

# Tight-Binding Model of Electronic Structures

Consider a collection of  $N$  atoms. The electronic structure of this system refers to its electronic wave function and the description of how it is related to the binding energy that keeps the atoms together. In an independent electron approximation, a single electron time-independent Schrödinger equation,

$$H\psi_v(\vec{r}) = \varepsilon_v\psi_v(\vec{r}), \quad (1)$$

is solved to find the eigenstates,  $\psi_v$  ( $v = 1, 2, \dots$ ), and the corresponding eigenenergies,  $\varepsilon_v$ , of the Hamiltonian operator,

$$H = -\frac{1}{2}\nabla^2 + V(\vec{r}), \quad (2)$$

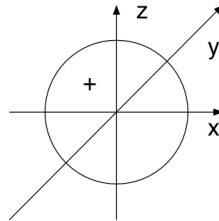
where  $V(\vec{r})$  is the potential energy operator and we have used the atomic unit. (For example, the density functional theory provides a framework to derive an effective single-electron potential energy operator, which incorporates the interaction among the many electrons [1-3].)

## §1. Tight-Binding Model

In the tight-binding model of electronic structures, single-electron wave functions are expanded in terms of atomic orbitals [4,5],

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi), \quad (3)$$

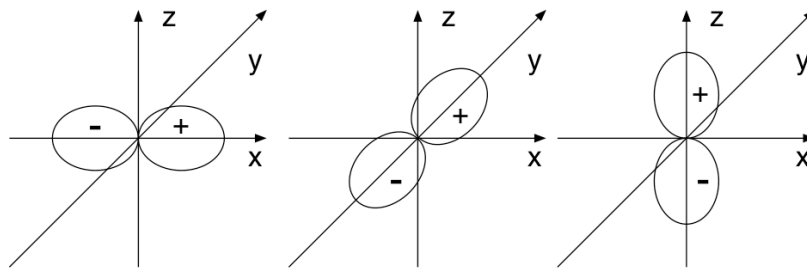
centered around each atom, where  $R_{nl}$  and  $Y_{lm}$  are radial and spherical-harmonics functions in polar coordinates. (This scheme is also called the linear combination of atomic orbitals, or LCAO.) In Eq. (3),  $n$ ,  $l$  and  $m$  are the principal, angular-momentum and magnetic quantum numbers, respectively. For example, 1s atomic orbital ( $n = 1$  and  $l = m = 0$ ) is spherically symmetric and is taken as positive definite (see the figure below).



For p atomic orbitals, we work with the Cartesian representation, such that the three orthogonal p orbitals are along the x, y and z axes [4-6] (see the figure below),

$$\psi_{nlm}(x, y, z) = \left(\frac{3}{4\pi}\right)^{1/2} R_{nl}(r) \begin{cases} x/r \\ y/r \\ z/r \end{cases}, \quad (4)$$

where  $r = \sqrt{x^2 + y^2 + z^2}$ .



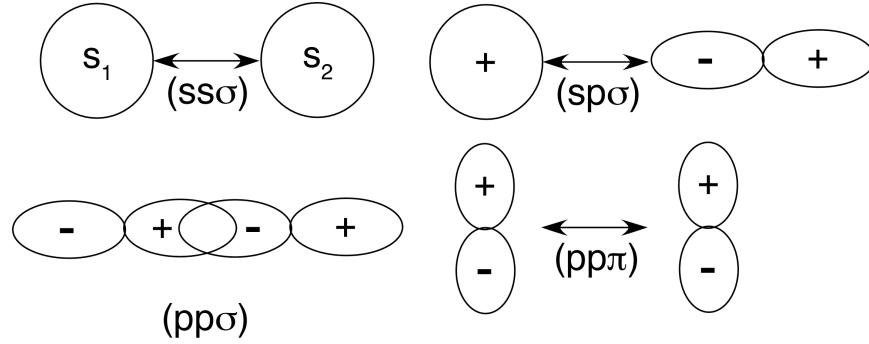
## HOPPING INTEGRALS

As a specific example, we consider a collection of silicon atoms, such as a silicon cluster. The electron configuration in a free silicon atom is  $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^2}$ , and thus there are four valance electrons (shown in bold) in the outer shell, which mainly contribute to the chemical bonding. We will represent the electronic structures of silicon clusters as a linear combination of four atomic orbitals per atom—one 3s orbital and three 3p orbitals,  $3p_x$ ,  $3p_y$  and  $3p_z$ , centered around each silicon atom,

$$\psi(\vec{r}) = \sum_{i=1}^N \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha} \psi_{\alpha}(\vec{r} - \vec{r}_i). \quad (5)$$

(The effects of inner shell electrons can be effectively included using pseudopotential methods [7].)

To solve the eigenvalue problem, Eq. (1), we need the Hamiltonian matrix elements between these atomic orbitals at different interatomic distances. In tight-binding methods, these so called hopping integrals are fitted as analytic functions of the interatomic distance,  $r$ . For the sp-bonding, there are only four nonzero hopping integrals as shown in the figure below, in which  $\sigma$  and  $\pi$  bondings are defined such that the axis of the involved p orbitals are parallel and normal to the interatomic vector, respectively.



In this lecture, we adopt the tight-binding model of silicon by Kwon, et al. [8], in which the hopping integrals are fitted as

$$h_{\lambda}(r) = \begin{cases} \langle s_1 | H | s_2 \rangle & \lambda = ss\sigma \\ \langle s_1 | H | p_{2d} \rangle & \lambda = sp\sigma \\ \langle p_{1d} | H | p_{2d} \rangle & \lambda = pp\sigma \\ \langle p_{1n} | H | p_{2n} \rangle & \lambda = pp\pi \end{cases}, \quad (6)$$

$$= h_{\lambda}(r_0) \left( \frac{r_0}{r} \right)^n \exp \left( n \left[ - \left( \frac{r}{r_{\lambda}} \right)^{n_{\lambda}} + \left( \frac{r_0}{r_{\lambda}} \right)^{n_{\lambda}} \right] \right)$$

whereas the diagonal Hamiltonian elements on each atom are given by

$$\begin{cases} \langle s | H | s \rangle = E_s \\ \langle p_x | H | p_x \rangle = \langle p_y | H | p_y \rangle = \langle p_z | H | p_z \rangle = E_p \end{cases}. \quad (7)$$

In Eq. (6),  $p_{1d}$  and  $p_{1n}$  denote the p orbitals parallel and normal to the bonding axis, respectively, centered at the first atom. The parameters in Eqs. (6) and (7) are listed in the tables below.

$r_0(\text{\AA})$	$n$	$E_s(\text{eV})$	$E_p(\text{eV})$
2.360352	2	-5.25	1.20

$\lambda$	ss $\sigma$	sp $\sigma$	pp $\sigma$	pp $\pi$
$h_i(r_0)$ (eV)	-2.038	1.745	2.75	-1.075
$n_i$	9.5	8.5	7.5	7.5
$r_i$ (Å)	3.4	3.55	3.7	3.7

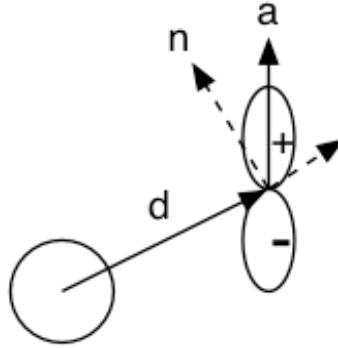
To convert the values into atomic units, divide all the lengths by the Bohr radius,  $a_B = 0.5291772083 \text{ \AA}$ , and all the energies by the Hartree energy,  $E_H = 27.2113834 \text{ eV}$ .

## §2. Projection of Hopping Integrals

In the tight-binding model presented in the previous section, the electronic wave functions are expanded in terms of the p orbitals along the Cartesian x, y and z axis, whereas the hopping integrals are parameterized for p orbitals that are parallel or normal to the bonding directions. To construct the Hamiltonian matrix elements, we need to decompose the Cartesian p orbitals into the bond-parallel and bond-normal p orbitals.

### PROJECTION OF S-P INTEGRALS

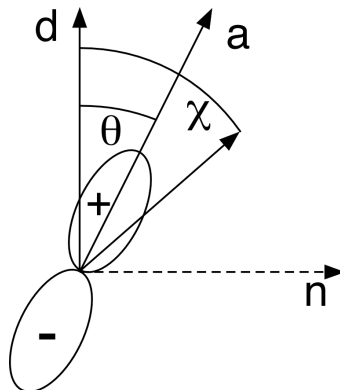
Consider the Hamiltonian matrix element,  $\langle s|H|p_\alpha\rangle$ , between the s orbital,  $|s\rangle$ , on one atom and one of the p orbitals,  $|p_\alpha\rangle$  ( $\alpha = x, y, z$ ), on another atom. Let  $\hat{d}$  be the unit vector along the bond from the first atom to the second. In the figure below,  $\hat{a}$  is the unit vector along one of the Cartesian (x, y or z) axes.



We first decompose the p orbital along  $\hat{a}$  into two p orbitals that are parallel and normal to  $\hat{d}$ , respectively (see the figure below):

$$|p_a\rangle = \hat{a} \cdot \hat{d} |p_d\rangle + \hat{a} \cdot \hat{n} |p_n\rangle, \quad (8)$$

where  $\hat{n}$  is the unit vector normal to  $\hat{d}$  within the plane spanned by  $\hat{d}$  and  $\hat{a}$ .



$\therefore$  Let  $\theta$  be the angle between vectors  $\hat{d}$  and  $\hat{a}$ . Consider an arbitrary point in the 3D space, whose polar angle from the  $\hat{d}$  axis is  $\chi$ . On this point, the value of the p basis function around the  $\hat{a}$  axis is given by

$$\begin{aligned} |p_a\rangle &= \cos(\chi - \theta) \\ &= \cos\chi \cos\theta + \sin\chi \sin\theta \\ &= \cos\theta |p_d\rangle + \sin\theta |p_n\rangle \\ &= \hat{a} \cdot \hat{d} |p_d\rangle + \cos\left(\frac{\pi}{2} - \theta\right) |p_n\rangle \\ &= \hat{a} \cdot \hat{d} |p_d\rangle + \hat{a} \cdot \hat{n} |p_n\rangle \end{aligned}$$

where we have used a trigonometric addition theorem to derive the second line from the first. //

The Hamiltonian matrix element is then given by

$$\langle s | H | p_a \rangle = \langle s | H (\hat{a} \cdot \hat{d} |p_d\rangle + \hat{a} \cdot \hat{n} |p_n\rangle) = (\hat{a} \cdot \hat{d}) h_{sp\sigma}(r), \quad (9)$$

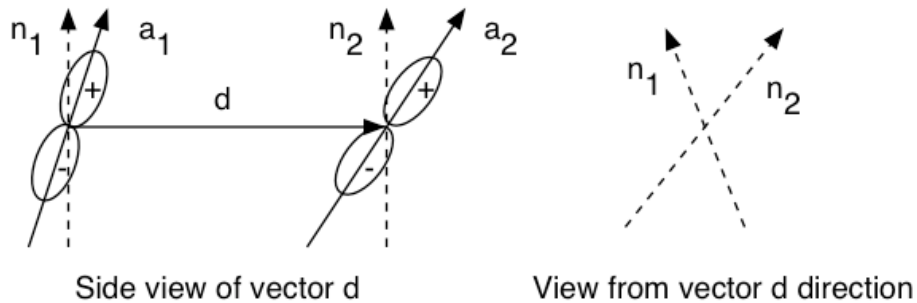
where  $h_{sp\sigma}(r)$  is the Hamiltonian matrix element in Eq. (6) evaluated at atomic distance  $r$ . Note the overlap between the  $|s\rangle$  and  $|p_n\rangle$  orbitals is zero by symmetry. To obtain explicit formula in terms of  $p_x$ ,  $p_y$  and  $p_z$  centered around the first second atom, let us introduce the directional cosines along the x, y and z axes as  $\hat{d} = (d_x, d_y, d_z)$ . Then

$$\begin{pmatrix} \langle s_1 | H | p_{2x} \rangle \\ \langle s_1 | H | p_{2y} \rangle \\ \langle s_1 | H | p_{2z} \rangle \end{pmatrix} = - \begin{pmatrix} \langle p_{1x} | H | s_2 \rangle \\ \langle p_{1y} | H | s_2 \rangle \\ \langle p_{1x} | H | s_2 \rangle \end{pmatrix} = \begin{pmatrix} d_x h_{sp\sigma}(r) \\ d_y h_{sp\sigma}(r) \\ d_z h_{sp\sigma}(r) \end{pmatrix}. \quad (10)$$

In Eq. (10), the matrix elements between the p orbitals on the first atom and the s orbital on the second atom are obtained simply by inverting the direction of the bonding unit vector,  $\hat{d}$ , i.e., changing the signs of the directional cosines.

### PROJECTION OF P-P INTEGRALS

Consider two unit vectors  $\hat{a}_1$  and  $\hat{a}_2$ , each of which is one of the Cartesian unit vectors, i.e.,  $\hat{x}$ ,  $\hat{y}$  and  $\hat{z}$ , along the x, y and z axes, respectively. Let  $\hat{d}$  be the unit vector along the bond between two atoms.



First, the p orbital along  $\hat{a}_1$  can be decomposed into two p orbitals that are parallel and normal to  $\hat{d}$ , respectively, as we did in Eq. (8):

$$|p_1\rangle = \hat{a}_1 \cdot \hat{d} |p_{d1}\rangle + \hat{a}_1 \cdot \hat{n}_1 |p_{n1}\rangle, \quad (11)$$

where  $\hat{n}_1$  is the unit vector normal to  $\hat{d}$  within the plane spanned by  $\hat{d}$  and  $\hat{a}_1$ . (We define the origins of  $|p_{d1}\rangle$  and  $|p_{n1}\rangle$  to be at the first atom.) The p orbital along  $\hat{a}_2$  is decomposed in a similar manner.

Now the Hamiltonian matrix element between  $|p_1\rangle$  and  $|p_2\rangle$  is given by

$$\begin{aligned} \langle p_1 | H | p_2 \rangle &= \left( \hat{a}_1 \cdot \hat{d} \langle p_{d1} | + \hat{a}_1 \cdot \hat{n}_1 \langle p_{n1} | \right) H \left( \hat{a}_2 \cdot \hat{d} |p_{d2}\rangle + \hat{a}_2 \cdot \hat{n}_2 |p_{n2}\rangle \right) \\ &= \left( \hat{a}_1 \cdot \hat{d} \right) \left( \hat{a}_2 \cdot \hat{d} \right) \langle p_{d1} | H | p_{d2} \rangle + \left( \hat{a}_1 \cdot \hat{n}_1 \langle p_{n1} | \right) H \left( \hat{a}_2 \cdot \hat{n}_2 |p_{n2}\rangle \right), \end{aligned} \quad (12)$$

where we have used the fact that the matrix elements between orthogonal p orbitals are zero by symmetry. Note that

$$\langle p_{d1} | H | p_{d2} \rangle = h_{pp\sigma}(r), \quad (13)$$

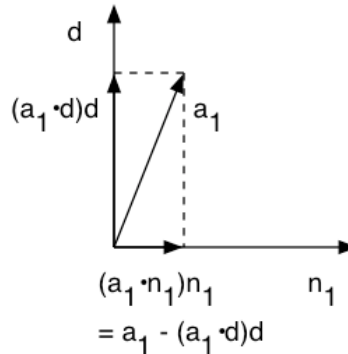
and

$$\begin{aligned} \left( \hat{a}_1 \cdot \hat{n}_1 \langle p_{n1} | \right) H \left( \hat{a}_2 \cdot \hat{n}_2 |p_{n2}\rangle \right) &= \left( \hat{a}_1 \cdot \hat{n}_1 \right) \left( \hat{a}_2 \cdot \hat{n}_2 \right) \langle p_{n1} | H | p_{n2} \rangle \\ &= \left( \hat{a}_1 \cdot \hat{n}_1 \right) \left( \hat{a}_2 \cdot \hat{n}_2 \right) \left( \hat{n}_1 \cdot \hat{n}_2 \right) h_{pp\pi}(r) \\ &= \left( \left( \hat{a}_1 \cdot \hat{n}_1 \right) \hat{n}_1 \right) \cdot \left( \left( \hat{a}_2 \cdot \hat{n}_2 \right) \hat{n}_2 \right) h_{pp\pi}(r) \\ &= \left( \hat{a}_1 - \left( \hat{a}_1 \cdot \hat{d} \right) \hat{d} \right) \cdot \left( \hat{a}_2 - \left( \hat{a}_2 \cdot \hat{d} \right) \hat{d} \right) h_{pp\pi}(r) \end{aligned} \quad (14)$$

where we have used the relation,

$$\left( \hat{a}_1 \cdot \hat{n}_1 \right) \hat{n}_1 = \hat{a}_1 - \left( \hat{a}_1 \cdot \hat{d} \right) \hat{d},$$

see the figure below.



Substituting Eqs. (13) and (14) in Eq. (12), we obtain

$$\langle p_1 | H | p_2 \rangle = \left( \hat{a}_1 \cdot \hat{d} \right) \left( \hat{a}_2 \cdot \hat{d} \right) h_{pp\sigma}(r) + \left( \hat{a}_1 - \left( \hat{a}_1 \cdot \hat{d} \right) \hat{d} \right) \cdot \left( \hat{a}_2 - \left( \hat{a}_2 \cdot \hat{d} \right) \hat{d} \right) h_{pp\pi}(r), \quad (15)$$

To obtain explicit formula in terms of  $p_x$ ,  $p_y$  and  $p_z$  centered around the first and second atoms, let us introduce the directional cosines along the x, y and z axes as  $\hat{d} = (d_x, d_y, d_z)$ . Then

$$\begin{aligned} & \begin{pmatrix} \langle p_{1x} | H | p_{2x} \rangle & \langle p_{1x} | H | p_{2y} \rangle & \langle p_{1x} | H | p_{2z} \rangle \\ \langle p_{1y} | H | p_{2x} \rangle & \langle p_{1y} | H | p_{2y} \rangle & \langle p_{1y} | H | p_{2z} \rangle \\ \langle p_{1z} | H | p_{2x} \rangle & \langle p_{1z} | H | p_{2y} \rangle & \langle p_{1z} | H | p_{2z} \rangle \end{pmatrix} \\ & = \begin{pmatrix} d_x^2 h_{pp\sigma} + (1-d_x^2) h_{pp\pi} & d_x d_y (h_{pp\sigma} - h_{pp\pi}) & d_x d_z (h_{pp\sigma} - h_{pp\pi}) \\ d_y d_x (h_{pp\sigma} - h_{pp\pi}) & d_y^2 h_{pp\sigma} + (1-d_y^2) h_{pp\pi} & d_y d_z (h_{pp\sigma} - h_{pp\pi}) \\ d_z d_x (h_{pp\sigma} - h_{pp\pi}) & d_z d_y (h_{pp\sigma} - h_{pp\pi}) & d_z^2 h_{pp\sigma} + (1-d_z^2) h_{pp\pi} \end{pmatrix}, \end{aligned} \quad (16)$$

where  $h_{pp\sigma}$  is a short-hand notation for  $h_{pp\sigma}(r)$ .

In summary, the Hamiltonian matrix in the tight-binding model consists of  $4 \times 4$  blocks, in which each atomic pair is assigned a block:

$$H = \begin{pmatrix} & & & & j & & \\ & & & & \vdots & & \\ & & & & & & \\ i & \dots & s_i s_j & s_i p_{jx} & s_i p_{jy} & s_i p_{jz} & \\ & & p_{ix} s_j & p_{ix} p_{jx} & p_{ix} p_{jy} & p_{ix} p_{jz} & \dots \\ & & p_{iy} s_j & p_{iy} p_{jx} & p_{iy} p_{jy} & p_{iy} p_{jz} & \\ & & p_{iz} s_j & p_{iz} p_{jx} & p_{iz} p_{jy} & p_{iz} p_{jz} & \\ & & & & \vdots & & \end{pmatrix}, \quad (17)$$

where the diagonal blocks ( $i = j$ ) are diagonal,

$$\begin{pmatrix} E_s & 0 & 0 & 0 \\ 0 & E_p & 0 & 0 \\ 0 & 0 & E_p & 0 \\ 0 & 0 & 0 & E_p \end{pmatrix}, \quad (18)$$

and the off-diagonal blocks ( $i \neq j$ ) are given by

$$\begin{pmatrix} h_{ss\sigma} & d_x h_{sp\sigma} & d_y h_{sp\sigma} & d_z h_{sp\sigma} \\ -d_x h_{sp\sigma} & d_x^2 h_{pp\sigma} + (1-d_x^2) h_{pp\pi} & d_x d_y (h_{pp\sigma} - h_{pp\pi}) & d_x d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_y h_{sp\sigma} & d_y d_x (h_{pp\sigma} - h_{pp\pi}) & d_y^2 h_{pp\sigma} + (1-d_y^2) h_{pp\pi} & d_y d_z (h_{pp\sigma} - h_{pp\pi}) \\ -d_z h_{sp\sigma} & d_z d_x (h_{pp\sigma} - h_{pp\pi}) & d_z d_y (h_{pp\sigma} - h_{pp\pi}) & d_z^2 h_{pp\sigma} + (1-d_z^2) h_{pp\pi} \end{pmatrix}. \quad (19)$$

Though two atomic basis functions on different atoms are not exactly orthogonal, we will ignore their overlaps and treat the  $4N$ -function basis set as an orthonormal basis set.

## References

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## Appendix A—Hamiltonian Matrix

Consider the energy eigenvalue problem,

$$H|\psi\rangle = \varepsilon|\psi\rangle. \quad (\text{A1})$$

As shown in Eq. (5), we expand the wave function,  $|\psi\rangle$ , in terms of atomic orbitals,

$$|\psi\rangle = \sum_{i=1}^N \sum_{\alpha \in \{s, p_x, p_y, p_z\}} c_{i\alpha} |i\alpha\rangle, \quad (\text{A2})$$

where  $|i\alpha\rangle$  is the  $\alpha$ -th atomic eigenstates ( $\alpha \in \{s, p_x, p_y, p_z\}$ ) of the  $i$ -th atom. Substituting Eq. (A2) into Eq. (A1) and multiplying the both sides by  $\langle i'\alpha'|$ , we obtain

$$\sum_{i\alpha} c_{i\alpha} \langle i'\alpha'|H|i\alpha\rangle = \varepsilon \sum_{i\alpha} c_{i\alpha} \langle i'\alpha'|i\alpha\rangle. \quad (\text{A3})$$

Using the orthonormality of the basis set,  $\langle i'\alpha'|i\alpha\rangle = \delta_{i'i} \delta_{\alpha\alpha'}$ , Eq. (A3) becomes

$$\sum_{i\alpha} H_{i'\alpha', i\alpha} c_{i\alpha} = \varepsilon c_{i'\alpha'}, \quad (\text{A4})$$

where the Hamiltonian matrix is defined as

$$H_{i'\alpha', i\alpha} = \langle i'\alpha'|H|i\alpha\rangle = \int d\vec{r} \psi_{\alpha'}^*(\vec{r} - \vec{r}_i) \left( -\frac{1}{2} \nabla^2 + V(\vec{r}) \right) \psi_{\alpha}(\vec{r} - \vec{r}_i). \quad (\text{A5})$$

In the  $4N \times 4N$  matrix in Eq. (17), the indices  $i$  and  $\alpha$  are combined as  $\kappa = 4(i - 1) + \alpha$ , where  $i \in \{1, 2, \dots, N\}$  and  $\alpha \in \{1 \leftrightarrow s, 2 \leftrightarrow p_x, 3 \leftrightarrow p_y, 4 \leftrightarrow p_z\}$ . With this indexing scheme, Eq. (A4) becomes an ordinary matrix eigenvalue problem,

$$\sum_{\kappa} H_{\kappa'\kappa} c_{\kappa} = \varepsilon c_{\kappa'}. \quad (\text{A6})$$



## Appendix B—Trigonometric Addition Theorem

In the proof of Eq. (8), we have used the trigonometric addition theorem,

$$\cos(\chi - \theta) = \cos \chi \cos \theta + \sin \chi \sin \theta, \quad (\text{B1})$$

which may be derived from the following identity,

$$\exp(i(\chi - \theta)) = \exp(i\chi)\exp(-i\theta). \quad (\text{B2})$$

The left-hand side of Eq. (B2) is

$$\exp(i(\chi - \theta)) = \cos(\chi - \theta) + i \sin(\chi - \theta), \quad (\text{B3})$$

whereas its right-hand side is

$$\begin{aligned} \exp(i\chi)\exp(-i\theta) &= [\cos(\chi) + i \sin(\chi)][\cos(\theta) - i \sin(\theta)] \\ &= [\cos(\chi)\cos(\theta) + \sin(\chi)\sin(\theta)] + i[\sin(\chi)\cos(\theta) - \cos(\chi)\sin(\theta)]. \end{aligned} \quad (\text{B4})$$

Comparison of the real parts of Eqs. (B3) and (B4) gives Eq. (B1).