

# Spectral fine structure of the atomic ground states based on full relativistic theory

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We focus on the full relativistic quantum mechanical calculations from boron to fluorine atoms with electronic configuration of  $1s^2 2s^2 2p^n$  ( $n = 1, 2, 3, 4,$  and  $5$ ), where  $1s^2 2s^2$  is the closed shell and  $2p^n$  is the open shell. Their active electrons in the open shell occupy all the six spinors as far as possible. Therefore, we suggest a new rule called “maximum probability” for the full symmetry group relativistic theory. Furthermore, the spectral fine structure of the atomic ground states based on the full relativistic theory and their intervals of L-S splitting are all reasonable. It is impossible to calculate the L-S splitting through non-relativistic quantum mechanics. The relativistic effect of atomic mass is increased significantly by about 12 folds from boron atom to fluorine atom.

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Symmetry plays an important role in the quantum mechanical theory. The quantum mechanical method has three levels: non-relativistic based on the single-point group, relativistic based on the double group, and relativistic based on the full symmetry group or quaternion symmetry.

The  $nP$  orbit for the non-relativistic theory based on the single-point group has three components,  $P_x$ ,  $P_y$ , and  $P_z$ , whereas the relativistic theory<sup>[1]</sup> based on the double group has relativistic orbit  $P^-$  with  $j = 1/2$  and  $P$  with  $j = 3/2$ . In the relativistic realm, the spin symmetry is lost and the single-point groups are replaced by double groups. For the double group<sup>[2,3]</sup>, a new symmetry operation  $\hat{E}$  exists, corresponding to a rotation of  $2\pi$ , in which the coordinates are recovered; however, the wave function is changed to negative. The number of symmetry operations will be doubled, whereas the number of classes and irreducible representations will generally not be doubled. For example, the single-point group  $C_{2V}$  has four symmetry operations and four irreducible representations, while the double group  $C'_{2V}$  has eight symmetry operations and only five irreducible representations. The number of symmetry operations and irreducible representations are 8 and 8 for the  $D_{2h}$  single-point group, and 16 and 10 for the  $D'_{2h}$  double group.

In consideration of the equivalence of space and time, the time reversal symmetry operation for the relativistic theory based on the full symmetry group or the quaternion symmetry is included in the symmetry group. The product of two symmetry operators is represented by the product of the corresponding unitary matrices in the theory of group representation; however, time reversal symmetry operation is an antiunitary operator. With the inclusion of both space and time operations, the group is called the full symmetry group, while their group representation is called a co-representation<sup>[4,5]</sup>, which is not unitary representation; however, it is still possible to break it down to irreducible form. The third level, i.e., relativistic quantum mechanical theory based on the full

symmetry group or quaternion symmetry, was first explored by the milestone research of Saue *et al.*<sup>[6,7]</sup>.

The time reversal operator, which is called Kramer operator<sup>[5,8]</sup>, is defined as follows:

$$\hat{K}\psi(r, t) = \psi^*(r, -t). \quad (1)$$

If Hamiltonian  $\hat{H}$  is a real function of  $r$ , then

$$\begin{aligned} \hat{K}\hat{H}(r)\psi(r, t) &= \hat{H}^*(r)\psi^*(r, -t) \\ &= \hat{H}(r)\psi^*(r, -t) = \hat{H}\hat{K}\psi(r, t), \end{aligned} \quad (2)$$

that is,

$$[\hat{H}, \hat{K}] = 0. \quad (3)$$

The commutator (3) is the necessary and sufficient condition for the two operators  $\hat{K}$  and  $\hat{H}$  having the same set of eigenfunctions, that is, the state is invariant to time reversal (motion reversal).

The time reversal operator is antiunitary<sup>[5,8]</sup>, as shown by

$$\langle \hat{K}\psi | \hat{K}\phi \rangle = \langle \psi | \phi \rangle^* = \langle \phi | \psi \rangle. \quad (4)$$

It is also an antilinear operator.

According to the Kramer theorem<sup>[3,8,9]</sup>, it can be proved that if  $\hat{K}^2 = -1$ , which corresponds to  $J$  value with half odd integer, i.e., fermions, there will be new double degeneracy by time reversal; if  $\hat{K}^2 = +1$ , which corresponds to  $J$  value with integer, i.e., bosons, there will be no double degeneracy.

The time-independent Dirac equation can be expressed as

$$\hat{h}_D\psi = E\psi, \quad (5)$$

$$\hat{h}_D = \beta' mc^2 + c(\alpha\hat{p}) + \hat{V}, \quad (6)$$

where  $\alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix}$ ,  $\beta' = \begin{bmatrix} 0 & 0 \\ 0 & 2I_2 \end{bmatrix}$ , and  $I_2$  is a  $2 \times 2$  unit matrix.

The Pauli spins matrices are

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \quad (7)$$

If  $\widehat{V} = 0$ , then it is the Dirac equation of free electrons.

The time reversal operator is defined using an equivalent method, i.e., Kramer theorem<sup>[3,8]</sup>. In such theorem, if  $\widehat{K}^2 = -1$ , that is,  $\widehat{K}^2\phi = -\phi = \bar{\phi}$  in which the state is recovered by twice the time reversal, the wave function is changed to negative; if  $\widehat{K}^2 = +1$ , that is,  $\widehat{K}^2\phi = \phi$  in which the state is recovered by twice the time reversal, the wave function is unchanged. Therefore, the operator can be expanded in terms of Kramer's partners,  $\{\phi\}$  and  $\{\bar{\phi}\}$ . For example, the Hermitian of one-electron operator<sup>[7,10]</sup> is as follows:

$$\hat{h}_D = \begin{pmatrix} A & B \\ -B^* & A^* \end{pmatrix} = \begin{pmatrix} \widehat{V} & -ic\hat{d}_z & 0 & -ic\hat{d}_- \\ -ic\hat{d}_z & -2mc^2 + \widehat{V} & -ic\hat{d}_- & 0 \\ 0 & -ic\hat{d}_+ & \widehat{V} & ic\hat{d}_z \\ -ic\hat{d}_+ & 0 & ic\hat{d}_z & -2mc^2 + \widehat{V} \end{pmatrix}, \quad (8)$$

where

$$\hat{d}_z = \frac{\partial}{\partial z}, \quad \hat{d}_\pm = \frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y}. \quad (9)$$

It can be easily determined that the following equations hold true:

$$A = \begin{pmatrix} \widehat{V} & -ic\hat{d}_z \\ -ic\hat{d}_z & -2mc^2 + \widehat{V} \end{pmatrix} = A^+, \quad (10)$$

$$B = \begin{pmatrix} 0 & -ic\hat{d}_- \\ -ic\hat{d}_- & 0 \end{pmatrix} = -B^+ = \begin{pmatrix} 0 & -ic\hat{d}_+ \\ -ic\hat{d}_+ & 0 \end{pmatrix}. \quad (11)$$

That is,  $A$  is a Hermitian and  $B$  is an antihermitian. For Kramer's partners, the Dirac operator  $\hat{h}_D$  can be expressed as<sup>[7]</sup>

$$\hat{h}_D = I_2 \otimes \begin{pmatrix} \widehat{V} & 0 \\ 0 & -2mc^2 + \widehat{V} \end{pmatrix} - c \overset{\vee}{i} \otimes \begin{pmatrix} 0 & \hat{d}_z \\ \hat{d}_z & 0 \end{pmatrix} - c \overset{\vee}{j} \otimes \begin{pmatrix} 0 & \hat{d}_y \\ \hat{d}_y & 0 \end{pmatrix} - c \overset{\vee}{k} \otimes \begin{pmatrix} 0 & \hat{d}_x \\ \hat{d}_x & 0 \end{pmatrix}, \quad (12)$$

where  $\hat{h}_D$  is expressed as the quaternion, which exhibits the time reversal symmetry.

Quaternion algebra<sup>[7,11]</sup> has been developed several years ago, however, limited applications of this in quantum mechanics have been made in recent years. The quaternion is expressed as follows:

$$q = \sum_{\lambda=0}^3 V_\lambda e_\lambda = V_0 + V_1 \overset{\vee}{i} + V_2 \overset{\vee}{j} + V_3 \overset{\vee}{k}, \quad (13)$$

where

$$e_1 = \overset{\vee}{i} \leftrightarrow i\sigma_z, \quad e_2 = \overset{\vee}{j} \leftrightarrow i\sigma_y, \quad e_3 = \overset{\vee}{k} \leftrightarrow i\sigma_x, \quad (14)$$

$\overset{\vee}{i}$ ,  $\overset{\vee}{j}$ , and  $\overset{\vee}{k}$  are quaternion units. Quaternion includes three-dimensional complex space and one-dimensional real space. Based on Eqs. (7)–(11), the quaternion algebra includes both time and space reversal symmetry and is called the full symmetry group, while its matrix representation is called co-representation. The  $\hat{h}_D$  in Eq. (12) is the Dirac operator of the full symmetry group. The Dirac equation can, therefore, be rewritten into the quaternion algebra form:

$${}^q\hat{h}_D {}^q\psi = E {}^q\psi. \quad (15)$$

Table 1 is the character table of the single group and full symmetry group of  $D_{2h}$ . The calculation is performed starting from  $D_{2h}$ , which is an Abelian, making it easy to solve the Dirac equation. However, the calculated atoms all belong to the  $O(3)$  group, under which  $D_{2h}$  is a subgroup; therefore, there is a need to derive their relationship. The relation of the single group and full symmetry group of  $D_{2h}$  derived in our calculation can be seen in Table 1.

The direct product of representations is also the irreducible representation or the direct sum of the representations, shown as

$$\Gamma^{(i)} \otimes \Gamma^{(j)} = \sum_k \chi_k^{(i,j)} \Gamma^{(k)},$$

where the coefficients  $\chi_k^{(i,j)}$  can be zero or positive integers. For example,

$$B_{1u} \otimes B_{2u} = B_{3g}.$$

From Table 1, the two fermion representations of the irreducible co-representations can be resolved by direct product decomposition into the direct sum of the  $D_{2h}$  group as follows:

$$E_{1u} \otimes E_{1u} \otimes E_{1u} \otimes E_{1u} = E_{1g} \otimes E_{1g} = A_g \oplus B_{1g} \oplus B_{2g} \oplus B_{3g}, \quad (16a)$$

$$E_{1u} \otimes E_{1u} = A_g \oplus B_{1g} \oplus B_{2g} \oplus B_{3g}, \quad (16b)$$

$$E_{1g} \otimes E_{1u} = A_u \oplus B_{1u} \oplus B_{2u} \oplus B_{3u}. \quad (16c)$$

For instance, the open shell of the four electrons of the oxygen atom is the fermion irrep  $E_{1u}$ , and its direct product decomposition is represented by Eq. (16a), where the

**Table 1. Character Table of the Single Group and Full Symmetry Group of  $D_{2h}$**

$D_{2h}$	$E$	$C_2(x)$	$C_2(z)$	$C_2(Y)$	$i$	$\sigma(yz)$	$\sigma(xy)$	$\sigma(xz)$
$A_g$	1	1	1	1	1	1	1	1
$B_{1g}$	1	-1	1	-1	1	-1	1	-1
$B_{2g}$	1	-1	-1	1	1	-1	-1	1
$B_{3g}$	1	1	-1	-1	1	1	-1	-1
$A_u$	1	1	1	1	-1	-1	-1	-1
$B_{1u}$	1	-1	1	-1	-1	1	-1	1
$B_{2u}$	1	-1	-1	1	-1	1	1	-1
$B_{3u}$	1	1	-1	-1	-1	-1	1	1
$E_{1g}$	2	0	0	0	2	0	0	0
$E_{1u}$	2	0	0	0	-2	0	0	0

**Table 2. States of Boron, Carbon, Nitrogen, Oxygen, and Fluorine**

	Non-Relativistic Single Group L-S Coupling	Relativistic Theory Double Group j-j Coupling	Relativistic Theory Full Symmetry Group with Time Reversals
B	${}^2P_{3/2}, {}^2P_{1/2}$	$J = 3/2, 1/2$ (Odd Parity)	Fermion Irreps $E_{1g}, E_{1u}$
C	${}^1S, {}^1D, {}^3P$	$J = 0, 2, 2, 1, 0$ (Even Parity)	Fermion Irreps $E_{1g}, E_{1u}$
N	${}^2P, {}^2D, {}^4S$	$J = 3/2, 1/2, 3/2, 5/2, 3/2$ (Odd Parity)	Fermion Irreps $E_{1g}, E_{1u}$
O	${}^1S, {}^1D, {}^3P$	$J = 0, 2, 0, 1, 2$ (Even Parity)	Fermion Irreps $E_{1g}, E_{1u}$
F	${}^2P_{1/2}, {}^2P_{3/2}$	$J = 1/2, 3/2$ (Odd Parity)	Fermion Irreps $E_{1g}, E_{1u}$

direct sum is

$$B_{1g} \oplus B_{2g} \oplus B_{3g}.$$

This corresponds to the ground state of the oxygen atom  $P_g$  of  $O(3)$ . Since all these atoms belong to the  $O(3)$  group, under which  $D_{2h}$  is a subgroup,  $O(3)$  can be resolved into its subgroup  $D_{2h}$  and the reversal process is generally impossible. However, for the full symmetry group, the reversal process is automatically permitted. Therefore, we have the following processes:

$$O(3) \rightleftharpoons D_{2h}.$$

The representation  $P_g$  of  $O(3)$ , i.e., the ground state of the oxygen atom, will then be reversibly related to  $D_{2h}$ :

$$P_g \rightleftharpoons B_{1g} \oplus B_{2g} \oplus B_{3g}.$$

This corresponds to the real part of the fermion representations in the quaternion symmetry. It can be proved that for the ground state of boron and fluorine atoms,  $P_u \rightleftharpoons B_{1u} \oplus B_{2u} \oplus B_{3u}$ , and for nitrogen,  $S_u \rightarrow A_u$ .

The description of the electronic states is different for the three theories<sup>[7,10,12]</sup>, which is listed in Table 2. The electronic configuration of B, C, N, O, and F is  $1s^2 2s^2 2p^n$  ( $n = 1, 2, 3, 4,$  and  $5$ ), where  $1s^2 2s^2$  is the closed shell and  $2p^n$  is the open shell. These states are determined by the open shell. The states of the non-relativistic theory based on the single group is derived from L-S coupling, whereas the states of the relativistic theory based on the double group is derived from j-j coupling, in which the spin symmetry is lost. There are two fermion irreducible co-representations for the  $D_{2h}$  group with inversion under the relativistic theory with time reversals, i.e.,  $E_{1g}$  and  $E_{1u}$ .

The calculation of atoms B, C, N, O, and F was performed. Relativistic effects are important in quantum mechanical calculations<sup>[12,13]</sup>; however, there are only a few literature that focused on the calculations of atoms B, C, N, O, and F in terms of the full symmetry group. Carbon isotope shifts can be used to measure isotope abundances in gas clouds<sup>[14–17]</sup>.

The calculation presented in this letter follows that used in previous studies<sup>[10,18]</sup>. For the electronic configuration of B, C, N, O, and F,  $1s^2 2s^2 2p^n$  ( $n = 1, 2, 3, 4,$  and  $5$ ), there will be three Kramer's partners,  $\{\phi\}$  and  $\{\bar{\phi}\}$ , and six spinors for six  $2p$  electrons. There are four electrons included in the closed shell, whereas 1, 2, 3, 4, and 5 active electrons are in the open shell for B, C, N, O, and F atoms, respectively. The results

are listed in Tables 3 and 4, where NAE denotes the number of active electrons and NS denotes the number of spinors—which is possibly an even number (i.e., 2, 4, and 6, where 6 is the largest number of spinors).

From Table 3, it is clear that the ground state, i.e., the lowest energy, is the combination of the number of active electrons in the open shell and the largest number of spinors. For the F atom, there is only one possible combination, i.e., NAE/NS=5/6; the calculating L-S splitting  ${}^2P_{3/2}^0 - {}^2P_{1/2}^0$  is  $393.53 \text{ cm}^{-1}$  and the experimental result is  $404 \text{ cm}^{-1}$ . For the O atom, there are two combinations, 4/4 and 4/6, where the energy of 4/6 is the ground state and its L-S splitting  ${}^3P_2 - {}^3P_1$  is  $152.5 \text{ cm}^{-1}$  and  ${}^3P_1 - {}^3P_0$  is  $227.4 \text{ cm}^{-1}$ , which are in agreement with the experimental results (i.e., the energy series  ${}^3P_2 < {}^3P_1 < {}^3P_0$  of L-S splitting is also correct); however, its L-S splitting for the combination of 4/4 is zero. The ground state of the O atom is  ${}^3P_{1,2,3}$ , with its L-S splitting being impossible to be calculated by non-relativistic quantum mechanics. For the ground state  ${}^4S_{3/2}^0$  of the N atom, both the orbital angular momentum and its magnetic moment are zero, the quadruplet is only formal; and there is no L-S splitting. For the C atom, the energy of 2/6 is the ground state and its L-S splitting  ${}^3P_0 - {}^3P_1$  is  $19.3 \text{ cm}^{-1}$  and  ${}^3P_1 - {}^3P_2$  is  $57.81 \text{ cm}^{-1}$  (i.e., energy series  ${}^3P_0 < {}^3P_1 < {}^3P_2$  of L-S splitting is also correct), which are quite contrary to that of the O atom. The other combinations of 2/4 and 2/2 have higher energy and the energy series of L-S splitting is unreasonable.

This is unexpected for the B atom; the energy for the combination of 1/6 is not the lowest and the L-S splitting of the ground state remains to be reasonable, whereas for the combination of 1/2, the L-S splitting of the ground state is unreasonable.

Following Hund's rules of non-relativistic theory, the three p electrons of the N atom, for example, are distributed on three p orbits with parallel spin. However, for the relativistic theory, the spin symmetry is lost, thus the active electrons in the open shell will occupy all the six spinors as far as possible, that is, the combination of 3/6 represents the ground state. Therefore, we suggest a new rule called "maximum probability" for the full symmetry group relativistic theory.

The spectrum is a representation of the atomic or molecular structure. Therefore, many studies have been focused in the area of atomic, molecular, and optical physics.

**Table 3. Energy and L-S Splitting for the Ground State with NAE/NS**

Atom	NAE/NS	$-E$ (a.u.)	L-S Splitting for Ground State ( $\text{cm}^{-1}$ )	Experimental Result ( $\text{cm}^{-1}$ )
F	5/6	99.450905346174636	${}^2P_{3/2}^0 - {}^2P_{1/2}^0$ 393.53 (7.383)	404.14 <sup>[19]</sup>
O	4/6	74.801166939033578	${}^3P_2 - {}^3P_1$ 152.5 (2.849)	158.27 <sup>[20]</sup>
			${}^3P_1 - {}^3P_0$ 227.4 (4.274)	226.98 <sup>[20]</sup>
	4/4	74.774831415504366	${}^3P_2 - {}^3P_1$ 0.00	158.27
N	3/6	54.303368894079128	${}^3P_1 - {}^3P_0$ 0.00	226.98
			${}^4S_{3/2}^0$ 0.00 (23354)	0.00 <sup>[20]</sup>
C	2/6	37.612879416357814	${}^4S_{3/2}^0$ 190.31	0.00
			${}^3P_0 - {}^3P_1$ 19.3 (0.3617)	16.42 <sup>[19]</sup>
B	2/4	37.609420372085978	${}^3P_1 - {}^3P_2$ 57.81 (1.085)	43.41 <sup>[19]</sup>
			${}^3P_0 - {}^3P_1$ 9.91	16.42
	2/2	37.592150575605643	${}^3P_1 - {}^3P_2$ 19.97	43.41
B	1/6	24.365066796634650	${}^3P_0 - {}^3P_1$ 0.00	16.42
			${}^3P_1 - {}^3P_2$ 0.00	43.41
			${}^2P_{1/2}^0 - {}^2P_{3/2}^0$ 23.96 (0.4499)	15.29 <sup>[21]</sup>
1/4	24.365085504231715	${}^2P_{1/2}^0 - {}^2P_{3/2}^0$ 23.53	15.29	
1/2	24.365139583498639	${}^2P_{1/2}^0 - {}^2P_{3/2}^0$ 0.00	15.29	

Note: values in brackets are calculated by non-relativistic quantum mechanics.

From the B atom to the F atom, the relativistic effect is increased by about 12 folds, making the relativistic effect remarkable.

In conclusion, the electronic configuration of the B atom to the F atom is  $1s^22s^22p^n$  ( $n = 1, 2, 3, 4,$  and  $5$ ), wherein four electrons are in the closed shell and their active electrons in the open shell occupy all the six spinors as far as possible. Therefore, we suggest a new rule called “maximum probability” for the full symmetry group relativistic theory, which is relatively different from the non-relativistic theory. Furthermore, the spectral fine structure of the atomic ground states based on the full relativistic theory and their interval of L-S splitting are all reasonable. It is impossible to calculate the L-S splitting through non-relativistic quantum mechanics. The relativistic effect of the atomic mass for the same period is significant, which records an increase of about 12 folds from the B atom to the F atom.

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