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Lawrence Radiation Laboratory
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THE "RADIAL KINETIC ENERGY" TERM IN THE SCHROEDINGER EQUATION FOR A CENTRAL FORCE

Frank S. Crawford, Jr.

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Frank S. Crawford, Jr.

Lawrence Radiation Laboratory
University of California
Berkeley, California

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ABSTRACT

A straightforward derivation is given for the Hermitian operator

$$p_r \equiv \frac{1}{r}\frac{\hbar}{i}\frac{\partial}{\partial r}r$$

corresponding to the radial component of linear momentum in the central force problem. The purpose is purely pedagogical; we believe that the radial term of the Schroedinger equation in spherical coordinates is more comprehensible when it appears in the form

$$(p_r^2/2m)\psi = \left[\left(\frac{1}{r}\frac{\hbar}{i}\frac{\partial}{\partial r}r\right)^2/2m\right]\psi$$

than when it appears, as it does in most textbooks, in the form

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

The latter expression is usually arrived at by a tedious transformation of variables done "in the appendix"; instead one may derive p_r with a minimum of algebra and with the focus where it belongs, on the concepts of quantum mechanics.

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

$$\int \psi^* H\psi \, d\tau = \int (H\psi)^* \psi \, d\tau , \tag{1}$$

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

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

i.e.,

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

When one deals with a central potential

$$V(\underset{\sim}{r}) = V(r),$$

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 $\underset{\sim}{p}^2/2m$ by transforming the Laplacian operator $\underset{\sim}{\nabla}^2$ [times $(-\hbar^2/2m)$] from Cartesian to spherical coordinates. Then $\underset{\sim}{L}^2$, the square of the Hermitian operator

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

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

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

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]

DERIVATION OF RADIAL MOMENTUM OPERATOR

A straighforward 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 non-commutative 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 expended in transforming the Laplacian to spherical coordinates.

For $r \neq 0$ one can resolve the classical linear momentum $\underset{\sim}{p}$ into a radial component $\hat{r} \cdot \underset{\sim}{p} \equiv p_r$ and a transverse component that has the same <u>magnitude</u> (although not the same direction) as $\hat{r} \times \underset{\sim}{p}$, where $\hat{r}$ is the unit

vector $\underset{\sim}{r}/r$. Thus the kinetic energy can be written

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

The second term can be written

$$\frac{(\underset{\sim}{r}\times\underset{\sim}{p})^2}{2mr^2} = \frac{\underset{\sim}{L}^2}{2mr^2} ,$$

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

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

One then returns to the Schroedinger equation and writes

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

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

$$\left[\frac{p_r^2}{2m} + \frac{\hbar^2 L(L+1)}{2mr^2} + V(r)\right] R(r) = E R(r). \qquad (3)$$

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

$$\int \psi^* (A\psi)\, d\tau = \int (A^\dagger \psi)^* \psi\, d\tau . \tag{4}$$

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. (4). Therefore 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. The Hermitian operator to be associated with p_r is then clearly

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

i.e.,

$$p_r = \frac{\hbar}{2i}(\hat{r} \cdot \underset{\sim}{\nabla} + \underset{\sim}{\nabla} \cdot \hat{r}). \tag{5}$$

This operator is easily evaluated in spherical coordinates. The algebra is in footnote 3. We obtain

$$p_r = \frac{1}{r}\left(\frac{\hbar}{i}\frac{\partial}{\partial r}\right) r .\,^{4} \tag{6}$$

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 (3) becomes

$$\left[\frac{1}{2m} \frac{1}{r} \left(\frac{\hbar}{i} \frac{\partial}{\partial r} \right)^2 r + \frac{L(L+1)\hbar^2}{2mr^2} + V(r) \right] R(r) = E R(r). \tag{7}$$

In Eq. (7) the radial kinetic energy term has a more convenient form than that in Eq. (2). For instance, from Eq. (7) one sees by inspection that if one multiplies the radial equation by r and defines $rR(r) \equiv u(r)$, one obtains 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 $\psi(\underset{\sim}{r}) = R(r)\, Y_L^M(\theta, \phi)$, the question of the Hermiticity of p_r is just the question

$$\int_0^\infty R^*(p_r R)\, r^2 dr \stackrel{?}{=} \int_0^\infty (p_r R)^* R\, r^2 dr. \tag{8}$$

Starting with the left-hand side of Eq. (8) (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 $r = \infty$. (We will later find that this condition need not always hold.) The minus sign introduced in the integration by parts is canceled by the complex conjugation of $i = \sqrt{-1}$. Thus we have

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

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

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

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

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

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

and the answer to $\stackrel{?}{=}$ in Eq. (8) is "yes."

This last demonstration is instructive in showing us that 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. (6) 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

$$p_r' = +\hbar k \ \text{(outgoing)}, \qquad \text{or} \qquad -\hbar k \ \text{(incoming)}.$$

At first sight it may seem that we actually have not solved the eigenfunction-eigenvalue problem, because in the derivation following Eq. (8) we assumed $u(r) \to 0$ at $r \to 0$ and $r \to \infty$ (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. (8)] 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. (3) 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. (3). 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 reason to require $\exp i\alpha = -1$, i.e. to require $u(r) = 0$ at $r = 0$.[5]

From Eq. (3) we see that there is only one other case for which a stationary state (definite E) may be simultaneously an eigenstate of p_r; that can occur if the potential is the rather peculiar function of r (and L),

$$V(r, L) = -\frac{\hbar^2 L(L+1)}{2mr^2} + \text{constant};$$

then the actual potential $V(r)$ is attractive and exactly cancels the effective centrifugal potential. This would correspond to a classical velocity-dependent potential

$$V(r, p) = -\frac{(\underline{r} \times \underline{p})^2}{2mr^2} + \text{constant}.$$

Since this potential does not seem to correspond to any physical system actually realized in nature, it is not surprising that the eigenvalues of p_r have little application.

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 4. No attempt was made to search the literature of quantum mechanics to see whether a similar treatment has been given elsewhere. See reference 4, however.

3. For clarity we include the operand wave function R(r). We have, for the first term in the parentheses of Eq. (5),

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

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

$$(\hat{r} \cdot \underline{\nabla} + \underline{\nabla} \cdot \hat{r})R = 2\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)R$$

$$= \frac{2}{r}\left(r\frac{\partial}{\partial r} + 1\right)R$$

$$= \frac{2}{r}\left(\frac{\partial}{\partial r} r\right)R,$$

and Eq. (6) follows from Eq. (5).

4. P. Dirac [The Principles of Quantum Mechanics (Oxford University Press, 3rd ed., 1947), p. 152] introduces the operator $p_r' \equiv (\hbar/i)(\partial/\partial r)$ 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. (6). 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 $(\hbar/i)(\partial/\partial r)$.

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

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