

On the Directed Orbital Model

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Abstract We suggest a directed orbital model for electrons moving in atom.

First we represent the arguments for suggesting such a model and then we show how to perform the calculation of wave function of atom using this model.

Key word directed orbital model

Introduction

After discovering Scrodinger equation the method of self-consistent field was developed. The most important concepts in this method are two; one is the concept of a state of one electron and the other is the concept of central force field which is used for effective field in which every electron moves.

Of course, the Slater determinant must be used for the total wave function in order to satisfy the requirement of antisymmetry of it under exchange of electrons.

The concept for the state of individual electron in such system of electrons as atom is, obviously, an approximate one. Up to now self-consistent field method is widely used and we are also using it[4–6]. But we must emphasize that the approximation of central force field is too rough and contains logical contradiction, therefore we will try to change it.

1. Arguments for Suggesting Directed Orbital Model

Here we consider the arguments for suggesting directed orbital model (DOM).

First, we must emphasize that approximation of the central force field contains logical contradiction physically. This can be shown by a simple example.

Let us consider the ground state of boron atom. In the central force field approximation the electrons are in the states of $1s^2 2s^2 2p$. It is obvious that the electron cloud of $2p$ electron is in no sense spherically symmetric and therefore the electrostatic field made by this electron greatly differs from spherically symmetric. This leads to the result that other electrons cannot move in a state with given eigen values of operators \vec{L}^2 and L_z . So we cannot say that other electrons move in $2s$ states. This shows that the concept that in boron atom every electron moves in some central force field contains logical contradiction. Similar conclusion holds for most of the other atoms. It is known from the study that even in helium atom, where two electrons move in $1s$ state, the part of wave function depending on distance between electrons takes important role. This means that even in helium atom the concept of central force field is not very good approximation.

Second, let us consider Stark effect in hydrogen atom.

The problem for the states of electron in hydrogen-like atom has great importance to understand the electron states in other atoms. Here hydrogen-like atom means a system in which only one electron moves in a field of point charge.

The state of an electron in an atom is characterized by quantum numbers n and l . Here the principal quantum number n , speaking strictly, has a physical meaning only for hydrogen-like atom. This shows that it is very important to understand the state of electron in hydrogen-like atom deeply.

In discussing the electron states in hydrogen-like atom we must first of all pay attention to the fact that the energy of electron depends only on principal quantum number n and it does not depend on orbital quantum number l . So, for example, $2s$ and $2p$ states have the same energy and arbitrary linear combination of ψ_{2s} and ψ_{2p} has the same energy of ψ_{2s} . This means that it is hard to judge what state atom has when there is no external electric field. Considering the Stark effect we can solve this problem.

If we take the direction of external electric field to be z -axis, then we get 4 states with $n=2$.

$$\psi_- = \frac{1}{\sqrt{2}}(\psi_{2s} - \psi_{2p,0}), \quad \psi_+ = \frac{1}{\sqrt{2}}(\psi_{2s} + \psi_{2p,0}), \quad \psi_1 = \psi_{2p,1}, \quad \psi_{-1} = \psi_{2p,-1}$$

Among them ψ_- has the lowest energy, ψ_+ has the highest energy and ψ_1 and ψ_{-1} have equal energy exactly.

Let us consider the case where the strength of external electric field diminishes slowly down to zero. Since the state ψ_- has the lowest energy, the electron in ψ_- state will remain in that state. But ψ_- is independent of strength of external electric field. This leads to the conclusion that after removing the external electric field the electron in the state $n=2$ will move still in ψ_- state and not in ψ_{2s} or ψ_{2p} states. The ψ_- state differs from the states with given quantum number l and in ψ_- state the electron cloud has sharp directivity. The probability for electron to be in places with $z>0$ is $1/8$ and that with $z<0$ is $7/8$. This means that electron cloud is concentrated in the region $z < 0$. The electron is attracted to this region by external electric field and remains there after removing the external electric field. We call such state as directed orbital[1].

We can draw conclusion that even in the absence of external electric field the electron in atomic can remain moving in directed orbital state.

If atom has several electrons, then some of them can make central force field and some others can make electric field, which is similar to external electric field in meaning that its electric field has directivity.

For example, in the case of boron atom the electrons in $1s$ state contribute to central force field whereas $2p$ electron gives rise to directed electric field. In such case for electron it is preferable to be in ψ_- state rather than in ψ_{2s} or ψ_{2p} state.

The ψ_- and ψ_+ states resemble the hybrid orbital encountered in the theory of molecules. But these differ in their physical meaning. Hybrid orbital arises only when atoms go into molecule. But the directed orbital is a state of electron in an isolated atom.

The states ψ_1 and ψ_{-1} have different energies when atom is placed in external magnetic field but in external electric field these have the same energy.

Third, argument for suggesting directed orbital model can be seen from Hund's rules. These are empirical rules determining the ground state of atom. According to these rules the total spin of an atom has maximum possible value. This means that the spin wave function of electrons has maximum symmetry under the exchange of electrons and therefore spatial wave function of electrons is maximally antisymmetric.

The other Hund's rule state is that the total angular momentum of electrons has maximum possible value. This can be interpreted as follows. In ground state the electrons must move as far from each other as possible. If in atom there are two outer electrons, these must move with angle between them of 180° . If three electrons move in one plane this angle is 120° . If there are four equivalent electrons with the same orientation of spins, then the angle between each two electrons must be $109^\circ 28'$.

Fourth, let us consider the process of chemical bonding.

As we can see, hybrid orbital is formed in the process of chemical bonding. But in this process there is a virtual intermediate state where electron reaches very high energy. For example, in order for carbon atom to make graphite the excitation energy of about $7 \sim 8\text{eV}$ is needed. Even for virtual state this must be considered to be too high.

But if three outer electrons of carbon atom with the same value of S_z are located at one plane the angle between two electrons is equal to 120° , then it is easy to be combined in graphite. In this case the electron with opposite value will make weak bond between neighboring layers.

If one can make four outer electrons in carbon atom to have the same spin, then these will have tetrahedral shape and this is the condition to produce diamond. So the important condition for producing diamond from graphite is that the outer electrons of carbon atoms must have the same spin. For example, in atoms of Ni, Co and Fe one can expect that such effect will be strong. In order to produce diamond it is also important that the lattice constants of corresponding materials must be close to that of diamond. The alloys such as NiMnCo and NiMnFe satisfy these two conditions. It is known that such alloys are good catalysts in producing diamond.

Fifth, it is important to analyze the solid state of inert gases.

The electron cloud in an isolated atom cannot be visualized in experiment. In many cases based on the result of experiment with gas one can judge about the inner state of individual atom. It is clear that in order to draw some conclusion from experimental data one must use some assumption about inner state of atom. Let us analyze some problems in this respect.

It is reasonable to think that in chemical bond the electrons in atom are in ground state. In this connection it is very interesting to analyze the structure of crystals obtained when inert gas turns to solid state at very low temperature. If atoms of inert gas have a spherical form, then in solid state the crystal must have hexagonal closest package. But only helium gas in solid state has such structure other inert gases such as Ne, Ar, Kr, Xe in solid state have cubic closest package of type CH_4 . We can understand only if we assume that in their atoms the electrons are in sp^3 hybrid orbital, in our terminology, in directed orbital.

It is interesting that in inert atoms the closed shell consisted of 8 electrons is not made of 4 pairs of electrons with opposite spins but it is made of two groups of four electrons which are bound in quartet[2]. This idea gives us possibility to understand the structure of solid state of inert gases. Since the atoms of inert gas interact with each other very weakly when inert gas turns to solid state the structure of electron cloud in every atom may be changed very little.

Sixth, we must emphasize that the notion of a state of one electron in atom is very conditional. For example, if there are two electrons with equal spin and one electron is in ns state and other one electron in state np_0 then total wave function can be written as following Slater determinant.

$$\begin{vmatrix} \psi_-(r_1) & \psi_+(r_1) \\ \psi_-(r_2) & \psi_+(r_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{2s}(r_1) - \psi_{2p,0}(r_1) & \psi_{2s}(r_1) + \psi_{2p,0}(r_1) \\ \psi_{2s}(r_2) - \psi_{2p,0}(r_2) & \psi_{2s}(r_2) + \psi_{2p,0}(r_2) \end{vmatrix} = \begin{vmatrix} \psi_{2s}(r_1) & \psi_{2p,0}(r_1) \\ \psi_{2s}(r_2) & \psi_{2p,0}(r_2) \end{vmatrix}$$

Now let us consider total wave function assuming that one electron is in ψ_- state and other one in ψ_+ state. Then corresponding total wave function has the form

$$\Psi_B(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_-(r_1) & \psi_+(r_1) \\ \psi_-(r_2) & \psi_+(r_2) \end{vmatrix} \alpha(\sigma_1) \alpha(\sigma_2).$$

So $\Psi_A(1, 2) = \Psi_B(1, 2)$.

This shows that we cannot distinguish between these two cases and therefore the concept of one-electron state in many-electron system does not have a rigorous meaning.

2. Wave Function of Boron Atom

The wave function of boron atom with 5 electrons in directed orbital model (DOM) may be written as following Slater determinant

$$\Psi = \frac{1}{5!} \begin{vmatrix} \varphi_1(x_1) & \varphi_2(x_1) & \varphi_3(x_1) & \varphi_4(x_1) & \varphi_5(x_1) \\ \varphi_1(x_2) & \varphi_2(x_2) & \varphi_3(x_2) & \varphi_4(x_2) & \varphi_5(x_2) \\ \varphi_1(x_3) & \varphi_2(x_3) & \varphi_3(x_3) & \varphi_4(x_3) & \varphi_5(x_3) \\ \varphi_1(x_4) & \varphi_2(x_4) & \varphi_3(x_4) & \varphi_4(x_4) & \varphi_5(x_4) \\ \varphi_1(x_5) & \varphi_2(x_5) & \varphi_3(x_5) & \varphi_4(x_5) & \varphi_5(x_5) \end{vmatrix} = \varphi_1 \varphi_2 \varphi_3 \varphi_4 \varphi_5$$

$$\begin{aligned} \varphi_1(x) &= \psi_{1s}(\vec{r}) \alpha(\sigma), \quad \varphi_2(x) = \psi_{1s}(\vec{r}) \beta(\sigma), \quad \varphi_3(x) = \psi_{2s}(\vec{r}) \beta(\sigma), \quad \varphi_4(x) = \psi_+(\vec{r}) \alpha(\sigma), \quad \varphi_5(x) = \psi_-(\vec{r}) \alpha(\sigma) \\ \psi_+(\vec{r}) &= C_0 \psi_{2s}(\vec{r}) + C_1 \psi_{2p,0}(\vec{r}) + C_2 \psi_{d,0}(\vec{r}), \quad \psi_-(\vec{r}) = C_0 \psi_{2s}(\vec{r}) - C_1 \psi_{2p,0}(\vec{r}) + C_2 \psi_{d,0}(\vec{r}) \end{aligned}$$

$$\begin{aligned}\psi_{1s}(\vec{r}) &= R_{1s}(r) Y_{0,0}(\theta, \varphi), \quad \psi_{2s}(\vec{r}) = R_{2s}(r) Y_{0,0}(\theta, \varphi) \\ \psi_{2p,0}(\vec{r}) &= R_{2p}(r) Y_{1,0}(\theta, \varphi), \quad \psi_{d,0}(\vec{r}) = R_d(r) Y_{2,0}(\theta, \varphi)\end{aligned}$$

$$\psi_{ns}(\vec{r}) = \sum_{i=1}^6 C_n(i) N_s(i) r^{n(i)-1} \exp(-Zs(i)r) Y_{0,0}(\theta, \varphi)$$

$$\psi_{2p,0}(\vec{r}) = \sum_{i=1}^4 C_p(i) N_p(i) r \exp(-Zp(i)r) Y_{1,0}(\theta, \varphi), \quad N_s(i) = \frac{[2Zs(i)]^{n(i)+1/2}}{\sqrt{[2n(i)]!}}, \quad N_p(i) = \frac{2}{\sqrt{3}} [Zp(i)]^{2.5}$$

The basis functions $\varphi_1 - \varphi_5$ are orthonormalized. The values of $n(i)$, $Zs(i)$, $Zp(i)$ and $C_n(i)$, $C_p(i)$ are taken from [3] and are listed below.

On the other hand, the one-electron basis functions in the central force field approximation are as follows $\psi_k = \varphi_k$ ($k=1, 2, 3$), $\psi_4 = \psi_{2s}\alpha$, $\psi_5 = \psi_{2p}\alpha$.

It is easy to show that the total wave functions in two approximations coincide if $C_2 = 0$. But in DOM the term $C_2\psi_d(\vec{r})\alpha(\sigma)$ must be taken into account.

Normalization and orthogonality lead us to the result that $C_1 = 1/\sqrt{2}$, $C_0 = \sqrt{1/2 - C_2^2}$.

So only C_2 is a free parameter.

The part in total energy depending on C_2 can be represented in the following form

$$dE = AC_2^2 + BC_0C_2, \quad A = A_1 + 4A_{1,4} - 2JA_{1,4} + 2A_{3,4} + A_{4,5}$$

$$A_1 = Zd \left(Zd - \frac{10}{3} \right) + 10 \int_0^\infty R_{2s}^2 r dr - \int_0^\infty \left[r \frac{d}{dr} (R_{2s}) \right]^2 dr$$

$$A_{1,4} = \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 \{ R_{1s}^2(r_1) [R_d^2(r_2) - R_{2s}^2(r_2)] + [R_d^2(r_1) - R_{2s}^2(r_1)] R_{1s}^2(r_2) \}$$

$$JA_{1,4} = \frac{2}{5} \int_0^\infty r_1^4 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 R_{1s}(r_1) R_d(r_1) R_{1s}(r_2) R_d(r_2) - 2 \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 R_{1s}(r_1) R_{2s}(r_1) R_{1s}(r_2) R_{2s}(r_2)$$

$$A_{3,4} = \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 \{ R_{2s}^2(r_1) [R_d^2(r_2) - R_{2s}^2(r_2)] + [R_d^2(r_1) - R_{2s}^2(r_1)] R_{2s}^2(r_2) \}$$

$$\begin{aligned}A_{4,5} &= 2 \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 \{ [R_d^2(r_1) - R_{2s}^2(r_1)] R_{2p}^2(r_2) + R_{2p}^2(r_1) [R_d^2(r_2) - R_{2s}^2(r_2)] \} + \\ &+ \frac{8}{35} \int_0^\infty r_1^4 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 [R_d^2(r_1) R_{2p}^2(r_2) + R_d^2(r_2) R_{2p}^2(r_1)] + \frac{4}{3} \int_0^\infty r_1^3 dr_1 \int_{r_1}^\infty dr_2 R_{2s}(r_1) R_{2p}(r_1) R_{2s}(r_2) R_{2p}(r_2) - \\ &- \frac{16}{15} \int_0^\infty r_1^3 dr_1 \int_{r_1}^\infty dr_2 R_{2p}(r_1) R_d(r_1) R_{2p}(r_2) R_d(r_2) - \frac{108}{245} \int_0^\infty r_1^5 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 R_{2p}(r_1) R_d(r_1) R_{2p}(r_2) R_d(r_2) \\ B &= \frac{8}{5\sqrt{5}} \int_0^\infty r_1^4 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 \{ R_{2s}(r_1) R_d(r_1) R_{2p}^2(r_2) + R_{2p}^2(r_1) R_{2s}(r_2) R_d(r_2) \} - \\ &- \frac{8}{3\sqrt{5}} \int_0^\infty r_1^3 dr_1 \int_{r_1}^\infty dr_2 \{ R_{2s}(r_1) R_{2p}(r_1) R_d(r_2) R_{2p}(r_2) + R_d(r_1) R_{2p}(r_1) R_{2s}(r_2) R_{2p}(r_2) \}\end{aligned}$$

The minimum of the total energy is reached when $A > 0$ and

$$C_2 = -\frac{1}{2} \sqrt{1 - \frac{A}{\sqrt{A^2 + B^2}}} \text{SGN}(B), \quad \Delta E_{\min} = \frac{1}{4} \left(A - \sqrt{A^2 + B^2} \right).$$

3. Directed Orbital for Carbon Atom

For carbon atom with configuration $1s^2 2s^2 2p^2$ the ground state is 3P .

This means that $S=1, L=1$. Directed orbital corresponding to this state are as follows

$$\begin{aligned} \varphi_1 &= \frac{1}{\sqrt{4\pi}} R_{1s} \alpha, \quad \varphi_2 = \frac{1}{\sqrt{4\pi}} R_{1s} \beta, \quad \varphi_3 = \frac{1}{\sqrt{4\pi}} R_{2s} \beta \\ \varphi_4 &= \frac{1}{\sqrt{4\pi}} (C_0 R_{2s} + \sqrt{3} C_1 R_{2p} P_1(\cos\theta) + \sqrt{5} C_2 R_d P_2(\cos\theta)) \alpha \end{aligned}$$

$$\varphi_5 = \frac{1}{\sqrt{4\pi}} \left\{ C_0 R_0 - \frac{C_1 R_1}{2} (P_1 - \sqrt{3} \sin\theta \cos\varphi) - \frac{\sqrt{5}}{8} C_2 R_2 \left(P_2 + 6\sqrt{3} \sin\theta \cos\varphi - \frac{9}{2} \sin^2\theta \cos(2\varphi) \right) \right\} \alpha$$

$$\varphi_6 = \frac{1}{\sqrt{4\pi}} \left\{ C_0 R_0 - \frac{C_1 R_1}{2} (P_1 + \sqrt{3} \sin\theta \cos\varphi) - \frac{\sqrt{5}}{8} C_2 R_2 \left(P_2 - 6\sqrt{3} \sin\theta \cos\varphi - \frac{9}{2} \sin^2\theta \cos(2\varphi) \right) \right\} \alpha$$

where $P_1 = P_1(\cos\theta)$ and $P_2 = P_2(\cos\theta)$ are Legendre polynomials.

From normalization and orthogonality we obtain $C_0 = \sqrt{1/3 - C_2^2/4}$, $C_1 = \sqrt{2/3 - 3C_2^2/4}$.

Therefore C_2 is the only free parameter.

Then the part of the total energy of carbon atom depending on C_2 can be written as follows $E = 3(E_4 + 2K_{14} + K_{34} + K_{45} - J_{14} - J_{45})$.

Since the matrix elements between states with different eigenvalues of angular momentum are zero we obtain $E_4 = C_0^2 \langle 2s | h | 2s \rangle + C_1^2 \langle 2p | h | 2p \rangle + C_2^2 \langle d | h | d \rangle$.

The part depending on C_2 can be written as follows

$$E_4 = C_2^2 \{ \langle d | h | d \rangle - \langle 2s | h | 2s \rangle / 4 - 3 \langle p | h | 2p \rangle / 4 \}.$$

where $\langle d | h | d \rangle = Z d^2 / 2 - 2Zd$.

For calculation of K_{14} we need only the part of $|\psi_4|^2$ depending only on r and θ which can be written as

$$\frac{1}{4\pi} [C_0^2 R_0^2 + C_1^2 R_1^2 + C_2^2 R_d^2] \rightarrow \frac{1}{4\pi} C_2^2 \left[R_d^2 - \frac{1}{4} R_0^2 - \frac{3}{4} R_1^2 \right].$$

$$K_{14} \text{ can be written as follows } K_{14} = C_2^2 \iint \frac{1}{r_1} r_1^2 dr_1 r_2^2 dr_2 R_{1s}^2 \left[R_d^2(r_2) - \frac{1}{4} R_0^2(r_2) - \frac{3}{4} R_1^2(r_2) \right].$$

For K_{34} we have the same formula in which R_{1s} is replaced by R_{2s} .

For J_{14} we have

$$\begin{aligned} J_{14} &= \frac{2}{(4\pi)^2} \iint \frac{1}{r_1} r_1^2 dr_1 r_2^2 dr_2 R_{1s}(r_1) \times \{ C_0 R_{2s}(r_1) + \sqrt{3} C_1 R_{2p}(r_1) P_1(\cos\theta_1) + \sqrt{5} C_2 R_d(r_1) P_2(\cos\theta_1) \} \times \\ &\quad \times \{ C_0 R_{2s}(r_2) + \sqrt{3} C_1 R_{2p}(r_2) P_1(\cos\theta_2) + \sqrt{5} C_2 R_d(r_2) P_2(\cos\theta_2) \} \end{aligned}$$

In the formula for J_{14} the region of integration is $r_2 > r_1$. The formula for J_{14} can be transformed into the following form

$$J_{14} = 2 C_0^2 \int_0^\infty r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int_{r_1}^\infty r_2 dr_2 R_{1s}(r_2) R_{2s}(r_2) + \frac{2}{3} C_1^2 \int_0^\infty r_1^3 dr_1 R_{1s}(r_1) R_{2p}(r_1) \cdot \\ \cdot \int_{r_1}^\infty dr_2 R_{1s}(r_2) R_{2p}(r_2) + \frac{2}{5} C_2^2 \int_0^\infty r_1^4 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 R_{1s}(r_2) R_{2s}(r_2)$$

The formula for $K_{45} - J_{45}$ can be written as follows

$$K_{45} - J_{45} = \sum_{l=0}^4 B_l, \quad B_0 = \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r dr A_0, \quad B_1 = \int_0^\infty r_1^3 dr_1 \int_{r_1}^\infty dr A_1, \quad B_2 = \int_0^\infty r_1^4 dr_1 A_2 \\ A_0 = \frac{3}{2} C_1^4 R_1^2 R_1^2 + \frac{63}{32} C_2^4 R_2^2 R_2^2 + 3 C_0^4 C_1^2 (R_0^4 R_1^2 + R_1^4 R_0^2) + \frac{9 C_0^4 C_2^2}{4} (R_0^4 R_2^2 + R_2^4 R_0^2) + \frac{15 C_1^4 C_2^2}{8} (R_1^4 R_2^2 + R_2^4 R_1^2)$$

(Here, for example, $R_1^2 R_2^2$ means $R_1^2(1) R_2^2(2) = R_1^2(r_1) R_2^2(r_2)$.)

$$A_1 = -2 C_0^4 C_1^2 (R_0 R_1 R_0 R_1 + R_1^2 R_0^2) - C_0^4 C_1^2 C_2 (R_0 R_1 + R_1 R_0) / \sqrt{5} - 57 C_1^4 C_2^2 R_1 R_2 R_1 R_2 / 30 \\ A_2 = -\frac{9}{10} C_0^4 C_2^2 R_0 R_2 R_0 R_2 + \frac{3}{5\sqrt{5}} C_0^4 C_1^2 C_2 [R_0 R_2 R_1^2 + R_1^2 R_0 R_2] - \frac{3}{10} C_1^4 R_1^2 R_1^2 - \\ - \frac{45}{399} C_2^4 R_2^2 R_2^2 + \frac{3}{140} C_1^4 C_2^2 (R_1^2 R_2^2 + R_2^2 R_1^2).$$

4. Directed Orbital for Nitrogen Atom

For nitrogen the unit vectors are chosen as follows

$$\vec{n}_1 = (0, 0, 1), \quad \vec{n}_2 = (\sqrt{8}/3, 0, -1/3), \quad \vec{n}_3 = (-\sqrt{2}/3, \sqrt{2}/3, -1/3), \quad \vec{n}_4 = (-\sqrt{2}/3, -\sqrt{2}/3, -1/3)$$

Directed orbitals can be chosen as follows

$$\psi_{3+k}(r) = \frac{1}{\sqrt{4\pi}} [C_0 R_0 + \sqrt{3} C_1 R_1 P_1(\vec{n}_k \vec{n}) + \sqrt{5} C_2 R_2 P_2(\vec{n}_k \vec{n})] \quad (k = 1, 2, 3).$$

For Legendre polynomials we have

$$P_1(\vec{n}_1 \vec{n}) = P_1(\cos \theta), \quad P_1(\vec{n}_2 \vec{n}) = -\frac{1}{3} P(\cos \theta) + \frac{\sqrt{8}}{3} \sin \theta \cos \varphi, \quad P_1(\vec{n}_3 \vec{n}) = -\frac{1}{3} P(\cos \theta) - \frac{\sqrt{8}}{3} \sin \theta \cos \varphi \\ P_2(\vec{n}_1 \vec{n}) = P_2(\cos \theta), \quad P_2(\vec{n}_2 \vec{n}) = -\frac{1}{3} P_2(\cos \theta) - \frac{\sqrt{8}}{3} \cos \theta \sin \theta \cos \varphi + \frac{2}{3} \sin^2 \theta \cos(2\varphi)$$

The normalization and orthogonality lead to the result that $C_0 = 1/2$, $C_1 = \sqrt{3/4 - C_2^2}$.

And therefore C_0 has a definite value and only C_1 and C_2 are variables.

The part of energy depending on C_2 can be written as follows

$$\Delta E = 4 C_2^2 \{E_1 + 2E_{14} - J_{14} + E_{34}\} + 6 (K_{45} - J_{45}) \\ E_1 = \frac{1}{2} Z d^2 - 2 Z d - \langle 2p | h | 2p \rangle, \quad E_{14} = \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 \{R_{1s}^2 [R_2^2 - R_1^2] + [R_2^2 - R_1^2] R_{1s}^2\} \\ E_{34} = \int_0^\infty r_1^2 dr_1 \int_{r_1}^\infty r_2 dr_2 \{R_{2s}^2 [R_2^2 - R_1^2] + [R_2^2 - R_1^2] R_{2s}^2\}$$

$$\begin{aligned}
J_{14} &= \frac{2}{5} \int_0^\infty r_1^4 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 R_{1s} R_2 R_{1s} R_2 - \frac{2}{3} \int_0^\infty r_1^3 dr_1 \int_{r_1}^\infty dr_2 R_{1s} R_1 R_{1s} R_1 \\
K_{45} - J_{45} &= \sum_{k=0}^4 B_k, \quad B_0 = \int_0^\infty r_1^2 dr_1 A_0, \quad B_1 = \int_0^\infty r_1^3 dr_1 \int_{r_1}^\infty dr_2 A_1, \quad B_2 = \int_0^\infty r_1^4 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 A_2 \\
B_3 &= \frac{128}{735} C_1^2 C_2^2 \int_0^\infty r_1^5 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 R_{21} R_2 R_1 R_2, \quad B_4 = -\frac{128}{1323} C_2^4 \int_0^\infty r_1^6 dr_1 \int_{r_1}^\infty \frac{1}{r_2} dr_2 R_2^2 R_2^2 \\
A_0 &= \frac{8}{3} C_0^2 C_1^2 (R_0^2 R_1^2 + R_1^2 R_0^2) + \frac{8}{3} C_0^2 C_2^2 (R_0^2 R_2^2 + R_2^2 R_0^2) + \frac{16}{9} C_1^2 C_2^2 (R_1^2 R_2^2 + R_2^2 R_1^2) + \\
&\quad + \frac{16}{9} C_1^4 R_1^2 R_1^2 + \frac{16}{9} C_2^4 R_2^2 R_2^2 \\
A_1 &= -\frac{16}{9} C_0^2 C_1^2 R_0 R_1 R_0 R_1 - \frac{64}{45} C_1^2 C_2^2 R_1 R_2 R_1 R_2 - \frac{32}{9\sqrt{5}} C_0 C_1^2 C_2 [R_0 R_1 R_1 R_2 + R_1 R_2 R_0 R_1] \\
A_2 &= -\frac{16}{15} C_0^2 C_2^2 R_0 R_2 R_0 R_2 - \frac{32}{1125} C_1^4 R_1^2 R_1^2 - \frac{80}{441} C_2^4 R_2^2 R_2^2 - \frac{16}{315} C_1^2 C_2^2 (R_1^2 R_2^2 + R_2^2 R_1^2)
\end{aligned}$$

5. Results of Calculation and Discussion

We obtained the result that for boron, carbon and nitrogen atoms the values of C_2 giving the minimum of total energy and the minimum total energy are as follows[table].

Table. Values of C_2 and minimum energy value

Atom	Zd	C_2	ΔE
Boron	1.149 3	0.046 89	-0.003 000
Carbon	1.404 7	0.065 79	-0.003 310
Nitrogen	1.742 0	0.049 97	-0.014 566

The values of C_2 are comparatively small, but the most important result of this work is that in isolated atom the electrons move in the state of directed orbital.

Conclusion

According to [3] the difference in total energy between 3P and 1D states of carbon atom is 0.057 3.

In comparison with this value the value of 0.003 310 or 0.014 566 are not so small as may be seemed at first glance. More important is the result that in directed orbital model the mixture of d-type state arises naturally and it reduces the total energy.

This means that for electrons in isolated atom it is preferable to be in directed orbital state.

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