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Theoretical Study of Interesting Fine-Structure Splittings Based on a Scenario for Precise Calculations *

ZHANG Xiao-Le(张小乐)[1**], CHENG Cheng(程诚)[1], GAO Xiang(高翔)[1], LI Jia-Ming(李家明)[1,2]

[1] *Department of Physics, Shanghai Key Laboratory for Laser Fabrication and Material Science, Shanghai Jiaotong University, Shanghai 200240*

[2] *The Key Laboratory of Atomic and Molecular Nanosciences (Ministry of Education), Department of Physics, Tsinghua University, Beijing 100084*

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Based on the multi-configuration Dirac–Fock self-consistent field method, a scenario has been presented to calculate the fine-structure energy levels of C^{2+} and Si^{2+} excited states (3^1D_2 and $3^3D_{1,2,3}$). The Breit interactions and quantum electrodynamics corrections are added as perturbations. The present calculation results are found to be in excellent agreement with the experimental data. By means of the precise calculation procedure, we elucidate that four competitive mechanisms influence the interesting fine-structure splittings in C^{2+} and Si^{2+}, such as spin-orbit interactions, relativistic corrections of exchange interactions, the Breit interactions and electron correlation effects. Furthermore, the mechanism of relativistic correction of exchange interactions has been studied clearly. We elucidate that the inner shell $2p_{1/2,3/2}$ orbitals are essential to relativistic corrections of exchange interactions which are crucial for the final anomalous fine-structure splittings.

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In the precision physics stage, the study of fine-structure is not only a good way to estimate whether the theoretical computations are valid, but also provides knowledge about the detailed dynamics of electron-electron interactions.[1] There are many interesting features in the fine-structure splittings, such as the anomalous splitting (the higher total angular moment J, the lower total energy level) of $n^2D_{3/2,5/2}$ Rydberg series in Sodium.[2] In our previous works, we have studied different cases about fine structure splittings in some atoms and ions, such as the sodium-like,[3−5] helium-like[6] and nitrogen-like[7] isoelectronic sequence. We have elucidated four mechanisms of the anomalous fine-structure splittings, such as the spin-orbit interactions, the relativistic corrections of exchange interactions due to the relativistic effects of the nd orbital wavefunctions,[4] the Breit interactions and the electron correlation effects. Since the electron correlations are very important in two-valence-electron systems, it is also interesting to extend the fine-structure study to these systems. Calculations have already been carried out for the energy levels of magnesium.[8] Considering that the electron correlations become less important with the atomic number Z increasing in the isoelectronic sequence, so we perform the calculations to C^{2+} and Si^{2+} in order to elucidate the mechanisms clearly. In this Letter, using the GRASP-2K program,[9] which is based on the multi-configuration Dirac–Fock self-consistent field (MCDF-SCF)[10,11] and relativistic configuration interaction (RCI) methods, we use our recently proposed scenario[12] to perform the calculations for 3^3D_2, $3^3D_{1,2,3}$ states of C^{2+} and Si^{2+}. The calculated energy levels and fine-structure splittings are in excellent agreement with the experimental results. Through our calculations, we elucidate that there are also four competitive mechanisms influence the interesting fine structure splittings in C^{2+} and Si^{2+}.

We first present a brief summary of the theoretical methods and our calculation strategies. According to the theory of quantum electrodynamics (QED), in the Coulomb gauge, the interactions in atomic systems can be separated into two parts: longitudinal and transverse interactions. The longitudinal interactions are instantaneous, while the transverse interactions including the interactions with radiation fields can be treated as perturbations later. For an N-electron atom or ion, the Dirac–Coulomb Hamiltonian representing instantaneous longitudinal interactions can be expressed as

$$\widehat{H}_{\rm DC} = \sum_{i=1}^{N}\left[c\boldsymbol{\alpha}\cdot\boldsymbol{p}_i+(\beta-1)c^2-\frac{Z}{r_i}\right]+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}. \tag{1}$$

Based on the Dirac–Coulomb Hamiltonian given in Eq. (1), atomic state functions (ASFs) $|\Gamma PJM\rangle$ can be calculated by solving the eigenvalue problems,

$$\widehat{H}_{\rm DC}\,|\Gamma PJM\rangle = E_\Gamma\,|\Gamma PJM\rangle\,, \tag{2}$$

with a parity P, a total angular momentum J and a magnetic quantum number M. The Γ denotes the

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**Email: lele19861104@sina.com

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Γth atomic eigenstate function. The ASFs are the N-electron eigenstate wavefunctions, which are linear combinations of configuration state functions (CSFs) with the same P, J and M, namely,

$$|\Gamma PJM\rangle = \sum_{i=1}^{n_c} C_i^{\Gamma} |\gamma_i PJM\rangle, \tag{3}$$

where C_i^{Γ} are the mixing coefficients, γ represents all the information required to define the CSF uniquely. The CSFs $|\gamma PJM\rangle$, which form a quasi-complete basis set for an N-electron atomic system in Hilbert space, are linear combinations of Slater determinants of atomic orbital wavefunctions (AOs). The AOs reveal the atomic shell structure. By applying variational method to Eq. (2), we can obtain the mixing coefficients C_i^{Γ} as well as the AOs self-consistently. Note that the AOs form basis set for single electron in Hilbert space. More specifically, for C^{2+}, with the ground-state ($1s^2 2s^2$) configuration, we start with DF calculation to obtain the AOs of $1s$ and $2s$. With the obtained AOs fixed (i.e. $1s$, $2s$), we can perform MCDF-SCF calculations to obtain the AO of $2p$. The CSFs are generated by a single excitation from the reference ground-state configuration $1s^2 2s^2$ to a $1s^2 2s 2p$ configuration, denoted as $[1s^2 2s^2 - 2p]S$ shown in Table 1. With the same procedures, we can obtained the AOs of $2p$, $3s$, $3p$, $3d$. The calculation results of 3^1D_2, $3^3D_{1,2,3}$ states are listed in the column named as basis set ($n \leq 3$) in Table 2, from which we can find that the fine-structure splitting of $3^3D_{1,2,3}$ of C^{2+} is normal and the ratio of $\nu_{21}/\nu_{31} = (E_2 - E_1)/(E_3 - E_1)$ is 0.399, almost equal to 0.4, which is decided by pure spin-orbit interactions. Such feature demonstrates that the calculations of basis set ($n \leq 3$) have already taken spin-orbit interactions into account. The calculated fine structure splittings are in agreement with the experimental data[2] which means that the major mechanism of fine-structures splittings for C^{2+} is the spin-orbit interactions. However, for excitation energies, huge differences between theoretical and experimental excitation energies about 5% exist, which principally result from the electron correlations neglected in the present calculations with the basis set ($n \leq 3$). In atomic systems, there are infinite numbers of spectroscopy orbitals including continuum contribute to electron correlations. It is impossible to calculate all of them. In order to take into account the electron correlations adequately, pseudo-orbitals,[1,9,12] which are special linear combinations of infinite bound and continuum orbitals determined variationally are adopted. As for the pseudo-orbitals of $n = 4$, because we concern excitations from 2^1S_0 into $3^3D_{1,2,3}$ and 3^1D_2 eigenstates, we perform MCDF-SCF calculations to obtain the pseudo-orbitals of $4\bar{s}$, $4\bar{p}$, $4\bar{d}$ and $4\bar{f}$ separately by optimizing the total energies we concern (i.e. 2^1S_0, $3^3D_{1,2,3}$, 3^1D_2) without imposing the condition of appropriate number of radial nodes. The configurations used for each orbital with angular momentum l are created by single, double and some important triple excitations from the ground-state reference configuration $1s^2 2s^2$ to the orbitals of $n \leq 4$ with the same l. The AOs ($n \leq 3$) and pseudo AOs ($n = 4$) forming basis set ($n \leq 4$), with which the total energies are calculated by relativistic configuration interaction (RCI) method. Thus, more atomic configurations are added to fully consider the electron correlation effects. The CSFs are generated by single, double and some important triple excitations from the ground-state reference configuration $1s^2 2s^2$ to the orbitals with $n \leq 4$, denoted as $[1s^2 2s^2 - 4l]S, D, T$ shown in Table 1. The calculation results are listed in column named as basis set ($n \leq 4$) of Table 2, our calculation results without the Breit interactions and QED corrections for $3^3D_{1,2,3}$ agree with the experimental results[2] within 0.2%. Note that the fine-structure splittings ($\nu_{21} = 2.37\,\mathrm{cm}^{-1}$, $\nu_{31} = 5.92\,\mathrm{cm}^{-1}$) are about twice as much as the experimental data. The Breit interactions and QED corrections can be treated as perturbations. Among the perturbations, the Breit interactions are the dominant corrections. The results with the Breit interactions and QED corrections are shown in column named as with Breit of Table 2. The excitation energies also agree with the experimental results within 0.2%, however, the fine-structures ($\nu_{21} = 0.97\,\mathrm{cm}^{-1}$, $\nu_{31} = 3.58\,\mathrm{cm}^{-1}$) are now in good agreement with the experimental data. With the same procedures as basis set of $n = 4$,

we further construct the basis set of $n = 5$ and $n = 6$. Finally, our calculation results with Breit for 3^3D_{123} agree with the experimental data within 0.02% and fine-structure splittings ($v_{21} = 1.10\,\mathrm{cm}^{-1}$, $v_{31} = 3.91\,\mathrm{cm}^{-1}$) are in excellent agreement with the experimental results. we call the basis set which satisfies the desired accuracy of calculations quasi-complete bases set. From the comparison of calculations based on Basis set ($n \leq 3$) and Basis set ($n \leq 5$), there are also two minor mechanisms which affect the fine-structure splitting. The correlation effects give rise to the normal fine-structure splittings and the Breit interactions give rise to the anomalous fine-structure splitting. These two minor mechanisms will cancel with each other.

For Si^{2+}, we can perform similar calculations based on the same scenario. Different basis sets have been constructed and the calculation results are listed in Table 3. From the calculations based on Basis set ($n \leq 3$) of Si^{2+}, we find that the fine-structure splittings ($\nu_{21} = -0.51\,\mathrm{cm}^{-1}$, $\nu_{31} = -1.27\,\mathrm{cm}^{-1}$) are anomalous, which are different from C^{2+}. Because there is only one configuration of the type $1s^2 2s 3d$ for each symmetry, calculation based on Basis set ($n \leq 3$) is almost a single configuration calculation. Therefore, the fine-structure splittings can be understood by simple single-configuration type energy expressions

$$E(^3D_3) - E(^3D_1) = [\Delta(3d) - \Delta(3d_-)] + \Big\{ -\frac{1}{5}[G^2(1s3d) - G^2(1s3d_-)] - \frac{1}{5}[G^2(2s3d) - G^2(2s3d_-)]\Big\}$$
$$+ \Big\{ -\frac{1}{5}[G^2(3s3d) - G^2(3s3d_-)] - \frac{1}{3}[G^1(2p3d) - G^1(2p_-3d_-)] - \frac{1}{15}[G^1(2p3d)$$
$$- G^1(2p3d_-)] - \frac{4}{35}[G^3(2p3d) - G^3(2p_-3d)] - \frac{9}{35}[G^3(2p_-3d) - G^3(2p3d_-)]\Big\}, \quad (4)$$

$$E(^3D_2) - E(^3D_1) = \Big\{\frac{2}{5}[\Delta(3d) - \Delta(3d_-)]\Big\} + \Big\{ -\frac{2}{25}[G^2(1s3d) - G^2(1s3d_-)] - \frac{2}{25}[G^2(2s3d) - G^2(2s3d_-)]\Big\}$$
$$\cdot \Big\{ -\frac{2}{25}[G^2(3s3d) - G^2(3s3d_-)] - \frac{2}{15}[G^1(2p3d) - G^1(2p_-3d_-)] - \frac{2}{75}[G^1(2p3d)$$
$$- G^1(2p3d_-)] - \frac{8}{175}[G^3(2p3d) - G^3(2p_-3d)] - \frac{18}{175}[G^3(2p_-3d) - G^3(2p3d_-)]\Big\}, \quad (5)$$

where $2p$ represents the $2p_{3/2}$ orbital; $2p_-$ represents the $2p_{1/2}$ orbital. The first brace term represents the spin-orbit interactions. The second brace term represents the relativistic corrections of exchange interactions between the excited orbital $3d_{3/2,5/2}$ and the inner shell orbitals $1s$ and $2s$. The third brace term represents the relativistic corrections of exchange interactions between the excited orbital $3d_{3/2,5/2}$ and inner shell orbitals $2p_{1/2,3/2}$ and $3s$. In the nonrelativistic limit, the second and third terms reduce to zero exactly. Therefore, the fine-structure splittings should be completely determined by spin-orbit interactions. However, for full relativistic calculations, the second and third terms become nonzero naturally, The theoretical calculation results of Eqs. (4) and (5) are listed in Table 4. For $E_3 - E_1$ of Si^{2+}, the spin-orbit interactions make the fine-structure splittings normal ($10.218\,cm^{-1}$). The exchange interactions due to $1s$ and $2s$ orbitals make the fine-structure splittings anomalous ($-0.011\,cm^{-1}$, $-0.223\,cm^{-1}$ respectively). Although the exchange interactions due to $1s$ and $2s$ orbitals will result in the anomalous splittings of fine-structure, when compared with spin-orbit interactions, it can be negligible. Thus it will not make the ultimate splittings of the fine-structure anomalous. However, when the contributions of inner shell $2p_{1/2,3/2}$ orbitals ($-10.796\,cm^{-1}$) are included into consideration, the relativistic correction of exchange interactions will overcome the spin-orbit interactions and the final fine-structure splittings of Si^{2+} will become anomalous. Therefore, such behavior demonstrates that the existence of inner shell $2p_{1/2,3/2}$ orbitals are essential for the relativistic correction of exchange interactions and the final anomalous fine-structure splittings. Let us return to discuss the fine-structure splittings of C^{2+} calculated with the Basis set ($n \le 3$). It is interesting to note that, for $E_3 - E_1$, only the first and second terms of Si^{2+} exist, i.e. the spin-orbit interactions ($3.817\,cm^{-1}$) and exchange interactions due to $1s$ and $2s$ orbitals ($-0.013\,cm^{-1}$, $0.302\,cm^{-1}$ respectively). Therefore, the spin-orbit interactions almost dominate the fine structure splittings of C^{2+}.

Table 1. Process of constructing quasi complete basis set for C^{2+}. S represents the single excitation, D the double excitation and T the important triple excitation.

	Orbital to be optimized	Configurations	Energy levels to be optimized
Single ground-dstate configuration (DF)	$1s2s$	$[1s^22s^2]$	2^1S_0
Basis set($n \le 2$)	$2p$	$[1s^22s^2 - 2p]S$	$2^3P_{0,1,2}, 2^1P_1$
Basis set($n \le 3$)	$3l$	$[1s^22s^2 - 3l]S$	N^1S_0, N^1S_1, $N^3P_{0,1,2}$, N^1P_1, $N^3D_{1,2,3}$, N^1D_2 ($N \le 3$)
Basis set($n \le 4$)	4l	$[1s^22s^2 - 4l]S, D, T$	$2^1S_0, 3^3D_{1,2,3}, 3^1D_2$
Quasi complete basis set($n \le 5$)	$5l$	$[1s^22s^2 - 5l]S, D, T$	$2^1S_0, 3^3D_{1,2,3}, 3^1D_2$

Table 2. Our calculation of excitation energy (in cm^{-1}) and fine structures of C^{2+}: $3s3d\,^3D_{1,2,3}, 3s3d\,^1D_2$. Here, υ_{21} and υ_{31} represent the $^3D_2 - {}^3D_1$ and $^3D_3 - {}^3D_1$ fine-structure interval, respectively. Here $\Delta = (E_{\rm theor} - E_{\rm NIST})/E_{\rm NIST}$ represents the differences between our calculation results of RCI with Breit and the NIST data.[2]

Excited states	Expt[8]	Basis set ($n \le 3$)	Δ	Basis set					
				Basis set ($n \le 4$) RCI			Quasi basis set ($n \le 5$) RCI		
				No breit	With breit	Δ	No breit	With breit	Δ
$^3D_1$	270010.83	257363.10	4.7%	269632.26	269609.57	−0.07%	270021.44	270001.17	0.02%
$^3D_2$	270011.93	257364.74	4.7%	269634.63	269610.54	−0.15%	270023.92	270002.27	−0.004%
$^3D_3$	270014.74	257367.21	4.7%	269638.18	269613.15	−0.15%	270027.64	270005.08	−0.004%
$^1D_2$	276482.86	263468.66	4.7%	276321.16	276297.96	−0.15%	276550.82	276529.87	−0.004%
υ_{21}	1.10	1.64		2.37	0.97		2.48	1.10	
υ_{31}	3.91	4.11		5.92	3.58		6.20	3.91	

Table 3. Our calculation of excited energy (in cm^{-1}) and fine structures of Si^{2+}: $3s3d^3D_{1,2,3}$, $3s3d^1D_2$.

Excited states	Exp[2]	Basis set ($n \leq 3$)	Δ	Basis set						
				Basis set ($n \leq 4$) RCI		Basis set ($n \leq 5$) RCI		Quasi basis set ($n \leq 6$) RCI		
				No breit	With breit	No breit	With breit	No breit	With breit	Δ
$^3D_1$	142948.25	134501.42	−5.91%	142984.63	142954.88	143069.04	143041.24	143472.37	143445.03	0.37%
$^3D_2$	142945.84	134500.91	−5.91%	142983.52	142952.03	143068.19	143038.64	143471.68	143442.63	0.37%
$^3D_3$	142943.74	134500.15	−5.91%	142981.85	142948.64	143066.90	143035.66	143470.95	143440.23	0.37%
$^1D_2$	165765.00	147723.11	−10.88%	169989.73	169963.34	166268.19	166244.78	166441.22	166416.71	0.34%
υ_{21}	−2.41	−0.51		−1.11	−2.85	−0.86	−2.60	−0.69	−2.41	
υ_{31}	−4.51	−1.27		−2.78	−6.24	−2.14	−5.58	−1.42	−4.80	

Table 4. Mechanism of exchange interactions owing to the relativistic effect of electron orbitals (in cm^{-1}). $\Delta_{so} = E_2 - E_1$ represents the spin-orbit interaction which leads to normal energy splitting, e.g. for Si^{2+}, it represents the term of $2/5[\Delta(3d) - \Delta(3d_-)]$ in Eq. (5). RCEI: relativistic correction of exchange interactions; e.g. for $E_3 - E_1$ (Si^{2+}), RCEI ($1s$) denotes the relativistic correction of exchange interaction owing to $1s$ orbital which represents the term $-1/5[G^2(1s3d) - G^2(1s3d_-)]$ in Eq. (4).

	Si^{2+}						C^{2+}	
	$E(^3D_3) - E(^3D_1)$			$E(^3D_2) - E(^3D_1)$			$E(^3D_3) - E(^3D_1)$	$E(^3D_2) - E(^3D_1)$
Δ_{so}	10.218			4.087			3.817	1.527
RCEI ($1s$)	−0.011			−0.004			−0.013	−0.0005
RCEI ($2s$)	−0.223			−0.089			0.302	0.121
RCEI ($3s$)	−0.463			−0.185				
RCEI ($2p_-, 2p$)	−13.561	The total anomalous splitting due to $2p$	−10.796	−5.424	The total anomalous splitting due to $2p$	−4.318		
	−0.175			−0.070				
	5.600			2.240				
	−2.660			−1.064				
The final splitting		−1.275			−0.509		4.106	1.649

As shown in Table 3, because the calculations based on Basis set ($n \leq 3$) only consider few electron correlations, to obtain the precise results, we should enlarge our basis set by MCDF-SCF calculations. Since the electron correlations in Si^{2+} are more complicated than C^{2+}, we have to extend our basis set to $n = 6$ and finally obtain the quasi-complete basis set. Along with the enlargement of our basis sets, the difference between our calculations and experimental excitation energies[2] are converged. With all the mechanisms affecting fine-structure splittings taken into account, our calculations of fine-structure ($\nu_{21} = -2.41\,cm^{-1}$ $\nu_{31} = -4.80\,cm^{-1}$) are also in good agreement with the experimental data.

Finally, we would like to conclude by the following comments. Based on the multi-configuration Dirac–Fock self-consistent field (MCDF-SCF)[10,11] and relativistic configuration interaction (RCI) methods, we have calculated the energy levels of 3^3D_2, $3^3D_{1,2,3}$ states of C^{2+} and Si^{2+} with high precision using our recently proposed scenario[12] of constructing the quasi-complete basis set. Our calculation results of excitation energies of 3^1D_2, $3^3D_{1,2,3}$ of C^{2+} and Si^{2+} as well as their fine-structure splittings are in excellent agreement with the experimental data.[2] With the precise theoretical calculations, we elucidate the mechanisms of such interesting fine-structure splittings in C^{2+} and Si^{2+}. Furthermore, we also elucidate that the inner shell $2p_{1/2,3/2}$ orbitals are the key factors for the relativistic correction of exchange interactions, which is essential for the final anomalous fine-structure splitting of Si^{2+}. Besides the precise calculations for $3^3D_{1,2,3}$, our scenario should also be valid to calculate other higher excited states of other many-electron atomic systems, which would be very useful in related scientific fields.

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