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SYMMETRY GROUP OF THE HYDROGEN MOLECULAR ION (A SYSTEM WITH SEPARABLE VARIABLES)

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A larger (than the geometric) symmetry group of the hydrogen molecular ion is found. In terms of this symmetry, the von Neumann—Wigner theorem is found to be applicable to the hydrogen molecular ion. The results are extended to the case of an arbitrary system with separable variables.

LET the Hamiltonian H of a certain quantum-mechanical system be invariant with respect to the group of transformations G. Then the eigenvalues of the operator H (energy levels, or terms) may be classified according to the irreducible representations of the group G. In most cases the transformations of the group G are geometrical, i.e., reduce to rotations and reflections of ordinary space. However, there exist quantum mechanical systems which require for the description of all of its properties more than purely geometrical transformations G. The hydrogen atom is an example of such a system. The purely geometrical symmetry group G is the group O_3. However, this group is not capable of explaining the multiplicity of the degeneracy of the hydrogen atom energy levels. It was shown by Fock[1] that the complete symmetry group $\tilde{G}$ of the hydrogen atom, which explains all its properties (including the multiplicity of the degenerate energy levels), is isomorphic to the group of rotations in the four dimensional space O_4. In this example the symmetry group $\tilde{G}$ contains along with the purely geometrical transformations G transformations of a more general type.

In this paper we want to bring another example of a physical system where the complete symmetry group does not reduce to purely geometrical transformations. We consider the molecular hydrogen ion (and also the more general problem of the motion of an electron in the field of two different Coulomb centers with charges Z_1 and Z_2). The geometrical symmetry group of this problem is the group O_2, which contains rotations about the axis of the molecule and reflections in the planes passing through the molecular axis. In the case of the molecular hydrogen ion ($Z_1 = Z_2 = 1$) one has an additional element of symmetry—reflection in a plane lying in the middle between the two nuclei. What then distinguishes the molecular hydrogen ion from other two-atomic molecules and requires us to search for a higher (than geometrical) symmetry group for this system? It turns out that the molecular hydrogen ion H_2^+ and the problem on the motion of an electron is the field of two different Coulomb centers do not obey (if one takes this H_2^+ symmetry to mean the geometrical symmetry) the von Neumann—Wigner theorem[2] which forbids the crossing of terms with the same symmetry. In the case of the two-atomic molecule, a special case of which is the molecular hydrogen ion H_2^+, this theorem forbids the crossing of electronic terms with the same values of the quantum number Λ (the absolute value of the projection of the orbital angular momentum of the electron on the molecular axis) and the same symmetry with respect to reflection in the plane situated between the nuclei.

Let us recall (see Bethe[3]) the main results relevant to the molecular hydrogen ion. As is well known the problem of determining the electronic terms for the molecular hydrogen ion allows a complete separation of variables in the elliptic coordinate system ξ, η, φ:

$$\xi = \frac{r_1 + r_2}{R}, \qquad \eta = \frac{r_1 - r_2}{R}, \tag{1}$$

where r_1 and r_2 are the distances from the nuclei, and R is the distance between the nuclei. The angle φ is measured around the molecular axis. If one looks for a stationary solution of the Schrödinger equation in the form

$$\psi = F(\xi) G(\eta) e^{im\varphi}, \tag{2}$$

then for each of the factors $F(\xi)$ and $G(\eta)$ one obtains an equation of the Sturm-Liouville type:

$$\frac{d}{d\xi}\left[(\xi^2-1)\frac{dF}{d\xi}\right] + \left[-\frac{m^2}{\xi^2-1}+R(Z_1+Z_2)\xi-p^2\xi^2+A\right]F=0, \qquad (3)$$

$$\frac{d}{d\eta}\left[(1-\eta^2)\frac{dG}{d\eta}\right] + \left[-\frac{m^2}{1-\eta^2}+R(Z_2-Z_1)\eta+p^2\eta^2-A\right]G=0 \qquad (4)$$

(to the molecular hydrogen ion corresponds the case $Z_1 = Z_2 = 1$), where

$$p^2 = -R^2E/2, \qquad (5)$$

Here E is the energy (excluding the Coulomb repulsion of the nuclei), and A is a separation constant. It is convenient to characterize each of the factors $F(\xi)$ and $G(\eta)$ by the number of nodes (zeroes). Since each of these two equations contains m^2 and the common separation constant A, the eigenvalues of the energy and the eigenfunctions have the form

$$E_{n_1 n_2 |m|}(R) = E(n_1, n_2, m^2; R), \qquad (6)$$

$$\psi_{n_1 n_2 m} = F_{n_1 n_2 |m|}(\xi)\, G_{n_1 n_2 |m|}(\eta)\, e^{im\varphi}. \qquad (7)$$

In order to make clear which of the electronic terms (6) cross, it is sufficient to know what these terms go into in two limiting cases: for R = 0 and R = ∞. As the distance R between the nuclei is varied the number of nodes n_1 and n_2 cannot change.1) [3] When R = 0 our system goes over into a unified hydrogen atom with energy levels (expressed in terms of elliptic quantum numbers n_1, n_2, m) described by the formula[3]

$$E(n_1, n_2, m^2; 0) = -2(n_1+n_2+|m|+1)^{-2}. \qquad (8)$$

At R = ∞, we have infinitely separated atom and ion of hydrogen. The energy in this limiting case has the form[3]

$$E(n_1, n_2, m^2; \infty) = -{}^1/_2(n_1+n_2'+|m|+1)^{-2}, \qquad (9)$$

where

$$n_2' = \begin{cases} n_2/2, & \text{if } n_2 \text{ is even} \\ (n_2-1)/2, & \text{if } n_2 \text{ is odd} \end{cases} \qquad (10)$$

Knowing the energy levels in these two limiting cases it is easily shown which of the terms of the same symmetry certainly cross. These are, for example, the terms $E_{300}(R)$ and $E_{040}(R)$. Examples for crossing of terms in the same symmetry in the case of the motion of an electron in the field of two different Coulomb centers may be found in the work of Gershteĭn and Krivchenkov.[4]

Let us show now that the here-demonstrated violation of the von Neumann-Wigner theorem is only apparent and due to the fact that the geometrical symmetry group does not exhaust the entire symmetry which our system possesses. In the work of Gershteĭn and Krivchenkov[4] (and also in the work of Smirnov[5]) the inapplicability of the von Neumann—Wigner theorem to the molecular hydrogen ion was connected with the separability of variables in this problem. It is therefore natural to ascertain the symmetries possessed by systems that allow a complete separation of variables. If the variables separate in the Schrödinger equation, then they also separate in the Hamilton-Jacobi equation which arises in the corresponding classical system.

Let the classical Hamilton-Jacobi equation of some mechanical system allow complete separation of variables, i.e., let the action have the form

$$S_0 = \sum_{i=1}^{f} S_i(q_i), \qquad (11)$$

where f is the number of degrees of freedom of the system under consideration. In that case as is well known[6], we can use a canonical transformation to go over to new variables, where the role of generalized momenta is played by the action variables

$$I_i = \frac{1}{2\pi}\oint \frac{\partial S_0}{\partial q_i}\, dq_i, \qquad (12)$$

and the generalized coordinates are the so-called angle variables

$$w_i = \partial S_0 / \partial I_i. \qquad (13)$$

If the Hamiltonian function is expressed in terms of these new variables then it will contain only the action variables I_i:

$$H = H(I_1, I_2, \ldots, I_f). \qquad (14)$$

Thus the angle variables are cyclic. It is obvious that the Hamiltonian function (14) is invariant with respect to a shift of the origin from which the angles w_i are measured by an arbitrary quantity α_i. A change of the origin from which the angles w_i are measured is equivalent to a rotation in certain planes. In order to find these planes let us perform

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1)In view of the continuous dependence on R, the number of nodes can change only as a result of confluence of two nodes; this, however is impossible because the solution of a second-order equation cannot have a multiple zero.

one more canonical transformation to the variables P_i and Q_i:

$$P_i = \sqrt{2I_i}\cos w_i, \qquad Q_i = \sqrt{2I_i}\sin w_i. \tag{15}$$

In terms of the variables P_i and Q_i, the Hamiltonian has the form

$$H = H\left(\frac{P_1^2+Q_1^2}{2}, \frac{P_2^2+Q_2^2}{2}, \dots, \frac{P_f^2+Q_f^2}{2}\right). \tag{16}$$

It is now obvious that our Hamiltonian is invariant with respect to rotations by arbitrary angles α_i in the P_i and Q_i planes (it is important to emphasize that these rotations are canonical transformations). Since rotations in different planes are entirely independent, the symmetry group of our mechanical system has the form

$$SO_2 \otimes SO_2 \otimes \dots \otimes SO_2, \tag{17}$$

where SO_2 is the group of pure rotations (without reflections) in a plane.

Thus the symmetry group of the mechanical system for which the Hamilton-Jacobi equation can be completely separated has the form of a direct product of two-dimensional rotation groups, one SO_2 group for each degree of freedom. It is not hard to see that the resultant symmetry does not reduce to geometrical, since the rotation SO_2 takes place not in configuration space (as is the case for the conventional geometrical symmetry) but in phase space.

In the previous considerations it was presupposed that the mechanical system under discussion does not contain some geometrical axis of symmetry. Let us consider now the mechanical problem of the motion of a charge in the field of two Coulomb centers. In that case the system possesses a geometrical symmetry under rotations (and reflections) with respect to an axis passing through the nuclei, and consequently the coordinate $q_3 = \varphi$ is cyclic. In that case relations (12) and (13) will be valid only for the values of indices i = 1, 2. For the case i = 3 the relation (12) must be replaced by

$$I_3 = P_\varphi \equiv L_z. \tag{18}$$

In place of Eq. (16) we shall obtain

$$H = H\left(\frac{P_1^2+Q_1^2}{2}, \frac{P_2^2+Q_2^2}{2}, L_z^2\right). \tag{16$'$}$$

The symmetry group now has the form

$$SO_2 \otimes SO_2 \otimes O_2, \tag{19}$$

where the two groups SO_2 correspond to the variables ξ and η, and the group O_2 corresponds to the angle φ.

It is now necessary to modify these results for the quantum mechanical case. It seems natural that in the case of the molecular hydrogen ion the symmetry group will coincide with the symmetry group of the corresponding classical problem, i.e., with Eq. (19). Further, since the quantum numbers n_1, n_2, and $\Lambda \equiv |m|$ do not change as the distance R between the nuclei is varied, it would be natural to consider them as indices of an irreducible representation of the group (19). In that case there is no difficulty with the von Neumann–Wigner theorem since two different terms differ in at least one of the quantum numbers n_1, n_2, and Λ and thus possess a different symmetry from the point of view of the group (19). Let us show that this is indeed the case.

First of all we introduce the operators

$$\hat{N}_1, \hat{N}_2, \hat{N}_\phi \equiv \hat{L}_z,$$

which are defined by the relations

$$\hat{N}_1\psi_{n_1n_2m} = n_1\psi_{n_1n_2m}, \qquad \hat{N}_2\psi_{n_1n_2m} = n_2\psi_{n_1n_2m}, \qquad \hat{N}_\phi\psi_{n_1n_2m} = m\psi_{n_1n_2m}, \tag{20}$$

where $\psi_{n_1n_2m}$ are the eigenfunctions of the molecular hydrogen ion (7). The so-introduced operators $\hat{N}_1$ and $\hat{N}_2$ are closely connected to the classical action variables (12). Indeed, the quantization condition in the quasi-classical approximation has the form ($\hbar = 1$)

$$I_k \equiv \frac{1}{2\pi}\oint p_k dq_k = n_k + \gamma_k, \qquad n_k = 0, 1, 2, \dots, \quad k = 1, 2; \tag{21}$$

here I_k is determined by Eq. (12) and γ_k are certain numbers (usually equal to 1/2); Eq. (21) differs from the quantities defined by Eq. (20) only by the additive constant γ_k.

The close connection between the quantities (12) and (20) is also emphasized by the fact that the quantities (12) are adiabatic invariants in classical mechanics, whereas in quantum mechanics the quantum numbers of states are adiabatic invariants, i.e., in our case, the quantum numbers n_1, n_2, and m.

The concrete form of the operators (20) depends on the form of the eigenfunctions $\psi_{n_1n_2m}$, i.e., in the final analysis on the representation chosen by us. Passing from one representation to another is equivalent in quantum mechanics to a canonical transformation in classical mechanics. We are, apparently, interested in the representation which is equivalent to the classical variables: action-angle—Eq. (12), and (13).

It would seem that the desired representation may be achieved by the following procedure. Let us suppose that the wave functions are periodic functions of the angle variables w_1, w_2, ϕ with period 2π, and the operators $\hat{N}_k$ have the form

$$\hat{N}_k = -i\frac{\partial}{\partial w_k}, \quad k = 1, 2; \quad \hat{N}_\phi = -i\frac{\partial}{\partial \phi}. \tag{22}$$

Then the eigenfunctions of our problem would be given in this representation by

$$\psi_{n_1 n_2 m} = (2\pi)^{-3/2} \exp(in_1 w_1 + in_2 w_2 + im\phi). \tag{23}$$

However in that case we would not be able to exclude negative values for the quantum numbers n_1 and n_2, which by definition are non-negative.

This difficulty can be overcome by using instead of the representation (22) a certain modification of the representation which was first introduced by Fock[7] in connection with the problem of the oscillator, and was subsequently studied in detail by Bargmann[8]. In our modified Fock representation (which for brevity sake we shall call simply the Fock representation) the wave functions are entire analytical functions of two complex variables z_1 and z_2, and periodic functions of the real angle ϕ with period 2π. The scalar product of two wave functions in this representation is defined as follows

$$(u, v) = \frac{1}{\pi^2} \int\int\int\int_{-\infty}^{+\infty} \int_0^{2\pi} \{u(z_1, z_2, \phi)\}^* \cdot$$
$$\cdot v(z_1, z_2, \phi) \exp(-|z_1|^2 - |z_2|^2)\, d^2z_1 d^2z_2\, d\phi,$$
$$d^2z = d(\operatorname{Re} z)\, d(\operatorname{Im} z). \tag{24}$$

The operators $\hat{N}_1$, $\hat{N}_2$, and $\hat{N}_\phi$ have the form

$$\hat{N}_1 = z_1\frac{\partial}{\partial z_1}, \quad \hat{N}_2 = z_2\frac{\partial}{\partial z_2}, \quad \hat{N}_\phi = -i\frac{\partial}{\partial \phi}. \tag{25}$$

The normalized eigenfunctions in our problem have the form

$$\psi_{n_1 n_2 m} = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{n_1!\, n_2!}} z_1^{n_1} z_2^{n_2} e^{im\phi},$$
$$n_1, n_2 = 0, 1, 2, \ldots; \quad m = 0, \pm 1, \pm 2, \ldots . \tag{26}$$

The Hamiltonian may be expressed in the form

$$H = E\left(z_1\frac{\partial}{\partial z_1}, z_2\frac{\partial}{\partial z_2}, -\frac{\partial^2}{\partial \phi^2}; R\right), \tag{27}$$

where the function $E(N_1, N_2, L_z^2; R)$ is given by Eq. (6). It should be emphasized that writing the Hamiltonian in the form (27) is somewhat symbolic. However, even from this symbolic form it follows that the Hamiltonian does not change its form under the transformation

$$z_k \rightarrow z_k e^{i\alpha_k}, \quad k = 1, 2,$$
$$\phi \rightarrow \phi + \alpha,$$
$$\phi \rightarrow -\phi, \tag{28}$$

i.e., under independent rotations in the plane of the complex variables z_1 and z_2 and under rotations and reflections with respect to the angle ϕ.

Thus the symmetry group of our quantum mechanical problem has the form

$$SO_2 \otimes SO_2 \otimes O_2, \tag{29}$$

i.e., it coincides with the symmetry group (19) of the corresponding classical problem. The operators $\hat{N}_1$, $\hat{N}_2$, and $\hat{N}_\phi$ are, as is easily seen, the infinitesimal operators of the group (29). In addition, there is connected with the group (29) the operator $\hat{\sigma}$, whose action on the wave function reduces to the replacement of the angle ϕ by $-\phi$:

$$\hat{\sigma}\psi(z_1, z_2, \phi) = \psi(z_1, z_2, -\phi). \tag{30}$$

As a result of the relations (20) and (30), the irreducible representations of the group (29) are one-dimensional for $\Lambda = |m| = 0$ and two-dimensional for $\Lambda = |m| > 0$. Thus the quantum numbers n_1, n_2, and Λ are indeed the indices of an irreducible representation of the group (29) or, in other words, the symmetry indices of the group (29), as was already proposed by us above.

Let us try to answer the following question: how can we concretely realize the Fock representation Eqs. (24)–(27)? The kernel of the corresponding unitary transformation has the form

$$K_R(z_1, z_2, \phi; \xi, \eta, \varphi) = \sum_{n_1 n_2 m} \frac{z_1^{n_1} z_2^{n_2} e^{im\phi}}{(2\pi n_1!\, n_2!)^{1/2}} \psi^*_{n_1 n_2 m}(\xi, \eta, \varphi; R). \tag{31}$$

With the help of this kernel one may obtain the ψ function in the Fock representation (24)–(27), if it is known in the original x-representation:

$$\psi(z_1, z_2, \phi) = \int\int\int K_R(z_1, z_2, \phi; \xi, \eta, \varphi) \cdot$$
$$\cdot \psi(\xi, \eta, \varphi; R)\, d\tau_{\xi, \eta, \varphi}. \tag{32}$$

It is clear that the kernel (31) does not have a simple analytical form. Nevertheless what is important to us is that such a kernel exists.

Let us formulate our results. We have established the symmetry group of the molecular hydrogen ion (and also for the problem of the motion of an electron in a field of two different centers). This group turns out to be wider than the original geometrical group. In terms of this larger symmetry group the von Neumann–Wigner theorem turns out to be applicable also to the molecular hydrogen ion. The results obtained for the molecular hydrogen ion can be generalized without difficulties to the case of an arbitrary quantum mechanical system, which allows a complete separability of variables.

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