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Hartree-Fock-Slater Method for Materials Science

The DV-Xα Method for Design and Characterization of Materials

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Hartree-Fock-Slater Method for Materials Science

The DV-Xα Method for Design and Characterization of Materials

With 132 Figures and 33 Tables

Springer

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Preface

The aim of this book is to present and explain the discrete variational (DV) Xα molecular orbital method for calculations of the electronic structure and properties of molecules. With recent advance of computers, several self-consistent molecular orbital methods have been developed. The DV-Xα method is one such method.

The approximation for the exchange potential, now denoted by the Xα potential, was first introduced in 1951 by J.C. Slater. The Xα method is usually called as the Hartree–Fock–Slater method for atoms. J. Korringa (1947), W. Kohn and N. Rostoker (1954) proposed the Korringa–Kohn–Rostoker (KKR) method to calculate electronic states of solids with a translational symmetry by the use of the multiple scattering approach. Though this approach was believed to be suitable for energy band calculations, K.H. Johnson (1967) demonstrated that this approach is also applicable to isolated molecules, using the Xα potential. Johnson's method was called the multiple scattering (MS) Xα or scattered wave (SW) Xα method. After the work of Johnson, complicated molecules or surfaces, without any periodic boundary conditions, could be calculated with a similar method of solid state physics.

The DV-Xα method first appeared in 1970 in Chicago and was developed by D.E. Ellis, H. Adachi (one of the editors and authors of this book), and other young researchers at that time. In contrast, to multiply scattered spherical waves used for the MS-Xα or SW-Xα method, the wave functions in the DV-Xα method are expressed by a linear combination of atomic orbitals (LCAO). The atomic wave functions are given in numerical form and the matrix elements in the secular equation are calculated numerically with the DV-integration method. The advantage of the DV-Xα method is the possibility to obtain realistic molecular potentials and wave functions with relatively small basis set. This method is also applicable to molecules or clusters both for ground and excited states, which have no translational symmetry.

Based on this merit, the DV-Xα method has been used for design of alloys and ceramics, surface and interface chemistry, and core level spectroscopies, because, in such systems, the added atoms, surface, or core hole are regarded as an impurity to break the periodic boundary condition. Recently the DV-Xα method has been applied to design of various kinds of industrial materials, such as electric batteries, catalysts, etc.

The reason for such wide applications is in the fact that by using the DV-Xα method it is easy to converge the electronic structure of clusters that contain any atomic number elements up to $Z = 115$; any kind of unstable valence states, such as Fe^{5+}; any bond length, such as an iron in the earth's core; or a very short-lived transition state, such as the 1s core hole state. The DV-Xα method is still advancing including the relativistic effect, spin multiplet, and spin-orbital interaction.

This book presents various topics of the DV-Xα method from the basic concept to important applications and is divided into three parts. The first part is fundamental and the basic principle of the DV-Xα method is explained in Chap. 1. The second part is devoted to materials science. Chapters 2 to 7 describe alloy design, lattice imperfections, ceramics, magnetic properties, optical materials and heavy elements. The third part covers applications for spectroscopy. X-ray spectroscopy, core hole spectroscopy and Auger spectroscopy are discussed in Chaps. 8 to 10.

We wish to thank Dr. I. Kishida for his efforts to transform many complicated mathematical formulae into TeX. It is also a pleasure to thank Claus Ascheron of Springer for his encouragement and patience over the course of preparing this book.

Kyoto, Oct. 2005

Hirohiko Adachi
Jun Kawai
Takeshi Mukoyama

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Part I

Fundamental

1

DV-Xα Method and Molecular Structure

Hirohiko Adachi

1.1 Molecular Orbital Theory

In a molecule, the potential acting on an electron can be expressed as a summation of the potentials of the constituent atoms. In such a model, the electron moves about in the attracting field of their nuclei; in other words, the valence electron can move all over the molecule, because the potential barrier is depressed midway between the atoms where the atomic potentials overlap (see Fig. 1.1).

Molecular orbital theory addresses such an electron system. The molecular orbital corresponds to the wave function of the electron moving about in the molecule. In order to obtain the molecular orbital ϕ_l, we need to solve the Schrödinger equation for the molecule, written as

$$h\phi_l(r) = \varepsilon_l \phi_l(r) \ , \tag{1.1}$$

where h is the one-electron Hamiltonian for the molecule, given by

$$h(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) \ . \tag{1.2}$$

Because it is impossible to solve the partial differential equation of (1.1) rigorously, we need to make an approximation of the solution to the equation. In most molecular orbital (MO) methods, an MO wave function ϕ_l is expressed by a linear combination of atomic orbitals (LCAO) written as

$$\phi_l = \sum_l C_{il}\chi_i \ , \tag{1.3}$$

where C_{il} is the coefficient and χ_i the atomic orbital as a basis function. In order to find a solution to the Schrödinger equation, the Rayleigh–Ritz variational method is usually employed to obtain a secular equation. The

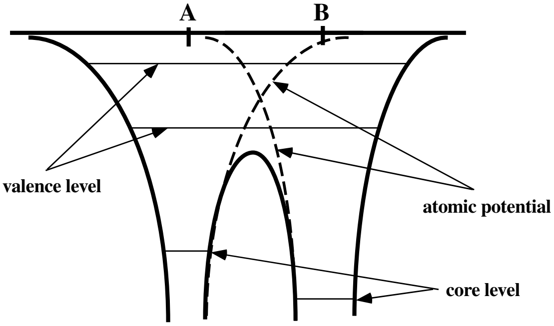

Fig. 1.1. Schematic diagram of the molecular potential resulting from superimposing atomic potentials

molecular orbital can be obtained by solving the secular equation written in a matrix formula as

$$(\underset{\sim}{\boldsymbol{H}} - \underset{\sim}{\boldsymbol{\varepsilon}} \cdot \underset{\sim}{\boldsymbol{S}}) \cdot \underset{\sim}{\boldsymbol{C}} = 0 , \tag{1.4}$$

where $\underset{\sim}{\boldsymbol{H}}$ and $\underset{\sim}{\boldsymbol{S}}$ are the matrices whose elements are the so-called resonance and overlap integrals, respectively. Solving the equation yields the eigenvalue $\underset{\sim}{\boldsymbol{\varepsilon}}$ and eigenvector $\underset{\sim}{\boldsymbol{C}}$, which correspond to the one-electron energy and the coefficient of the LCAO wave function for the molecular orbital, respectively. The matrix elements H_{ij} and S_{ij} in the secular equation are given by integrals of atomic orbitals as

$$S_{ij} = \int \chi_i \chi_j \, \mathrm{d}v , \tag{1.5}$$

$$H_{ij} = \int \chi_i H \chi_j \, \mathrm{d}v , \tag{1.6}$$

and are referred to as the "resonance integral" and "overlap integral," respectively, as mentioned above. For the case of $i = j$, we sometimes call the integral H_{ii} the "Coulomb integral." In the MO calculation, we should first evaluate the matrix elements H_{ij} and S_{ij} of (1.5) and (1.6) to construct the secular equation and then solve it by diagonalizing the matrix to obtain $\underset{\sim}{\boldsymbol{\varepsilon}}$ and $\underset{\sim}{\boldsymbol{C}}$ as the eigenvalue and eigenvector. Thus, we obtain the eigenvalue ε_l, which corresponds to the one-electron MO energy and the eigenvector to the coefficient C_{il} for the atomic orbital i in the LCAO wave function of the lth molecular orbital.

Next, we try to understand the spatial distribution of electronic charge. We can analyze the result of the MO calculation with the aid of the Mulliken population analysis [1]. In this method, the total number of electrons in the system can be written as

$$n = \sum_l \sum_i \sum_j Q_{ij}^l , \quad Q_{ij}^l = f_l C_{il} C_{jl} S_{ij} , \tag{1.7}$$

where f_l is the occupation number of the lth MO level. Q_{ij}^l and Q_i^l are related by

$$Q_i^l = \sum_j Q_{ij}^l \ , \tag{1.8}$$

are the contributions of the lth MO state to the orbital population Q_i and the overlap population Q_{ij}, defined as

$$Q_i = \sum_l \sum_j Q_{ij}^l \ , \tag{1.9}$$

and

$$Q_{ij} = \sum_l Q_{ij}^l \ . \tag{1.10}$$

They are regarded as the effective number of electrons in the ith atomic orbital, and the strength of the covalent interaction between atomic orbitals i and j, respectively. When the value of Q_{ij} is positive, the interaction between atomic orbitals i and j is bonding, while an antibonding interaction occurs in the case of a negative overlap population. The sum of Q_i over all i belonging to atom A,

$$Q_{\mathrm{A}} = \sum_{i \in \mathrm{A}} Q_i \ , \tag{1.11}$$

is the effective charge of the atom. Thus, the net charge of atom A, N_{A}, is given by the difference between the atomic number Z_{A} and Q_{A}; thus,

$$N_{\mathrm{A}} = Z_{\mathrm{A}} - Q_{\mathrm{A}} \ . \tag{1.12}$$

The bond overlap population (BOP), Q_{AB}, which is defined as the sum of Q_{ij} over all i belonging to atom A and all j belonging to atom B – namely,

$$Q_{\mathrm{AB}} = \sum_{i \in \mathrm{A}} \sum_{i \in \mathrm{B}} Q_{ij} \ , \tag{1.13}$$

is considered as a measure of strength of covalent bonding between atoms A and B.

1.2 Discrete Variational (DV) Xα Molecular Orbital Method

In the conventional first-principle molecular orbital method, an analytical function such as the Gaussian-type orbital (GTO) or the Slater-type orbital (STO) is utilized as the basis functions of the LCAO of (1.3), so that the analytical integrations for $\boldsymbol{H}$ and $\boldsymbol{S}$ are feasible. In such a case, a large number of basis functions is necessary to represent an atomic orbital. This means that a large-scale computation for the preparation of the matrix elements is inevitable with this method.

In the discrete variational Xα (DV-Xα) method [2–4], we adopt an LCAO MO function given by (1.3) similar to the usual MO method, but we use the real atomic orbital for the basis function χ_i instead of the analytical function, so that one can prepare basis functions, each of which corresponds to one atomic orbital. This drastically reduces the required computational memory and time. The atomic orbital used as the basis function can be obtained by numerically solving the Schrödinger equation for an atom. The atomic orbital wave function is given by

$$\chi = R_{\mathrm{n}l}(r) \cdot \boldsymbol{y}_{l\mathrm{m}}(\theta, \phi) , \tag{1.14}$$

where $\boldsymbol{y}_{l\mathrm{m}}$ are the well-known spherical harmonics, and $R_{\mathrm{n}l}$ is the radial wave function, which we can calculate numerically with the following equation for a given atom:

$$\left\{ -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} + V(r) \right\} R_{\mathrm{n}l}(r) = \varepsilon_{\mathrm{n}l} R_{\mathrm{n}l}(r) . \tag{1.15}$$

The numerical computation of the above equation is practicable by the use of a computer code similar to that introduced by Herman and Skillman [5]. Figure 1.2 shows the radial wave functions $R_{\mathrm{n}l}$ for C and O atoms, which can be used for MO calculations of a molecule that contains these atoms.

The atomic orbital χ is the product of $R_{\mathrm{n}l}$ and the spherical harmonics $\boldsymbol{y}_{l\mathrm{m}}$, as shown by (1.14). We use the numerical atomic orbital thus obtained for the

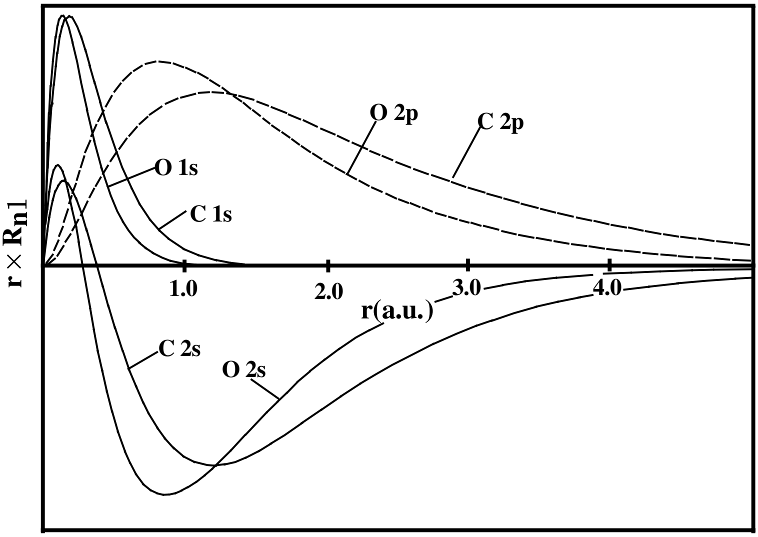

Fig. 1.2. Radial wave function of atomic orbitals for C and O atoms

basis function in the DV-Xα MO method; naturally, analytical integrations for the resonance and overlap matrix elements, H_{ij} and S_{ij}, are impossible to carry out. Instead, a numerical integration [4, 6] should be adopted for the calculation of H_{ij} and S_{ij}. In this method, the integration is replaced by a summation; namely,

$$\int \mathrm{d}\boldsymbol{r} \cdot g(\boldsymbol{r}) \Rightarrow \sum_{k=1}^{N} \omega(\boldsymbol{r}_k) \cdot g(\boldsymbol{r}_k) \ . \tag{1.16}$$

Here $g(\boldsymbol{r})$ is the integrand, and $\omega(\boldsymbol{r}_k)$ is the weight of the sampling point $\boldsymbol{r}_k$. For the integration, we first take a total of N sampling points in three-dimensional real space to calculate the integrand values at each sampling point, and then sum up the integrand values multiplied by the weight of the point over all sampling points. The matrix elements are thus given by

$$H_{ij} = \sum_{k=1}^{N} \omega(\boldsymbol{r}_k)\chi_i(\boldsymbol{r}_k)h(\boldsymbol{r}_k)\chi_j(\boldsymbol{r}_k) \ , \tag{1.17}$$

$$S_{ij} = \sum_{k=1}^{N} \omega(\boldsymbol{r}_k)\chi_i(\boldsymbol{r}_k)\chi_j(\boldsymbol{r}_k) \ , \tag{1.18}$$

where $h(\boldsymbol{r}_k)$ is the one-electron Hamiltonian given by

$$h(\boldsymbol{r}_k) = -\frac{1}{2}\nabla^2 + V(\boldsymbol{r}_k) \ . \tag{1.19}$$

$V(\boldsymbol{r}_k)$ is the effective molecular potential and is written by

$$V(\boldsymbol{r}_1) = -\sum_{\nu} \frac{Z_\nu}{|\boldsymbol{r}_1 - \boldsymbol{R}_\nu|} + \int \frac{\rho(\boldsymbol{r}_2)}{r_{12}} \mathrm{d}\boldsymbol{r}_2 - 3\alpha \left\{ \frac{3}{8\pi}\rho(\boldsymbol{r}_1) \right\}^{1/3} \ , \tag{1.20}$$

where Z_ν and $\boldsymbol{R}_\nu$ are the atomic number and position of atom ν, respectively. The molecular charge density is given by

$$\rho(\boldsymbol{r}) = \sum_{l} \rho_l(\boldsymbol{r}) = \sum_{l} f_l |\phi_l(\boldsymbol{r})|^2 \ . \tag{1.21}$$

Thus, the first and second terms of (1.20) are the attractive potential from the nuclei and the repulsive potential of the electron cloud of the whole system, respectively. The third term is the exchange-correlation potential proposed by Slater [7, 8], and α is the scaling parameter, the only parameter used in this method.

In performing the DV numerical integration described above, we have to generate the N sampling points. We first take three random numbers, a_k, b_k, and c_k, which are distributed between 0 and 1, to set the kth sampling point $\boldsymbol{r}_k$. We can choose these numbers, for example, to be the decimal parts of $a_k = k \times 2^{1/2}$, $b_k = k \times 3^{1/2}$, and $c_k = k \times 5^{1/2}$, for $k = 1$ to N. In order to determine the point $\boldsymbol{r}_k(r_k, \theta_k, \phi_k)$ in polar coordinates using a_k, b_k, and c_k, we set

$$\left.\begin{aligned} &\cos\theta_k = 2b_k - 1 , \\ &\phi_k = 2\pi c_k , \\ &r_k = \ln \frac{\exp(a_k/A)}{1 + \{1 - \exp(a_k/A)\} \exp(-R_0)} , \end{aligned}\right\} \tag{1.22}$$

where A is an adjustable parameter and R_0 is chosen to be a value near the atomic radius. Both are parameters of the Fermi-like distribution function for the sampling point (see Fig. 1.3).

Then, the density of the sampling point is given by

$$d(r) = \frac{A}{4\pi r^2 \{1 + \exp(r - R_0)\}} . \tag{1.23}$$

The sampling points are distributed around a given atom according to the above equations. For a molecular calculation, we take these points around all constituent atoms. The density of the sampling point $\boldsymbol{r}$ can be given by the sum of contributions from all atoms in the molecule; thus,

$$D(\boldsymbol{r}) = \sum_\nu t_\nu \cdot d_\nu(\boldsymbol{r}_\nu) , \quad \sum_\nu t_\nu = 1 . \tag{1.24}$$

Consequently, the weight of the sampling point is

$$\omega(\boldsymbol{r}) = \frac{1}{N \times D(\boldsymbol{r})} . \tag{1.25}$$

The distribution of the sampling points for a diatomic molecule is displayed in Fig. 1.4. The sampling points are relatively condensed near the nucleus where the variations of the wave functions and the potential are rapid, while the points are dilute far from the nucleus since these functions change smoothly.

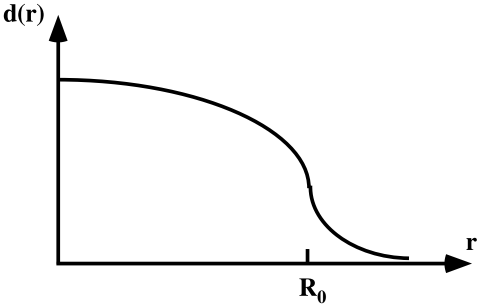

Fig. 1.3. Density of the sampling point of a Fermi-like function

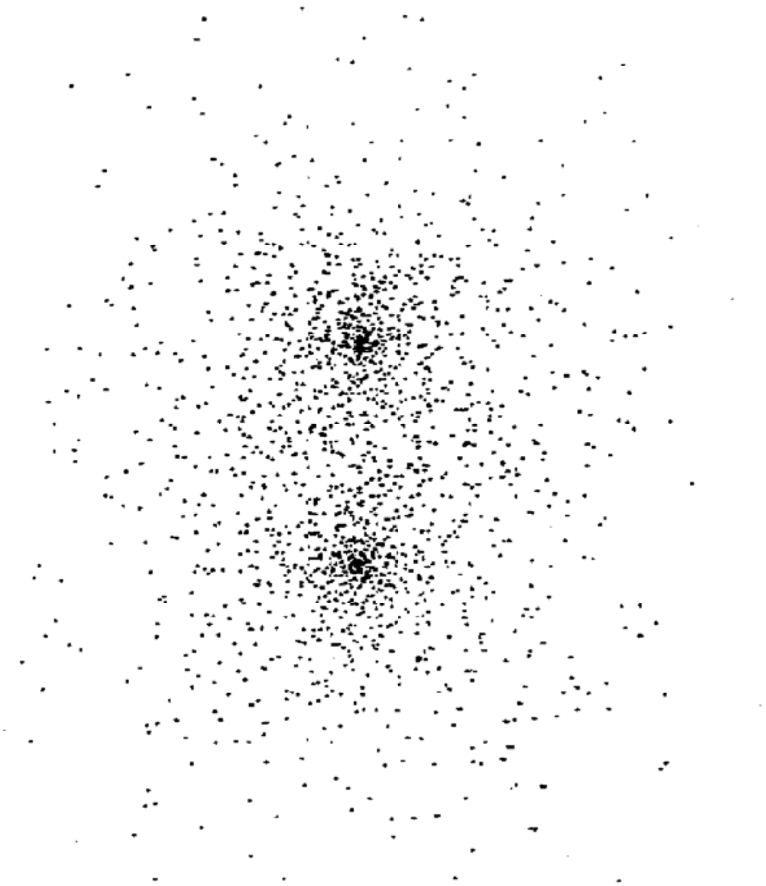

Fig. 1.4. Projection of 2000 sampling points around the C and O atoms in a CO molecule

Next, we should evaluate the integrand at a given sampling point constructed by the atomic orbital functions and potential function, as given in (1.17) and (1.18). The radial part of the atomic orbital given by (1.14) is previously calculated using (1.15). The molecular potential is also expressed by (1.20); thus, we are able to evaluate the integrand value at the point.

Figure 1.5 illustrates how to estimate the values of atomic orbital functions at a sampling point $\boldsymbol{r}$ locating around the nuclei. The integrand is multiplied by the weight $\omega(\boldsymbol{r})$ for each sampling point and then summed up over all the sampling points to obtain the integral values of H_{ij} and S_{ij}. The secular equation thus composed can be solved by an ordinary matrix diagonalization to obtain the eigenvalues and eigenvectors.

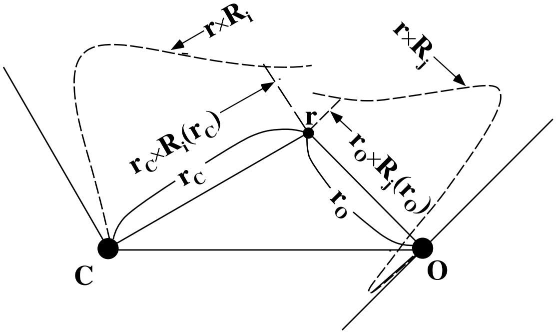

Fig. 1.5. Evaluation of the radial wave functions of atomic orbitals for C and O atoms at a sampling point $\boldsymbol{r}$

1.3 Molecular Orbital Calculation of H_2

Next we are going to perform an actual calculation of the molecular orbital. The simplest case of a molecular problem is a hydrogen molecule. Consider two hydrogen atoms A and B approaching each other to form a hydrogen molecule. In this case, we have an LCAO molecular orbital given by

$$\phi = C_{\mathrm{A}}\chi_{\mathrm{A}} + C_{\mathrm{B}}\chi_{\mathrm{B}} \ , \tag{1.26}$$

where χ_{A} and χ_{B} are $H \times 1s$ orbitals of atoms A and B. The secular equation (1.4) can thus be expressed as

$$\begin{array}{c} (H_{\mathrm{AA}} - \varepsilon)C_{\mathrm{A}} + (H_{\mathrm{AB}} - \varepsilon S_{\mathrm{AB}})C_{\mathrm{B}} = 0 \\ (H_{\mathrm{BA}} - \varepsilon S_{\mathrm{BA}})C_{\mathrm{A}} + (H_{\mathrm{BB}} - \varepsilon)C_{\mathrm{B}} = 0 \end{array} \ , \tag{1.27}$$

where we can set

$$\varepsilon_0 = H_{\mathrm{AA}} = H_{\mathrm{BB}} \ , \quad S_{\mathrm{BA}} = S_{\mathrm{AB}} \ , \quad H_{\mathrm{BA}} = H_{\mathrm{AB}} \ , \tag{1.28}$$

since the atoms A and B are equivalent. Then, the eigenvalue ε can be obtained by solving the determinantal equation

$$\begin{vmatrix} \varepsilon_0 - \varepsilon & H_{\mathrm{AB}} - \varepsilon S_{\mathrm{AB}} \\ H_{\mathrm{AB}} - \varepsilon S_{\mathrm{AB}} & \varepsilon_0 - \varepsilon \end{vmatrix} = (\varepsilon_0 - \varepsilon)^2 - (H_{\mathrm{AB}} - \varepsilon S_{\mathrm{AB}})^2 = 0 \ . \tag{1.29}$$

Then, we have two values

$$\varepsilon_{\pm} = \frac{\varepsilon_0 \pm H_{\mathrm{AB}}}{1 \pm S_{\mathrm{AB}}} \tag{1.30}$$

for eigenvalues; namely, the orbital energies for the H_2 molecule. Because the molecular wave function ϕ_l is normalized, we have

$$\int |\phi_l|^2 \, \mathrm{d}v = C_{\mathrm{A}}^2 + C_{\mathrm{B}}^2 + 2C_{\mathrm{A}}\ C_{\mathrm{B}}S_{\mathrm{AB}} = 1 \ . \tag{1.31}$$