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# Quantum Mechanics of Electronic Structure of Simple Molecules.

By

MASAO KOTANI, KIMIO OHNO and KUNIFUSA KAYAMA.

With 49 Figures.

## I. Introduction.

The subject of discussion in this article is the quantum-mechanical theory of simple molecules, i.e., systems consisting of  $N$  electrons and several nuclei, forming a stable entity. As is well known, such molecules can rotate and vibrate, and give rise to series of rotational and vibrational energy levels. Our main concern in the present article is, however, with the motion of *electrons* in these molecules, and rotations and vibrations of the molecules will not be dealt with in detail.

**1. Separation of electronic and nuclear motions.** The study of the electronic motion in molecules provides the basis on which the nature of chemical bonds and the mechanism of various electronic processes can be theoretically understood. Theory gives, for any fixed values of the distances between the nuclei (we denote them symbolically by  $R$ ), the electronic ground state and a series of electronic excited states, with energies  $E_0(R)$  and  $E_1(R)$ ,  $E_2(R)$ , ... respectively. These  $E_k(R)$  where  $k=0, 1, \dots$  play the role of potentials for the forces acting between the nuclei in the respective electronic states. The properties of chemical bonds are usually derived from  $E_0(R)$  for the electronic ground state, and once this  $E_0(R)$  is known the treatment of rotation and vibration is not very difficult. The procedure described here is based on the *adiabatic approximation*, or *Born-Oppenheimer approximation*, according to which the large difference between nuclear and electronic masses enables us to separate the electronic motion and the nuclear motion to a very high degree of accuracy. An outline of the BORN-OPPENHEIMER approximation will now be given briefly.

Let the masses, charges and coordinates of the particles concerned be denoted as follows:

Particle	Mass	Charge	Coordinates
Nucleus $a$	$M_a$	$Z_a e$	$\mathbf{R}_a(X_a, Y_a, Z_a)$ $a = 1, 2, \dots, Q.$
Electron $k$	$m$	$-e$	$\mathbf{r}_k(x_k, y_k, z_k)$ $k = 1, 2, \dots, N.$

Then the Schrödinger equation for our system is

$$\left\{ -\frac{\hbar^2}{2} \sum_{a=1}^Q \frac{\Delta_a}{M_a} - \frac{\hbar^2}{2m} \sum_{k=1}^N \Delta_k + V \right\} \Psi = E \Psi, \quad (1.1)$$

$$V = \sum_{i < k} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_k|} - \sum_{k,a} \frac{Z_a e^2}{|\mathbf{r}_k - \mathbf{R}_a|} + \sum_{a < b} \frac{Z_a Z_b e^2}{R_{ab}},$$

where  $R_{ab} = |\mathbf{R}_b - \mathbf{R}_a|$  and  $\Delta_a$  and  $\Delta_k$  are Laplacian operators acting on the coordinates  $\mathbf{R}_a$  and  $\mathbf{r}_k$  respectively. By writing (1.1) we have neglected all relativistic effects involving spin-dependent terms. This is sufficiently accurate for the purpose of studying the properties of chemical bonds in lighter molecules.

Now, the nuclear masses are very much larger than the electronic mass, and intuitively we may expect the nuclei to move much more slowly than the electrons. Thus we should be able to study the motion of the electrons neglecting the motion of the nuclei completely and treating their coordinates as parameters. Following this idea, we set up the Schrödinger equation for the electronic motion, dropping the nuclear kinetic energy terms from (1.1):

$$\left\{ -\frac{\hbar^2}{2m} \sum_k \Delta_k + V \right\} \Psi^{\text{el}} = E^{\text{el}}(R) \Psi^{\text{el}}. \quad (1.2)$$

The eigenvalue of this equation is called the "electronic energy", and is a function of the internuclear distances  $R$ .  $[V$ , and consequently  $E^{\text{el}}(R)$ , contains the inter-nuclear repulsion  $\sum_{a < b} \frac{Z_a Z_b e^2}{R_{ab}}$  so that  $E^{\text{el}}(R)$  is not strictly electronic. We shall call

$E^{\text{el}}(R) - \sum_{a < b} \frac{Z_a Z_b e^2}{R_{ab}}$  the "purely electronic energy".] In general, the Schrödinger equation (1.2) gives a series of discrete eigenvalues  $E_0(R) < E_1(R) < E_2(R) < \dots$ , and the corresponding eigenfunctions are denoted by  $\Psi_0^{\text{el}}, \Psi_1^{\text{el}}, \Psi_2^{\text{el}}, \dots$ . For the sake of simplicity, we assume that the eigenvalues are not degenerate, but this is not essential for the following discussion. We can represent the functions  $E_0(R), E_1(R), \dots$  as surfaces in a space spanned by  $E$  and  $R$ . These are called the (adiabatic) electronic energy surfaces.

Now we consider the nuclear motion. The electronic energy  $E_n^{\text{el}}(R)$  discussed above is the potential energy  $V$  averaged with respect to electronic coordinates in the electronic state  $n$ , and intuitively we expect  $E_n^{\text{el}}(R)$  to play the role of the potential energy for the motion of the nuclei. Written wave-mechanically, this amounts to assuming the following Schrödinger equation for the nuclei:

$$\left\{ -\frac{\hbar^2}{2} \sum_a \frac{\Delta_a}{M_a} + E^{\text{el}}(R) \right\} \Psi^{\text{nucl}} = E \Psi^{\text{nucl}}. \quad (1.3)$$

In the following, let us confine ourselves, for simplicity, to the case of the diatomic molecule. Then Eq. (1.3) can be dealt with as follows: Since the potential contains only  $\mathbf{R}_a - \mathbf{R}_b$ , it is convenient to transform coordinates from  $\mathbf{R}_a, \mathbf{R}_b$  to  $\mathbf{R}_G$  and  $\mathbf{R}$ , where

$$\begin{aligned} \mathbf{R}_G &= \frac{M_a \mathbf{R}_a + M_b \mathbf{R}_b}{M_a + M_b} && (\text{centre of mass}), \\ \mathbf{R} &= \mathbf{R}_a - \mathbf{R}_b && (\text{relative coordinate}). \end{aligned}$$

We are not interested, however, in the motion of the molecule as a whole, so that  $\Psi^{\text{nucl}}$  may be assumed as a function of  $\mathbf{R}$  only, and  $E^{\text{el}}$  is a function only of the magnitude  $R$  of the internuclear distance. Thus we have

$$\left\{ -\frac{\hbar^2}{2M} \Delta + E^{\text{el}}(R) \right\} \Psi^{\text{nucl}} = E \Psi^{\text{nucl}}, \quad (1.4)$$

<sup>1</sup> There are  $\frac{Q(Q-1)}{2}$  internuclear distances in all. However, most of them are redundant and only  $3Q - 6$  ( $3Q - 5$  for linear molecules) of them are necessary to determine  $E^{\text{el}}(R)$ , since  $3Q$  is the number of degrees of freedom of the  $Q$  nuclei and  $E^{\text{el}}$  clearly does not depend on the three coordinates which specify the position of the centre of mass of the nuclear system or on another three (two for linear molecules) which determine the spatial orientation.

where  $\Delta$  refers to the relative coordinate  $\mathbf{R}$ , and  $M$  is the reduced mass

$$M = \frac{M_a M_b}{M_a + M_b}. \quad (1.5)$$

The problem (1.4) is essentially the same as the problem of a single particle of mass  $M$  subject to a central potential  $E^{\text{el}}(R)$  from a fixed point. In order to solve it we introduce spherical coordinates  $R, \Theta, \Phi$  for  $\mathbf{R}$ , and put

$$\Psi^{\text{nuc}} = \frac{f(R)}{R} Y(\Theta, \Phi). \quad (1.6)$$

Physically  $f(R)$  describes the molecular vibration, while  $Y(\Theta, \Phi)$  represents the state of rotation. In order that (1.6) may satisfy (1.4),  $Y(\Theta, \Phi)$  must be spherical harmonics of a certain order  $J$ :

$$Y(\Theta, \Phi) = \sum_{M_J} c_{M_J} P_J^{|M_J|}(\cos \Theta) e^{i M_J \Phi}. \quad (1.7)$$

The order  $J$  determines the magnitude of the angular momentum of rotation as  $\hbar \sqrt{J(J+1)}$ . By means of the differential equation satisfied by the spherical harmonics, we can derive from (1.4) the wave equation to be satisfied by  $f(R)$ :

$$\left\{ -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + E^{\text{el}}(R) + \frac{\hbar^2 J(J+1)}{2M R^2} \right\} f(R) = E f(R). \quad (1.8)$$

In case stable binding occurs in the electronic state  $n$ ,  $E_n^{\text{el}}(R)$  must have a minimum at some positive value  $R_0$ , and the internuclear distance  $R$  oscillates in the neighbourhood of  $R_0$ . According to (1.8) the potential energy of this one-dimensional motion is  $E_n^{\text{el}}(R) + \frac{\hbar^2 J(J+1)}{2M R^2}$ , of which the second term comes from the centrifugal force due to rotation. If the rotational quantum number  $J$  is not very large, the centrifugal potential is very small compared with  $E_n^{\text{el}}(R)$ , at least for

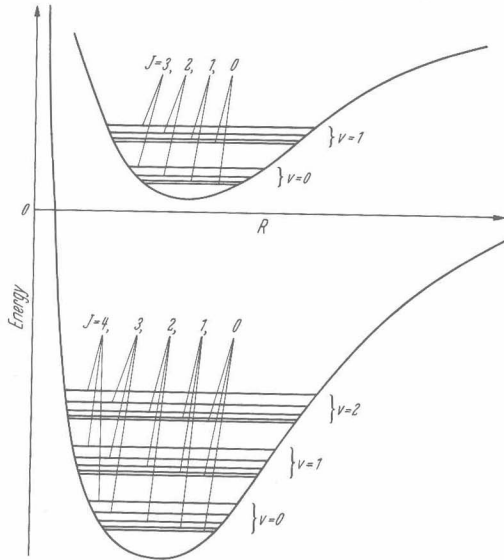


Fig. 1. Schematic diagram of electronic, vibrational and rotational levels.

$R \gtrsim R_0$ , and may be treated as an additive constant  $\frac{\hbar^2 J(J+1)}{2M R_0^2}$ . This means that the effective potential is just the potential  $E_n^{\text{el}}(R)$  for the nonrotating state displaced by a constant.

On the assumption that  $E_n^{\text{el}}(R)$  has a minimum for  $R = R_0$ , which is not too shallow, the wave equation gives a finite number of discrete levels whose eigenfunctions and eigenvalues are

$$f_{nvJ}(R) \quad \text{and} \quad E_{nvJ}, \quad v = 0, 1, 2, \dots$$

If the centrifugal potential may be regarded as a constant,  $f_{nv,J}(R)$  does not depend on  $J$  and  $E_{nvJ}$  takes the form

$$E_{nvJ} = E_n^{\text{el}}(R_0) + E_{nv}^{\text{vib}} + \frac{\hbar^2 J(J+1)}{2M R_0^2}. \quad (1.9)$$

Here the second and the third terms are called the vibrational and rotational energies respectively. If the shape of the potential  $E_n^{\text{el}}(R)$  near the minimum is assumed to be parabolic, the vibration is harmonic with circular frequency  $\omega_n = \sqrt{\frac{E_n^{\text{el}''}(R_0)}{M}}$ , and the eigenvalues are given by the familiar expression

$$E_{nv}^{\text{vib}} = \hbar \omega_n \left(v + \frac{1}{2}\right). \quad (1.10)$$

$E_{n0}^{\text{vib}} = \frac{1}{2} \hbar \omega_n$  is the energy of zero-point vibration, in which the root-mean-square values of momentum and displacement (coordinate) are related by HEISENBERG'S uncertainty principle. The binding energy of the molecule under consideration is

$$E_0^{\text{el}}(\infty) - \{E_0^{\text{el}}(R_0) + E_{00}^{\text{vib}}\}. \quad (1.11)$$

In the present article, however, we use the word "binding energy" in the sense of  $E_0^{\text{el}}(\infty) - E_0^{\text{el}}(R_0)$ , that is, the depth of the potential minimum measured from its value at  $R = \infty$ , and denote it by  $D$ .

The quantity (1.11), which is smaller than  $D$  by  $E_{00}^{\text{vib}} = \frac{1}{2} \hbar \omega_0$ , is referred to as "dissociation energy".

It is sometimes convenient to represent  $E_0^{\text{el}}(R)$  by an analytical expression, for which the vibrational Schrödinger equation (1.8) can be solved exactly. The most usual method is to use MORSE'S formula<sup>1</sup>

$$\left. \begin{aligned} E_0^{\text{el}}(R) - E_0^{\text{el}}(R_0) \\ = D \{1 - e^{-\beta(R-R_0)}\}^2. \end{aligned} \right\} \quad (1.12)$$

This expression does not represent the behaviour of  $E_0^{\text{el}}(R)$  near  $R=0$  correctly, but this is not serious because  $f(R)$

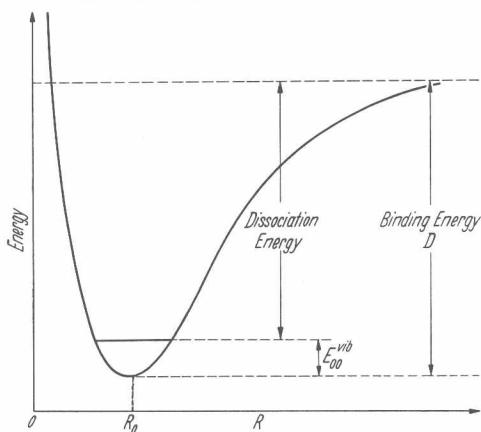


Fig. 2. Potential energy curve.

vanishes almost completely near  $R=0$ . The curve corresponding to (1.12) is called the Morse curve.

In order to construct the Morse function for a given electronic state of a given diatomic molecule from empirical data, we have to find the values of three parameters:  $D$ ,  $R_0$ ,  $\beta$ .  $D$  can be obtained by adding the zero-point energy  $\frac{1}{2} \hbar \omega_0$  to the observed "dissociation energy",  $R_0$  can be determined from the separation of rotational energy levels, and  $\beta$  is related to known quantities through the relation

$$\beta = \sqrt{\frac{M}{2D}} \omega_0. \quad (1.13)$$

This is derived from (1.12) by equating the curvature of  $E_0^{\text{el}}(R)$  at  $R_0$  to  $M\omega_0^2$ .

Returning to our original problem, we have to prove the following

*Theorem:* The eigenfunctions of (1.1) are given by

$$\Psi = \Psi^{\text{el}} \cdot \Psi^{\text{nucl}} \quad (1.14)$$

provided that quantities of order  $\left(\frac{m}{M}\right)^{\frac{1}{2}}$  can be considered negligible compared to unity. The corresponding eigenvalue  $E$  is the same as that of the nuclear wave equation (1.3).

<sup>1</sup> P. M. MORSE: Phys. Rev. **34**, 57 (1929).



*Proof*<sup>1</sup>: It is easy to see that the product function (1.14) actually satisfies (1.1) if one is allowed to put

$$\left. \begin{aligned} -\frac{\hbar^2}{2M_a} \Delta_a \Psi &= \Psi^{\text{el}} \cdot \left( -\frac{\hbar^2}{2M_a} \Delta_a \Psi^{\text{nuc}} \right) \\ \text{and a similar relation for } -\frac{\hbar^2}{2M_b} \Delta_b \Psi. \end{aligned} \right\} \quad (1.15)$$

However, this is not exact, because  $\Psi^{\text{el}}$  contains nuclear coordinates as parameters; the exact expression is as follows:

$$\left. \begin{aligned} -\frac{\hbar^2}{2M_a} \Delta_a \Psi &= \Psi^{\text{el}} \cdot \left( -\frac{\hbar^2}{2M_a} \Delta_a \Psi^{\text{nuc}} \right) - \frac{\hbar^2}{M_a} (\text{grad}_a \Psi^{\text{el}}) \cdot (\text{grad}_a \Psi^{\text{nuc}}) + \\ &\quad + \left( -\frac{\hbar^2}{2M_a} \Delta_a \Psi^{\text{el}} \right) \cdot \Psi^{\text{nuc}}. \end{aligned} \right\} \quad (1.16)$$

The reason why the second and third terms on the right side of (1.16) may be neglected is found in the fact that  $\Psi^{\text{nuc}}$  varies with the nuclear coordinates much more rapidly than  $\Psi^{\text{el}}$  does. As an estimate of the order of magnitude, differentiation with respect to a coordinate may be considered as a multiplication by a certain quantity  $\lambda$  of the dimension of a reciprocal length. Since Eq. (1.2) contains no other constants than  $\hbar^2/m$  and  $e$ , the multiplicative constant  $\lambda$  for the electronic wave function  $\Psi^{\text{el}}$  must be of the order of  $\frac{m e^2}{\hbar^2} = \frac{1}{a_H}$  (Reciprocal Bohr radius). However,  $\lambda$  for the nuclear function  $\Psi^{\text{nuc}}$  is much larger. This can be seen in the following way:  $\Psi^{\text{nuc}}$  contains the vibrational function  $f(R)$ , which is confined essentially within the classical amplitude of vibration. If we denote this by  $l$ , then  $\lambda$  for  $\Psi^{\text{nuc}}$  is roughly  $1/l$ . From HEISENBERG's uncertainty relation,  $l \sim \frac{\hbar}{p}$ , where  $p$  is some average value of the absolute value of linear momentum. For the purpose of estimating  $p$  we put

$$\begin{aligned} \frac{p^2}{2M} &\sim E^{\text{el}}(R_0 \pm l) - E^{\text{el}}(R_0) \approx \frac{1}{2} E^{\text{el}''}(R_0) l^2, \\ E^{\text{el}''}(R_0) &\sim \frac{m e^4}{\hbar^2} \cdot \frac{m^2 e^4}{\hbar^4} = \frac{m^3 e^8}{\hbar^6}. \end{aligned}$$

These relations give

$$p \sim \left( \frac{M}{m} \right)^{\frac{1}{4}} \frac{m e^2}{\hbar}.$$

This shows that  $\lambda$  for  $\Psi^{\text{nuc}}$  is  $(M/m)^{\frac{1}{4}}$  times larger than  $\lambda$  for  $\Psi^{\text{el}}$ . This is what we desired to prove.

Furthermore we can easily estimate the order of magnitude of electronic, vibrational and rotational energies. The order of magnitude of electronic energy [absolute value of  $E^{\text{el}}(R)$ , energy differences between different electronic states, etc.] is  $\frac{m e^4}{\hbar^2}$ , which is the unique expression of the dimension of energy built from the universal constants contained in the wave equation (1.2). The vibrational energy is of the order of  $\frac{p^2}{M} \sim \left( \frac{m}{M} \right)^{\frac{1}{2}} \frac{m e^4}{\hbar^2}$  while the rotational energy is  $\frac{\hbar^2}{M a_H^2} \sim \frac{m}{M} \frac{m e^4}{\hbar^2}$ . These results give us some idea of the spacing of various

<sup>1</sup> The proof will be given only for the case of diatomic molecules. The reader is referred to BORN and OPPENHEIMER's original paper for a thorough and more general treatment, M. BORN and J.R. OPPENHEIMER: Ann. d. Phys. **84**, 457 (1927).

energy levels. Up to this point, our specific proofs and explanations have been confined to the case of diatomic molecule but, as we can easily see, most of the results hold good also for general polyatomic molecules.

In the present article we deal almost exclusively with the electronic Schrödinger equation, so that it is very convenient to use the unit system in which the electronic mass,  $m$ , the elementary charge (the absolute value of the electronic charge)  $e$  and  $(2\pi)^{-1}$  times PLANCK'S constant,  $\hbar$ , are reduced to one. This unit system is called the atomic system. The best values available at present of these atomic constants seem to be those determined by J.W.M. DuMOND, E.R. COHEN et al. from carefully selected high precision measurements related to atomic constants<sup>1</sup>. Those values are as follows:

$$\begin{aligned} m &= (9.1083 \pm 0.0003) \times 10^{-28} \text{ g}, \\ e &= (4.80286 \pm 0.00009) \times 10^{-10} \text{ e.s.u.}, \\ \hbar &= (1.05443 \pm 0.00004) \times 10^{-27} \text{ erg sec.} \end{aligned}$$

Some of the derived units in this system are given here:

$$\begin{aligned} (\text{length}) \quad a_H &\equiv \frac{\hbar^2}{m e^2} = (5.29172 \pm 0.00002) \times 10^{-9} \text{ cm}, \\ (\text{energy}) \quad 2R_\infty h c &\equiv \frac{m e^4}{\hbar^2} = (4.35916 \pm 0.00014) \times 10^{-11} \text{ erg}, \\ (\text{time}) \quad \frac{\hbar^3}{m e^4} &= (2.4189 \pm 0.0002) \times 10^{-17} \text{ sec}, \\ (\text{velocity}) \quad \frac{e^2}{\hbar} &= (2.18767 \pm 0.00006) \times 10^8 \text{ cm/sec.} \end{aligned}$$

Another important constant  $c$ , the light velocity in vacuum, is not used in our "atomic units", but is essential for relativistic effects:

$$c = (2.997930 \pm 0.000003) \times 10^{10} \text{ cm/sec.}$$

The ratio of the velocity  $e^2/\hbar$  to  $c$  is the so-called fine structure constant:

$$\alpha \equiv \frac{e^2}{\hbar c} = (7.29729 \pm 0.00003) \times 10^{-3}.$$

In molecular physics the energy is frequently expressed in electron volts (ev) and in wave-number units ( $\text{cm}^{-1}$ ), and in the literature in chemistry the thermal unit kcal/mol is widely used. The following table will be useful for conversion between any two of these units.

Table 1. *Relation between various units of energy.*

	in a. u.	in ev	in $\text{cm}^{-1}$	in Cal/mol <sup>2</sup>	in erg
1 a. u.	1	27.20976	$2.194746 \times 10^5$	$6.27709 \times 10^2$	$4.35916 \times 10^{-11}$
1 ev	0.0367515	1	$8.06603 \times 10^3$	23.0692	$1.60206 \times 10^{-12}$
1 $\text{cm}^{-1}$	$4.55634 \times 10^{-6}$	$1.23977 \times 10^{-4}$	1	$2.86005 \times 10^{-3}$	$1.98618 \times 10^{-16}$
1 Cal/mol	$1.59310 \times 10^{-3}$	0.0433478	$3.49644 \times 10^2$	1	$6.94456 \times 10^{-14}$
1 erg	$2.29402 \times 10^{10}$	$6.24196 \times 10^{11}$	$5.03479 \times 10^{15}$	$1.43998 \times 10^{13}$	1

<sup>1</sup> COHEN, DuMOND, LAYTON and ROLLETT: Rev. Mod. Phys. **27**, 363 (1955). — E.R. COHEN and J.W.M. DuMOND: Vol. XXXV of this Encyclopedia. — COHEN, CROWE and DuMOND: Fundamental Constants of Physics. New York: Interscience Publishers 1957.

<sup>2</sup> The Calorie is defined as 4.1840 joule.

If the energy and coordinates are measured in atomic units, the Schrödinger equation for the electronic motion in molecules is written as follows

$$\left\{ -\frac{1}{2} \sum_k \Delta_k + \sum_{i < k} \frac{1}{|\mathbf{r}_i - \mathbf{r}_k|} - \sum_{k,a} \frac{Z_a}{|\mathbf{r}_k - \mathbf{R}_a|} - \sum_{a < b} \frac{Z_a Z_b}{R_{ab}} \right\} \Psi = E(R) \Psi. \quad (1.17)$$

Here we have dropped the superscript el to  $\Psi$  and  $E(R)$ . This equation is the starting point for the developments to be described in the present article.  $|\mathbf{r}_i - \mathbf{r}_k|$ ,  $|\mathbf{r}_k - \mathbf{R}_a|$  etc. are sometimes written as  $r_{ik}$ ,  $r_{ak}$  etc., respectively.

**2. Symmetry groups of molecules.** When we deal with the electronic structure of molecules neglecting the kinetic energy of nuclei (adiabatic approximation), the nuclei are regarded simply as centres of force, and the Hamiltonian of the electron system of each molecule has the same spatial symmetry as the nuclear skeleton of the molecule. This spatial symmetry is described by the assembly of geometrical operations, such as rotations, reflections, inversion, rotary reflections, etc., which have the effect of permuting equivalent nuclei among themselves and which leave the nuclear architecture of the molecule unchanged. These geometrical operations are called "symmetry operations" of a molecule, and the assembly of all symmetry operations of a molecule is said to form the "symmetry group" of this molecule.

For the full explanation of the mathematical theory of the symmetry group the reader is referred to JAGODZINSKI's article on Crystallography (Vol. VII, Part 1): we describe here briefly only those aspects of the theory which are needed in our molecular theory.

Consider a molecule, and suppose that all the nuclei of this molecule are held fixed, usually at their respective equilibrium points. Let  $P, Q, \dots$  denote symmetry operations allowed by this nuclear configuration. If we first apply  $P$  to the molecule, and then apply  $Q$  to the result of operation  $P$ , the result is equivalent to that of a single operation, which is called the product of  $P$  and  $Q$ , and is denoted by  $QP$ . Since the nuclear framework remains unchanged by each of  $P$  and  $Q$ , the same holds for the product  $QP$ , so that the product of two symmetry operations is a symmetry operation. The multiplication of operators is not necessarily commutative:  $PQ \neq QP$ , but is always associative  $P(QR) = (PQ)R$ . Every symmetry group contains the particular operation  $E$  (identity), which leaves all points unmoved;  $E$  satisfies  $EP = PE = P$  with any operation  $P$ . If the operation  $P$  displaces  $A$  to  $B$ , then the operation which displaces  $B$  back to  $A$  is also a symmetry operation of the same molecule, and is denoted by  $P^{-1}$  (reciprocal of  $P$ ). The equation  $PP^{-1} = P^{-1}P = E$  holds for any  $P$ .

An operation  $P$  of a symmetry group  $\mathcal{G}$  is said to be conjugate to another operation  $Q$  ( $Q \in \mathcal{G}$ ) when there exists at least one operation  $S \in \mathcal{G}$  satisfying  $P = SQS^{-1}$ . Since  $P = SQS^{-1}$  gives  $Q = S^{-1}PS^{-1}$ , and since  $S^{-1}$  also belongs to  $\mathcal{G}$ , the relation of being conjugate is a mutual (reversible) one. If  $P$  is conjugate to both  $Q$  and  $R$ ,  $Q$  and  $R$  are mutually conjugate (transitivity), the set of all operations which are conjugate to a particular operation of  $\mathcal{G}$  being called a class of conjugate operations, or simply a class, of  $\mathcal{G}$ . The operations of  $\mathcal{G}$  are divided into a certain number of classes. If  $P$  is a rotation of angle  $\varphi$  about an axis  $l$ , and  $l$  is displaced to  $l'$  by operation  $S$ , operation  $SPS^{-1}$  is the rotation through the same angle  $\varphi$  about the axis  $l'$ . Similarly, if  $P$  is a rotary reflection,  $SPS^{-1}$  is also rotary reflection through the same angle, in which the reflecting plane

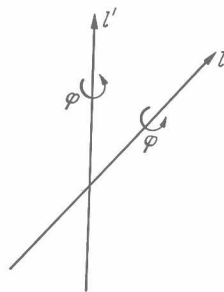


Fig. 3. Rotations about axes  $l$  and  $l'$ .

as well as the rotation axis are displaced according to the operation  $S$ . In general, we can say that two conjugate operations  $P, Q$  are operations of the same character, and differ only in their orientation in space; and the rotation axes and/or reflection planes of two conjugate operations are equivalent in the sense that there exists an operation  $S (\in \mathfrak{G})$  which transforms the axis and/or the plane of  $P$  into those of  $Q$ . In short, we may say that conjugate operations are equivalent.

*Example 1.* Group  $C_{3v}$ . Triangular pyramidal molecule.  $\text{NH}_3$ ,  $\text{ClCH}_3$ , etc. We assume that  $\text{H}_3$  forms a (horizontal) regular triangle, and that the N nucleus is situated at a point above the centre of gravity of  $\text{H}_3$ . The symmetry group consists of the following 6 operations,

$E$ , identity,

$\sigma_a(\pi), \sigma_b(\pi), \sigma_c(\pi)$ , reflections through the plane containing the main symmetry axis  $l$  and passing through  $a, b, c$  respectively,

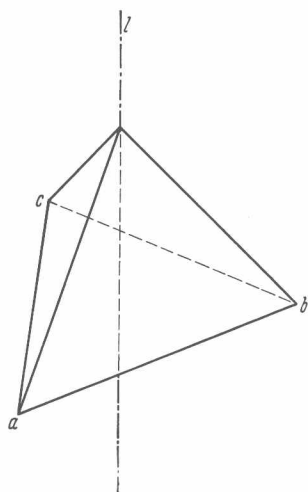


Fig. 4. Equilateral triangular pyramid.

$C\left(\frac{2\pi}{3}\right), C\left(-\frac{2\pi}{3}\right)$ , rotations of angle  $+\frac{2\pi}{3}$  and  $-\frac{2\pi}{3}$  about the axis  $l$ .

These 6 operations are classified into 3 classes:

$$E, \{\sigma_a(\pi), \sigma_b(\pi), \sigma_c(\pi)\}$$

and

$$\left\{C\left(\frac{2\pi}{3}\right), C\left(-\frac{2\pi}{3}\right)\right\}.$$

Table 2

$\begin{smallmatrix} Q \\ P \end{smallmatrix}$	$E$	$\sigma_a$	$\sigma_b$	$\sigma_c$	$C_+$	$C_-$
$E$	$E$	$\sigma_a$	$\sigma_b$	$\sigma_c$	$C_+$	$C_-$
$\sigma_a$	$\sigma_a$	$E$	$C_+$	$C_-$	$\sigma_c$	$\sigma_b$
$\sigma_b$	$\sigma_b$	$C_-$	$E$	$C_+$	$\sigma_a$	$\sigma_c$
$\sigma_c$	$\sigma_c$	$C_+$	$C_-$	$E$	$\sigma_b$	$\sigma_a$
$C_+$	$C_+$	$\sigma_c$	$\sigma_a$	$\sigma_b$	$C_-$	$E$
$C_-$	$C_-$	$\sigma_b$	$\sigma_c$	$\sigma_a$	$E$	$C_+$

We give the so-called multiplication table for  $C_{3v}$  in Table 2. In the table  $\sigma_a(\pi)$ ,  $C\left(\frac{2\pi}{3}\right)$ , ... are abbreviated as  $\sigma_a, C_+, \dots$ .

*Example 2.* Group  $T_d$ . Tetrahedral molecule.  $\text{CH}_4$ , etc. We assume  $\text{H}_4$  to form a regular tetrahedron and C to be at its centre. The symmetry group is the "Tetraederdrehspiegelungsgruppe", consisting of 24 operations. They are classified into 5 classes:

$E$ .

$C\left(\frac{2\pi}{3}\right)$  and  $C\left(-\frac{2\pi}{3}\right)$  around each of four triple axes ( $\text{CH}_a, \text{CH}_b, \text{CH}_c$ , and  $\text{CH}_d$ ).

$C_x(\pi), C_y(\pi), C_z(\pi)$ . Rotations of angle  $\pi$  around straight lines connecting midpoints of pairs of non-intersecting edges. We have 3 pairs, and 3 straight lines are orthogonal among themselves. These are chosen as  $x, y$  and  $z$  axes.

$\sigma_{ab}, \sigma_{ac}, \sigma_{ad}, \sigma_{bd}, \sigma_{cd}$ . Reflections through planes containing one edge and the centre of the tetrahedron.

$S_x^+, S_x^-, S_y^+, S_y^-, S_z^+, S_z^-$ . Rotations of angle  $\pm\frac{\pi}{2}$  around the  $x$  axis followed by reflection through the  $yz$  plane. Similarly with the  $y$  and  $z$  axes.

*Example 3.* Group  $C_{\infty v}$ . Linear asymmetric molecules NO, HCN, etc. We take the straight lines passing through all nuclei as the  $z$  axis. The group contains an infinite number of operations.

Class	Operations
$E$	$E$
$C(\pm \varphi)$	$C(\varphi), C(-\varphi)$ (2 operations)
$C(\pi)$	$C(\pi)$ (1 operation)
$\sigma_v(\alpha)$	reflection through a plane containing the $z$ -axis ( $\infty$ operations), $\alpha$ is the azimuth of the normal to the plane

*Example 4.* Group  $D_{\infty h}$ . Linear symmetric molecules  $N_2$ , OCO, etc. We take the Cartesian  $xyz$  axes in such a way that the  $z$  axis coincides with the molecular axis and the origin at the centre of symmetry. The classes are as follows:

Class	Operations
$E$	$E$
$C(\pm \varphi)$	$C(\varphi), C(-\varphi)$
$C(\pi)$	rotation through the angle $\pi$ around the $z$ -axis
$\sigma_v(\alpha)$	reflection through a plane containing the $z$ -axis
$I$	inversion through the origin
$R'_\alpha$	rotations through the angle $\pi$ around any straight line passing through the origin and perpendicular to the $z$ -axis, the azimuth of the line is $\alpha$
$S(\pm \varphi)$	$S(\varphi), S(-\varphi): C(\varphi), C(-\varphi)$ followed by $\sigma_h$
$\sigma_h$	reflection through the $xy$ -plane

**3. Symmetry properties of electronic wave functions in molecules.** We now define the operation of symmetry operators on electronic wave functions of molecules. Consider a symmetry operation  $P$  and a wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ . If the operation  $P$  displaces the point  $\mathbf{r}$  to point  $\mathbf{r}'$ , in particular  $\mathbf{r}_1$  to  $\mathbf{r}'_1, \mathbf{r}_2$  to  $\mathbf{r}'_2, \dots$ , then  $\Psi'(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \equiv P\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is defined by the identity

$$\Psi'(\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N) \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (3.1)$$

In other words,  $\Psi'$  is the same function as  $\Psi$  if the former is viewed from the coordinate system  $\Sigma'$  and the latter from  $\Sigma$ ,  $\Sigma'$  being obtained from  $\Sigma$  by the application of operation  $P$  to the fundamental vectors of the coordinate system. The function  $P\Psi$  is, as it were, internally the same as  $\Psi$ , and is different from  $\Psi$  only in external orientation in space, so that the scalar product of two wave functions is not altered by applying the same symmetry operations to both:

$$\int \Psi'_1{}^* \Psi'_2 dv = \int \Psi_1{}^* \Psi_2 dv, \quad (3.2)$$

where

$$\Psi'_1 \equiv P\Psi_1, \quad \Psi'_2 \equiv P\Psi_2.$$

If  $P$  displaces  $\mathbf{r}_i$  to  $\mathbf{r}'_i$ , and  $Q$  shifts  $\mathbf{r}'_i$  to  $\mathbf{r}''_i$ , the functions  $\Psi, \Psi' \equiv P\Psi$  and  $\Psi'' \equiv Q\Psi'$  are related according to

$$\begin{aligned} \Psi''(\mathbf{r}''_1, \mathbf{r}''_2, \dots) &\equiv \Psi'(\mathbf{r}'_1, \mathbf{r}'_2, \dots) \\ &\equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots). \end{aligned}$$

Now, the product operation  $R \equiv QP$  displaces  $\mathbf{r}_i$  directly to  $\mathbf{r}''_i$ , so that we have  $\Psi'' = R\Psi$ . This proves that

$$(QP)\Psi = Q(P\Psi). \quad (3.3)$$

The important use of symmetry operators in molecular quantum mechanics consists in deriving from one solution of the Schrödinger equation other solutions (eigenfunctions) of the same energy (eigenvalue). The electronic wave function  $\Psi$  of a molecule can, in principle, be obtained by solving the Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \quad (3.4)$$

for the system of (say,  $N$ ) electrons moving in the Coulomb field due to atomic nuclei, and exerting Coulomb repulsions upon each other. Let the symmetry group of this molecule be  $\mathfrak{G}$ , and consider a symmetry operation  $P$  contained in  $\mathfrak{G}$ . Since the Hamiltonian  $\mathcal{H}$  is invariant under the transformation  $P$ ,  $P^{-1}\mathcal{H}P = \mathcal{H}$  so that we have  $P\mathcal{H} = \mathcal{H}P$ . By applying  $P$  to (3.4), we find that  $\Psi' \equiv P\Psi$  satisfies the same Schrödinger equation as  $\Psi$  with the same eigenvalue  $E$ . Thus from (3.4) it follows that

$$\mathcal{H}\Psi' = E\Psi'. \quad (3.5)$$

If  $E$  is non-degenerate and there exists only one independent solution for the value of  $E$ ,  $\Psi'$  must be a constant multiple of  $\Psi$ :

$$\Psi' = u\Psi. \quad (3.6)$$

Since  $\Psi$  and  $\Psi'$  have the same normalization integrals,  $u$  must be unimodular:  $|u| = 1$ . In the more general case in which  $E$  is a degenerate eigenvalue, we have a finite number (say,  $f$ ) of linearly independent solutions  $\Psi_1, \Psi_2, \dots, \Psi_f$  and the general solution of (3.4) for this particular value of  $E$  is a linear combination of these  $f$   $\Psi$ 's. As we have seen above, the functions  $P\Psi$  are also solutions of (3.4) for the same value of  $E$ , so that we must have

$$P\Psi_i = \sum_{k=1}^f u_{ki}(P) \Psi_k, \quad i = 1, 2, \dots, f. \quad (3.7)$$

In this way we obtain an  $f$ -dimensional matrix

$$U(P) = (u_{ik}(P)) \quad (3.8)$$

for each  $P$ . If we apply the operator  $Q$  to (3.7), we have by (3.3)

$$(Q\Psi)_i = \sum_{h=1}^f \left\{ \sum_{k=1}^f u_{hk}(Q) u_{ki}(P) \right\} \Psi_h. \quad (3.9)$$

If  $R = QP$ , (3.9) must be the same as

$$R\Psi_i = \sum_{h=1}^f u_{hi}(R) \Psi_h \quad (3.10)$$

so that we obtain, by equating the coefficients of  $\Psi_h$  on the right-hand sides,

$$u_{hi}(R) = \sum_{k=1}^f u_{hk}(Q) u_{ki}(P),$$

or in matrix notation

$$U(R) = U(Q) \cdot U(P). \quad (3.11)$$

Thus we obtain a matrix  $U(P)$  for each operation  $P$ , and these matrices satisfy the same multiplication relations as the operators themselves. Mathematically these matrices are said to form a (matrix) representation of the symmetry group. We denote representations by the symbol  $\Gamma$ , and distinguish different representations by subscripts as  $\Gamma_1, \Gamma_2$ , etc.

If  $\Psi_1, \Psi_2, \dots, \Psi_f$  constitute an orthonormal set

$$(\Psi_i, \Psi_j) \equiv \int \Psi_i^* \Psi_j dv = \delta_{ij}, \quad (3.12)$$

the transformed functions  $P\Psi_1, P\Psi_2, \dots, P\Psi_f$  do the same because scalar products  $(\Psi_i, \Psi_j)$  are invariant under the symmetry operations:

$$(P\Psi_i, P\Psi_j) = (\Psi_i, \Psi_j) = \delta_{ij}. \quad (3.13)$$

Substituting (3.10) into (3.13), and using (3.12), we find

$$\sum_h u_{hi}(P)^* u_{hj}(P) = \delta_{ij}, \quad (3.14)$$

or in matrix form

$$U(P)^\dagger \cdot U(P) = \mathbf{1}, \quad (3.15)$$

where  $^\dagger$  denotes the hermitian conjugate, and  $\mathbf{1}$  denotes the unit matrix. Eqs. (3.14) and (3.15) show that matrices  $U(P)$  are unitary, and in such cases the representation itself is said to be unitary.

In the absence of a magnetic field, eigenfunctions of the Schrödinger equation can be taken to be real. In this case, the matrices are also real, and, if the basic functions  $\Psi_1, \Psi_2, \dots$  are mutually orthogonal, the representation matrices are obtained as orthogonal matrices. The representation is then orthogonal.

In this way, to each energy level  $E$  belongs a representation of the symmetry group of the molecule. The spatial symmetry of wave functions is expressed completely by the representation which belongs to this energy level. Accordingly, we can classify energy levels of a molecule by means of the kind of representations generated by the wave functions of this level. Then our next problem is: How many different kinds of representations are possible for the group such as  $C_{\infty v}$  and  $D_{\infty h}$ , and how can we characterize each kind of representation?

Before we can answer these questions, we have to explain the concepts of equivalence and irreducibility of representations. If a set of matrices (with dimension  $f > 1$ )

$$U(P), \quad U(Q), \dots \quad (3.16)$$

forms a representation  $\Gamma$  of the symmetry group  $\mathfrak{G}$ , we can derive from  $\Gamma$  an infinite number of representations in the following manner: Let  $T$  be a constant  $f$ -dimensional square matrix whose determinant does not vanish, and put

$$\bar{U}(P) = T^{-1} U(P) T, \quad \bar{U}(Q) = T^{-1} U(Q) T, \dots \quad (3.17)$$

Then the set

$$\bar{U}(P), \quad \bar{U}(Q), \dots \quad (3.18)$$

forms also a representation of  $\mathfrak{G}$ , because  $\bar{U}(P) \bar{U}(Q) = \bar{U}(R)$  is an immediate consequence of  $U(P) U(Q) = U(R)$ :

$$\begin{aligned} \bar{U}(P) \cdot \bar{U}(Q) &= T^{-1} U(P) T \cdot T^{-1} U(Q) T = T^{-1} U(P) U(Q) T \\ &= T^{-1} U(R) T = \bar{U}(R). \end{aligned} \quad (3.19)$$

Two representations, whose matrices are connected by a relation of the form (3.17), are said to be equivalent. Since  $T$  can be chosen in an infinite number of ways, we would have an infinite number of representations if we considered equivalent representations to be different as long as their matrices were different.

For our present purpose, however, we should regard the equivalent representations as essentially the same, as shown by the following considerations.

If the energy level  $E$  is degenerate ( $f \geq 2$ ), the choice of  $f$  linearly independent solutions  $\Psi_1, \Psi_2, \dots, \Psi_f$  can be made in an infinite number of different ways. If  $(\Psi_1, \Psi_2, \dots, \Psi_f)$  and  $(\bar{\Psi}_1, \bar{\Psi}_2, \dots, \bar{\Psi}_f)$  are two orthonormal bases, they are related through a unitary transformation:

$$\bar{\Psi}_i = \sum_{j=1}^f t_{ji} \Psi_j. \quad (3.20)$$

Applying the operator  $P$  to (3.20), we have

$$P\bar{\Psi}_i = \sum_{j=1}^f t_{ji} P\Psi_j = \sum_{k=1}^f \sum_{j=1}^f u_{kj}(P) t_{ji} \Psi_k.$$

On the other hand, we can write, using the representation matrix  $\bar{U}(P)$  generated by the new basis

$$P\bar{\Psi}_i = \sum_{h=1}^f \bar{u}_{hi}(P) \bar{\Psi}_h = \sum_{k=1}^f \sum_{h=1}^f t_{kh} \bar{u}_{hi}(P) \Psi_k.$$

Equating the coefficients of  $\Psi_k$  in these two expressions for  $P\bar{\Psi}_i$ , we obtain

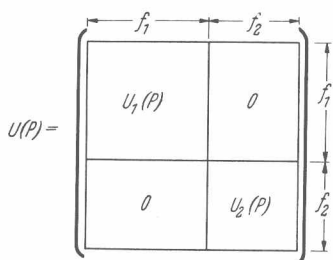


Fig. 5. Representation matrix  $U(P)$  of dimension  $f_1 + f_2$ .

$$U(P) T = T \bar{U}(P),$$

where  $T = (t_{ij})$ . Since  $T$  is unitary  $T^{-1} = T^\dagger$  exists, and this relation can be written as

$$\bar{U}(P) = T^{-1} U(P) T. \quad (3.21)$$

This result shows that the representation  $\Gamma\{U(P), U(Q), \dots\}$  is equivalent to the representation  $\Gamma'\{\bar{U}(P), \bar{U}(Q), \dots\}$ . Thus, the representation associated with a definite energy level is changed into another one which is equivalent to the former. Hence,

in order to consider the representation belonging to each energy level as definite without mentioning the choice of basic functions explicitly, we should regard equivalent representations as essentially the same.

The second point we have to discuss is the irreducibility of a representation. If we take two representations  $\Gamma_1\{U_1(P), \dots\}$  and  $\Gamma_2\{U_2(P), \dots\}$  of dimensions  $f_1$  and  $f_2$  respectively, and build the  $(f_1 + f_2)$ -dimensional matrix  $U(P)$  as shown in Fig. 5, we obtain a new representation  $(\Gamma_1 + \Gamma_2)\{U(P), U(Q), \dots\}$  of dimension  $f = f_1 + f_2$ . However, such representations are simply sums of two representations, and we need not give special treatment to them. In general, a representation, all matrices of which can be brought into the form of Fig. 5 simultaneously by a suitable choice of basic functions, is called *reducible*, and a representation for which this is not possible is said to be *irreducible*. In the case of reducible representations, there exists a sub-set of functions  $\Psi_1, \Psi_2, \dots, \Psi_{f_1}$ , with  $1 \leq f_1 < f$ , which are transformed among themselves by all the operators of the group, but this cannot occur in the case of irreducible representations.

The representation  $\Gamma$  which belongs to an energy level  $E$  of a molecule is in general irreducible. This can be seen from the following reasoning. If  $\Gamma$  were reducible, we could choose  $f$  basic functions  $\Psi_1, \Psi_2, \dots, \Psi_f$  in such a way as to put the representation matrices in the reduced form. Then, functions of the sets  $\{\Psi_1, \Psi_2, \dots, \Psi_{f_1}\}$  and  $\{\Psi_{f_1+1}, \dots, \Psi_f\}$  would be transformed separately, without mixing functions of the two sets. Therefore, from the standpoint of the symmetry of the molecule there would be no reason for the energy values of these two sets of wave functions to be equal. If they happen to be equal, this equality is not



required from the geometrical symmetry, but is quite accidental at least of our present point of view and we talk of an "accidental degeneracy". Disregarding such accidental degeneracy, therefore, we can assume that the representation of each energy level is always irreducible.

The main problem we have presented above can be formulated as follows: To determine the possible kinds of inequivalent, irreducible representations of a given symmetry group. The answer to this problem is given by the following

*Theorem.* For any group consisting of a finite number of elements (operations) the number of its inequivalent, irreducible representations is finite, and is equal to the number of classes of conjugate elements in that group.

Further details concerning this fundamental theorem will be discussed in the following subsections, where a convenient method of characterizing representations will also be given.

As an example, let us consider the tetrahedral group  $T_d$ . As was explained in Example 2 of Sect. 2,  $T_d$  has five classes, so that it should have five irreducible representations, which we can actually construct in the following way: First of all, every group has a trivial one-dimensional representation called the identical representation in which we associate +1 with all elements. This representation of  $T_d$  is denoted by  $A_1$ . We obtain another one-dimensional representation  $A_2$ , by associating +1 with all pure rotations and -1 with all reflections and rotary reflections. Introducing  $x, y, z$  axes as in Example 2 of Sect. 2, we find that the transformations of  $x, y, z$  give a three-dimensional representation, which we denote by  $T_1$ . Again, by reversing the sign of matrices corresponding to reflections and rotary reflections we obtain another three-dimensional representation  $T_2$ . Finally the quadratic form  $ax^2 + by^2 + cz^2$  ( $a + b + c = 0$ ) is transformed into itself by the operations of  $T_d$ , so that we obtain a two-dimensional representation  $E$  by choosing, e.g.,  $\frac{x^2 - y^2}{\sqrt{2}}$  and  $\frac{2z^2 - x^2 - y^2}{\sqrt{6}}$  as basic functions. The representation derived from  $E$  by reversing the sign of reflections, etc. is found to be equivalent to  $E$  itself. In this way we have obtained five irreducible representations  $A_1, A_2, E, T_1$ , and  $T_2$ , and the fundamental theorem asserts that any irreducible representation of  $T_d$  must be equivalent to one of these.

For later use, we give here representation matrices in the particular coordinate system explained above for typical elements, choosing one from each class:

Table 3

Representation	Element				
	$E$	$C_4\left(\frac{2\pi}{3}\right)$	$C_2(\pi)$	$\sigma_{ac}$	$S_6^+$
$A_1$	1	1	1	1	1
$A_2$	1	1	1	-1	-1
$E$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$
$T_1$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
$T_2$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$