Complex Variables in Quantum Mechanics

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The general representation theory of quantum mechanics requires one to represent the states of a dynamical system by functions of a set of real variables q'_r, each of which has a domain consisting of either discrete points or a continuous range of points, or possibly both together. A dynamical variable is represented by a function of two such sets of real variables q'_r and q''_r forming a generalized "matrix". In this paper we shall show that in certain cases it is advantageous to consider some of our variables q'_r as complex variables and to suppose the representatives of states and dynamical variables to depend on them in accordance with the theory of functions of a complex variable.

In the usual theory the domains of the q'_r's are the eigenvalues of certain observables q_r. This significance of the q'_r's of course gets lost when we consider them as complex variables, but we have, however, some beautiful mathematical features appearing instead, and we gain a considerable amount of mathematical power for the working out of particular examples.

1—The Fundamental Theorem

Suppose we have in our representation a variable q whose domain consists of all points from 0 to ∞. This q may be, for example, the radius r in a system of polar co-ordinates, or a cartesian co-ordinate of a particle which is restricted to lie in a half of total space by an impenetrable plane barrier. The wave function representing any state will now be a function $(q\,|)$ of the variable q and of other variables which may be necessary to describe other degrees of freedom, which we do not need to mention explicitly.

Let us pass to a representation in terms of the momentum variable p conjugate to q. The wave function representing a state will now be

$$(p\,|) = h^{-\frac{1}{2}}\int_0^\infty e^{-ipq/\hbar}\,dq(q\,|). \tag{1}$$

In the usual theory the variable p is restricted to be real, but we shall now allow it to be complex. We consider the function $(p\,|)$ as a function of a complex variable defined by (1) for all values of p in the lower half-plane (i.e. all values of p for which the pure imaginary part of p is a negative multiple of i). We can easily see that *it must be regular in this domain.* For this purpose we note the physical requirement that the function $(q|)$ must be everywhere finite, or else contain singularities of a kind (such as the δ function) which give a finite integral when multiplied by a continuous function and integrated. Further, $|(q|)|$ must remain bounded as $q \to \infty$. It follows that when p is in the lower half-plane the integral (1) is absolutely convergent, and thus $(p|)$ cannot become infinite. Also, the function $(p|)$ defined by (1) in the lower half-plane is always single-valued and thus cannot have branch points in this domain. It follows that it must be regular in this domain.

By the principle of analytical continuation we may extend the domain of definition of our function $(p|)$ over the real axis into the upper half-plane. The formula (1) will still be valid on the real axis, except possibly at certain points where the function $(p|)$ has a singularity, but will not be valid beyond, unless $(q|)$ tends to zero very rapidly as q tends to infinity.

The conjugate imaginary of a wave function $(p|)$ is a function $(|p)$ which is regular for all values of p in the upper half-plane. A dynamical variable α is represented by a function $(p'|\alpha|p'')$ of the two variables p' and p'', which is similar to $(p|)$ in its dependence on p' and to $(|p)$ in its dependence on p''. Thus $(p'|\alpha|p'')$ is a regular function of p' in the lower half-plane and a regular function of p'' in the upper half-plane.

In our general scheme of quantum mechanics, whenever we have to do an integration over p, it will be of the type of an integral along the real axis

$$\int_{-\infty}^{\infty} (\ldots|p)\,dp(p|\ldots), \tag{2}$$

where the integrand contains two factors, the first $(\ldots|p)$ being similar to $(|p)$ and therefore regular in the upper half-plane and the second $(p|\ldots)$ being similar to $(p|)$ and therefore regular in the lower half-plane. From the theory of functions we know that we may distort the path of integration in any way provided we do not pass over a singularity in the integrand. We are thus led to our fundamental theorem, that *in performing an integration* (2), *we may choose any contour extending from $-\infty$ to ∞ such that the first factor of the integrand is regular everywhere above this contour and the second is regular everywhere below it.*

It may happen that the integral (2) along the real axis is indefinite as it stands, owing to the presence of certain kinds of singularity in the integrand on the real axis. Let us examine what interpretation quantum mechanics requires us to give to the integral in such a case.

The most important kind of singularity is a simple pole. Suppose we have a simple pole on the real axis in the second factor $(p|\ldots)$. Then this factor must correspond to a wave function $(q|\ldots)$ in the q variable of the form e^{iaq} for large q, a being some real number. To see this, we put

$$(q|) = h^{\frac{1}{2}} e^{iaq}$$

in (1), obtaining

$$(p|) = \int_0^\infty e^{-ipq/\hbar} e^{iaq} dq$$

$$= \frac{i\hbar}{p-a\hbar}\left[e^{-i(p-a\hbar)q/\hbar}\right]_0^\infty \tag{3}$$

$$= \frac{-i\hbar}{p-a\hbar} \tag{4}$$

for p in the lower half-plane, and also for p on the real axis, except at the point $p = a\hbar$. (This involves neglecting the oscillating part of (3) for $q = \infty$, which is the usual practice in quantum mechanics.) Thus we have a simple pole at the point $a\hbar$.

When the second factor in (2) is of the form (4), to obtain the value of the integral (2) according to the usual procedure of quantum mechanics, we must first substitute for $(p|)$ the value (3) taken to some large definite upper limit g instead of to ∞, and then, after evaluating the integral, make $g \to \infty$. This gives us for the critical part of the integral from $a\hbar - \epsilon$ to $a\hbar + \epsilon$, ϵ being small,

$$\int_{a\hbar-\epsilon}^{a\hbar+\epsilon} (\ldots|p)\, dp(p|) = i\hbar \int_{a\hbar-\epsilon}^{a\hbar+\epsilon} (\ldots|p)\,[e^{-i(p-a\hbar)g/\hbar} - 1]\frac{dp}{p-a\hbar}$$

$$= i\hbar \int_{-g\epsilon/\hbar}^{g\epsilon/\hbar} \left(\ldots|a\hbar + \frac{\hbar x}{g}\right)[e^{-ix} - 1]\frac{dx}{x},$$

where $p = a\hbar + \hbar/g\,.x$. In the limit $g \to \infty$, this becomes

$$i\hbar(\ldots|a\hbar)\int_{-\infty}^{\infty}[e^{-ix} - 1]\,dx/x = \pi\hbar(\ldots|a\hbar).$$

This value for the integral (2) from the point $a\hbar - \epsilon$ to the point $a\hbar + \epsilon$ is the same as that which we should have obtained if we had done a contour integration along a small semicircle in the lower half-plane with centre $a\hbar$ and radius ϵ.

Thus we see that, when we are doing an integration of the type (2) in which there is a simple pole on the real axis in the second factor of the integrand, we must avoid the singularity by distorting our path of integration into the lower half-plane. Similarly, it may be shown that if there is a simple pole in the first factor of the integrand, we must avoid it by distorting our path of integration into the upper half-plane. These distortions are in the directions allowed by our fundamental theorem.

Our theory would break down if both factors of the integrand had a simple pole at the same point on the real axis. This case, however, is never met with in practice. It would make the integral (2) infinitely great, according to the quantum-mechanical significance.

Poles of higher order than the first on the real axis will not ordinarily occur in our integrand (2), since a wave function $(p|)$ involving such a pole would correspond to a wave function $(q|)$ which increases without limit as $q \to \infty$ and is therefore not allowed physically. We may, however, sometimes wish to work with an operator whose representative $(p'|\alpha|p'')$ involves such a pole in p' or p''. In these cases the operator will be defined so that, in performing an integration (2), we must avoid the singularity by distorting our path of integration from the real axis in the direction allowed by our fundamental theorem.

If a singularity of a different nature from a pole (i.e. a branch point without a pole superposed) occurs on the real axis, it will not give rise to any uncertainty in the integration through it. We may then distort the path of integration in the direction allowed by our fundamental theorem without altering the value of the integral. In this way we see that *our fundamental theorem is always valid, with any array of singularities on the real axis.*

2—Conditions at Infinity

It is a rather ugly feature of our fundamental theorem that the path of integration must begin at $-\infty$ and end at ∞. We might even sometimes meet with divergence at these points. It is thus necessary to make a closer investigation of the conditions at infinity.

Let us suppose first that both the factors in the integrand in (2) are regular at infinity, so that for large values of p they can be expanded in power series in p^{-1}, and let us suppose further that the constant terms in these series vanish. Then we have for large p

$$\left.\begin{aligned}(p|\ldots) &= a_1p^{-1}+a_2p^{-2}+a_3p^{-3}+\ldots\\ (\ldots|p) &= b_1p^{-1}+b_2p^{-2}+b_3p^{-3}+\ldots\end{aligned}\right\}. \tag{5}$$

Thus the total integrand is of the form

$$(\ldots|p)(p|\ldots) = c_2p^{-2}+c_3p^{-3}+\ldots. \tag{6}$$

If this is integrated over a large semicircle of radius R, extending from the point R to the point $-R$ in either the upper or the lower half-plane, the result will tend to zero as $R \to \infty$. Thus we may take as our path of integration in (2) a closed contour, extending from $-R$ to R along the real axis and going back to $-R$ along a large semicircle in either the upper or the lower half-plane.

Let us now suppose one of the factors (5) contains a constant term, say the first, so that we have

$$(p\,|\,...) = a_0 + a_1 p^{-1} + a_2 p^{-2} + \dots. \tag{7}$$

The integrand (6) will now contain the term $a_0 b_1 p^{-1}$ and (provided $b_1 \neq 0$) it will no longer have a precise meaning to integrate it from $-\infty$ to ∞. Let us examine what meaning quantum mechanics would require us to give to this integral.

We must see what the important terms in (7) and the second of equations (5) correspond to in the q-representation. The term a_0 in (7) would be given, according to (1), by the q-wave function

$$(q\,|\,0) = a_0 h^{\frac{1}{2}}\,\delta(q),$$

the function $\delta(q)$ here being understood to lie entirely on the positive side of the point $q = 0$, so that

$$\int_0^\infty \delta(q) f(q)\, dq = f(0). \tag{8}$$

Again, the $b_1 p^{-1}$ term in the second of equations (5) would, according to the conjugate imaginary of equation (1), namely

$$(\,|\,p) = h^{-\frac{1}{2}} \int_0^\infty (\,|\,q)\, dq\, e^{ipq/\hbar},$$

be given by the constant q-wave function

$$(1\,|\,q) = -ih^{\frac{1}{2}}\hbar^{-1} b_1.$$

The integrated product of these two wave functions is

$$\int_0^\infty (1\,|\,q)\, dq (q\,|\,0) = -2\pi i a_0 b_1 \int_0^\infty \delta(q)\, dq = -2\pi i a_0 b_1,$$

the δ function being interpreted in accordance with (8). From the transformation theory of quantum mechanics, the product must have the same value when evaluated in the p-representation, so that we must have

$$-2\pi i a_0 b_1 = \int (1\,|\,p)\, dp (p\,|\,0) = a_0 b_1 \int p^{-1}\, dp.$$

The domain of integration here is along the real axis, the pole at the origin being skirted, in accordance with our previous work, by a deviation into the upper half-plane, since the singularity occurs in the first factor of the integrand. It is now clear that, to get the right result, we must complete our path of integration by a large semicircle in the lower half-plane and make it into a closed contour.

We can now see that, if a constant term appears in either of the expansions (5), we have to avoid the point at infinity in our path of integration in a somewhat analogous way to that in which we must avoid a simple pole on the real axis. If the constant term appears in the second factor, we must close up our path of integration by a large semicircle in the lower half-plane, and similarly if it appears in the first factor, we must close up our path of integration by a large semicircle in the upper half-plane. We cannot have a constant term in both factors. It would make the integral infinitely great, like a simple pole in both factors at the same point on the real axis.

We can now generalize our fundamental theorem to read as follows: *In performing an integration* (2) *we may choose any closed contour which divides the complex plane into two regions, such that the first factor of the integrand is regular in one of the regions* (*the one on the left-hand side of the contour*), *and the second factor is regular in the other. A constant term in either factor is here to be counted as having a singularity at the point at infinity.*

If either of the expansions (5) contains positive powers of p, these would correspond in the q-representation to terms involving derivatives of $\delta(q)$. Such terms do not seem to be of any practical importance as wave functions. We might possibly have to deal with an operator whose representative contains terms of this type, in which case we would define the operator in such a way that, when its representative occurs in an integrand, we must treat the singularity at infinity in accordance with our generalized fundamental theorem. Other independent types of singularity that may occur at infinity in the integrand would not affect the validity of our generalized fundamental theorem.

3—Some Simple Operators

To obtain the representatives of operators in our complex p-representation, it is often not very convenient to make a direct transformation from the q-representation, but it is better to get the result by an argument which works entirely with the p-representation. The following work provides some simple illustrations of this.

We do not need to use the δ function in connexion with our complex variable p. We have the reciprocal function playing the part of the δ function. For example, the "unit matrix" is now

$$(p'|1|p'') = \frac{-i}{2\pi}\frac{1}{p'-p''}. \tag{9}$$

To verify this, let us multiply this matrix into an arbitrary function $(p'|)$ in accordance with our fundamental theorem. The result is

$$\frac{-i}{2\pi}\int\frac{1}{p'-p''}\,dp''(p''|), \tag{10}$$

the integral being taken along a closed contour such that the factor $1/(p'-p'')$ is regular in the domain on the left of the contour and the factor $(p''|)$ is regular in the domain on the right. Thus the simple pole at p' in the first factor must occur in the domain on the right of the contour, and must be the only singularity of the integrand in this domain. We may take the contour to be a small circle going clockwise round the pole at p', and we then see that the integral has the value $(p'|)$. Thus the right-hand side of (9) plays the part of the unit matrix.

Similarly, the operator of multiplication by p is represented by the matrix

$$(p'|p|p'') = \frac{-i}{2\pi}\frac{p'}{p'-p''}, \tag{11}$$

since when this matrix is multiplied into an arbitrary function $(p'|)$ in accordance with our rules, the result will be (10) multiplied by the factor p'. It is a little surprising that the matrix (11) is not hermitian. Its conjugate, obtained by interchanging p' and p'', and writing $-i$ for i, is

$$(p'|\overline{p}|p'') = \frac{-i}{2\pi}\frac{p''}{p'-p''}, \tag{12}$$

which differs from (11) by a constant. If we multiply the matrix (12) into an arbitrary function $(p'|)$, the constant will make its presence felt by the fact that the first factor in the integrand of

$$\int(p'|\overline{p}|p'')\,dp''(p''|)$$

must be counted as having a singularity at infinity, and thus we must choose our path of integration such that the point at infinity is in the domain on the right, as well as the point p'. We may thus choose the path as in fig. 1, when the integral around the large circle will give the contribution of the constant part of (12).

To understand the physical significance of this constant part, we note that it is the representative of $i\hbar\,\delta(q)$, thus

$$\begin{aligned} i\hbar(p'|\delta(q)|p'') &= i\hbar\,h^{-1}\int_0^\infty\int_0^\infty e^{-ip'q'/\hbar}\,dq'\,\delta(q')\,\delta(q'-q'')\,dq''\,e^{ip''q''/\hbar} \\ &= i/2\pi \\ &= (p'|\overline{p}-p|p''), \end{aligned} \tag{13}$$

where $\delta(q)$ is assumed to lie in the domain 0 to ∞, in accordance with (8). Thus the lack of hermitianness of the operator p is associated with a δ function at $q = 0$ and is of importance only when we operate on wave functions in q which do not vanish at the origin.

The dynamical variable q corresponds to the operator $i\hbar\, d/dp$. This is represented by the matrix

$$(p'|q|p'') = \frac{-\hbar}{2\pi}\frac{1}{(p'-p'')^2}, \tag{14}$$

because, when we multiply this matrix into an arbitrary $(p'|)$, we get

$$\frac{-\hbar}{2\pi}\int\frac{1}{(p'-p'')^2}dp''(p''|),$$

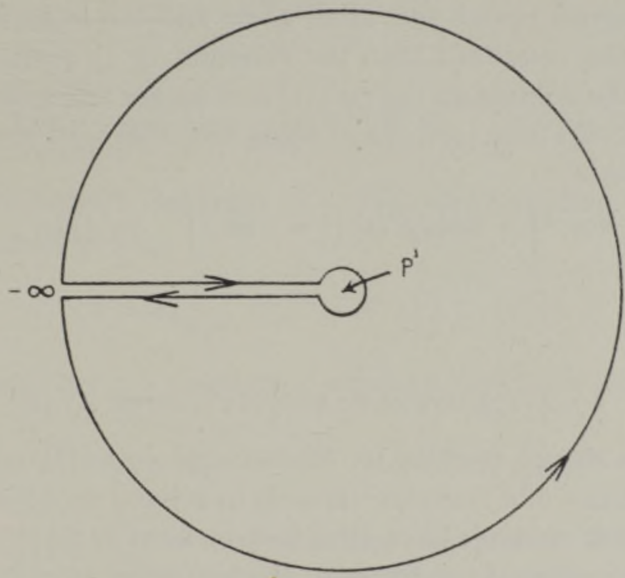

Fig. 1

the path of integration being the same as with (10), which gives

$$i\hbar\frac{d(p'|)}{dp'}.$$

Since q corresponds to $i\hbar$ times the operator of differentiation, q^{-1} must correspond to $-i\hbar^{-1}$ times the operator of integration. There is an arbitrary constant of integration associated with the operation of integration. This corresponds to the fact that we may add on an arbitrary multiple of $\delta(q)$ to the result of an operation of multiplication by q^{-1}. If we want to have no multiple of $\delta(q)$ in the result, we must choose our constant of integration so that when our wave function is expanded in the form (7) the constant term vanishes. This is equivalent to putting the point at infinity as the lower limit in our integral.

We may represent q^{-1} by the matrix

$$(p'|q^{-1}|p'') = -h^{-1}\log(p'-p'').$$

To verify this result, we note that when we multiply this matrix into an arbitrary $(p'|)$ we get

$$-h^{-1}\int \log(p'-p'')\,dp''(p''|), \tag{15}$$

where the path of integration must be such that the point p' and the point at infinity are in the domain on the right, and may thus be chosen as in fig. 1. The integrals round the small circle and the large circle will then vanish (from the condition that the function $(p'|)$ must not have any singularity in the domain on the right†) and we are left with the difference of the integral (15) from $-\infty$ to p' along two sheets of the log function, which difference is

$$-h^{-1}\int_{-\infty}^{p'} 2\pi i\,dp''(p''|) = -i\hbar^{-1}\int_{-\infty}^{p'}(p''|)\,dp'',$$

as required.

4—Application to the Hydrogen Atom

The present theory enables us to use the powerful methods of the theory of functions of a complex variable in solving problems in quantum mechanics. These methods have already been used in many cases, notably in Schrödinger's original treatment of the hydrogen atom in 1926, but we have here put them on a systematic basis. As an example we shall now show how the treatment of the hydrogen atom appears in the present theory.

We take the radius r to be our co-ordinate q, and we then have to solve the differential equation

$$\left[\hbar^2\left\{\frac{d^2}{dq^2}+\frac{2}{q}\frac{d}{dq}-\frac{n(n+1)}{q^2}\right\}+2m\left(W+\frac{e^2}{q}\right)\right](q|) = 0, \tag{16}$$

† We require also the condition that the expansion of $(p'|)$ in the form (7) shall contain no p^{-1} term, as well as no constant term. If this condition is not fulfilled, the integral round the large circle will be infinitely great. The wave function $(p'|)$ then corresponds to a wave function $(q'|)$ which does not vanish at the origin and to which therefore the operator q^{-1} cannot legitimately be applied, as the square of the modulus of the resulting function would not be integrable.

W being the eigenvalue, and n being the order of the spherical harmonic concerned. Expressed in terms of the p variable, this equation reads

$$\left[-p^2+2\int p+n(n+1)\int\int+2mW-2ime^2\hbar^{-1}\int\right](p|)=0, \tag{17}$$

the integral sign being here used as an operator (in the sense of the preceding section with no constant term).

To obtain the solution of (17), we simply have to transcribe Schrödinger's solution of (16) into the p-representation. Schrödinger first eliminates the term $n(n+1)/q^2$ in (16) by making a transformation of the type

$$(q|)=q^{\alpha}(q|)^*$$

with $$\alpha=n \text{ or } -n-1.$$

This leads to

$$\left[\hbar^2\left\{\frac{d^2}{dq^2}+\frac{2(\alpha+1)}{q}\frac{d}{dq}\right\}+2m\left(W+\frac{e^2}{q}\right)\right](q|)^*=0, \tag{18}$$

which is Schrödinger's equation (7′). The corresponding transformation in the p-representation is

$$(p|)=\left(\frac{d}{dp}\right)^{\alpha}(p|)^* \quad \text{or} \quad \left(\int\right)^{-\alpha}(p|)^*, \tag{19}$$

according to whether α is positive or negative, and leads to the equation

$$\left[-p^2+2(\alpha+1)\int p+2mW-2ime^2\hbar^{-1}\int\right](p|)^*=0. \tag{20}$$

The solution of (18) is given by Schrödinger's equation (12) in the form of an integral over a complex variable z, which is obviously playing the part of $i/\hbar$ times our variable p. The integrand here, apart from the factor $e^{ipq/\hbar}$, is therefore the solution of (20). Thus

$$(p|)^*=(p-c_1)^{\alpha_1-1}(p-c_2)^{\alpha_2-1}, \tag{21}$$

where c_1 and c_2 are the roots of

$$p^2-2mW=0$$

and $$\alpha_1=\frac{-2ime^2/\hbar}{c_1-c_2}+\alpha+1, \quad \alpha_2=\frac{-2ime^2/\hbar}{c_2-c_1}+\alpha+1.$$

For large values of p, we have

$$(p|)^*=p^{\alpha_1+\alpha_2-2}=p^{2\alpha},$$

and hence $(p|)$ is proportional to p^{α}. Now we require $(p|)$ not to have any singularity at ∞ and so we must take the negative value for α, namely $-n-1$.

For $n>0$, we may use the other solution $\alpha = n$ provided we discard from it all the terms involving non-negative powers of p in its expansion in the form (5) in descending powers of p. One can easily see that this must give the previous solution again, since there can be no p^{-1}, $p^{-2} \dots p^{-n}$ terms in the $\alpha = n$ solution on account of its being, according to (19), the n-fold derivative of $(p|)^*$. The discard will be taken into account automatically if we arrange to have the point at infinity on the right-hand side of our contour of integration (instead of the left-hand side as it should be according to the fundamental theorem) whenever we use this solution in an integrand.

Our wave function $(p|)$ has singularities at the two points c_1 and c_2. For any positive value of W, these points are both on the real axis and our wave function is alright. But for negative W, one of these points, say c_1, will be in the lower half-plane, where our wave function is not allowed to have any singularity. We now get a permissible wave function only when the point c_1 becomes regular owing to α_1 being a positive integer, i.e. when

$$\frac{me^2/\hbar}{(-2mW)^{\frac{1}{2}}} - n$$

is a positive integer, s say. This leads to the Bohr formula

$$W = -\frac{me^4}{2\hbar^2(n+s)^2}.$$

The case of $n = 0$ is a little exceptional in that then (21) is not really a solution of (20). This may be seen from the fact that (21) is now of the form p^{-2} for large p, so that the first term of (20) will contribute a constant for large p, and no other term in (20) can contribute another constant to cancel with this one. Thus, we should have a constant term on the right-hand side of (20), which would correspond to a $\delta(q)$ term on the right-hand side of (18), implying a failure of our solution at the origin. The fact that this solution is allowed by quantum mechanics shows that our theory does not always automatically give the correct boundary conditions at the origin.

The above example shows the great superiority of the p-representation in dealing with this kind of problem, in that it allows the wave function $(p|)^*$ to be expressed in finite form. In fact, we may say that Schrödinger's (1926) treatment is effectively a treatment in the p-representation, his complex variable z playing the part of our p. Any subsequent calculations that we may wish to make, such as the evaluation of matrix elements, may be conveniently carried out with the wave functions $(p|)^*$ and the machinery of contour integration. The work will be specially simple for the discrete states, since the wave function then has only one singularity, and any contour integration may be performed round a small circle enclosing this singularity.

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On the Pattern of Proteins

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1—Introduction

Any theory as to the structure of the molecule of simple native protein must take account of a number of facts belonging to many different domains of science. As our starting point we take the following:

(*a*) The molecules are largely, if not entirely, made up of amino- and imino-acid molecules. They contain peptide linkages, but in general few —NH_2 groups not belonging to side chains, and, in some cases, possibly none (Cohn 1928).

(*b*) There is a general uniformity among proteins of widely different chemical composition (Jordan Lloyd 1926; Astbury and Lomax 1935); presumably, therefore, there is a simple general plan in the arrangement of the amino- and imino-acid residues characteristic of proteins in general.

(*c*) A large number of crystalline proteins have highly symmetrical crystals (Schimper 1881); unlike the low symmetrical forms of most organic compounds, these usually possess triad or hexad axes. Insulin (Crowfoot 1935) and pepsin (Bernal and Crowfoot 1934) crystals are of trigonal type. In the case of insulin this symmetry has been shown to be possessed by the molecules themselves (Crowfoot 1935). In other cases also, by analogy