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ABSTRACT

We discuss the Hermitian operator p_r that corresponds to the radial component of linear momentum in the central-force problem. The purpose is purely pedagogical—i.e., we are slightly unhappy with the usual manner in which the term

$$-\left(\frac{\hbar^2}{2mr^2}\right)\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)$$

makes its entrance, in a derivation of the Schroedinger equation in spherical coordinates.

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INTRODUCTION

The Schroedinger equation for the stationary states $\psi(\underset{\sim}{r})$ of a single particle subject to a potential $V(\underset{\sim}{r})$ can be written in the form

$$H\psi(\underset{\sim}{r}) = E\psi(\underset{\sim}{r}).$$

The operator H is obtained from the classical Hamiltonian function

$$H = \frac{\underset{\sim}{p}^2}{2m} + V(\underset{\sim}{r})$$

by substituting operators for the dynamical variables $\underset{\sim}{r}$ and $\underset{\sim}{p}$. The requirement that the eigenvalues E be real leads to the demand that the operator H be Hermitian, i.e. one demands

$$\int \psi^* H\psi\, d\tau = \int (H\psi)^* \psi\, d\tau , \qquad (1)$$

where $d\tau$ is the three-dimensional volume element, and the integral extends over all space.

If one is dealing with Cartesian coordinates one uses the operators

$$p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad \text{(etc., for y and z).}$$

(That p_x is Hermitian is checked by replacing H in the left side of Eq. (1) by p_x and integrating once by parts, with $\psi \to 0$ at infinity.)

Then one obtains the Hermitian operator

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x\,y\,z)\,,$$

i.e.,

$$H = -\frac{\hbar^2}{2m}\,\nabla^2 + V(xyz)\,.$$

When one deals with a central potential

$$V(\mathbf{r}) = V(r),$$

one naturally uses spherical coordinates r, θ, and φ. In most textbooks one proceeds now to obtain the Hermitian operator corresponding to the kinetic energy $\mathbf{p}^2/2m$ by transforming the Laplacian operator ∇^2 [times $(-\hbar^2/2m)$] from Cartesian to spherical coordinates. Then $\mathbf{L}^2$, the square of the Hermitian operator

$$\mathbf{L} = \mathbf{r}\times\mathbf{p} = \mathbf{r}\times\frac{\hbar}{i}\,\nabla\,,$$

is recognized in the "angular" part of the Laplacian, and one finds

$$H = -\frac{\hbar^2}{2m}\,\frac{1}{r^2}\,\frac{\partial}{\partial r}\,r^2\,\frac{\partial}{\partial r} + \frac{\mathbf{L}^2}{2mr^2} + V(r)\,.$$

In this form the "radial" part of the kinetic-energy operator is rather puzzling. It corresponds to the classical radial kinetic energy $p_r^2/2m$. But one does not easily recognize here the square of a Hermitian operator p_r, and the operator p_r is not usually discussed at all.[1] This can be mystifying to the student, and is therefore poor pedagogy.

DERIVATION OF RADIAL MOMENTUM OPERATOR

A straightforward and elementary derivation will now be given, in which the Hermitian operator corresponding to the radial momentum p_r enters naturally.[2] At the same time the student is (lightly) exercised in the noncommutative algebra of operators, and finally obtains the radial kinetic-energy operator in its most useful form. All of this can be done with somewhat less algebra than is often expended in transforming the Laplacian to spherical coordinates.

For $r \neq 0$ one can resolve the classical linear momentum $\underline{p}$ into a radial component $\hat{r} \cdot \underline{p} \equiv p_r$ and a transverse component that has the same magnitude (although not the same direction) as $\hat{r} \times \underline{p}$, where $\hat{r}$ is the unit vector $\underline{r}/r$. Thus the kinetic energy can be written

$$\frac{p^2}{2m} = \frac{(\hat{r} \cdot \underline{p})^2}{2m} + \frac{(\hat{r} \times \underline{p})^2}{2m} .$$

The second term can be written

$$\frac{(\underline{r} \times \underline{p})^2}{2mr^2} \equiv \frac{\underline{L}^2}{2mr^2} ,$$

where $\underline{L} \equiv \underline{r} \times \underline{p}$ is the angular momentum. One easily shows that the operator $\underline{L} = \underline{r} \times (\hbar/i)\underline{\nabla}$ is Hermitian, and so is $\underline{L}^2$. At this point one profitably studies the eigenfunction-eigenvalue problem for $\underline{L}^2$ (and for L_z) and finds

$$\underline{L}^2\, Y_L^M(\theta,\phi) = \hbar^2 L(L+1)\, Y_L^M(\theta,\phi).$$

One then returns to the Schroedinger equation and writes

$$\psi(\underline{r}) = R(r)\, Y_L^M(\theta,\phi) ,$$

thus obtaining the "radial equation" for R(r), namely

$$\left[\frac{p_r^2}{2m} + \frac{\hbar^2 L(L+1)}{2mr^2} + V(r)\right] R(r) = E\,R(r). \tag{2}$$

It is now natural to look for the Hermitian operator corresponding to p_r. For the classical momentum $\underset{\sim}{p}$ we have $p_r = \hat{r}\cdot\underset{\sim}{p} = \underset{\sim}{p}\cdot\hat{r}$, analogous to the Cartesian component $p_x = \hat{x}\cdot\underset{\sim}{p} = \underset{\sim}{p}\cdot\hat{x}$. We now replace $\underset{\sim}{p}$ by the operator $\underset{\sim}{p} = (\hbar/i)\underset{\sim}{\nabla}$. In the Cartesian case we have $p_x = \hat{x}\cdot(\hbar/i)\underset{\sim}{\nabla} = (\hbar/i)\underset{\sim}{\nabla}\cdot\hat{x} = (\hbar/i)(\partial/\partial x)$. In the spherical case, since $\hat{r}$ is not a fixed direction, $\hat{r}\cdot(\hbar/i)\underset{\sim}{\nabla}$ and $(\hbar/i)\underset{\sim}{\nabla}\cdot\hat{r}$ are not equal, and in fact neither $\hat{r}\cdot\underset{\sim}{p}$ nor $\underset{\sim}{p}\cdot\hat{r}$ is Hermitian, and therefore neither can represent p_r. In seeing why these operators are not Hermitian we will be naturally led to the correct Hermitian operator for p_r.

The Hermitian conjugate $A^\dagger$ of an operator A is defined by the relation

$$\int \psi^* (A\psi)\, d\tau = \int (A^\dagger\psi)^* \psi\, d\tau. \tag{3}$$

If $A^\dagger = A$ then A is said to be Hermitian, and one then immediately finds that the eigenvalues of A are real. A vector operator $\underset{\sim}{A} = A_x\hat{x} + A_y\hat{y} + A_z\hat{z}$ is Hermitian if its components are Hermitian. Thus $\hat{r} = \underset{\sim}{r}/r$ and $\underset{\sim}{p} = (\hbar/i)\underset{\sim}{\nabla}$ are easily seen to be Hermitian. If A and B are Hermitian operators, then $(AB)^\dagger = B^\dagger A^\dagger = BA$, as follows directly from the defining Eq. (3). Thus AB is not in general Hermitian (unless BA = AB). However, AB + BA is Hermitian. For vector Hermitian operators, $(A_xB_x)^\dagger = B_x^\dagger A_x^\dagger = B_xA_x$, etc., for y and z, so that $(\underset{\sim}{A}\cdot\underset{\sim}{B})^\dagger = \underset{\sim}{B}\cdot\underset{\sim}{A}$. Thus $\underset{\sim}{A}\cdot\underset{\sim}{B}$ is not in general

Hermitian, but $\underset{\sim}{A} \cdot \underset{\sim}{B} + \underset{\sim}{B} \cdot \underset{\sim}{A}$ is. Thus the Hermitian operator to be associated with p_r is clearly

$$p_r = \frac{1}{2}\,(\hat{r} \cdot \underset{\sim}{p} + \underset{\sim}{p} \cdot \hat{r}) \,,$$

i.e.,

$$p_r = \frac{\hbar}{2i}\,(\hat{r} \cdot \underset{\sim}{\nabla} + \underset{\sim}{\nabla} \cdot \hat{r}) \,. \tag{4}$$

This operator is easily evaluated in spherical coordinates. For clarity we include the operand wave function R(r). We have for the first term in the parentheses of Eq. (4),

$$\hat{r} \cdot \underset{\sim}{\nabla} R = \frac{\partial}{\partial r} R \,.$$

The second term is

$$\begin{aligned}
\underset{\sim}{\nabla} \cdot \hat{r} R &= \underset{\sim}{\nabla} \cdot \left(\frac{\underset{\sim}{r}}{r} R\right) \\
&= \frac{R}{r} (\underset{\sim}{\nabla} \cdot \underset{\sim}{r}) + R\, \underset{\sim}{r} \cdot \underset{\sim}{\nabla} \frac{1}{r} + \frac{1}{r} \underset{\sim}{r} \cdot \underset{\sim}{\nabla} R \\
&= \frac{R}{r}\, 3 + R\, r \left(-\frac{1}{r^2}\right) + \frac{1}{r}\, r \frac{\partial}{\partial r} R \\
&= \left(\frac{2}{r} + \frac{\partial}{\partial r}\right) R \,.
\end{aligned}$$

Thus we have

$$\begin{aligned}
(\hat{r} \cdot \underset{\sim}{\nabla} + \underset{\sim}{\nabla} \cdot \hat{r}) R &= 2\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) R \\
&= \frac{2}{r} \left(r \frac{\partial}{\partial r} + 1\right) R \\
&= \frac{2}{r} \left(\frac{\partial}{\partial r}\, r\right) R \,.
\end{aligned}$$

Finally we have from Eq. (4)

$$p_r = \frac{1}{r} \left(\frac{\hbar}{i} \frac{\partial}{\partial r}\right) r. \tag{5}$$[2,3]

Then for p_r^2 we have

$$p_r^2 = \left(\frac{1}{r}\, \frac{\hbar}{i}\, \frac{\partial}{\partial r}\, r\right) \left(\frac{1}{r}\, \frac{\hbar}{i}\, \frac{\partial}{\partial r}\, r\right) \,,$$

i. e.,

$$p_r^2 = \frac{1}{r}\left(\frac{\hbar}{i}\frac{\partial}{\partial r}\right)^2 r .$$

The radial equation (1) becomes

$$\left[\frac{1}{2m}\frac{1}{r}\left(\frac{\hbar}{i}\frac{\partial}{\partial r}\right)^2 r + \frac{L(L+1)\hbar^2}{2mr^2} + V(r)\right] R(r) = E\,R(r).$$

This is just the form one wishes for the radial kinetic-energy term; one sees by inspection that if one multiplies the radial equation by r and defines $rR(r) \equiv u(r)$, one has the useful "equivalent one-dimensional" form

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial r}\right)^2 + \frac{L(L+1)\hbar^2}{2mr^2} + V(r)\right] u(r) = E\,u(r).$$

HERMITICITY OF RADIAL MOMENTUM OPERATOR

Next we check that p_r is indeed Hermitian. In doing so we gain more insight into the way in which $u(r) = rR(r)$ enters naturally.

In spherical coordinates, with the separation $\psi(\underset{\sim}{r}) = R(r)\,Y_L^M(\theta,\varphi)$, the question of the Hermiticity of p_r is just the question

$$\int_0^\infty R^*(p_rR)\,r^2\,dr \overset{?}{=} \int_0^\infty (p_rR)^*\,R\,r^2\,dr. \tag{6}$$

Starting with the left-hand side of Eq. (6) (and setting $\hbar = 1$ for convenience) we introduce $u = rR$; we then integrate once by parts, demanding that $u(r)$ vanish at $r = 0$ and $r = \infty$. The minus sign introduced in the integration by parts is cancelled by the complex conjugation of $i = \sqrt{-1}$. Thus we have

$$\int_0^\infty R^* (p_r R)\, r^2\, dr = \int_0^\infty R^* \left(\frac{1}{r} \frac{1}{i} \frac{\partial}{\partial r} r R\right) r^2\, dr$$

$$= \int_0^\infty u^* \left(\frac{1}{i} \frac{\partial}{\partial r}\right) u\, dr$$

$$= \frac{1}{i} \left[|u(\infty)|^2 - |u(0)|^2 \right] - \frac{1}{i} \int_0^\infty \left(\frac{\partial u^*}{\partial r}\right) u\, dr$$

$$= 0 + \int_0^\infty \left(\frac{1}{i} \frac{\partial}{\partial r} u\right)^* u\, dr$$

$$= \int_0^\infty \left(\frac{1}{r} \frac{1}{i} \frac{\partial}{\partial r} r R\right)^* R\, r^2\, dr$$

$$= \int_0^\infty (p_r R)^* R\, r^2\, dr ,$$

and the answer to $\overset{?}{=}$ in Eq. (6) is "yes."

This last demonstration is instructive in showing us how the operator $(\hbar/i)(\partial/\partial r)$ is in a certain sense Hermitian with respect to the wave function $u(r)$, for which "the inverse-square law" (for a conserved flux) has been factored out in order to reduce the three-dimensional problem to an equivalent one-dimensional problem.

EIGENFUNCTIONS OF RADIAL MOMENTUM OPERATOR

Lastly we look at the eigenfunction-eigenvalue problem for p_r. We have

$$p_r R(r) = p_r' R(r) ,$$

where p_r is given by Eq. (5) and p'_r is the eigenvalue. That is, for $r \neq 0$,

$$\left(\frac{1}{r}\,\frac{\hbar}{i}\,\frac{\partial}{\partial r}\,r\right) R = p'_r R,$$

i.e.,

$$\left(\frac{\hbar}{i}\,\frac{\partial}{\partial r}\right) u(r) = p'_r\, u(r),$$

where $u = rR$. This differential equation has the solutions

$$u = \exp(ikr) \qquad \text{(outgoing wave)}$$

and

$$u = \exp(-ikr) \qquad \text{(incoming wave)},$$

where k is real and positive, and where

$$p'_r = +\hbar k \;\text{(outgoing)}, \quad \text{or} \quad -\hbar k \;\text{(incoming)}.$$

At first sight it may seem that we actually have <u>not</u> solved the eigenfunction-eigenvalue problem, because in the derivation following Eq. (6) we assumed $u(r) \rightarrow 0$ at $r \rightarrow 0$ and $r \rightarrow \infty$ (in the step in which we integrated by parts), whereas our present solution, $u = \exp(\pm ikr)$, does not vanish at $r = 0$ or at infinity. Nevertheless, the integrated term [in the derivation of Eq. (6)] still gives zero, because it has the <u>same</u> value at $r = 0$ and at infinity, namely $u^* u = 1$. Thus $u = \exp(\pm ikr)$ is an acceptable eigenfunction. Of course, these eigenfunctions are unnormalizable, in essentially the same way that the free-particle eigenfunctions of p_x, namely $\exp(\pm ikx)$, are unnormalizable.

From Eq. (2) we see that the eigenfunctions of p_r correspond to stationary states (definite energy) only for free particles

[V(r) = constant] in an S state (L = 0); otherwise, we may not replace p_r^2 by a constant in Eq. (2). For free particles in an S state, flux conservation is satisfied if we have the linear combination

$$u(r) = \exp(-ikr) + \exp(i\alpha)\exp(ikr).$$

There seems to be no compelling reason to require that $\exp i\alpha = -1$, i.e. to require $u(r) = 0$ at $r = 0$.[4]

From Eq. (2) we see that there is another special case for which a stationary state (definite E) may be simultaneously an eigenstate of p_r; that can occur if V(r) is the rather peculiar function of r (and L),

$$V(r) = -\frac{\hbar^2 L(L+1)}{2mr^2} .$$

FOOTNOTES AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission.

1. See for instance David Bohm, Quantum Theory (Prentice-Hall, New York, 1951); L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Co., New York, 1955); E. Merzbacher, Quantum Mechanics (John Wiley and Sons, Inc., New York, 1961); J. L. Powell and B. Crasemann, Quantum Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1961); V. Rojansky, Introductory Quantum Mechanics (Prentice-Hall, New York, 1946); and Linus Pauling and E. B. Wilson, Jr., Introduction to Quantum Mechanics (McGraw-Hill Book Co., Inc., New York, 1935).

2. The derivation of p_r given here is not found in the representative sample of popular texts listed in references 1 and 3. No attempt was made to search the vast literature of quantum mechanics to see whether a similar treatment has been given elsewhere. See reference 3, however.

3. P. Dirac [The Principles of Quantum Mechanics (Oxford University Press, 3rd ed., 1947), p. 152] introduces the operator $p_r' = (\hbar/i)(\partial/\partial r)$ and then shows that $p_r' - i\hbar r^{-1}$ is canonically conjugate to r. L. Landau and E. Lifshitz [Quantum Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), p. 108, footnote] mention without discussion the operator p_r of our Eq. (5). E. C. Kemble [The Fundamental Principles of Quantum Mechanics (McGraw-Hill Book Co., New York, 1937), pp. 297 and 335, footnote] discusses the unsatisfactory character of the operator $(\hbar/i)(\partial/\partial r)$.

4. For a discussion of boundary conditions at r = 0, see B. H. Armstrong and E. A. Power, Am. J. Phys. 31, 262 (1963).