizability programs. All the coefficients given by Drachman [44] were reproduced.

C. Assessment of polarizability uncertainties

The CICP calculation is semiempirical in nature, so an *a priori* determination of the uncertainty is problematic. However, comparisons with high-precision experiments and high-precision calculations make it possible to place some bounds on the polarizabilities.

The polarizabilities are evaluated by oscillator strength sum rules, so the uncertainties in the polarizabilities are largely determined by the uncertainties in the oscillator strengths. The underlying accuracy of the one electron-core–valence interaction can be deduced by examination of line strengths for the alkali-metal-like ions. A systematic comparison of the $3s \rightarrow 3p$ line strengths for the Na and isoelectronic systems Mg^+, Al^{2+}, and Si^{3+} revealed a consistent trend when the HF plus core polarization (HFCP) [a model based on similar physics to the present CICP model], a MBPT calculation, and CI-BSR were contrasted [45]. The MBPT calculation was a relativistic all-order single-double calculation which treats all single and double excitations from a Dirac-Fock reference state to all orders of many-body perturbation theory. The spread between the line strengths was generally about 1%, with the HFCP line strengths being the smallest and the BSR-CI being the largest with the MBPT line strength being intermediate in size. The highest-precision experiments gave line strengths closer to the HFCP and BSR-CI values. A reasonable conclusion would be that the present model is capable of predicting the resonant oscillator strengths of low Z Na-like ions to an accuracy of 0.5% better [45].

There are additional uncertainties associated with the prediction of the resonant oscillator strength of Mg-like ions. Unfortunately, there have not been any really high-precision lifetime experiments upon the Mg-like ions. The most refined *ab initio* calculations were a CI+MBPT calculation which gave a Mg line strength of 16.24(16) [40,46], while the BSR-CI calculation gave 16.05 [31]. An earlier CICP-type calculation [47] on Mg gave 16.24 for the line strength. Therefore an uncertainty of 1% or 0.117 a.u. has been assigned to the CICP line strength. The rest of the valence and core transitions only contribute 0.303 a.u. to the dipole polarizability. The uncertainty in the core polarizability of 0.1624 a.u. has been estimated at 5% or 0.0080 a.u. [45]. The rest of the valence f-value distribution will be conservatively assumed to have a relative uncertainty twice as large as that of the resonant transition, giving a contribution of 0.0028 a.u. In total, this gives a relative uncertainty of 1.1% or an overall uncertainty of 0.129 a.u. in α_1.

The uncertainties in the nonadiabatic polarizabilities β_1 and γ_1 are slightly smaller than that of α_1 since the higher power in the energy denominator means they are less susceptible to errors coming from the core polarizability and other valence transitions. The uncertainties in the quadrupole and octupole polarizabilities can be assumed to be roughly the same size as that of the dipole polarizability—i.e., 1%. The uncertainty in C_6 is therefore $(0.358+6\times 0.127)/2=1.1$ a.u.

The major errors in the α_{112} and α_{1111} evaluations arise from the restricted excitation space used in the sum rules. An indication of the error can be estimated by evaluating the polarizabilities in the restricted space. The ground-state dipole polarizability was 11.386 a.u., while the quadrupole polarizability was 34.95 a.u. The $3s3p\ ^1P^0$ static dipole polarizability was 12.31 a.u. These polarizabilities are all within 3% of sum-rule values when the entire excitation space is included. The multiplicative structure of the α_{112} and α_{1111} polarizabilities suggests that the relative uncertainties should be added and the uncertainties can be assessed as 9% and 12%, respectively. Errors in the evaluation of α_{112} and α_{1111} do not have a major impact in the derived values of C_7 and C_8. For example, a 13% error in α_{112} would result in a 4% change in C_7, while a 12% error in α_{1111} would lead to a 1.5% change in C_8.

D. Polarization plot

Polarizabilities can be extracted from experimental data using a polarization plot. This is based on a similar procedure that is used to determine the ionization limits of atoms [48]. Assuming that the dominant terms leading to departures from hydrogenic energies are C_4 and C_6 terms, we can write

$$\frac{\Delta E}{\Delta\langle r^{-4}\rangle} = C_4 + C_6\frac{\Delta\langle r^{-6}\rangle}{\Delta\langle r^{-4}\rangle}. \tag{17}$$

In this expression, ΔE is the energy difference between two states of the same n, but different L—i.e., $\Delta E=E(n,L)-E(n,L')$. $\Delta\langle r^{-6}\rangle$ and $\Delta\langle r^{-4}\rangle$ are the differences in the radial excitation values of the two states.

There are other corrections that can result in Eq. (17) departing from a purely linear linear form. These are relativistic energy shifts, Stark shifts due to a residual electric field, and polarization shifts due to the C_7 and C_8 (and possibly higher-order) terms of Eq. (5). The energy difference be-

TABLE IV. Various energy corrections (in units of MHz) for some $n=19$ energy intervals of Si^{+}. The L_1 and L_2 columns give the ℓ values of the adjacent Rydberg states. All first- and second-order polarization corrections were computed using the C_n values listed in Table III. The relativistic corrections were computed using Eq. (21), while the Stark shift corrections are those used in Komara *et al.* [7].

n	L_1	L_2	ΔE_{rel}	ΔE_4	ΔE_6	ΔE_7	ΔE_8	ΔE_{8L}	ΔE_{sec}	ΔE_{ss}
19	9	10	4.0968	658.6201	−6.3133	−1.2900	0.2835	2.8728	0.4738	−0.0833
19	10	11	3.3843	364.9377	−2.2672	−0.3697	0.0644	0.7944	0.1430	−0.0987
19	11	12	2.8428	212.5616	−0.8843	−0.1172	0.0165	0.2436	0.0477	−0.1025
19	12	13	2.4217	129.0478	−0.3687	−0.0402	0.0046	0.0810	0.0172	−0.0837
19	13	14	2.0876	81.1276	−0.1623	−0.0147	0.0014	0.0287	0.0067	−0.0269
19	13	15	3.9059	133.6673	−0.2369	−0.0204	0.0019	0.0393	0.0094	0.0711
19	13	16	5.5038	168.5725	−0.2724	−0.0226	0.0020	0.0434	0.0106	0.3910

tween the (n,L) and (n,L') states can be written

$$\Delta E = \Delta E_4 + \Delta E_6 + \Delta E_7 + \Delta E_8 + \Delta E_{8L} + \Delta E_{\text{rel}} + \Delta E_{\text{sec}} + \Delta E_{\text{ss}}, \tag{18}$$

where ΔE_n arises from the polarization terms of order $\langle r^{-n}\rangle$.

Dividing Eq. (18) through by $\Delta\langle r^{-4}\rangle$ and replacing ΔE_6 by $C_6\Delta\langle r^{-6}\rangle$ gives

$$\frac{\Delta E}{\Delta\langle r^{-4}\rangle} = C_4 + C_6\frac{\Delta\langle r^{-6}\rangle}{\Delta\langle r^{-4}\rangle} + \frac{\Delta E_7 + \Delta E_8 + \Delta E_{8L}}{\Delta\langle r^{-4}\rangle} + \frac{\Delta E_{\text{rel}} + \Delta E_{\text{sec}} + \Delta E_{\text{ss}}}{\Delta\langle r^{-4}\rangle}. \tag{19}$$

The influence of the Stark shifts, relativistic shifts, and second-order polarization correction can be incorporated into the polarization plot by simply subtracting the energy shifts.

The corrected energy shift ΔE_{c1} is derived from the experimental energy shifts [7] as

$$\frac{\Delta E_{c1}}{\Delta\langle r^{-4}\rangle} = \frac{\Delta E_{\text{obs}}}{\Delta\langle r^{-4}\rangle} - \frac{\Delta E_{\text{rel}} + \Delta E_{\text{sec}} + \Delta E_{\text{ss}}}{\Delta\langle r^{-4}\rangle}. \tag{20}$$

An approximate result is used for the relativistic energy correction. This is taken as

$$E_{\text{rel}} = -\frac{\alpha^2 Z^4}{2n^3}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right). \tag{21}$$

The corrections due to relativistic effects for the Rydberg states of Si^{+} for which RESIS data existed are listed in Table IV. Corrections due to energy shifts from other sources are also given in Table IV.

The second-order correction ΔE_{sec} used the analytic results of Drake and Swainson [49,50]. There was one issue in applying the Drake-Swainson formulation. Equations (41) and (42) of [49] imply a second-order energy correction that scales as Z^{10} for a fixed polarizability, whereas the actual Z scaling should be Z^6. A Z^6 scaling is also compatible with the text just after Eq. (15) of [50]. The Stark shift correction ΔE_{ss} used the Stark shift coefficients tabulated by Komara *et al.* [7] and their value for the background electric field.

The second corrected energy is defined by further subtracting the polarization shifts ΔE_7, ΔE_8, and ΔE_{8L}:

$$\frac{\Delta E_{c2}}{\Delta\langle r^{-4}\rangle} = \frac{\Delta E_{\text{c1}}}{\Delta\langle r^{-4}\rangle} - \frac{\Delta E_7 + \Delta E_8 + \Delta E_{8L}}{\Delta\langle r^{-4}\rangle}. \tag{22}$$

The radial expectation values needed for the polarization energy shift were computed with the formulas of Bockasten [51], while the C_n values were taken from Table III.

Table IV shows the sizes of all the corrections to the energies of the Rydberg states used in the RESIS analysis. The RESIS data start for the $(n,L)=(19,9)-(19,10)$ interval. The largest energy correction to any of the levels comes from the C_4 term. The next largest term is ΔE_6, which is 1.1% of ΔE_4 for (19,9)-(19,10) interval.

One finds that ΔE_{8+8L} is larger than ΔE_7 for the (19,9)-(19,10) interval largely due to the impact of the C_{8L} term. The impact of the higher multipole corrections ΔE_7 and ΔE_{8+8L} diminishes as L increases. The $\Delta E_{7,8,8L}$ corrections for the (19,9)-(19,10) interval amount to about 40% of the ΔE_6 energy shift. As mentioned by Drachman [44], a condition for the usefulness of the polarization series is that the $\Delta E_{7,8,8L}$ corrections should be smaller than the ΔE_6 corrections. Therefore, the series, Eq. (5), is justified for the current (n,L) values of Si^{+} for which RESIS data exists.

The previous analysis of Komara *et al.* [7] did not explicitly include the contribution from C_7, C_8, and C_{8L} terms. In a later analysis, Snow *et al.* [4] underestimated the possible influence of these terms on the polarization plot. However, this omission had only a marginal impact on the derived dipole polarizability.

Figure 1 shows the polarization plot for Si^{+}. One feature is the irregularity in the plot for the smallest values of $\frac{\Delta\langle r^{-6}\rangle}{\Delta\langle r^{-4}\rangle}$. This irregularity occurs for the two states that were resolved by increasing the microwave intensity so as to make two- and three-photon transitions detectable. The high microwave intensities do lead to a significant ac Stark shift, which in turn entails making corrections to the energy intervals. The easiest way to deal with the problem is to remove these two points from the linear regression analysis used to derive the dipole and quadrupole polarizabilities. It is noted in passing that little information describing the details of the Stark shift correction is available.

A notable aspect of Fig. 1 are the slopes of the ΔE_{c1} and ΔE_{c2} plots. The ΔE_{c1} data points show a distinct departure from a purely linear curve. This indicates that polarization

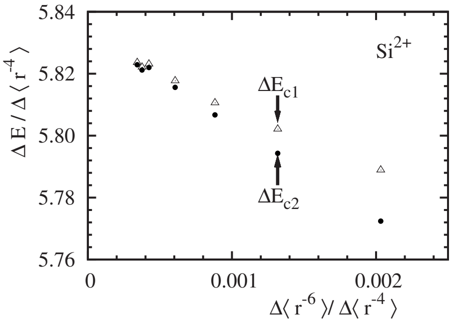

FIG. 1. The polarization plot of the fine-structure intervals of Si$^+$ for the $n=19$ Rydberg levels. The ΔE_{c1} intervals are corrected for relativistic, second-order, and Stark shifts. The ΔE_{c2} intervals account for $\langle r^{-7}\rangle$ and $\langle r^{-8}\rangle$ shifts.

corrections beyond C_6/r^6 have an impact on the energy splittings. On the other hand, the ΔE_{c2} polarization plot has no detectable nonlinear features apart from the first two points at the smallest values of $\frac{\Delta\langle r^{-6}\rangle}{\Delta\langle r^{-4}\rangle}$, which were influenced by ac Stark shifts. This indicates that inclusion of the ΔE_7 and ΔE_{8+8L} corrections takes into account most of the higher-order polarization effects.

A linear regression was applied to the five single-photon data points in Fig. 1. The intercept was 5.8343, which translates to a polarizability of 11.669(9) a.u. The dipole polarizability originally derived in Komara *et al.* was 11.666(4) a.u. [7]. The inclusion of the higher-multipole corrections to the polarization energy leads to the derived dipole polarizability changing by an amount equal to the stated uncertainty of the original experiment.

The slope was −30.543. Using $\beta_1=15.145$ a.u. gives a quadrupole polarizability of $\alpha_2=-61.09+90.87=29.78$ a.u. This is about 6 a.u. smaller than the CICP quadrupole polarizability of 35.75 a.u. The previous analysis of Komara *et al.* [7] did not present an estimate of the quadrupole polarizability.

1. Uncertainties in α_1 and α_2

The difference between the experimental $C_6=-30.543$ and the calculated C_6 of −27.56(110) is used to assign an uncertainty to the derived α_1. A pair of linear regressions were performed with C_6 fixed to be −26.45 and −34.62, respectively, to estimate the uncertainty in the intercept. The polarizability with error limits was 11.669(9) a.u.

The value of α_2 derived from the polarization plot experiment is susceptible to large errors due to the cancellations implicit in the calculation. The uncertainty is

$$\delta\alpha_2 = 2\,\delta C_6 + 6\,\delta\beta_1. \tag{23}$$

The uncertainty in β is small since the dipole polarizability is well reproduced. Assigning a relative uncertainty of 0.5% to β_1 gives $6\delta\beta_1=0.5$. The major source of uncertainty in C_6 is the possible impact of higher-order adiabatic and nonadiabatic polarizabilities. This was estimated to be half the difference in the slopes of the ΔE_{c1} and ΔE_{c2} plots depicted in Fig. 1. This choice was motivated by the discussion of Drachman on the convergence of the polarization series [44]. Therefore, using $2\delta(C_6)=10.0$ gives $\delta\alpha_2=10.5$ a.u. The RESIS and CICP quadrupole polarizabilities agree when the relatively large uncertainty is taken into consideration.

2. Estimate of the resonant oscillator strength

An estimate of Si^{2+} resonant oscillator strength can be derived from the experimental oscillator strength via the relation

$$f_{3s^2\rightarrow 3s3p} = (\Delta E_{3s^2\rightarrow 3s3p})^2(\alpha_1-\alpha_{\text{core}}-\alpha') = 0.377649^2 \times (11.669-0.1624-0.1396) = 1.621. \tag{24}$$

The α' polarizability is the valence polarizability with the resonant transition removed. Incorporating the uncertainties given previously gives a final value of 1.621(3) for the resonant oscillator strength. This oscillator strength is compatible with the CICP oscillator strength and incompatible with the BSR-CI oscillator strength.

IV. CONCLUSIONS

The polarizabilities of the Si^{2+} ion ground state have been calculated with the sum-over-states approach in conjunction with some large-basis CI calculations. The higher-order polarizabilities are used to make corrections to the RESIS fine-structure intervals of the Lundeen group [2]. A polarization plot is then made, yielding a revised polarizability of 11.669(9) a.u. This is marginally larger than the original experimental value of 11.666(4) a.u. [7]. The dipole polarizability obtained from the CICP model is 11.688 a.u.

A semiempirical CI calculation based on a HF core is seen to give an accurate dipole polarizability for Si^{2+}, and by implication it should be able to accurately predict the polarizabilities of other Mg-like atoms and ions. This difference between CICP and experimental polarizabilities of 0.2% was fortuitious. While the high level of agreement between CICP and CI+MBPT calculations of the Mg ground-state polarizability [21,47,40] did suggest that a CICP accuracy of better than 1% was achievable, an accuracy of 0.2% indicates that there has been some fortunate cancellation of errors. Earlier in this paper, a first-principles estimate of the uncertainty in the ground state polarizability of 1.1% was made. The present CICP calculation was partly done in order to establish a better estimate of the uncertainty that could be translated to Al$^+$. A conservative, after-the-fact conclusion would be that the CICP approach is capable of predicting the ground-state polarizabilities of Mg-like ions to an accuracy of 0.5% or better. The circumstances that conspired to make the CICP very accurate for Si^{2+} can be expected to apply to other Mg-like ions such as Al$^+$ provided the CICP methodology is applied in a consistent manner.

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