QUANTUM-MECHANICALLY CORRECT FORM OF HAMILTONIAN FUNCTION FOR CONSERVATIVE SYSTEMS

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Abstract

Dirac showed that, if in the Hamiltonian H momenta η_r conjugate to the coordinates ξ_r are replaced by $(h/2\pi i)\partial/\partial\xi_r$, the Schrödinger equation appropriate to the coordinate system ξ_r is $(H-E)\psi_\xi=0$. Applied to coordinate systems other than cartesian this usually leads to incorrect results. The difficulty is here traced partially to the way in which ψ_ξ is normalized and partly to the choice of H. In H expressions such as $qpq^{-1}p$ and p^2 are not equivalent, and the simplified form is generally incorrect. A formula satisfying all the requirements of quantum mechanics for a Hamiltonian of a conservative system, in an arbitrary coordinate system, is therefore developed

$$H=\frac{1}{2\mu}\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g^{-1/4}p_r g^{1/2}g^{rs}p_s g^{-1/4}+U$$

This formula is applied to a case of plane polar coordinates and leads to correct results.

SCHRÖDINGER,[1] and Eckart[2] have shown that the correct differential equation for the Schrödinger ψ function can be obtained if in the Hamiltonian function H we replace momenta p_x, p_y, and p_z by the differential operators $(h/2\pi i)\partial/\partial x$, $(h/2\pi i)\partial/\partial y$, and $(h/2\pi i)\partial/\partial z$ respectively and write

$$(H-E)\psi=0, \tag{1}$$

where E is the total energy of the system. Later the method was extended by Epstein[3] to non-conservative systems. Still later Dirac[4] has shown that, if ψ_ξ be regarded as the transformation function for transforming matrices from a scheme in which a set of coordinates ξ_r ($r=1, 2, \cdots n$, where n is the number of degrees of freedom) is represented by diagonal matrices to a scheme in which energy is a diagonal matrix, Eq. (1) will hold provided that in H we replace each momentum η_r, conjugate to ξ_r, by the differential operator $(h/2\pi i)\partial/\partial\xi_r$. Dirac's method of proof has an advantage in that it is valid even if ξ_r are not cartesian, but are any set of coordinates in which $\partial/\partial\xi_r$ has a meaning.

However, the application of this method to any but the cartesian coordinates leads almost invariably to erroneous results. To illustrate the difficulties, let us consider the case of the hydrogen atom in space polar coordinates.

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[1] E. Schrödinger, Ann. d. Physik **79**, 745 (1926).

[2] C. Eckart, Phys. Rev. **28**, 711 (1926).

[3] P. S. Epstein, Proc. Nat. Acad. Sci. **12**, 637 (1926).

[4] P. A. M. Dirac, Proc. Roy. Soc. **A113**, 621 (1927).

If we write the Schrödinger equation in cartesian coordinates

$$\nabla^2\psi_x(x,y,z) + \frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi_x(x,y,z) = 0 \tag{2}$$

and transform this to polar coordinates, we obtain

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_x(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_x(r,\theta,\phi)}{\partial\theta}\right)$$
$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_x(r,\theta,\phi)}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi_x(r,\theta,\phi)=0 \tag{3}$$

We have used the symbol ψ_x to indicate that, while in (2) ψ is regarded as a function of x, y, z, and in (3) as a function of r, θ, ϕ, it is the same function of position, so that

$$\psi_x(x,y,z)=\psi_x(r,\theta,\phi),$$

for the corresponding values of the coordinates. Eq. (3) is the equation used by Schrödinger in his treatment of the hydrogen atom.

If, however, we start with the Hamiltonian function in polar coordinates

$$H=\frac{1}{2\mu}\left\{p_r^2+\frac{1}{r^2}p_\theta^2+\frac{1}{r^2\sin^2\theta}p_\phi^2\right\}-\frac{e^2}{r} \tag{4}$$

and put $p_r=(h/2\pi i)\partial/\partial r$, $p_\theta=(h/2\pi i)\partial/\partial\theta$, $p_\phi=(h/2\pi i)\partial/\partial\phi$, Eq. (1) leads to

$$\frac{\partial^2\psi_r(r,\theta,\phi)}{\partial r^2}+\frac{1}{r^2}\frac{\partial^2\psi_r(r,\theta,\phi)}{\partial\theta^2}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_r(r,\theta,\phi)}{\partial\phi^2}$$
$$+\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)\psi_r(r,\theta,\phi)=0, \tag{5}$$

which obviously differs from (3).

2. Part of the difficulty is due to the difference in the ways in which ψ_x and ψ_r are normalized. For ψ_x we have

$$\iiint\psi_x\psi_x^*dxdydz=\iiint\psi_x\psi_x^*r^2\sin\theta\,drd\theta d\phi=1 \tag{6}$$

while for ψ_r, according to Dirac,[5]

$$\iiint\psi_r\psi_r^*drd\theta d\phi=1 \tag{7}$$

integration being extended over the whole space. The relation between ψ_x and ψ_r must therefore be

$$\psi_x=(r^2\sin\theta)^{-1/2}\psi_r. \tag{8}$$

[5] P. A. M. Dirac, Proc. Roy. Soc. **A113**, 629 (1927).

If we substitute ψ_x from (8) into (3) we obtain a correct equation for ψ_r, which however is still inconsistent with (5).

We are thus led to the conclusion that (4) is not a quantum-mechanically correct Hamiltonian function. It is easy to see that one can put (4) into many classically equivalent forms which will differ greatly quantum-mechanically. Thus, a term such as p_r^2 may be written $r^{-1}p_r r p_r$, $r^{-1}p_r r^2 p_r r^{-1}$, $r p_r r^{-3} p_r r^2$, etc., which are not equivalent if p_r does not commute with r. We shall now develop a method of obtaining the quantum-mechanically correct form of the Hamiltonian function in an arbitrary coordinate system. In the present paper we shall restrict ourselves to non-relativistic conservative systems.

3. In a conservative system of N particles, if the kinetic energy of one, say kth, particle expressed as a function of coordinates $q_{1k}, q_{2k}, \cdots q_{nk}$ and momenta $p_{1k}, p_{2k}, \cdots p_{nk}$, is written for short $T_k(q_k, p_k)$, the Hamiltonian for the entire system may be written

$$H=\sum_{k=1}^{k=N} T_k(q_k, p_k)+U(q_{11}, q_{21}, \cdots, q_{n1}, q_{12}, \cdots, q_{nN}). \tag{9}$$

The potential energy U is not a function of momenta and will therefore be identical with its classical form. Thus, extension to systems with more than one particle involves merely a simple summation. Therefore, for the sake of simplicity, we limit ourselves to the case of a single moving particle, extension to the general case being obvious from (9).

4. The Schrödinger equation in cartesian coordinates of n dimensions, n being the number of degrees of freedom, is

$$\frac{\partial^2\psi_x}{\partial x_1^2}+\frac{\partial^2\psi_x}{\partial x_2^2}+\cdots+\frac{\partial^2\psi_x}{\partial x_n^2}+\frac{8\pi^2\mu}{h^2}(E-U_x)\psi_x=0 \tag{10}$$

where ψ_x is supposed normalized so that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\psi_x\psi_x^* dx_1 dx_2\cdots dx_n=1 \tag{11}$$

An arbitrary coordinate system $u_1, u_2, \cdots u_n$ may be characterized by the coefficients, g_{rs} say, in the expression for the square of an element of length in terms of the u's, thus

$$\begin{aligned} ds^2&=g_{11}du_1^2+2g_{12}du_1du_2+\cdots+g_{22}du_2^2+2g_{23}du_2du_3+\cdots+g_{nn}du_n^2\\ &=\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g_{rs}du_r du_s,\quad g_{rs}=g_{sr}. \end{aligned} \tag{12}$$

As is usual, we will denote by g the determinant

$$g=\begin{vmatrix} g_{11} & g_{12} & g_{13}\cdots g_{1n}\\ g_{21} & g_{22} & g_{23}\cdots g_{2n}\\ \cdot & \cdot & \cdot\ \cdot\ \cdot\ \cdot\\ g_{n1} & g_{n2} & g_{n3}\cdots g_{nn} \end{vmatrix} \tag{13}$$

We shall also need the notation

$$g^{rs} = (\text{minor of } g_{rs} \text{ in } g)/g \tag{14}$$

We now wish to transform Eqs. (10) and (11) to the coordinate system u. In doing this, we regard $\psi_x\psi_x^*$, on account of its physical significance, as invariant function of position. Thus, in the expression for ψ_x we imagine $x_1, x_2, \cdots$ replaced by their values in terms of u's, so that

$$\psi_x(x_1, x_2, \cdots, x_n) = \psi_x(u_1, u_2, \cdots, u_n).$$

We retain the subscript x to distinguish this function of position from ψ_u which would be obtained by the use of (1) in the coordinate system u directly.

The formulae of transformation for expressions such as (10) and (11) are known.[6] We obtain

$$\sum_{r=1}^{r=n} \sum_{s=1}^{s=n} g^{-1/2} \frac{\partial}{\partial u_r}\left(g^{1/2} g^{rs} \frac{\partial \psi_x}{\partial u_s}\right) + \frac{8\pi^2\mu}{h^2}(E - U_u)\psi_x = 0 \tag{10'}$$

and

$$\int\int \cdots \int \psi_x \psi_x^* g^{1/2} du_1 du_2 \cdots du_n = 1. \tag{11'}$$

The corresponding normalizing equation for ψ_u is[5]

$$\int\int \cdots \int \psi_u \psi_u^* du_1 du_2 \cdots du_n = 1 \tag{15}$$

so that combining (11') and (15) we obtain

$$\int \int \cdots \int \psi_x \psi_x^* g^{1/2} du_1 du_2 \cdots du_n = \int \int \cdots \int \psi_u \psi_u^* du_1 du_2 \cdots du_n \tag{16}$$

Consideration of the way in which matrices are constructed, by the use of ψ_x and ψ_u respectively, shows that Eq. (16) must hold even if the integrands are both multiplied by an arbitrary function of u's. We must therefore have

$$\psi_x = g^{-1/4}\psi_u \tag{17}$$

Substituting ψ_x from (17) into (10') and multiplying the resulting equation by $-h^2 g^{1/4}/8\pi^2\mu$ we obtain

$$\frac{1}{2\mu} \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} g^{-1/4} \frac{h}{2\pi i} \frac{\partial}{\partial u_r}\left(g^{1/2} g^{rs} \frac{h}{2\pi i} \frac{\partial}{\partial u_s} g^{-1/4}\psi_u\right) + U_u\psi_u - E\psi_u = 0 \tag{18}$$

This is in the form (1) and is therefore the desired differential equation for ψ_u. Replacing the differential operators $(h/2\pi i)\partial/\partial u$ by the corresponding

[6] F. D. Murnaghan, Vector Analysis and the Theory of Relativity, 46–48.

momenta, we obtain the expression for H in the quantum-mechanically correct form

$$H=\frac{1}{2\mu}\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g^{-1/4}p_r g^{1/2}g^{rs}p_s g^{-1/4}+U \tag{19}$$

In the classical case, when the order of factors is immaterial, this reduces to the usual form

$$H=\frac{1}{2\mu}\sum_{r=1}^{r=n}\sum_{s=1}^{s=n} g^{rs}p_r p_s+U \tag{20}$$

5. Let us apply these results to plane polar coordinates. Here $u_1=r$, $u_2=\theta$, $g_{11}=1$, $g_{22}=r^2$, $g_{12}=g_{21}=0$, $n=2$; therefore $g=r^2$, $g^{11}=1$, $g^{22}=1/r^2$, $g^{12}=g^{21}=0$. Using Eq. (19)

$$H=\frac{1}{2\mu}r^{-1/2}(p_1 r p_1 r^{-1/2}+p_2 r\cdot r^{-2}p_2 r^{-1/2})+U \tag{21}$$

This can be considerably simplified. Operating on ψ

$$\begin{aligned}
H\psi&=\frac{1}{2\mu}\left(\frac{h}{2\pi i}\right)^2 r^{-1/2}\left(\frac{\partial}{\partial r}r\frac{\partial}{\partial r}r^{-1/2}+\frac{\partial}{\partial\theta}r^{-1}\frac{\partial}{\partial\theta}r^{-1/2}\right)\psi+U\psi\\
&=\frac{1}{2\mu}\left(\frac{h}{2\pi i}\right)^2\left(\frac{\partial^2\psi}{\partial r^2}+\frac{1}{4}r^{-2}\psi+r^{-2}\frac{\partial^2\psi}{\partial\theta^2}\right)+U\psi\\
&=\frac{1}{2\mu}\left\{\left(\frac{h}{2\pi i}\frac{\partial}{\partial r}\right)^2+r^{-2}\left(\frac{h}{2\pi i}\frac{\partial}{\partial\theta}\right)^2-\frac{h^2}{16\pi^2}r^{-2}\right\}\psi+U\psi\\
&=\frac{1}{2\mu}\left\{p_r{}^2+r^{-2}\left(p_\theta{}^2-\frac{h^2}{16\pi^2}\right)\right\}\psi+U\psi
\end{aligned}$$

So that

$$H=\frac{1}{2\mu}\left\{p_r{}^2+r^{-2}\left(p_\theta{}^2-\frac{h^2}{16\pi^2}\right)\right\}+U, \tag{22}$$

which is just the Hamiltonian used by Dirac[7] in agreement with Pauli,[8] but it is here obtained without any special assumptions.

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[7] P. A. M. Dirac, Proc. Roy. Soc. **A110,** 561 (1926).
[8] W. Pauli, Zeits. f. Physik **36,** 336 (1926).