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Theoretical study of the isotope effects on the detachment thresholds of Si^-

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The isotope effects in Si^- bound levels are studied using the multiconfiguration Hartree-Fock *ab initio* approach. Large-scale calculations are carried out for the $3p^3\ {}^4S^o$, ${}^2D^o$, and ${}^2P^o$ multiplets of Si^- and the $3p^2\ {}^3P$ multiplet of Si. We predict an anomalous isotope shift on the electron affinity, dominated by the specific mass shift, with a value of $-0.66(6)$ m^{-1} for the 30-28 isotope pair. We also report hyperfine-structure parameters for the studied multiplets. We provide the values of level electric-field gradients at the nucleus that could be of interest in a study of the metastable silicon isotopes. Relativistic corrections are estimated using nonrelativistic orbitals in the Breit-Pauli and fully relativistic frameworks.

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I. INTRODUCTION

In recent decades, the interest in the isotope effects in negative ions has grown as the experimental techniques have evolved [1,2]. In particular, the isotope shift (IS) in the electron affinity, i.e., the shift of a negative-ion binding energy from one isotope to another, has gradually become accessible experimentally [3–5] and theoretically [5–8]. The study of isotope shifts on atomic transitions is a rather old subject and previous advances in our understanding of atomic structure are tightly linked to advances in experimental techniques permitting the measurement of isotope effects [9]. The laser photodetachment techniques attained such a level of accuracy that there are new possibilities for understanding negative ions and isotope effects.

Silicon is the third-period atom of the carbon-group; its lowest configuration is [Ne]$3s^23p^2$. The silicon negative ion binds the three multiplets arising from the $3p^3$ configuration, i.e., the ground state ${}^4S^o_{3/2}$ and the excited ${}^2D^o_{3/2,5/2}$ and ${}^2P^o_{1/2,3/2}$ states. Scheer *et al.* [10] have measured the binding energy of the ${}^2D^o_{3/2}$ and ${}^2D^o_{5/2}$ states, 0.527 234(25) and 0.525 489(20) eV, respectively, but were not able to detect the weakly bound ${}^2P^o$ whose best binding energy measurement to date is due to Kasdan *et al.* of 29(5) meV [11]. Blondel *et al.* [12] and Chaibi *et al.* [13] later measured the ^{28}Si electron affinity ${}^eA$, i.e., the ${}^4S^o_{3/2}$-${}^3P_0$ threshold, using the laser photodetachment microscopy technique and obtained ${}^eA({}^{28}Si^-) = 1\,120\,724.4(6)$ m^{-1} $= 1.389\,521\,0(7)$ eV.

There are two stable isotopes of silicon with zero spin: ^{28}Si (92.23%) and ^{30}Si (3.10%). The third stable silicon isotope is ^{29}Si (4.67%), which has a spin $I = 1/2$. Lee and Fairbank studied experimentally the $3s^23p^2\ {}^3P_2 \rightarrow 3s3p^3\ {}^3D^o_3$ transition isotope shifts and, in the case of ^{29}Si, its hyperfine structure [14]. This work was motivated by the possibility of using the metastable ^{31}Si ($I = 3/2$), decaying by β radiation into ^{31}P, for quantum computing applications [15]. Incidentally, it also determined the hyperfine constant of a state belonging to the ground multiplet of a silicon isotope. Wendt *et al.* [16] also conducted a two-photon Doppler-free study of isotope effects on the $3s^2\,3p^2\ {}^3P_{0,1,2} \rightarrow 3s^23p4p\ {}^3P_{0,1,2}$ transitions.

In the present work, we use an approach similar to that used for previous studies of the IS on the ${}^eA$ in neighboring elements sulfur [5] and chlorine [8]. This method, relying on a systematic reduction of the single and double excitations of a set of reference configurations, has been proven to work efficiently for computing isotopes shifts as well as hyperfine structure parameters [17], despite the strong emphasis that this approach puts on providing accurate energies. It has also been successfully used for studying the weakly bound $2p^3\ {}^2D^o$ excited state of C^- [7]. With respect to C^-, the challenge in Si^- is to correctly describe the correlation of the outer electron with the larger $1s^22s^22p^6$ core. This has been proven to be the bottleneck in S^- and Cl^- studies. One problem is to obtain a balanced description of the neutral atom and negative ion. Following previous works [5,8,18], we solve this issue by using orbitals specifically optimized for valence correlation to describe core-valence correlation.

In Sec. II we briefly lay out the theoretical background. The calculations of the isotope shifts and hyperfine parameters, as well as their reliability, are detailed in Secs. III and IV, respectively. We summarize in Sec. V.

II. THEORY

A. Mass isotope shift

At the nonrelativistic level, the energy corrected for the first-order mass shift is [8,19]

$$\delta E^{M'M} = \left[\frac{\mu}{M} - \frac{\mu'}{M'}\right]\left(E_\infty - \frac{\hbar^2}{m_e}S_{\rm SMS}\right), \qquad (1)$$

where $\mu = m_eM/(m_e + M)$ is the electron reduced mass, m_e is the electron mass, and M is the bare nucleus mass. Here E_∞ is the total binding energy of the atomic system and $S_{\rm SMS}$ is the specific mass shift parameter, both calculated with an infinite nucleus mass

$$S_{\rm SMS} = -\langle\Psi_\infty|\sum_{i<j}\nabla_i\cdot\nabla_j|\Psi_\infty\rangle. \qquad (2)$$

The first term of (1) contains the normal mass shift (NMS) and the second the specific mass shift. The atomic masses are taken from Audi *et al.* [20].

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B. Field isotope shift

It was shown for sulfur [5] and chlorine [18] that even if the field shift (FS) on the electron affinity due to the effect of the finite nucleus volume on the energy levels is below the current experimental resolution, it may constitute a non-negligible correction to the total isotope shift on the electron affinity of p-block atoms. This shift can be estimated using

$$\delta E_{\mathrm{FS}}^{M'M} = \frac{h a_0^3}{4Z} f(Z)^{M'M} [\langle r^2 \rangle_M - \langle r^2 \rangle_{M'}] 4\pi \Delta\rho(\mathbf{0}), \tag{3}$$

where $f(Z)$ is a scaling factor correcting for the relativistic effects, $\langle r^2 \rangle$ is the isotope-dependent rms radius, and $\Delta\rho$ is the change in the spinless total electron density [21] at the origin

$$\Delta\rho(\mathbf{0}) = \rho_{\mathrm{Si}}(\mathbf{0}) - \rho_{\mathrm{Si}^-}(\mathbf{0}). \tag{4}$$

The mean square radii of the nucleus charge densities of the different stable isotopes of Si ($A = 28,29,30$) are reviewed in Refs. [22,23], offering a large choice of nuclear shape parameters for silicon. We therefore choose to estimate the field shift from the averaged values of Angeli [24], $\langle r^2 \rangle^{1/2} = 3.1223(24), 3.1168(50), 3.1332(40)$ fm, respectively, for $A = 28,29,30$. The value for $f(Z)/c = 1.1099\ \mathrm{m}^{-1}/\mathrm{fm}^2$ is taken from Aufmuth *et al.* [25].

C. Hyperfine interaction

The hyperfine structure of a J level is caused by the interaction of the angular momentum of the electron cloud $\mathbf{J}$ and of the nucleus $\mathbf{I}$, forming the total atomic angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The theory underlying the computation of hyperfine structures can be found in Refs. [26–29]. The diagonal hyperfine-interaction energy correction is usually expressed in terms of the hyperfine magnetic dipole A_J and electric quadrupole B_J constants expressed in MHz. It is possible to further decompose the nonrelativistic hyperfine interaction in terms of the J-independent orbital a_l, spin dipole a_{sd}, contact a_c, and electric quadrupole b_q electronic hyperfine parameters defined in Refs. [26,27].

D. The multiconfiguration Hartree-Fock expansion

The multiconfiguration Hartree-Fock (MCHF) approach consists in variationally solving the time-independent Schrödinger equation in the space defined by the ansatz [30]

$$\Psi(\gamma L S M_L M_S \pi) = \sum_i c_i \Phi(\gamma_i L S M_L M_S \pi), \tag{5}$$

where $\Phi(\gamma_i L S M_L M_S \pi)$ are configuration state functions (CSFs) built on orthonormal one-electron radial functions. In practice, we mostly use a multireference interacting (MR-I) scheme [5]. It consists in selecting in the expansion (5) the CSFs that interact to first order with a multireference CSF set. This MR-I space is defined in a given one-electron orbital basis set $\lceil n_{\max} l_{\max} \rceil$ containing in total $n_{\max} - l$ orbitals of angular momentum quantum number $l \leqslant l_{\max}$. In order to include higher-order correlation effects, the linear problem in larger CSF spaces is solved by optimizing the c_i only. We refer to this model as configuration-interaction (CI) calculations. Because the specific mass shift on the electron affinity is mainly sensitive to valence correlation and the hyperfine-interaction constants are sensitive to core correlation, we settle for different approaches in Secs. III and IV. All nonrelativistic calculations, including the ones of the isotope shift parameters, are performed using the ATSP2K package [31].

E. Relativistic corrections

In order to estimate relativistic corrections, we compare nonrelativistic calculations to the corresponding relativistic calculations that have similar variational contents. To do so, the relativistic ansatz

$$\Psi(\Gamma J M \pi) = \sum_i c_i \Phi(\gamma_i J M \pi) \tag{6}$$

is constructed on orbitals optimized at the nonrelativistic level. This has been proven to work for hyperfine structures of second-period atoms [7,32,33]. For third-period atoms, the reliability of this scheme has not been established. It has been used for estimating relativistic effects on the hyperfine structures of the ground states of S, S$^-$, and Cl [18], but this study is not conclusive on the accuracy of the computed corrections. We compare the Breit-Pauli configuration-interaction (BPCI) method [30] and the relativistic configuration-interaction method using the Pauli approximation (RCIP) [34]. Such a comparison has recently been performed for excited states of fluorine [33], showing a good consistency between the two approaches.

For differential effects such as the electron affinity and its isotope shift, one has to strike a balance in the nonrelativistic approach as well as in the relativistic one. Except in the case of carbon and its negative ion [7], no attempt to achieve this within our framework has been successful. However, as previously emphasized for systems in which it is unrealistic to consider series of calculations converging toward an exact solution [5], it is necessary to define some guideline to assess the balance of the calculations performed on the neutral and the negative ion. We use the electron affinity itself as the natural guideline. Since the specific mass shift is much more sensitive to correlation effects than the energy, it is necessary to subtract relativistic corrections on the reference electron affinity, even if relativistic corrections on the isotope shift are not considered. When the nuclear spin is zero, nonrelativistic results for the electron affinity can be compared to reference nonrelativistic binding energies ${}^{e}A_{\mathrm{ref}}^{\mathrm{nr}}(LS)$, which are obtained by averaging the fine-structure experimental thresholds on the electronic J angular momenta and subtracting a theoretical estimation of the scalar non-fine structure relativistic effects $\Delta E_{\mathrm{theor}}^{NF}$ [18]

$${}^{e}A_{\mathrm{ref}}^{\mathrm{nr}} = {}^{e}A_{\mathrm{expt}}^{AV} - \Delta E_{\mathrm{theor}}^{NF}. \tag{7}$$

The BPCI and RCIP calculations are performed using the ATSP2K package [31] and the GRASP2K package [34], respectively.

III. DETACHMENT THRESHOLDS AND THEIR ISOTOPE SHIFTS

We perform Hartree-Fock (HF) frozen-core valence ($n = 3$) MCHF calculations on the Si ${}^3P$ and Si$^-$ ${}^4S^o$, ${}^2D^o$, and ${}^2P^o$

TABLE I. Total energies E and $S_{\rm SMS}$ parameters of the $3p^2\ {}^3P$ state of silicon calculated by closed-core MCHF and open-core CI calculations. We use two different multireferences $\mathcal{M}1$ and $\mathcal{M}2$ [see Eq. (9) and (10)]. The energies are given in hartrees E_h and $S_{\rm SMS}$ in units of a_0^{-2}.

	$\mathcal{M}1$		$\mathcal{M}2$	
nl	E	$S_{\rm SMS}$	E	$S_{\rm SMS}$
	frozen-core MR-I, MCHF			
$4f$	−288.936115	−44.70051	−288.936207	−44.70080
$5g$	−288.938949	−44.69585	−288.939102	−44.69631
$6h$	−288.939673	−44.69836	−288.939841	−44.69886
$7i$	−288.939967	−44.70029	−288.940139	−44.70087
$8k$	−288.940104	−44.70062	−288.940278	−44.70121
$9k$	−288.940156	−44.70064	−288.940331	−44.70124
$10k$	−288.940176	−44.70067	−288.940351	−44.70126
	relaxed-core MR-I, MCHF			
$10k$	−288.940236	−44.70410	−288.940410	−44.70461
	HF core MR-CV-I, CI			
$10k$	−288.974565	−44.47343	−288.975221	−44.47000

states. Fully variational valence MCHF calculations are also carried out for Si ${}^3P$ and Si$^-$ ${}^4S^o$.

We use a MR-I approach similar to that used in previous works [5,8]. For Si$^-$, the multireference (MR) $\mathcal{M}$ is

$$\mathcal{M} = [\mathrm{Ne}]\{3s,3p\}^3\{3,4\}^2\ {}^4S^o,{}^2D^o,{}^2P^o, \tag{8}$$

where the Ne-like core is kept closed, two electrons are allowed to be excited in correlation orbitals $\{3d,4s,4p,4d,4f\}$, and the three remaining valence electrons are distributed among the spectroscopic $\{3s,3p\}$ orbitals. More flexibility has to be given to the negative-ion model since it is a system containing one more electron than the neutral atom. An all-electron series of calculations converging toward the exact wave functions for the anion and corresponding neutral, as performed, for instance, in the case of carbon [7], is intractable in the present case. In general, the best one can hope for when performing *ab initio* calculations is to narrow down an interval in which the targeted property most likely lies by tailoring computational models to the task at hand. It is therefore necessary to use guidelines for assessing the robustness of the error bars. Hence, for the neutral silicon atom, we choose two multireference expansions defined as follows:

$$\mathcal{M}1 = [\mathrm{Ne}]\{3s,3p\}^2\{3\}^2\ {}^3P, \tag{9}$$

$$\mathcal{M}2 = [\mathrm{Ne}]\{3s,3p\}^2\{3\}^1\{3,4\}^1\ {}^3P. \tag{10}$$

We further generate the full MR-CV-I $\lceil 10k \rceil$ sets using the above multireferences and allowing at most one hole in the $n = 2$ shell to describe valence and core-valence (CV) correlation. As advocated in Ref. [8], we use the frozen-core $\lceil 10k \rceil$ orbital basis sets in open-core CI calculations. The MR-CV-I expansion of ${}^2D^o$, however, is too large to be tractable. Our results for the total energy and $S_{\rm SMS}$ parameter of the investigated states are reported in Tables I and II.

With the experimental fine structure of the neutral atom, we obtain the J-averaged electron affinity

$${}^eA^{AV}_{\rm expt}({}^4S^o) = 11\,356.93\ \mathrm{cm}^{-1}. \tag{11}$$

To estimate the scalar relativistic shift, we perform Dirac-Fock (DF) calculations with GRASP2K [34] and compare them to Hartree-Fock results. We obtain $\Delta E^{NF}_{\rm theor}({}^4S^o) = -75.1\ \mathrm{cm}^{-1}$ and

$${}^eA^{\rm nr}_{\rm ref}({}^4S^o) = 11\,432\ \mathrm{cm}^{-1}. \tag{12}$$

Note that de Oliveira *et al.* [35] obtain $\Delta E^{NF}_{\rm theor}({}^4S^o) = -63.47\ \mathrm{cm}^{-1}$ when including correlation effects. Scheer *et al.* [10] measure the ${}^2D^o$ fine structure at 14.08(20) cm^{-1} so that the corresponding ${}^eA^{AV}_{\rm expt}$ is

$${}^eA^{AV}_{\rm expt}({}^2D^o) = 4393.7(3)\ \mathrm{cm}^{-1}. \tag{13}$$

We calculate $\Delta E^{NF}_{\rm theor}({}^2D^o) = -60.05\ \mathrm{cm}^{-1}$ so that

$${}^eA^{\rm nr}_{\rm ref}({}^2D^o) = 4454\ \mathrm{cm}^{-1}. \tag{14}$$

TABLE II. Total energies E and $S_{\rm SMS}$ parameters of all bound states of Si$^-$ $3p^3$ calculated by closed-core MCHF and open-core CI calculations. The energies are given in hartrees E_h and $S_{\rm SMS}$ in units of a_0^{-2}.

	${}^4S^o$		${}^2D^o$		${}^2P^o$	
nl	E	$S_{\rm SMS}$	E	$S_{\rm SMS}$	E	$S_{\rm SMS}$
	frozen-core MR-I, MCHF					
$4f$	−288.985203	−44.77505	−288.949710	−44.75223	−288.928666	−44.74459
$5g$	−288.990582	−44.77066	−288.957542	−44.75069	−288.938660	−44.74419
$6h$	−288.991886	−44.77157	−288.959439	−44.74967	−288.941004	−44.74002
$7i$	−288.992360	−44.77456	−288.960126	−44.75275	−288.941837	−44.74061
$8k$	−288.992579	−44.77503	−288.960372	−44.75362	−288.942200	−44.74286
$9k$	−288.992662	−44.77525	−288.960577	−44.75402	−288.942338	−44.74311
$10k$	−288.992698	−44.77524	−288.960631	−44.75418	−288.942397	−44.74330
	relaxed-core MR-I, MCHF					
$10k$	−288.992749	−44.77487				
	HF core MR-CV-I, CI					
$10k$	−289.026801	−44.54629			−288.975331	−44.52808

TABLE III. Theoretical electron affinities, specific mass shifts (SMS), total mass shifts (MS), field shifts (FS), and total isotope shifts IS on the detachment thresholds of Si$^-$ for the 30-28 isotopic pair. For the ^3P-$^4S^o$ valence MCHF calculations, we present the results of both HF frozen-core ([Ne] HF) and relaxed-core approaches. All values are in cm^{-1}.

Approach	${}^eA^{\rm nr}$	SMS	MS[a]	FS	IS[a]
			^3P-$^4S^o$		
valence relaxed	11506(19)	−0.02023(8)	−0.00558(8)	0.00010(6)	−0.00548(14)
valence [Ne] HF	11508(20)	−0.02130(9)	−0.00666(9)	0.00010(6)	−0.00656(15)
plus core valence	11392(72)	−0.0214(5)	−0.0067(5)	0.00010(7)	−0.0066(6)
other theory[b]	11425				
${}^eA^{\rm nr}_{\rm ref}$	11432				
			^3P-$^2D^o$		
valence	4470(19)	−0.01526(9)	−0.00971(9)	0.00007(5)	−0.00963(14)
${}^eA^{\rm nr}_{\rm ref}$	4454				
			^3P-$^2P^o$		
valence	468(20)	−0.01214(9)	−0.01184(15)	0.00006(4)	−0.01178(19)
${}^eA^{\rm nr}_{\rm ref}$	438(40)				

[a] The NMS is taken from experiment: 0.014 647, 0.005 558, and 0.000 306(53) cm^{-1} for the $^4S^o$, $^2D^o$, and $^2P^o$ thresholds, respectively.

[b] Nonrelativistic results from Ref. [35]. Their scalar relativistic correction yields ${}^eA^{\rm nr}_{\rm ref} = 11\,420$ m^{-1}.

The Si$^-$($^2P^o$) detachment threshold is 234(40) cm^{-1} [11]. Its fine structure is unknown. Neglecting the possible effect of the $^2P^o$ fine structure and using the HF-DF value for $\Delta E^{NF}_{\rm theor}(^2P^o) = -54.24$ cm^{-1}, we deduce

$$ {}^eA^{AV}_{\rm expt}(^2P^o) = 384(40)\ \text{cm}^{-1} \tag{15}$$

and

$$ {}^eA^{\rm nr}_{\rm ref}(^2P^o) = 438(40)\ \text{cm}^{-1}. \tag{16}$$

As explained in Sec. II E, calculating relativistic corrections on differential effects including interelectron correlation is delicate. By comparing Hartree-Fock results to Dirac-Fock mass shift parameters calculated using the RIS3 program [36], we estimate relativistic corrections smaller than 1% and hence neglect them.

The final prediction is the window between the results obtained from the models based on $\mathcal{M}1$ and $\mathcal{M}2$. This interpolation is expected to provide robust error bars since the ${}^eA$ and $\Delta S_{\rm SMS}$ trends in series of calculations are highly correlated [7,8]. Table III presents the IS on the ${}^eA$ of Si for the 30-28 isotope pair. The uncertainty on the FS is dominated by the uncertainty on the proton distribution $\delta\langle r^2\rangle$. We have an overall good agreement of our nonrelativistic calculations with the ${}^eA^{\rm nr}_{\rm ref}$ and the calculation of de Oliveira *et al.* [35]. One can easily deduce the hyperfine averaged IS for the isotopic pairs involving ^{29}Si with these results. To the contrary of what has been observed in the calculations of isotope shifts on the electron affinities of sulfur and chlorine, the relaxed-core MCHF calculations disagree with the open-core CI results, the latter being close to the results obtained in frozen-core calculations. We observe a breakdown of the MR-CV-I approach for the $^2P^o$ detachment threshold. Indeed, this model leads to ${}^eA^{\rm nr}_{\rm theor}(^2P^o) = 96(72)$ cm^{-1}, which, compared to the value of 468(20) cm^{-1} obtained using the closed-core MR-I model, reveals unphysical bias in the $^2P^o$ state open-core calculations. This is due to a significant difference of the role of the orbitals and mixing coefficients in the Si$^-$($^2P^o$) and neutral silicon closed-core expansions due to so-called quasisymmetries in the MCHF energy functional [37]. This effect was already encountered, but not fully understood, in neutral sulfur calculations [5].

IV. HYPERFINE STRUCTURE

For computing hyperfine structures, it is not necessary to get a balance between different states, but inner correlation is of crucial importance. In this context, we opt for a different systematics in the construction of the MCHF ansatz: an all-electron series of MR-I calculations, hereafter referred as open-core (OC) MCHF calculations. The multireference is itself a closed-core CSF set including all single and double (SD) excitations of the valence in the $n = 3$ layer but omitting the $3s^2 \rightarrow 3d^2$ excitation. In order to avoid too many redundancies in the variational parameters, the core orbitals are kept frozen to their HF shape in all calculations. Single, double, and triple (SDT) excitations of $\{3s^23p^w, 3s^13p^w3d^1\}$ ($w = 2$ for Si and $w = 3$ for Si$^-$) in $\lceil 4f \rceil$ and $\lceil 5g \rceil$ are added to the $n_{\rm max} = 11$ expansions through configuration interaction.

The results for the hyperfine parameters are given in Tables IV–VI for Si(^3P) and Si$^-$ ($^4S^o$, $^2D^o$, and $^2P^o$). For neutral silicon and Si$^-$ $^4S^o$, we also compare these results with calculations performed with the orbitals $\lceil 10k \rceil$ optimized on valence correlation expansions of Sec. II D, as done in Ref. [18]. In Tables IV and V, the calculation V stands for the valence MCHF calculation, $\cup$ CV stands for the core-valence CI calculation (at most one hole in the core), and the CI calculation $\cup$ CC includes also the double excitations from the core. As analyzed in Ref. [18], this latter approach yields good results, despite a slower convergence with the number of correlation layers. They are only used as an indicator of the quality of the results.

TABLE IV. Hyperfine parameters, in units of a_0^{-3}, obtained from the OC-MCHF and CI calculations performed for the silicon $3p^2\,{}^3P$ term.

	Si ^3P			
nl	a_l	a_{sd}	a_c	b_q
$4f$	2.42451	0.49677	1.84461	0.99652
$5g$	2.42181	0.49928	1.08012	0.97866
$6h$	2.42420	0.50223	0.41961	0.99904
$7i$	2.36871	0.49710	0.57705	0.94872
$8k$	2.36633	0.49087	0.77783	0.95023
$9k$	2.37003	0.49268	0.62625	0.96203
$10k$	2.36975	0.49204	0.69278	0.95866
$11k$	2.36960	0.49224	0.66352	0.96032
$\cup$ MR-SDT $\lceil n'l' \rceil$, CI				
$4f$	2.37499	0.49344	0.61067	0.96516
$5g$	2.37663	0.49385	0.57875	0.96640
MR-I $\lceil 10k \rceil$				
V	2.00503	0.41095	0.83596	0.78085
$\cup$ CV	2.41588	0.49439	1.83006	0.98781
$\cup$ CC	2.36143	0.48519	0.62423	0.96704

The a_c Fermi contact contribution represents the contact interaction between the nucleus and the electron spins. It is well known that this parameter is highly sensitive to spin polarization of the electron cloud at the origin and often shows erratic convergence in a sequence of MCHF calculations [32]. This difficulty arises from the fact that the relevant CSFs having unpaired s electrons coupled as $(nsms)\,{}^3S$ have very small mixing coefficients c_i in (5). From Tables IV–VI only, it is unclear if convergence has been reached for this parameter. The convergence of a_c is especially important for the ground state of the anion Si$^-$ $^4S^o$ as it is the only nonzero contribution to the magnetic dipole hyperfine constant. The most important CSFs for a_c are single excitations $ns \rightarrow n's$ of the dominant configurations, in particular, to s orbitals with a large contact term $\langle \delta(r) \rangle$. In Table VII, the evolution of the a_c hyperfine parameter calculated with the sequence of OC-MCHF $\lceil nl \rceil$ correlation models is put in line with the $\langle \delta(r) \rangle$, mean radius $\langle r \rangle$, and occupation number q of the s orbitals of the most complete OC-MCHF $\lceil 11k \rceil$ calculation. The orbital reorganization when extending the orbital active set is weak enough to allow a meaningful correlation. Oscillations occur up to $n = 8$, but stabilization appears even if the $\langle \delta(r) \rangle_{ns}$ values of the last correlation layers are quite large. Adding higher excitations through MR SDT excitations has a major effect (see Table V) and triple excitations to other layers than $n = 4,5$ might impact a_c even more.

TABLE V. Hyperfine parameters, in units of a_0^{-3}, obtained from the OC-MCHF and CI calculations performed for the Si$^-$ $3p^3\,{}^4S^o$ and $^2D^o$ terms.

	Si$^-$ $^4S^o$	Si$^-$ $^2D^o$			
nl	a_c	a_l	a_{sd}	a_c	b_q
$4f$	1.57325	3.48007	0.71108	0.53265	0.00085
$5g$	0.89446	3.47959	0.71891	0.32564	0.00492
$6h$	−0.47211	3.38189	0.70974	−0.10365	0.02545
$7i$	−0.18712	3.39307	0.71769	−0.01380	0.02526
$8k$	0.00010	3.39448	0.71475	0.03436	0.02491
$9k$	−0.27006	3.40187	0.71222	−0.07060	0.02242
$10k$	−0.18106	3.39954	0.71275	−0.04981	0.02365
$11k$	−0.19180	3.39838	0.71207	−0.05451	0.02341
$\cup$ MR-SDT $\lceil n'l' \rceil$, CI					
$4f$	−0.32457	3.40735	0.71481	−0.09401	0.02533
$5g$	−0.35984	3.40164	0.71508	−0.10138	0.02662
MR-I $\lceil 10k \rceil$					
V	−0.00364				
$\cup$ CV	1.05388				
$\cup$ CC	−0.24534				

TABLE VI. Hyperfine parameters, in units of a_0^{-3}, obtained from the OC-MCHF and CI calculations performed for the Si$^-$ $3p^3\,{}^2P^o$ term.

	Si$^-$ $^2P^o$			
nl	a_l	a_{sd}	a_c	b_q
$4f$	1.71550	−0.35163	0.63690	0.01448
$5g$	1.68124	−0.35213	0.28606	−0.01104
$6h$	1.68176	−0.35420	0.01997	−0.01138
$7i$	1.68515	−0.35677	0.06590	−0.01515
$8k$	1.68653	−0.35637	0.10389	−0.01458
$9k$	1.68501	−0.35361	−0.01197	−0.01099
$10k$	1.68502	−0.35423	−0.00046	−0.01227
$11k$	1.68393	−0.35370	−0.00183	−0.01217
$\cup$ MR-SDT $\lceil n'l' \rceil$, CI				
$4f$	1.68787	−0.35510	−0.04520	−0.01535
$5g$	1.68448	−0.35850	−0.04697	−0.03724

The nonrelativistic electric-field gradient at the nucleus b_q of neutral silicon can be estimated to be accurate to about 0.5 %. However, like the a_c parameters of Si$^-$ $^4S^o$, b_q is remarkably small for the Si$^-$ $^2D^o$ and $^2P^o$ multiplets. This is expected from the fact that, within a nonrelativistic framework,

TABLE VII. Mean values and occupation numbers q of the OC-MCHF $\lceil 11k \rceil$ s orbitals and evolution of the a_c hyperfine parameter along the sequence of OC-MCHF $\lceil nl \rceil$ calculations.

nl	$\langle \delta(r) \rangle$	$\langle r \rangle$	q	a_c
$1s$	820.8	0.111	1.99959667	
$2s$	58.1	0.563	1.99676579	
$3s$	3.5	2.299	1.93575762	
$4s$	194.8	0.845	0.00349874	1.57
$5s$	2002.7	0.400	0.00056144	0.89
$6s$	130.8	2.929	0.00318797	−0.47
$7s$	1646.7	0.945	0.00009859	−0.19
$8s$	5183.8	0.433	0.00002211	0.00
$9s$	189.9	3.073	0.00008889	−0.27
$10s$	4976.3	0.747	0.00000190	−0.18
$11s$	6542.0	0.480	0.00000029	−0.19

TABLE VIII. Relativistic corrections on $A\frac{I}{\mu_I}$ (MHz per units of μ_N) of each considered state evaluated by comparing SD-MCHF calculations to corresponding RCIP and BPCI results.

	Si ^3P				Si$^-$ $^4S^o$		Si$^-$ $^2D^o$				Si$^-$ $^2P^o$			
	$J=1$		$J=2$		$J=3/2$		$J=3/2$		$J=5/2$		$J=1/2$		$J=3/2$	
nl	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI
$4f$	−0.48	−0.52	1.72	2.05	−0.37	−0.25	0.35	0.34	0.67	0.93	2.47	3.27	0.21	0.32
$5g$	−1.40	−1.62	2.23	2.53	−1.04	−1.19	0.50	0.64	1.36	1.73	3.20	4.07	−0.10	−0.04
$6h$	−2.36	−2.85	1.73	1.77	−2.05	−2.76	0.15	0.37	1.10	1.36	6.33	7.85	−0.14	−0.20
$7i$	−2.49	−2.98	1.77	1.89	−2.21	−2.97	0.22	0.48	1.21	1.52	6.85	8.60	−0.16	−0.21

b_q vanishes for a p^3 open shell. Relativistic corrections are evaluated by performing MCHF and the corresponding Breit-Pauli and RCIP calculations on the set of SD excitations of the main configuration, as explained in Sec. II E. The relativistic corrections are the differences between the so-obtained hyperfine constants. They are presented for quantities that are independent of the nuclear parameters, i.e., $A\frac{I}{\mu_I}$ in Table VIII and B/Q in Table IX. There has been no test of which of the two methods is most reliable in this specific context, so we interpret the difference between their results as uncertainties. Overall, the agreement between BPCI and RCIP relativistic corrections is satisfactory since they yield uncertainties that are of the same order of magnitude as the degree of convergence of the nonrelativistic hyperfine constants.

The ^{29}Si isotope has a spin $I = 1/2$, with a magnetic moment of $\mu(^{29}\mathrm{Si}) = -0.555\,29(3)\mu_B$ [38]. The calculated A_J hyperfine constants are presented in Table X. As complementary information, the B/Q nuclear-independent constants are also given as they could be useful for the study of metastable isotopes of silicon with a nonzero electric quadrupole moment. We compare our results with the experimental value of Lee and Fairbank [14] for $A_2(^3P)$ and with the constants calculated in the open-core CI approach. This comparison indicate a high degree of convergence of the nonrelativistic calculations, i.e., to less than 1%, except in the case of the small magnetic dipole constants $A_1(^3P)$ of Si and $A_{3/2}(^4S^o)$ of Si$^-$. In the latter case, this is due to the fact that only the problematic Fermi contact term (see the above discussion) contributes to the hyperfine constant. In the case of the $A_1(^3P)$ constant, this relative lack of convergence is due to large cancellation effects. For a single open-shell configuration $l^w LSJ$, the ratio between the orbit and spin dipole contributions to the A_J magnetic dipole hyperfine constant is purely angular

$$\frac{A_J^{\mathrm{dip}}}{A_J^{\mathrm{orb}}} = (-)^{L+S+J+l+1}\frac{g_s}{2}\sqrt{\frac{90l(l+1)}{(2l+3)(2l+2)(2l-1)}} \times \begin{Bmatrix} L & S & J \\ L & S & J \\ 2 & 1 & 1 \end{Bmatrix} \Big/ \begin{Bmatrix} L & S & J \\ 1 & J & L \end{Bmatrix}, \quad (17)$$

where $g_s = 2.002\,32$ is the electron gyromagnetic ratio. For a p^2 or p^4 open shell forming ^3P, we have $A_1^{\mathrm{dip}}/A_1^{\mathrm{orb}} = -\frac{g_s}{2}$, implying that the two contributions cancel each other. This explains why the C, O, Si, and S $A_1(^3P)$ constants are small. However, for higher Z the deviation from the LS coupling increases and the $A_1(^3P)$ constant becomes relatively large (see, e.g., Refs. [39,40]).

The drastic effect of relativity on $B_{3/2}/Q$ values in Si$^-$ is striking. Within the nonrelativistic approximation, we have $B_{3/2}(^2D^o)/B_{5/2}(^2D^o) = +7/10$. The violation of this relation is due to the small (0.035%), symmetric $3p^3\,{}^2D^o$–$3p^3\,{}^2P^o$ mixing at the single-configuration level of approximation. In this 2×2 interaction problem, only the cross term between the $^2D^o$ and $^2P^o$ CSFs gives a nonzero $B_{3/2}$. This means that the relativistic corrections to the electric-field gradients of the two states are equal in magnitude and of opposite signs, as approximately observed in Table IX. Because the main configuration has an occupation of about 95% in both multiplets, the relativistic cross terms and electron correlation contributions to b_q are of the same order of magnitude.

To complete our work, we report in Table XI the theoretical off-diagonal hyperfine constants [28] that affect the splitting in nonzero external magnetic fields where J is no longer a good quantum number.

TABLE IX. Relativistic corrections on B/Q (MHz/b) of each considered state evaluated by comparing SD-MCHF calculations to corresponding RCIP and BPCI results.

	Si ^3P				Si$^-$ $^4S^o$		Si$^-$ $^2D^o$				Si$^-$ $^2P^o$	
	$J=1$		$J=2$		$J=3/2$		$J=3/2$		$J=5/2$		$J=3/2$	
nl	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI	RCIP	BPCI
$4f$	0.28	0.41	0.04	−1.23	0.00	−0.00	8.97	9.01	0.01	0.01	−8.86	−8.89
$5g$	0.46	0.69	−1.12	−2.60	−0.00	−0.01	8.61	8.63	0.01	0.01	−9.40	−9.41
$6h$	0.28	0.53	−1.32	−2.86	−0.00	−0.01	9.18	9.17	0.03	−0.01	−9.45	−9.38
$7i$	0.28	0.57	−1.39	−3.01	−0.00	−0.01	9.28	9.28	0.04	0.01	−9.55	−9.49

TABLE X. Hyperfine constants A_J and B_J/Q (in MHz) calculated with the hyperfine parameters reported in Tables IV–VI. Relativistic corrections (RCs) and their errors are estimated from Tables VIII and IX.

	Si (^3P)				Si$^-$ ($^4S^o$)
Calculation	A_1	A_2	B_1/Q	B_2/Q	$A_{3/2}$
OC-MCHF	−6.73	−163.38	112.82	−225.64	4.52
∪ MR-SDT	−5.17	−162.34	113.54	−227.07	8.48
plus RCs	−2.1(3)	−164.37(7)	114.0(2)	−229.3(8)	11.4(5)
Expt. [16]	8(10)	−163(2)			
Expt. [14]		−160.1(1.3)			

	Si$^-$ ($^2D^o$)			
Calculation	$A_{3/2}$	$A_{5/2}$	$B_{3/2}/Q$	$B_{5/2}/Q$
OC-MCHF	−111.07	−173.25	−3.85	−5.50
∪ MR-SDT	−111.50	−173.09	−4.38	−6.25
plus RCs	−111.9(2)	−174.6(2)	4.90(0)	−6.23(2)

	Si$^-$ ($^2P^o$)		
Calculation	$A_{1/2}$	$A_{3/2}$	$B_{3/2}/Q$
OC-MCHF	−488.10	−93.90	2.86
∪ MR-SDT	−492.63	−92.53	8.75
plus RCs	−501.2(1.0)	−92.15(3)	−0.77(3)

V. CONCLUSION

We reported values of isotope shifts and hyperfine splittings of all bound states of Si$^-$. We also provided the isotope shifts on the binding energy of those states and the hyperfine structure constants of the $3p^2\,{}^3P$ lowest multiplet of Si. For the latter, we obtained satisfactory agreement with experiment. We also found good consistency between the calculated photodetachment thresholds and their nonrelativistic experimental values ${}^{e}A^{\rm nr}_{\rm ref}$, deduced by subtracting the experimental data and the relativistic corrections.

Most hyperfine constants were determined to about ∼1%. These results could be useful for analyzing experimental spectra where the hyperfine structure might not be resolved, but still be significant at the level of the experimental uncertainty, as is the case of recent laser photodetachment microscopy experiments on P$^-$ [41].

We presented a systematic comparison of configuration-interaction relativistic methods based on nonrelativistic orbitals (BPCI and RCIP) for a third-period atom. The overall consistency between the so-deduced corrections, in particular in the cases where they account for a large fraction of the hyperfine constants, provides evidence that they yield useful estimates of relativistic effects. This is particularly interesting in the context of nonrelativistic methods, as it is in general necessary to consider the impact of relativity on the results [33].

TABLE XI. Off-diagonal hyperfine constants $A_{J,J'}$ and $B_{J,J'}/Q$ (in MHz).

	Si (^3P)			
Calculation	$A_{1,0}$	$A_{2,1}$	$B_{2,0}/Q$	$B_{2,1}/Q$
OC-MCHF	−79.26	−95.86	−97.71	−56.41
∪ MR-SDT	−81.97	−97.04	−98.32	−56.77
plus RCs	−84.37(3)	−100.78(27)	−98.88(19)	−57.16(14)

	Si$^-$ ($^2D^o$)		Si$^-$ ($^2P^o$)	
Calculation	$A_{5/2,3/2}$	$B_{5/2,3/2}/Q$	$A_{3/2,1/2}$	$B_{3/2,1/2}/Q$
OC-MCHF	−63.22	−0.60	−28.25	0.62
∪ MR-SDT	−64.03	−0.68	−28.91	1.89
plus RCs	−65.56(19)	−2.36(1)	−29.76(16)	2.94(1)

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