L. C. Biedenharn and R. M. Thaler, Phys. Rev. **104**, 1643 (1956).
H. C. Brinkman (unpublished).
G. Burkhardt, G. Elwert, and A. Unsöld, Z. Astrophys. **25**, 310 (1948).
S. Chandrasekhar, *Radiative Transfer*, (Oxford University Press, New York, 1950), Sec. 22.3.
G. Elwert, Ann. Physik **34**, 178 (1939).
G. Elwert, Z. Naturforsch. **3a**, 477 (1948).
G. Elwert, Z. Naturforsch. **9a**, 637 (1954).
A. Erdélyi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, Vol. II.
A. Erdélyi, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I.
J. A. Gaunt, Proc. Roy. Soc. (London) **A126**, 654 (1930).
I. P. Grant, Monthly Notices Roy. Astron. Soc. **118**, 241 (1958).
J. Greene, "Bremsstrahlung from a Maxwellian Gas," AEC Research and Development Report, PM-S-41, NYO-7905 (1958); Astrophys. J. **130**, 693 (1959).
T. Guggenberger, Z. Physik **149**, 523 (1957).
W. Heitler, *The Quantum Theory of Radiation*, (Oxford University Press, New York, 1954), 3rd ed., Sec. 25.
G. Hettner, Z. Physik **150** 182 (1958).
R. Huby and H. C. Newns, Proc. Phys. Soc. (London) **A64**, 619 (1951).
W. J. Karzas and R. Latter, The Rand-Corporation Research Memorandum RM-2010-AEC, ASTIA Document Number AD1560461 (1957/1958) (unpublished).
T. V. Kazachevskaya and G. S. Ivanov-Kholodny, Soviet Astron.-AJ **3**, 937 (1960).
P. Kirkpatrick and L. Wiedmann, Phys. Rev. **67**, 321 (1945).
H. W. Koch and J. W. Motz, Revs. Modern Phys. **31**, 920 (1959).
H. A. Kramers, Phil. Mag. **46**, 836 (1923).
R. M. Kulsrud, Astrophys. J. **119**, 386 (1954).
K. Kummerer, Z. Physik **147**, 373 (1957).
L. D. Landau and E. M. Lifshitz, *The Classical Theory of Fields*, (Pergamon Press, London, 1959), p. 200.
W. Magnus und F. Oberhettinger, *Formeln und Sätze für die speziellen Funktionen der mathematischen Physik* (Springer-Verlag, Berlin, Germany, 1948).
A. W. Maue, Ann. Physik **13**, 161 (1932).
L. McLean, Phil. Mag. **18**, 845 (1934).
D. H. Menzel and C. L. Pekeris, Monthly Notices Roy. Astron. Soc. **96**, 77 (1935).
L. Oster, Z. Astrophys. **47**, 169 (1959).
L. Oster, Revs. Modern Phys. **33**, 525 (1961).
F. Sauter, Ann. Physik **18**, 486 (1933).
P. A. G. Scheuer, Monthly Notices Roy. Astron. Soc. **120**, 231 (1960).
S. F. Smerd and K. C. Westfold, Phil. Mag. **40**, 831 (1949).
A. Sommerfeld, Ann. Physik **11**, 257 (1931).
A. Sommerfeld and A. W. Maue, Ann. Physik **23**, 589 (1935).
A. Sommerfeld, *Atombau und Spektrallinien*, (Friedrich Vieweg and Sohn, Braunschweig, Germany, 1939), Vol. II, Chap. VII, Sec. 5, (12) (In the formula a factor $8\pi/3$ is missing).
J. Stickforth, Z. Physik **164**, 1 (1961).
K. A. Ter-Martirosyan, J. Exptl. Theoret. Phys. (U.S.S.R.) **22**, 284 (1952).
R. M. Thaler, M. Goldstein, J. L. McHale, and L. C. Biedenharn, Phys. Rev. **102**, 1567 (1956).
C. F. Wandel, T. Hesselberg Jensen, and O. Kofoed-Hansen, Nuclear Instr. and Methods. **4**, 249 (1959).
G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1958).
R. Weinstock, Phys. Rev. **61**, 584 (1942).
G. Wentzel, Z. Physik **27**, 257 (1924).

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The Normal Constants of Motion in Quantum Mechanics Treated by Projection Technique*

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1. INTRODUCTION

IN the treatment of both one-particle and many-particle systems, the constants of motion play an important role in studying the time-dependent phenomena and the stationary states. In the classical theory, the constants of motion were physical quantities like the energy, the momentum, the angular momenta, etc. In quantum theory, the list of the constants of motion has been considerably extended and includes, not only the spin and the total angular momentum, but also such operators as the permutations, the translations, the crystal symmetry operators, etc. The physical quantities are represented by Hermitian operators, whereas the latter quantities correspond to another type of operators, the so-called *normal operators*, which may be considered as a generalization of the Hermitian operators. The normal constants of motion are essential for classifying the energy levels, and we will here give a short outline of their theory by means of a projection operator formalism.

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2. NORMAL OPERATORS

Two operators F and $F^\dagger$ are said to be mutually *adjoint*, if their expectation values are conjugate complex for all normalizable functions Φ, so that $\langle\Phi|F^\dagger|\Phi\rangle = \langle\Phi|F|\Phi\rangle^*$. Here and in the following, we are using bracket notations of the type $\langle\Phi_1|\Phi_2\rangle = \int \Phi_1^*\Phi_2(dx)$, $\langle\Phi_1|F|\Phi_2\rangle = \int \Phi_1^* F_{\text{op}}\Phi_2(dx)$ and $||\Phi||^2 = \langle\Phi|\Phi\rangle$. Putting $\Phi = \Phi_1 + \Phi_2$ and $\Phi = \Phi_1 + i\Phi_2$ and combining the two relations, one obtains the basic matrix formula $\langle\Phi_1|F^\dagger|\Phi_2\rangle = \langle\Phi_2|F|\Phi_1\rangle^*$ and the "turn-over rule,"

$$\langle F\Phi_1|\Phi_2\rangle = \langle\Phi_1|F^\dagger\Phi_2\rangle\,. \tag{1}$$

An operator is said to be self-adjoint, $F^\dagger = F$, or Hermitian, if it always has real expectation values, and vice versa. An operator Λ is said to be *normal*, if it commutes with its own adjoint operator $\Lambda^\dagger$, so that

$$\Lambda\Lambda^\dagger = \Lambda^\dagger\Lambda\,. \tag{2}$$

The Hermitian operators are hence a special class of the normal operators. On the other hand, a normal operator may always be written as the sum of an Hermitian and an anti-Hermitian component (see the Appendix), but we note that it is usually more feasible to develop the theory by means of the more general concept of the normal operators.

If Φ_k is an eigenfunction to Λ associated with the eigenvalue λ_k, so that

$$\Lambda\Phi_k = \lambda_k\Phi_k\,, \tag{3}$$

by using (1) and (2) one obtains

$$\begin{aligned}\|(\Lambda^\dagger - \lambda_k^*)\Phi_k\|^2 &= \int |(\Lambda^\dagger - \lambda_k^*)\Phi_k|^2(dx)\\ &= \langle(\Lambda^\dagger - \lambda_k^*)\Phi_k|(\Lambda^\dagger - \lambda_k^*)\Phi_k\rangle\\ &= \langle\Phi_k|(\Lambda - \lambda_k)(\Lambda^\dagger - \lambda_k^*)|\Phi_k\rangle\\ &= \langle\Phi_k|(\Lambda^\dagger - \lambda_k^*)(\Lambda - \lambda_k)\Phi_k\rangle = 0\end{aligned} \tag{4}$$

i.e.,

$$\Lambda^\dagger\Phi_k = \lambda_k^*\Phi_k\,. \tag{5}$$

This means that Φ_k is also an eigenfunction to the adjoint operator $\Lambda^\dagger$ associated with the eigenvalue λ_k^*. Using this property, one can now easily show that eigenfunctions Φ_k and Φ_l associated with different eigenvalues, $\lambda_k \neq \lambda_l$, are necessarily orthogonal,

$$\langle\Phi_k|\Phi_l\rangle = 0\,, \quad \lambda_k \neq \lambda_l\,, \tag{6}$$

since

$$\begin{aligned}\lambda_k\langle\Phi_k|\Phi_l\rangle &= \langle\lambda_k^*\Phi_k|\Phi_l\rangle = \langle\Lambda^\dagger\Phi_k|\Phi_l\rangle = \langle\Phi_k|\Lambda\Phi_l\rangle\\ &= \langle\Phi_k|\lambda_l\Phi_l\rangle = \lambda_l\langle\Phi_k|\Phi_l\rangle\,,\end{aligned} \tag{7}$$

i.e.,

$$(\lambda_k - \lambda_l)\langle\Phi_k|\Phi_l\rangle = 0\,.$$

The normal operators have, hence, orthogonal eigenfunctions in the same way as the Hermitian operators, but the eigenvalues λ_k for the former are in general complex numbers.

A special class of normal operators is represented by the unitary operators U, satisfying the relations $UU^\dagger = U^\dagger U = 1$, where the first part indicates that U is normal and the second part that $\lambda_k^*\lambda_k = 1$, i.e., $|\lambda_k| = 1$, for all k.

3. NORMAL CONSTANTS OF MOTION

A normal operator Λ is said to be a constant of motion of the system under consideration if it commutes with its Hamiltonian H:

$$\Lambda H = H\Lambda\,. \tag{8}$$

The fundamental importance of such an operator depends on the fact that the eigenfunctions Φ_k and Φ_l are not only orthogonal but are also *noninteracting* with respect to H, so that

$$\boxed{\langle\Phi_k|H|\Phi_l\rangle = 0\,, \quad \lambda_k \neq \lambda_l} \tag{9}$$

Using (6) and (8), we have

$$\begin{aligned}\lambda_k\langle\Phi_k|H|\Phi_l\rangle &= \langle\lambda_k^*\Phi_k|H|\Phi_l\rangle = \langle\Lambda^\dagger\Phi_k|H|\Phi_l\rangle\\ &= \langle\Phi_k|\Lambda H|\Phi_l\rangle = \langle\Phi_k|H\Lambda|\Phi_l\rangle = \lambda_l\langle\Phi_k|H|\Phi_l\rangle\,,\end{aligned} \tag{10}$$

i.e.,

$$(\lambda_k - \lambda_l)\langle\Phi_k|H|\Phi_l\rangle = 0\,,$$

which proves the theorem. This property can often be used to obtain an essential simplification of the treatment of the energy problem, whether one considers a single expectation value or a full energy matrix. For this purpose, it is convenient to partition the entire Hilbert space into the subspaces associated with the different eigenvalues λ_k to Λ, and this can be done using a projection operator technique.

Let us consider an arbitrary trial function Φ which has been found, for instance, by some general physical arguments and which is hence not necessarily an exact solution to the Schrödinger equation. This trial function may be considered as a superposition of pure Λ functions:

$$\Phi = \textstyle\sum_k \Phi_k\,, \tag{11}$$

where the different components Φ_k are associated with different eigenvalues λ_k. If such a resolution exists, it is certainly unique. Assuming that there would be two resolutions, $\Phi = \sum_k\Phi_k' = \sum_k\Phi_k''$, one has after subtraction $0 = \sum_k(\Phi_k' - \Phi_k'')$. Because of the orthogonality (6), one obtains for the normalization integral $0 = \sum_k||\Phi_k' - \Phi_k''||^2$, which leads to

$\Phi_k' = \Phi_k''$ and proves the uniqueness theorem except for an irrelevant zero function. The existence theorem is further discussed below; see (25).

By using (6) and (9), one obtains now for the expectation value of the energy

$$\langle H_{\text{op}}\rangle_{\text{AV}} = \frac{\langle\Phi|H_{\text{op}}|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \frac{\sum_k\langle\Phi_k|H|\Phi_k\rangle}{\sum_k\langle\Phi_k|\Phi_k\rangle} \tag{12}$$

In order to analyze this expression, it is feasible to introduce the energy expectation value E_k associated with the component Φ_k, i.e.,

$$E_k = \frac{\langle\Phi_k|H|\Phi_k\rangle}{\langle\Phi_k|\Phi_k\rangle}, \tag{13}$$

and the weight factor

$$\omega_k = \frac{\langle\Phi_k|\Phi_k\rangle}{\langle\Phi|\Phi\rangle}, \tag{14}$$

which is always positive. In this way, we obtain

$$\langle H_{\text{op}}\rangle_{\text{AV}} = \sum_k \omega_k E_k, \tag{15}$$

with $\sum_k\omega_k = 1$, showing that $\langle H\rangle$ is a weighted average of the component energies E_k without any interference between the different λ values. It follows that at least one of the energies E_k is lower than $\langle H\rangle$, unless they are all equal and, if the trial function is not a pure eigenfunction to Λ, one can hence always lower the energy by a "component analysis." This is of importance in understanding the nature of the chemical bond; see Sec. 5. Of still greater importance is the theorem that each one of the quantities E_k is an upper bound to the lowest true energy of the same Λ type, and that the variation principle can hence be applied to each one of the subspaces characterized by the different eigenvalues λ_k.

Projection Operator Formalism

Equation (11) may be interpreted geometrically as the resolution of a given vector Φ into orthogonal components Φ_k along axes and into subspaces defined by the eigenstates to Λ. Such a component analysis can be carried out by means of a set of operators O_k having the selective property

$$O_k\Phi = \Phi_k. \tag{16}$$

From this relation follows that O_k is an eigenoperator to Λ, so that $\Lambda O_k = O_k\Lambda = \lambda_k O_k$ and further that $O_k^2 = O_k$, i.e., O_k is a projection operator. According to (3) and (5), the operators Λ and $\Lambda^\dagger$ have the same eigenfunctions which means that $O_k = O_k{}^\dagger$. The operator O_k is hence an Hermitian projection operator having only the eigenvalues 0 and 1; it will project on the entire subspace associated with the eigenvalue λ_k, and the quantity $g_k = \text{Tr}(O_k)$ is an integer giving its dimensions and the order of the degeneracy of the eigenvalue. In summary, we have

$$\Lambda O_k = O_k\Lambda = \lambda_k O_k, \tag{17}$$

$$O_k^2 = O_k, \quad O_k^\dagger = O_k, \quad \text{Tr}(O_k) = g_k. \tag{18}$$

Instead of (6) and (9), one obtains further the operator relations:

$$O_k O_l = 0, \quad O_k H O_l = 0, \quad (\lambda_k \neq \lambda_l). \tag{19}$$

The expansion (11) corresponds now to the formula $1 = \sum_k O_k$, which is a resolution of the identity[1] in terms of the projection operators O_k. It directly follows further from (17) that $\Lambda = \sum_k\lambda_k O_k$, and the more general formula

$$f(\Lambda) = \sum_k f(\lambda_k)O_k, \tag{20}$$

for any polynomial function f of Λ. The essential question is now whether the basic expansion (11) exists and whether one can find some expressions for the corresponding projection operators O_k.

For the essential applications of the theory of normal constants of motion, it is sufficient to assume that the operator Λ has a *finite discrete* eigenvalue spectrum $\lambda_1, \lambda_2, \lambda_3, \cdots \lambda_n$ with the degeneracies $g_1, g_2, g_3, \cdots g_n$. The projection operators O_k are then conveniently expressed in the product form[2]:

$$O_k = \prod_{l\neq k}\frac{\Lambda - \lambda_l}{\lambda_k - \lambda_l} \tag{21}$$

and, even for multiple eigenvalues, each factor is taken only once. We note that, in the expansion (11), each one of the factors $(\Lambda - \lambda_l)$ will annihilate the corresponding eigenfunction Φ_l according to (3), and the denominator is chosen so that Φ_k will survive the operation in an unchanged form, i.e., with the factor 1.

Let us now introduce the reduced characteristic polynomial $F(z) \equiv \prod_l (z - \lambda_l)$ of degree n in the complex variable z. The associated function

$$O_k(z) = \frac{F(z)}{(z - \lambda_k)F'(\lambda_k)} \tag{22}$$

is a polynomial of degree $(n - 1)$ which has the value 1 for $z = \lambda_k$, and the value 0 for $z = \lambda l (l \neq k)$. It is interesting to study the function

$$G(z) \equiv 1 - \sum_k \frac{F(z)}{(z - \lambda_k)F'(\lambda_k)}, \tag{23}$$

[1] J. von Neumann, *Math. Grundlagen der Quantenmechanik* (Dover Publications, New York, 1943); M. H. Stone, *Linear Transformations in Hilbert Space and Their Applications to Analysis* (American Mathematical Society, Providence, Rhode Island, 1932).

[2] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955).

since it is a polynomial of degree $(n-1)$ having n different zero points: $z = \lambda_1, \lambda_2, \cdots \lambda_n$. The function $G(z)$ is hence identically vanishing for all values of z, and the relation $G(z) \equiv 0$ is a simple polynomial identity valid also if one substitues the operator Λ instead of the variable z. This gives the result

$$1 - \sum_k O_k = 0 , \tag{24}$$

which is the fundamental "resolution of the identity" needed in treating the normal constants of motion having a finite eigenvalue spectrum. Multiplying the arbitrary trial vector Φ by the operator $1 = \sum_k O_k$, one obtains

$$\Phi = \sum_k O_k \Phi = \sum_k \Phi_k ; \tag{25}$$

which proves the existence of the resolution (11) in this particular case. We have also proven the validity of (20) and, as a special case, we get $F(\Lambda) = 0$ which is the reduced Cayley-Hamilton equation for the operator Λ. We note that the operator O_k defined by (21) will project on the entire subspace connected with the eigenvalue λ_k, and that the quantity

$$\mathrm{Tr}(O_k) = g_k , \tag{26}$$

gives the order of the degeneracy.

Simultaneous Eigenfunctions to H and Λ

From the Schrödinger equation $H\Psi = E\Psi$ and (8) follows that

$$H(\Lambda\Psi) = E(\Lambda\Psi) , \tag{27}$$

showing that, in addition to Ψ, the function $\Lambda\Psi$ is also an eigenfunction to H associated with the same eigenvalue E. If the energy level is *nondegenerate*, this implies that $\Lambda\Psi$ is proportional to Ψ, i.e., $\Lambda\Psi = \lambda\Psi$, and Ψ is then a simultaneous eigenfunction to H and Λ.

The treatment of a *degenerate* energy level requires a somewhat different approach. Using (21) and (8), one obtains

$$HO_k = O_k H , \tag{28}$$

i.e., the projection operators O_k commute with H; the result is also easily derived directly from (16) provided that $1 = \sum_l O_l$. From (28) and (17) follows that

$$H(O_k\Psi) = E(O_k\Psi) , \quad \Lambda(O_k\Psi) = \lambda_k(O_k\Psi) , \tag{29}$$

which means that $O_k\Psi$ is a simultaneous eigenfunction to H and Λ, provided that

$$O_k\Psi \neq 0 . \tag{30}$$

According to (25), one has $\Psi = \sum_k O_k\Psi$, i.e., one may resolve Ψ into its Λ components, and we note that all nonvanishing components have the same energy E. By means of the Λ analysis, one is hence able to derive an ortho-normal and noninteracting subset of simultaneous eigenfunctions which are useful in describing the degeneracy. The orthonormalization of a series of projections $O_k\Psi_1$, $O_k\Psi_2$, $\cdots$ will be further discussed in the next section.

In some cases, the classification of the energy degeneracy by means of the eigenvalues λ_k to Λ may be complete; in other cases, the simultaneous eigenfunctions to H and Λ are still degenerate, and one may try to introduce further normal constants of motion commuting with both H and Λ to classify the remaining degeneracies. Examples from the theory of atomic energy levels tell us that it may be very difficult or perhaps even impossible to find enough normal constants of motion of a physical character to classify all degeneracies actually occurring in nature and this is probably still more accentuated in molecular and solid-state theory.

Relation (30) is of crucial importance in the theory, since it tells what λ_k values one can expect to find associated with a certain energy level E. It is also of interest to study the connection between the degeneracies of E and the degeneracies of a normal constant of motion Λ having the mutually commuting components $(\Lambda_1, \Lambda_2, \cdots \Lambda_m)$ which one has tried to make as complete as possible. In case there are further constants of motion Λ'_1, Λ'_2, $\cdots$, which commute with H but not with the selected operator Λ or with each other, one should observe that, according to (27), also the functions $\Lambda'_1\Psi$, $\Lambda'_2\Psi$, $\cdots$ are eigenfunctions to H associated with the same energy E, provided that they are not vanishing identically. If one starts from a *single* eigenfunction to H, one can in this way by means of the operators Λ'_1, Λ'_2, $\cdots$ span the degeneracy that is still inherent in the combined observable $(H_{op}, \Lambda_1, \Lambda_2, \cdots \Lambda_m)$. The approach is systematized by means of the theory of "ladder-operators." For example, if an angular momentum $\mathbf{M} = (M_x, M_y, M_z)$ is a constant of motion, one classifies the energy levels by means of the operator (M^2, M_z) and can transform the associated eigenfunctions into each other by means of the step-up and step-down operators $M_+ = M_x + iM_y$ and $M_- = M_x - iM_y$, respectively. As we will see in the following applications, one can often use this idea in a very elementary way, whereas a more profound theoretical treatment should be based on group theory and particularly group algebra. Research on this point is in progress.

4. SPLITTING OF SECULAR EQUATION

In quantum mechanics, the solution of the eigenvalue problem $H\Psi = E\Psi$ is to a very large extent based on Ritz's[3] expansion method. Introducing a complete basis $\{f_l\}$, one may express the wave function in the form $\Psi = \sum_l f_l c_l$, where one has to determine the coefficients c_l forming a column vector $\mathbf{C}$. For this purpose, we will introduce the energy matrix $\mathbf{H}$ and the metric matrix $\mathbf{\Delta}$ having the elements

$$H_{mn} = \langle f_m|H|f_n\rangle\,, \quad \Delta_{mn} = \langle f_m|f_n\rangle\,, \tag{31}$$

respectively. From $H\Psi = E\Psi$ follow immediately the relations $\sum_n(H_{mn} - E\Delta_{mn})c_n = 0$ or, in matrix form,

$$(\mathbf{H} - E\mathbf{\Delta})\mathbf{C} = 0\,, \tag{32}$$

where the eigenvalues E are determined by the so-called secular equation $\det\{H_{mn} - E\Delta_{mn}\} = 0$.

We will now study some of the expansion properties of the simultaneous eigenfunctions Ψ to H and Λ, satisfying the relations $H\Psi = E\Psi$ and $\Lambda\Psi = \lambda_k\Psi$. From the latter follows $O_k\Psi = \Psi$ and, letting O_k work on both sides of the expansion $\Psi = \sum_l f_l c_l$, one obtains

$$\Psi = \sum_l (O_k f_l)c_l\,. \tag{33}$$

This implies that, if the set $\{f_l\}$ is complete, one may expand an eigenfunction to Λ associated with the eigenvalue λ_k into the projections $\{O_k f_l\}$ of the basis. The set $\{O_k f_l\}$ spans a subspace of the total Hilbert space, which we will call the λ_k space. The functions in $\{O_k f_l\}$ are usually not orthogonal and show actually linear dependencies which make it possible to collect the terms in (33) so that a more rapidly convergent sum is obtained; one can also replace the set $\{O_k f_l\}$ by an orthonormal one; see below. The problem of the expansion of Ψ refers now entirely to the λ_k space, and we will obtain a simplified secular equation of type (32) which then may be treated by, e.g., the partitioning technique. Actually we will obtain such a simplified secular equation for each one of the eigenvalues λ_k, and together all these equations are equivalent to (32).

Conventionally the normal constants of motion have always been used to split the secular equation (32) based on a truncated or complete set $\{f_l\}$, and, for symmetry operators Λ, group-theoretical methods have been of essential importance. In studying, e.g., the atomic energy levels associated with a specific configuration l^N, Slater[4] could find the splitting of the energy levels in an ingeniously simple way by using the "diagonal sum rule" combined with the knowledge of which terms were to be expected in connection with the configuration l^N rendered by elementary combinatoric arguments. However, instead of this splitting of the total secular equation, we have here carried out a splitting of the basis $\{f_l\}$ into subsets $\{O_k f_l\}$ which are orthogonal, non-

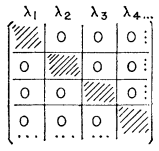

FIG. 1. Splitting of matrix $(\mathbf{H} - E\mathbf{\Delta})$ into independent parts by means of the projection operator formalism.

interacting with respect to H, and complete with respect to the subspaces associated with the eigenvalues λ_k to Λ; see (19) and (33). This splitting of the basis leads hence automatically to a splitting of the secular equation according to Fig. 1.

In the projection operator technique, there is a possibility of an obvious generalization, since one may start from different basic sets $\{f_l'\}$, $\{f_l''\}$, $\{f_l'''\}$, $\cdots$ in constructing the various projected subsets $\{O_1 f_l'\}$, $\{O_2 f_l''\}$, $\{O_3 f_l'''\}, \cdots$. This result is of particular importance if the original set $\{f_l\}$ depends on adjustable parameters α_1, α_2, α_3, $\cdots$, since one may now use different parameter values for the various λ_k types in order to obtain optimum convergency, etc. This generalization is still more valuable in the case when only a truncated basis is used.

Calculation of Matrix Elements

Let us now re-examine the properties of Ritz's expansion method in the case when the subspace associated with the eigenvalue λ_k is described by means of the projected subset

$$\Theta_{kl} = O_k f_l\,. \tag{34}$$

According to (33), we have $\Psi = \sum_l \Theta_{kl} c_l$, and, for the matrix elements with respect to the new basis, we obtain by means of (1), (18), and (28) that

$$\begin{aligned} H'_{mn} &= \langle \Theta_{km}|H|\Theta_{kn}\rangle = \langle O_k f_m|H|O_k f_n\rangle \\ &= \langle f_m|O_k^\dagger H O_k|f_n\rangle = \langle f_m|HO_k|f_n\rangle\,, \end{aligned} \tag{35}$$

$$\Delta'_{mn} = \langle \Theta_{km}|\Theta_{kn}\rangle = \langle f_m|O_k|f_n\rangle \tag{36}$$

The essential simplification comes from the relation $O_k^2 = O_k$. If the function (34) is expressed as a series, each matrix element is a double series which may be reduced to a single series by means of the "turn-over rule" and this relation.

[3] W. Ritz, J. reine angew. Math. **135**, 1 (1909).
[4] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

Construction of Orthonormal Subset

The functions Θ_{kl} are usually not linearly independent, and it is often convenient to replace them by an orthonormalized set Θ'_{kl}. Since we will here consider only a single subspace λ_k, we will drop the lower index k. Expanding the functions $\Theta_m(= \Theta_{km})$ into the complete set $\{f_\mu\}$, we obtain

$$\Theta_m = Of_m = \sum_\mu f_\mu \alpha_{\mu m} , \tag{37}$$

where the coefficients $\alpha_{\mu m} = \langle f_\mu | O | f_m \rangle$ are apparently the matrix elements of O. From the operator relation $O^2 = O$ follows immediately the matrix relation

$$\mathbf{a}^2 = \mathbf{a} , \tag{38}$$

showing that the matrix $\mathbf{a} = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \cdots)$ has only the eigenvalues 0 and 1, and that further each one of the column vectors $\mathbf{a}_\nu$ is an eigenvector to $\mathbf{a}$, so that $\mathbf{a}\mathbf{a}_\nu = \mathbf{a}_\nu$.

Let us consider[5] the functions Θ_1, Θ_2, Θ_3, $\cdots$ successively in order, and let us start by considering the expansion

$$\begin{aligned} \Theta_1 &= Of_1 = f_1\alpha_{11} + f_2\alpha_{21} + f_3\alpha_{31} + \cdots , \\ \Theta_2 &= Of_2 = f_1\alpha_{12} + f_2\alpha_{22} + f_3\alpha_{32} + \cdots , \end{aligned} \tag{39}$$

If $\alpha_{11} \neq 0$, we will fix the first function Θ_1 having the normalization integral $\Delta_{11} = \alpha_{11}$. It is then possible to determine a multiplier d_{12} so that $\alpha_{12} + \alpha_{11}d_{12} = 0$. Putting $\alpha'_{l2} = \alpha_{l2} + \alpha_{l1}d_{12}$ for $l \geq 2$, we then obtain

$$\Theta'_2 = O(f_2 + f_1 d_{12}) = 0 + f_2\alpha'_{22} + f_3\alpha'_{32} + \cdots . \tag{40}$$

The function Θ'_2 obtained by eliminating f_1 in the expansion of Θ_2 is automatically orthogonal to Θ_1 for, using the "turn-over rule" and (18), we get

$$\begin{aligned} \langle \Theta_1 | \Theta'_2 \rangle &= \langle Of_1 | \Theta'_2 \rangle = \langle f_1 | O\Theta'_2 \rangle \\ &= \langle f_1 | \Theta'_2 \rangle = \langle f_1 | f_2\alpha'_{22} + f_3\alpha'_{32} + \cdots \rangle = 0 . \end{aligned} \tag{41}$$

and the question is now only whether Θ'_2 is identically vanishing or not. For the normalization integral, we obtain similarly

$$\begin{aligned} \langle \Theta'_2 | \Theta'_2 \rangle &= \langle O(f_2 + f_1 d_{12}) | \Theta'_2 \rangle = \langle f_2 + f_1 d_{12} | \Theta'_2 \rangle \\ &= \langle f_2 + f_1 d_{12} | f_2\alpha'_{22} + f_3\alpha'_{32} + \cdots \rangle = \alpha'_{22} , \end{aligned} \tag{42}$$

showing that the function is nontrivial if $\alpha'_{22} \neq 0$. However, if $\alpha'_{22} = 0$, we can conclude that all the higher coefficients α'_{l2} are also vanishing: The function Θ_2 is then proportional to Θ_1 and may be omitted; in such a case, we will proceed in the set Θ_l until we find a function having a nonvanishing normalization integral connected with the coefficient for f_2.

[5] P. O. Löwdin, Advances in Chemical Physics (Interscience Publishers, Inc., New York 1959), Vol. 2, p. 290 ff.

Assuming that $\neq \alpha'_{22}$ 0, we will now consider the third function,

$$\Theta_3 = Of_3 = f_1\alpha_{13} + f_2\alpha_{23} + f_3\alpha_{33} + \cdots . \tag{43}$$

It is possible to eliminate f_1 and f_2 from this expansion by introducing two multipliers d_{13} and d_{23} such that

$$\alpha'_{l3} = \alpha_{l3} + \alpha_{l2}d_{23} + \alpha_{l1}d_{13} , \tag{44}$$

fulfilling the conditions $\alpha'_{13} = \alpha'_{23} = 0$. This gives

$$\begin{aligned} \Theta'_3 &= O(f_3 + f_2 d_{23} + f_1 d_{13}) \\ &= 0 + 0 + f_3\alpha'_{33} + f_4\alpha'_{43} + \cdots . \end{aligned} \tag{45}$$

As before, we can directly show that this function is automatically orthogonal with respect to Θ_1 and Θ'_2 and that the normalization integral is given by the expression

$$\langle \Theta'_3 | \Theta'_3 \rangle = \alpha'_{33} . \tag{46}$$

If $\alpha'_{33} = 0$, we have $\alpha'_{13} = 0$, and the function Θ_3 is then a linear combination of the functions Θ_1 and Θ'_2 and should be omitted in the orthogonalization process, which is here simply accomplished by means of the Gaussian elimination technique developed for solving equation systems. The connection between the matrices $\mathbf{a}$ and $\mathbf{a}'$ may be written in the form

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} & \alpha_{14} & \cdot \\ \alpha_{21} & \alpha_{22} & \alpha_{23} & \alpha_{24} & \cdot \\ \alpha_{31} & \alpha_{32} & \alpha_{33} & \alpha_{34} & \cdot \\ \alpha_{41} & \alpha_{42} & \alpha_{43} & \alpha_{44} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \begin{bmatrix} 1 & d_{12} & d_{13} & d_{14} & \cdot \\ 0 & 1 & d_{23} & d_{24} & \cdot \\ 0 & 0 & 1 & d_{34} & \cdot \\ 0 & 0 & 0 & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$

$$= \begin{bmatrix} \alpha_{11} & 0 & 0 & 0 & 0 & \cdot \\ \alpha_{21} & \alpha_{22} & 0 & 0 & 0 & \cdot \\ \alpha_{31} & \alpha'_{32} & \alpha'_{33} & 0 & \cdot & \cdot \\ \alpha_{41} & \alpha'_{42} & \alpha'_{43} & \alpha'_{44} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \tag{47}$$

where we have omitted all columns in the matrix $\mathbf{a}$ leading to identically vanishing columns in the matrix $\mathbf{a}'$.

The eigenvalue problem with respect to the energy H_{op} is now conveniently solved by means of the orthogonalized Λ-adapted set Θ_1, Θ'_2, Θ'_3, $\cdots$. Using the "turn-over rule" and (34), we obtain ($m \leq n$):

$$\begin{aligned} H'_{mn} &= \langle \Theta'_m | H_{op} | \Theta'_n \rangle \\ &= \langle O(\sum_{\mu=1}^{m} f_\mu d_{\mu m}) | H_{op} | \sum_{\nu=n} f_\nu \alpha'_{\nu n} \rangle \\ &= \sum_{\mu=1}^{m} \sum_{\nu=n} d^\dagger{}_{m\mu} \langle f_\mu | H | f_\nu \rangle \alpha'_{\nu n} . \end{aligned} \tag{48}$$

The single sum in (35) is here replaced by the sum of m such single sums, depending on the orthogonalization. The eigenvalue problem is in this way reduced to the form

$$\det\{H'_{mn} - E\alpha'_{mm}\delta_{mn}\} = 0\,, \tag{49}$$

and we note that there is an equation of this type associated with each eigenvalue λ_k to Λ. Hence, the projection operator formalism leads to a splitting of the original secular equation with respect to the various eigenstates of Λ, which is very convenient also for practical purposes.

5. EXCLUSION PRINCIPLE AND ANTISYMMETRY REQUIREMENT

Let us now consider a system of N identical fermions which obey the Pauli exclusion principle, and let $\mathbf{x}_i = (\mathbf{r}_i,\zeta_i)$ be the combined space-spin coordinate which is associated with the particle i. The spin-coordinate may describe the ordinary spin, the isotopic spin, etc., depending on the nature of the particles. The total Hamiltonian H is assumed to be symmetric in all coordinates $\mathbf{x}_i$, and the exclusion principle is now formulated so that the total wave function $\Psi = \Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\cdots\mathbf{x}_N)$ is required to be *antisymmetric* with respect to all permutations P of the coordinates $\mathbf{x}_1$, $\mathbf{x}_2$, $\cdots$ $\mathbf{x}_N$, so that

$$P\Psi = (-1)^p\Psi\,, \tag{50}$$

where p is the parity of the permutation. In this connection, it is convenient to introduce the operator

$$O_{AS} = (N!)^{-1}\sum_P (-1)^p P\,, \tag{51}$$

which satisfies the relations

$$PO_{AS} = (-1)^p O_{AS}\,,\quad O_{AS}^2 = O_{AS}\,,\quad O_{AS}^\dagger = O_{AS}\,. \tag{52}$$

The operator O_{AS} may hence be characterized as the antisymmetry projection operator which selects the "antisymmetric component" out of any trial function Φ, so that $P(O_{AS}\Phi) = (-1)^p(O_{AS}\Phi)$. Conventionally, the operator $A = (N!)^{1/2}O_{AS}$ is often called the "antisymmetrizer."

For the exact wave function Ψ satisfying the antisymmetry requirement (50), one obtains

$$O_{AS}\Psi = \Psi\,. \tag{53}$$

Since $HP = PH$, one has further $HO_{AS} = O_{AS}H$, which means that O_{AS} is a normal constant of motion which always has the value 1. We note that, for fermions, all further constants of motion have to commute with both H and O_{AS}.

Superposition of Configurations

In the discussions concerning the solution of the many-electron Schrödinger equation, the method of superposition of configurations or "configurational interaction" has played an important role, and we will now study this method from the points of view developed in this section[6]. For this purpose, we will introduce a discrete, orthonormal and complete set $\{\Psi_k\}$ of one-electron functions or spin-orbitals $\Psi_k(\mathbf{x})$, where $\mathbf{x} = (\mathbf{r},\zeta)$ is the space-spin coordinate, and assume the existence of the expansion

$$\Psi(\mathbf{x}) = \sum_k \Psi_k(\mathbf{x})c_k\,, \tag{54}$$

for every normalizable function $\Psi(\mathbf{x})$ of a single electronic coordinate. For a function of N electronic coordinates, one can then repeat the use of (54) for one coordinate at a time. This procedure leads finally to an expansion of the form:

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\cdots) = \sum_{klm\ldots} c_{klm\ldots}\Psi_k(\mathbf{x}_1)\Psi_l(\mathbf{x}_2)\Psi_m(\mathbf{x}_3)\cdots\,, \tag{55}$$

where each term in the right-hand sum is actually a so-called Hartree-product. We will now utilize the fact that the electrons obey Pauli's exclusion principle. Since Ψ is antisymmetric, one has according to (53) that $O_{AS}\Psi = \Psi$ and that

$$\begin{aligned}\Psi &= O_{AS}\Psi\\ &= (N!)^{-1}\sum_{klm\ldots}\det\{\Psi_k,\Psi_l,\Psi_m,\cdots\}c_{klm\ldots}\\ &= \sum_{k<l<m\ldots}\det\{\Psi_k,\Psi_l,\Psi_m,\cdots\}c_{klm\ldots}\,.\end{aligned} \tag{56}$$

Hence, every normalizable antisymmetric wave function Ψ may be expanded in Slater determinants built up from a complete basic set, and this theorem forms the basis for the method of "superposition of configurations." A selection K of N indices $k < l < m < \cdots$ is called an "ordered configuration" and, introducing the notations

$$\begin{aligned}\Psi_K &= (N!)^{-1/2}\det\{\Psi_k,\Psi_l,\Psi_m,\cdots\}\,,\\ C_K &= (N!)^{1/2}c_{klm\ldots}\,,\end{aligned} \tag{57}$$

one can write (56) in the condensed form

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N) = \sum_K \Psi_K(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)C_K\,. \tag{58}$$

In the N-electron configuration space, the Slater determinants Ψ_K form an orthonormal basis which completely spans the antisymmetric subspace. The linear system (32) takes the form

$$\sum_L (H_{KL} - E\delta_{KL})C_L = 0\,, \tag{59}$$

[6] P. O. Löwdin, Revs. Modern Phys. **32**, 328 (1960).

but the secular expansion can often be split still further if there are additional normal constants of motion.

Expansion in Projections of Slater Determinants

Let us assume that $\Lambda = \Lambda(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_N)$ is a normal operator, symmetric in all electronic coordinates, which commutes with the total Hamiltonian and with O_{AS} so that it is a constant of motion. Let us now consider a simultaneous antisymmetric eigenfunction Ψ to H and Λ. Letting the associated projection operator O_k work on both sides of (92), we have

$$\Psi = O_k\Psi = \sum_K (O_k\Psi_K)C_K\,, \tag{60}$$

showing that such a function may actually be expanded into the projections $\{O_k\Psi_K\}$ of the Slater determinants Ψ_K. The functions $O_k\Psi_K$ are usually not linearly independent and, by eliminating the redundancies, expansion (60) may often be considerably condensed. We note that the antisymmetry property is undisturbed by the projection, since O_k commutes with O_{AS}.

By means of the projection operators O_k, we can now split the antisymmetric subspace of the N-electron Hilbert space into smaller subspaces associated with the eigenvalues λ_k of Λ by splitting the basis $\{\Psi_K\}$ into the orthogonal and non-interacting bases

$$\{O_1\Psi_K\}\,,\quad \{O_2\Psi_K\}\,,\quad \{O_3\Psi_K\}\,,\cdots\,. \tag{61}$$

In the following we will use this technique for describing total wave functions of pure spin or pure angular momenta in general and for discussing properties connected with the total translational symmetry of a crystal.

6. EXCHANGE PHENOMENON AND NATURE OF CHEMICAL BOND

Let us consider a two-electron system characterized by the spinless Hamiltonian $H = H_{(0)} + H_1 + H_2 + H_{12}$, which is symmetric in the two space coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, so that the operator P_{12}^r is a normal constant of motion. In this section, we will omit the upper index r. Since $P_{12}^2 = 1$, the eigenvalues are ± 1 and, according to (21), the associated projection operators are given by the expressions:

$$\begin{aligned} O_{+1} &= \tfrac{1}{2}(1 + P_{12})\,,\\ O_{-1} &= \tfrac{1}{2}(1 - P_{12})\,, \end{aligned} \tag{62}$$

having the sum 1. Any trial function $\Phi = \Phi(1,2)$ of the space coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ may hence be resolved into a symmetric and antisymmetric component with respect to P_{12}:

$$\begin{aligned} \Phi(1,2) = {}& \tfrac{1}{2}[\Phi(1,2) + \Phi(2,1)]\\ &+ \tfrac{1}{2}[\Phi(1,2) - \Phi(2,1)]\,. \end{aligned} \tag{63}$$

According to the general theory, the two components are orthogonal and noninteracting with respect to H, and, by considering the possible spin functions and the antisymmetry requirement for the total wave function, it is easily seen that the first component corresponds to a singlet state with the spin factor $(\alpha_1\beta_2 - \beta_1\alpha_2)$ and the second component to a triplet state with the three possible spin factors $\alpha_1\alpha_2$, $(\alpha_1\beta_2 + \beta_1\alpha_2)$, and $\beta_1\beta_2$. By using (13), the energies of the two components are now easily obtained:

$${}^1E = \frac{\langle\Phi|H + HP|\Phi\rangle}{\langle\Phi|1 + P|\Phi\rangle}\,, \tag{64}$$

$${}^3E = \frac{\langle\Phi|H - HP|\Phi\rangle}{\langle\Phi|1 - P|\Phi\rangle} \tag{65}$$

where $P = P_{12}$. We note that these two energies are to be compared with the expectation value

$$\langle H\rangle = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle}\,, \tag{66}$$

and, according to (12), one of them must be lower, unless both are equal. The splitting of the average energy $\langle H\rangle$ into the two levels (64) and (65) depends on the fact that P_{12} *is a constant of motion*. The identity of the two electrons leads in this way to the so-called exchange phenomenon, which was first discovered for the helium atom by Heisenberg[7]. Later Heitler and London[7] found that the same symmetry splitting and energy lowering was responsible for the stability of the covalent chemical bond.

The "exchange integral" J associated with the space function Φ is conveniently described as the difference:

$$J = \tfrac{1}{2}({}^1E - {}^3E)\,. \tag{67}$$

Choosing Φ normalized so that $\langle\Phi|\Phi\rangle = 1$ and substituting the expressions (64) and (65) into (67), we obtain

$$J = \frac{\langle\Phi|HP|\Phi\rangle - \langle\Phi|P|\Phi\rangle\langle\Phi|H|\Phi\rangle}{1 - \langle\Phi|P|\Phi\rangle^2}\,. \tag{68}$$

We note that this quantity is invariant under a change of zero-point of the energy, so that $J' = J$ for $H' = H + \alpha$. If Φ is a mixture of the two exact space-eigenfunctions involved, the expression for J

[7] W. Heisenberg, Z. Physik **38**, 411 (1926); **39**, 499 (1926); **41**, 239 (1927); W. Heitler and F. London, *ibid.* **44**, 455 (1927).

will be exact, too. The formula is also a convenient starting point for discussing approximate theories. Only if Φ from the very beginning is either symmetric or antisymmetric, there is not enough information available about the other state, and the formula for J breaks down.

The importance of the quantity J depends on the fact that, for $J > 0$, one has ${}^3E < {}^1E$ and a parallel spin alignment in the ground state, whereas, for $J < 0$, one has ${}^1E < {}^3E$ and an antiparallel spin alignment in the ground state. This simple 2-electron model is the basis both for the theory of the chemical bond and for the theory of ferromagnetism and antiferromagnetism. For further comments, we refer to a recent paper[8].

7. ANGULAR MOMENTA

The projection operator technique described here is particularly important for treating the angular momenta as constants of motion[9]. Let $\mathbf{M} = (M_x, M_y, M_z)$ be a general angular momentum expressed in units of $\hbar$, defined by the commutation relation $\mathbf{M} \times \mathbf{M} = i\mathbf{M}$. As constants of motion, we will consider the operators M^2 and M_z having the eigenvalues $k(k+1)$ with $k = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots$ and $m = k, k-1, k-2, \cdots -k$, respectively. According to (21), the associated projection operators have the form

$$O_k(M^2) = \prod_{l \neq k} \frac{M^2 - l(l+1)}{k(k+1) - l(l+1)}, \quad (69)$$

$$O_k(M_z) = \prod_{\mu \neq m} \frac{Mz - \mu}{m - \mu}, \quad (70)$$

and, according to (16), these operators applied after each other give the analysis of an arbitrary trial function into components of pure angular momenta. In the case when the trial function has a definite $M_z = m(>0)$, one can expand $O_k(M^2)$ in terms of the step-up and step-down operators $M_+ = M_x + iM_y$, $M_- = M_x - iM_y$, respectively,

$$O_{km} = (2k+1)\frac{(k+m)!}{(k-m)!} \sum_{\nu=0}^{kmax-k} (-1)^\nu \times \frac{M_-^{k-m+\nu} M_+^{k-m+\nu}}{\nu!(2k+\nu+1)!}, \quad (71)$$

which form is sometimes more convenient than (69).

This approach has been applied to the spin degeneracy problem[10], and to the problem of separating space and spin in antisymmetric wave functions. Such a problem as the evaluation of the energy of the valence bond functions including overlap integrals, which has withstood all attacks along conventional lines, can be solved by the new technique. It has been successfully used in constructing atomic wave functions[11], and it has also been adapted to the nuclear shell model[12]. Also the connection with the group theoretical treatment has been studied[13].

In a many-particle system, one has $\mathbf{M} = \sum_i \mathbf{m}(i)$ and, since the projection operators (69) and (70) hence commute with the antisymmetrizer, the symmetrizer, etc., there are no complications coming from the Pauli-principle or the general symmetry requirements. In the atomic and nuclear cases, as well as in crystal theory, this leads to a very simple treatment of the problem of the coupling of a large number of angular momenta, which should be handled on an equivalent basis.

8. CYCLIC OPERATORS AND TRANSLATIONS

Cyclic Operators

Let us consider a normal constant of motion Θ which at the same time is a cyclic of order G, so that

$$\Theta^G = 1 \quad (72)$$

It is evident that Θ is a unitary operator having the eigenvalues θ satisfying the relation $\theta^G = 1$, i.e.,

$$\theta_\kappa = \exp(2\pi i\kappa/G), \quad -\tfrac{1}{2}G \leqslant \kappa < +\tfrac{1}{2}G \quad (73)$$

According to (21) and (22), the projection operator O_κ for selecting the state associated with the eigenvalue θ_κ is then given by

$$O_\kappa = \frac{1}{G}\frac{1-\Theta^{-G}}{1-\theta_\kappa\Theta^{-1}} = \frac{1}{G}\sum_{\nu=0}^{G-1} \theta_\kappa^\nu \Theta^{-\nu}, \quad (74)$$

where we have actually used an expansion in the adjoint operator $\Theta^\dagger = \Theta^{-1}$, which is particularly convenient for our purpose. It follows from the general relations (19) that the projection operators associated with different eigenvalues select wave functions which are not only orthogonal but also noninteracting with respect to every operator H, etc., with which the operator Θ commutes.

[8] P. O. Löwdin, Technical Note No. 46, Uppsala Quantum Chemistry Group, 1960 (unpublished); Revs. Modern Phys. **34**, 1 (1962).

[9] P. O. Löwdin, Technical Note No. 12, Uppsala Quantum Chemistry Group (1958) (unpublished).

[10] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955); Technical Note No. 2, Uppsala Quantum Chemistry Group (1957) (unpublished); Coll. Int. Centre Rech. Sci. **82**, 23 (Paris 1958).

[11] R. Fieschi and P. O. Löwdin, Technical Note No. 4, Uppsala Quantum Chemistry Group (1957) (unpublished); P. O. Löwdin, Proc. R. A. Welch Found. Conf. Chem. Res. II, 5 (1958); J. L. Calais and J. Linderberg, Technical Note No. 39, Uppsala Quantum Chemistry Group (1960) (unpublished).

[12] J. L. Calais, Technical Note No. 52, Uppsala Quantum Chemistry Group, (1960) (unpublished).

[13] H. McIntosh, J. Math. Phys. **1**, 453 (1960); J. L. Calais, Technical Note No. 25, Uppsala Quantum Chemistry Group (1959) (unpublished).

Examples of cyclic constants of motions are the permutations P in the case when H is symmetric in all the coordinates, so that $HP = PH$; see Sec. 6 and a forthcoming paper.

Another important example is provided by the cyclic organic molecules, i.e., the conjugated systems of symmetry D_{Gh}, of which the benzene molecule for $G = 6$ is the most well-known case[14]. The cyclic linear chain will be discussed further below.

Translation Operators

In order to prepare for the discussion of the three-dimensional translational symmetry of a crystal, we will here briefly study the linear chain. Let the system be described by the single coordinate x, and let T be a translation operator connected with the length defined by the relation:

$$T\Psi(x) = \Psi(x + a) . \tag{75}$$

It is easily shown that $T^\dagger = T^{-1}$, i.e., that T is a unitary and hence also normal operator. The system is said to have *translational symmetry* if $HT = TH$, and T is then a normal constant of motion. The further discussion is greatly simplified if we assume that the system satisfies the Born-von Kármán boundary condition, i.e., that it exists a large number G so that

$$\Psi(x + Ga) = \Psi(x) . \tag{76}$$

The wave function is hence periodic within the ground domain defined by G. Using (75), one can write this condition in the form $(T^G - 1)\Psi(x) \equiv 0$, which means that

$$T^G = 1 , \tag{77}$$

i.e., T is a cyclic operator of order G for all wave functions satisfying the periodicity condition. We can now apply the results previously obtained for the cyclic operators: the eigenvalues of T are given by (73) and the associated projection operators by (74), so that

$$O_\kappa = \frac{1}{G} \sum_{\nu=0}^{G-1} \exp(2\pi i\nu\kappa/G) T^{-\nu} . \tag{78}$$

Using the projection technique, an arbitrary trial function $\Phi = \Phi(x)$ may be resolved into eigenfunctions to T:

$$\Phi = \sum\nolimits_\kappa \Phi_\kappa , \tag{79}$$

$$\Phi_\kappa = O_\kappa \Phi = \frac{1}{G} \sum_{\nu=0}^{G-1} e^{2\pi i\nu\kappa/G} \Phi(x - \nu a) . \tag{80}$$

The functions given by (80) are known as the "Bloch functions" after Bloch[15] who derived them in a somewhat different way. The eigenvalue relation $T\Phi_\kappa = \theta_\kappa \Phi_\kappa$ is known as the "Bloch condition":

$$T\Phi_\kappa = e^{2\pi i\kappa/G} \Phi_\kappa , \tag{81}$$

and we note finally that, according to (9), eigenfunctions associated with different eigenvalues are not only orthogonal but also noninteracting with respect to H and all other operators commuting with T. In the next section, we will show that all these theorems are easily generalized to the case of three-dimensional translational symmetry, i.e., to crystals.

Let us finally consider the special case when $\Psi(x)$ is analytic within a sufficiently large region so that one may expand $\Psi(x + a)$ in Taylor series around the point x. According to (75), one obtains

$$T = \exp\{a(d/dx)\} = \exp\{(2\pi i/h)ap\} , \tag{82}$$

where $p = (h/2\pi i)d/dx$ is the momentum operator along the chain. Any eigenfunction to p will also be an eigenfunction to T, whereas the reverse is not true.

Translational Symmetry in Crystals

An ideal crystal is characterized by the translational symmetry which is basic for understanding its fundamental properties. Let $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ be the primitive translations of the ordinary lattice and $\boldsymbol{\beta}_1$, $\boldsymbol{\beta}_2$, $\boldsymbol{\beta}_3$ of the reciprocal lattice, so that $\mathbf{a}_k \cdot \boldsymbol{\beta}_l = \delta_{kl}$. The vectors $\mathbf{m} = \mu_1\mathbf{a}_1 + \mu_2\mathbf{a}_2 + \mu_3\mathbf{a}_3$, where (μ_1,μ_2,μ_3) is a triple of integers, connect equivalent points in the ordinary lattice, whereas the vector $\mathbf{K} = i_1\boldsymbol{\beta}_1 + i_2\boldsymbol{\beta}_2 + i_3\boldsymbol{\beta}_3$ for integer (i_1,i_2,i_3) connect equivalent points in the reciprocal lattice. Let further T_1, T_2, T_3 be the translational operators connected with the primitive translations $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, respectively, and defined by the relation

$$T_\nu \Psi(\mathbf{r}) = \Psi(\mathbf{r} + \mathbf{a}_\nu) , \quad \nu = 1,2,3 . \tag{83}$$

For the operator $T(\mathbf{m})$ connected with the general translation $\mathbf{m}$ one has $T(\mathbf{m}) = T_1^{\mu_1} T_2^{\mu_2} T_3^{\mu_3}$.

The treatment of the translational symmetry is greatly simplified, if one introduces the Born-von Kármán boundary condition:

$$\Psi(\mathbf{r} + G\mathbf{a}_\nu) = \Psi(\mathbf{r}) , \tag{84}$$

where G is a very large integer, which defines the periodically repeated microcrystal. Each microcrystal contains G^3 lattice points characterized by the triple (μ_1,μ_2,μ_3), and the inequality $0 \leqslant \mu_\nu \leqslant G - 1$ defines

[14] P. O. Löwdin, J. Chem. Phys. **21**, 496 (1953).

[15] F. Bloch, Z. Physik **52**, 555 (1929); **57**, 545 (1929).

a convenient "ground domain" (G). It follows from (13) that $T_\nu^G = 1$, i.e., the three translations will now be *cyclic operators* of order G having the eigenvalues $\exp(2\pi i\kappa_\nu/G)$ where κ_ν is an integer. The associated eigenvalue problem is now easily solved by the simple projection technique[16] which does not require any use of group theory. Generalizing the results in the preceding section to three dimensions, it is now convenient to label the simultaneous eigenfunctions to T_1, T_2, T_3 either by the triple of integers $(\kappa_1,\kappa_2,\kappa_3)$ or by the reduced wave vector:

$$\mathbf{k} = (\kappa_1\boldsymbol{\beta}_1 + \kappa_2\boldsymbol{\beta}_2 + \kappa_3\boldsymbol{\beta}_3)/G\,, \tag{85}$$

$$-G/2 < \kappa_\nu < +G/2\,, \tag{86}$$

where the inequality (86) defines a ground domain (G) containing G^3 points in k space. The eigenvalue relation may now be written in the form:

$$T(\mathbf{m})\Psi(\mathbf{k},\mathbf{r}) = \Psi(\mathbf{k},\mathbf{r}+\mathbf{m}) = \exp\{2\pi i\mathbf{k}\cdot\mathbf{r}\}\,\Psi(\mathbf{k},\mathbf{r})\,. \tag{87}$$

For $\mathbf{m}$ equal to the primitive translations, this gives the famous Bloch condition. The corresponding eigenfunctions may be found by means of the projection operators:

$$O_\mathbf{k} = G^{-3}\sum_{\mathbf{m}}^{(G)} \exp\{2\pi i\mathbf{k}\cdot\mathbf{m}\}\,T(-\mathbf{m})\,, \tag{88}$$

which fulfil the following basic relations:

$$O_\mathbf{k}^2 = O_\mathbf{k}\,,\quad O_\mathbf{k}^\dagger = O_\mathbf{k}\,,\quad O_\mathbf{k}O_\mathbf{l} = 0(\mathbf{k}\neq\mathbf{l})\,, \tag{89}$$

$$T(\mathbf{m})O_\mathbf{k} = \exp\{2\pi i\mathbf{k}\cdot\mathbf{m}\}\,O_\mathbf{k}\,. \tag{90}$$

One has further the "resolution of the identity" $1 = \sum_\mathbf{k} O_\mathbf{k}$ which implies that every trial function $\Phi(\mathbf{r})$ satisfying the periodicity condition (84) may be resolved into *Bloch components*, i.e.,

$$\Phi(\mathbf{r}) = \sum_{\mathbf{k}}^{(G)} O_\mathbf{k}\Phi(\mathbf{r}) = \sum_{\mathbf{k}}^{(G)} \Phi(\mathbf{k},\mathbf{r})\,, \tag{91}$$

which are not only orthogonal but also *noninteracting* with respect to every operator Ω which commutes with the translations T_1, T_2, T_3 according to the general formulas

$$O_\mathbf{k}^\dagger O_\mathbf{l} = 0\,,\quad O_\mathbf{k}^\dagger\Omega O_\mathbf{l} = 0\,, \tag{92}$$

for different reduced wave vectors ($\mathbf{k}\neq\mathbf{l}$). The fundamental relations (88)–(92) are easily verified directly. For a more detailed study of crystal theory on this basis, we will refer to another paper[17].

APPENDIX

Every normal operator Λ may be written as the sum of a Hermitean and an anti-Hermitian operator:

$$\Lambda = \tfrac{1}{2}(\Lambda+\Lambda^\dagger) + \tfrac{1}{2}(\Lambda-\Lambda^\dagger) = A + iB\,,$$
$$\Lambda^\dagger = \tfrac{1}{2}(\Lambda+\Lambda^\dagger) - \tfrac{1}{2}(\Lambda-\Lambda^\dagger) = A - iB\,,$$

where $A = \frac{1}{2}(\Lambda+\Lambda^\dagger)$ and $B = \frac{1}{2i}(\Lambda-\Lambda^\dagger)$ are self-adjoint. One has

$$\Lambda\Lambda^\dagger = A^2 + B^2 - i(AB-BA)\,,$$
$$\Lambda^\dagger\Lambda = A^2 + B^2 + i(AB-BA)\,,$$

and the operator Λ is normal, if and only if, $AB = BA$. On the other hand, every pair of commuting Hermitean operators may be combined into a normal operator. From the eigenvalue relations

$$\Lambda\Phi_k = \lambda_k\Phi_k\,,\quad \Lambda^\dagger\Phi_k = \lambda_k^*\Phi_k\,,$$

with $\lambda_k = a_k + ib_k$ follows, after addition and subtraction, that

$$A\Phi_k = a_k\Phi_k\,,$$
$$B\Phi_k = b_k\Phi_k\,.$$

Hence Φ_k is a simultaneous eigenfunction to the Hermitian operators A and B.

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[16] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955); p. 1512; Advances in Phys. **5**, 1 (1956); p. 56 ff.

[17] P. O. Löwdin, Technical Note No. 67, Uppsala Quantum Chemistry Group (1961); J. Appl. Phys. **33**, 251 (1962).