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The Schrödinger Wave Equation and Probability Interpretation

A The Wave Equation

With the Bohr relation for the energy, $E = \hbar\omega$, and the deBroglie relation for the momentum vector, $\vec{p} = \hbar\vec{k}$, we see the dispersion relation for waves, $\omega = f(\vec{k})$, goes over to a relation between energy and momentum. For a conservative system, this relation can be expressed through $E = H(\vec{p}, \vec{r})$, where H is the Hamiltonian function. In particular, for a free, nonrelativistic particle, of mass m, this "dispersion relation" becomes

$$E = \frac{(\vec{p} \cdot \vec{p})}{2m}. \tag{1}$$

Now, convert our wave packet expansion from an expansion in $\vec{k}$ to one in $\vec{p}$

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} A(\vec{p}) e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r} - Et)}, \tag{2}$$

so

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} E A(\vec{p}) e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r} - Et)}, \tag{3}$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} \frac{(\vec{p} \cdot \vec{p})}{2m} A(\vec{p}) e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r} - Et)}. \tag{4}$$

As a result, we get

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} + \frac{\hbar^2}{2m}\nabla^2\Psi = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p} \left[E - \frac{(\vec{p} \cdot \vec{p})}{2m}\right] e^{\frac{i}{\hbar}(\vec{p}\cdot\vec{r} - Et)} = 0, \tag{5}$$

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and the relation between E and $\vec{p}$ leads us to the wave equation for a free particle, the Schrödinger equation for a free particle,

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \Psi(\vec{r}, t). \tag{6}$$

The group velocity of a wave packet now becomes

$$\vec{v}_{\text{group}} = \frac{d\omega}{d\vec{k}} = \frac{dE}{d\vec{p}} = \frac{\vec{p}}{m} = \vec{v}_{\text{particle}}. \tag{7}$$

The uncertainty relations for waves go over to the Heisenberg uncertainty relations

$$\begin{aligned} \Delta k_x \Delta x \approx 2\pi \quad &\rightarrow \quad \Delta p_x \Delta x \approx h \\ \Delta k_y \Delta y \approx 2\pi \quad &\rightarrow \quad \Delta p_y \Delta y \approx h \\ \Delta k_z \Delta z \approx 2\pi \quad &\rightarrow \quad \Delta p_z \Delta z \approx h. \end{aligned} \tag{8}$$

For a particle subject to a conservative force derivable from a potential $V(x, y, z)$, with

$$E = H(\vec{p}, \vec{r}) = \frac{(\vec{p} \cdot \vec{p})}{2m} + V(x, y, z), \tag{9}$$

this relation between E and $\vec{p}$ gives the wave equation

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \Psi + V(x, y, z)\Psi. \tag{10}$$

Finally, we end with a remark about relativistic wave equations. The relation between energy and momentum for a relativistic particle, of rest mass m_0,

$$\frac{E^2}{c^2} - p^2 = m_0^2 c^2, \tag{11}$$

would lead us to a wave equation both second order in time and space derivatives, and again involving a single wave function $\Psi(\vec{r}, t)$. (See Problem 2). This equation leads to the so-called Klein–Gordon equation. An alternative solution for the relativistic wave equation was given by Dirac, whose wave equation is first order in both time and space derivatives. Essentially, it comes from the square root of the above dispersion relation and, therefore, leads to both positive and negative energy solutions. It is based not on a single Ψ, but on a number of ψ_α, actually, with $\alpha = 1, \ldots, 4$. We shall come back to the Dirac equation near the end of the book.

B The Probability Axioms

To use the Schrödinger wave equation, we need to understand the physical meaning of the wave function, Ψ. We begin with a few remarks:

1. The particle and the wavefield are equally real. (The wavefield is not a ghost field guiding the particle.) Both are pictures in the human mind to account for physical reality; both, however, have their limitations.

2. In practice, the wavefield is used in the following way: The result of a certain experiment lets us represent the particle motion by a wave packet at a certain time. The wave equation is then used to predict how the experiment evolves in time.

3. Because of the uncontrollable interaction of object and measuring instrument, we are led to a probability description.

The probability of finding a particle within a volume element $dxdydz$ about a point x, y, z at a time t, will be given by

$$W(x, y, z; t)dxdydz,$$

where $W(x, y, z; t)$ is a probability density. This probability density must satisfy certain sensibility restrictions; i.e., $W(x, y, z; t)$ must be a sensible probability density:

$$W \geq 0. \tag{12}$$

A negative probability density makes no sense. To make W patently positive, it makes sense to let the probability density be given by

$$W(\vec{r}; t) = \Psi^* \Psi. \tag{13}$$

Note, in optics or electromagnetism, physically measurable quantities, such as energy or intensity, are proportional to the square of the amplitude of the wave, or if the amplitude can be complex to the absolute value squared. Also,

$$\frac{d}{dt} \int_{\text{all space}} d\vec{r} \;\; W(\vec{r}, t) = 0. \tag{14}$$

The probability of finding the particle somewhere is independent of time. In non-relativistic quantum mechanics, we are building a theory of indestructible particles. Also,

$$\int_{\text{all space}} d\vec{r} \;\; W \quad \text{is Galilean invariant.} \tag{15}$$

All observers agree one particle exists somewhere.

The conservation of probability leads to a continuity equation. Because Ψ can be complex, the Schrödinger equation is really two equations

$$\begin{aligned} -\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2 \Psi + V\Psi \\ +\frac{\hbar}{i}\frac{\partial \Psi^*}{\partial t} &= -\frac{\hbar^2}{2m}\nabla^2 \Psi^* + V\Psi^*. \end{aligned} \tag{16}$$

Multiplying the first of these equations by $-\Psi^*$, the second equation by Ψ, and adding the two resultant equations, assuming also the potential function is real, we get

$$\frac{\hbar}{i}\frac{\partial}{\partial t}(\Psi^* \Psi) = \frac{\hbar^2}{2m} \text{div}(\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*). \tag{17}$$

This relation has the form of a continuity equation

$$\frac{\partial W}{\partial t} + \operatorname{div}\vec{S} = 0, \tag{18}$$

if we choose

$$\vec{S} = \frac{\hbar}{2mi}(\Psi^* \overrightarrow{\nabla} \Psi - \Psi \overrightarrow{\nabla} \Psi^*), \tag{19}$$

where this equation must be interpreted as a probability density current; i.e., as the probability per second per unit area normal to the direction of $\vec{S}$ that the particle be streaming in the direction of $\vec{S}$. The integral form of the continuity equation could be written as

$$\frac{d}{dt}\int_{\text{Vol.}} d\vec{r}\Psi^*\Psi + \int_{\text{Surf.}} dA(\vec{S}\cdot\vec{n}) = 0, \tag{20}$$

where the volume integral is over a finite volume and the surface integral is over the surface surrounding this finite volume, dA being an element of surface area and $\vec{n}$ being the outward normal to the surface. In integral form, this equation says: The time rate of change of probability of finding the particle within the finite volume must be the negative of the probability of the net outflow of the particle. If we let the volume grow to include all of our 3-D space and if we assume Ψ and $\Psi^* \to 0$ sufficiently fast as a function of r as the surface recedes to infinity, the surface integral will go to zero and our second probability restriction is satisfied.

Finally, examine the Galilean invariance. Suppose observers in a primed reference frame are moving with velocity, v, parallel to the x-direction. Then,

$$x = x' + vt', \qquad y = y', \qquad z = z', \qquad t = t', \tag{21}$$

with

$$\frac{\partial}{\partial t'} = 1\frac{\partial}{\partial t} + v\frac{\partial}{\partial x}, \quad \frac{\partial}{\partial x'} = 1\frac{\partial}{\partial x} + 0\frac{\partial}{\partial t}, \quad \frac{\partial}{\partial y'} = \frac{\partial}{\partial y}, \quad \frac{\partial}{\partial z'} = \frac{\partial}{\partial z}. \tag{22}$$

In addition, the wave function must also change under the Galilean transformation, according to

$$\Psi'(x', y', z'; t') = \Psi(x, y, z; t)e^{-\frac{i}{\hbar}(mvx - \frac{1}{2}mv^2t)}. \tag{23}$$

Comparing the Schrödinger equations in the primed and unprimed frames, we are led to

$$W' = W; \qquad \vec{S}' = \vec{S} - \vec{v}\Psi^*\Psi. \tag{24}$$

If observers in the unprimed frame see no streaming of probability to right or left, $(\vec{S}) = 0$, observers in the primed frame will see a streaming to the left, as they should because a particle in a region with $W \neq 0$ will appear to be moving in the direction of $-\vec{v}$ to an observer in the primed frame.

A final remark: If Ψ is real everywhere, $\vec{S}$ is zero everywhere; then, no transport of probability exists. A probability density with a real Ψ corresponds to a situation in which particles will stream in the $+x$ and $-x$ directions with equal probability.

Note, we need complex Ψ's to describe beams of particles streaming toward or away from a target.

C The Calculation of Average Values of Dynamical Quantities

On the atomic scale, we cannot give an exact orbit description, e.g., $x(t)$, for the motion of a particle. We can, however, give the probability theory average value of dynamical variables, such as x, as functions of the time. Define this average or expectation value of x through

$$\langle x \rangle = \int d\vec{r}\, x\, \Psi^*(\vec{r}, t)\Psi(\vec{r}, t); \tag{25}$$

or, similarly,

$$\langle x^n \rangle = \int d\vec{r}\, x^n\, \Psi^*(\vec{r}, t)\Psi(\vec{r}, t). \tag{26}$$

The question then arises, how do we define the corresponding expectation value of a momentum component, $\langle p_x \rangle$? It will be convenient to define a momentum space probability density, so the probability of finding a particle in the momentum range $dp_x dp_y dp_z$ about some value p_x, p_y, p_z is given by

$$\phi^*(\vec{p}, t)\phi(\vec{p}, t)dp_x dp_y dp_z,$$

so

$$\langle p_x \rangle = \int d\vec{p}\; p_x \phi^*(\vec{p}, t)\phi(\vec{p}, t), \tag{27}$$

where $\phi(\vec{p}, t)$ is the Fourier transform of $\Psi(\vec{r}, t)$. Comparing with eq. (2), and letting $\phi(\vec{p}, t) = A(\vec{p})e^{-\frac{i}{\hbar}Et}$,

$$\phi(\vec{p}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{r}\,' \Psi(\vec{r}\,', t)e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}\,'}, \tag{28}$$

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int d\vec{p}\phi(\vec{p}, t)e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}, \tag{29}$$

$$\Psi(\vec{r}, t) = \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r}\,' \Psi(\vec{r}\,', t)e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}\,')}. \tag{30}$$

Note

$$\begin{aligned} \int d\vec{p}\phi^*(\vec{p}, t)\phi(\vec{p}, t) &= \underline{\frac{1}{(2\pi\hbar)^3} \int d\vec{p}} \int d\vec{r}\Psi^*(\vec{r}, t) \underline{\int d\vec{r}\,' \Psi(\vec{r}\,', t)e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}\,')}} \\ &= \int d\vec{r}\Psi^*(\vec{r}, t)\underline{\Psi(\vec{r}, t)}, \end{aligned} \tag{31}$$

where the underlined quantities in the first line of this equation give $\Psi(\vec{r}, t)$ via the use of eq. (30). This relation between $\Psi(\vec{r}, t)$ and its Fourier transform $\phi(\vec{p}, t)$ is known as Parseval's theorem. Note, the probability of finding the particle *somewhere*, with *some* momentum, is equal to 1 for a theory of one particle.

The same type of Fourier transformation can also be used to express the expectation value $\langle p_x \rangle$ in terms of a space rather than a momentum integral

$$\begin{aligned}
\langle p_x \rangle &= \int d\vec{p}\ \ p_x \phi^*(\vec{p}, t)\phi(\vec{p}, t) \\
&= \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r} \Psi^*(\vec{r}, t)\ \ p_x \int d\vec{r}\,' \Psi(\vec{r}\,', t) e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}\,')} \\
&= \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \int d\vec{r} \Psi^*(\vec{r}, t) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \int d\vec{r}\,' \Psi(\vec{r}\,', t) e^{\frac{i}{\hbar}\vec{p}\cdot(\vec{r}-\vec{r}\,')} \right) \\
&= \int d\vec{r} \Psi^*(\vec{r}, t) \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(\vec{r}, t),
\end{aligned} \tag{32}$$

so $\langle p_x \rangle$ can also be evaluated through

$$\langle p_x \rangle = \int d\vec{r} \Psi^*(\vec{r}, t) \frac{\hbar}{i} \left(\frac{\partial}{\partial x} \Psi(\vec{r}, t) \right). \tag{33}$$

Similarly,

$$< p_x^2 >= \int d\vec{r} \Psi^*(\vec{r}, t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \Psi(\vec{r}, t) \right). \tag{34}$$

Finally, by the same technique, we could express $\langle x \rangle$ in terms of momentum rather than space integrals

$$\langle x \rangle = \int d\vec{p} \phi^*(\vec{p}, t) i\hbar \left(\frac{\partial}{\partial p_x} \phi(\vec{p}, t) \right). \tag{35}$$

D Precise Statement of the Uncertainty Principle

Now that we have defined $\langle x \rangle$, $< x^2 >$, and so on precisely in terms of the probability densities, we can formulate the Heisenberg uncertainty principle more precisely. Taking the usual statistical definition of the uncertainty, Δx,

$$\begin{aligned}
(\Delta x)^2 &= < (x - \langle x \rangle)^2 >=< x^2 > -2\langle x \rangle \langle x \rangle + \langle x \rangle^2 \\
&= < x^2 > -\langle x \rangle^2,
\end{aligned} \tag{36}$$

and, similarly, for Δp_x. The precise statement of the Heisenberg uncertainty principle is then

$$\begin{aligned}
\Delta p_x \Delta x &\geq \tfrac{1}{2}\hbar \\
\Delta p_y \Delta y &\geq \tfrac{1}{2}\hbar \\
\Delta p_z \Delta z &\geq \tfrac{1}{2}\hbar.
\end{aligned} \tag{37}$$

For simplicity, give a derivation only for one-dimensional (1-D) motion and consider the motion to be in the x-direction. To prove the uncertainty relation, consider

the following integral, a function of a real parameter λ,

$$I(\lambda) \equiv \int_{-\infty}^{\infty} dx \left| (x - \langle x \rangle)\Psi + i\lambda\left(\frac{\hbar}{i}\frac{\partial \Psi}{\partial x} - \langle p_x \rangle \Psi\right)\right|^2. \tag{38}$$

Note, through its definition, $I(\lambda) \geq 0$. Writing out all of the terms

$$\begin{aligned} I(\lambda) = & \int_{-\infty}^{\infty} dx \Psi^*(x - \langle x \rangle)^2 \Psi \\ & + \lambda\hbar \int_{-\infty}^{\infty} dx \left(\Psi^* \frac{\partial \Psi}{\partial x} + \Psi \frac{\partial \Psi^*}{\partial x}\right)(x - \langle x \rangle) \\ & + \lambda^2 \hbar^2 \int_{-\infty}^{\infty} dx \frac{\partial \Psi^*}{\partial x}\frac{\partial \Psi}{\partial x} \\ & + \lambda^2 \langle p_x \rangle \frac{\hbar}{i} \int_{-\infty}^{\infty} dx \left[\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x}\right] \\ & + \lambda^2 \langle p_x \rangle^2 \int_{-\infty}^{\infty} dx \Psi^* \Psi. \end{aligned} \tag{39}$$

Now, note term (2) (in the second line) can be rewritten

$$\int_{-\infty}^{\infty} dx \frac{\partial(\Psi^*\Psi)}{\partial x}(x - \langle x \rangle) = \left[(x - \langle x \rangle)\Psi^*\Psi\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \Psi^*\Psi = -1, \tag{40}$$

where we have assumed $\Psi \to 0$ sufficiently fast as $x \to \pm\infty$, so the integrated term is zero. Similarly, term (3) can be rewritten as

$$\hbar^2 \int_{-\infty}^{\infty} dx \frac{\partial \Psi^*}{\partial x}\frac{\partial \Psi}{\partial x} = \hbar^2 \left[\Psi^* \frac{\partial \Psi}{\partial x}\right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} dx \Psi^* \left(-\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}\right) = < p_x^2 > . \tag{41}$$

Finally, in term (4), rewrite

$$\frac{\hbar}{i} \int_{-\infty}^{\infty} dx \frac{\partial \Psi^*}{\partial x}\Psi = \frac{\hbar}{i}\left[\Psi^*\Psi\right]_{-\infty}^{\infty} - \int dx \Psi^* \frac{\hbar}{i}\frac{\partial \Psi}{\partial x} = -\langle p_x \rangle, \tag{42}$$

so the full expression of term (4) can be rewritten as $-2\langle p_x \rangle^2$. Putting together all of the terms, we then get

$$I(\lambda) = (\Delta x)^2 - \hbar\lambda + (\Delta p_x)^2 \lambda^2 \geq 0. \tag{43}$$

With $I(\lambda) = a\lambda^2 + b\lambda + c$, the requirement, $I(\lambda) \geq 0$, is met if $b^2 - 4ac \leq 0$. Thus, $\hbar^2 - 4(\Delta x)^2(\Delta p_x)^2 \leq 0$, and, therefore,

$$\Delta p_x \Delta x \geq \tfrac{1}{2}\hbar. \tag{44}$$

Thus, in the most favorable wave packet, the so-called minimum wave packet, we can have the minimum uncertainty, $\frac{1}{2}\hbar$. We shall see later this is true for a Gaussian wave packet.

E Ehrenfest's Theorem: Equations of Motion

Classically, the Hamiltonian for a single particle of mass m,

$$H = \frac{\vec{p}^{\,2}}{2m} + V(x, y, z), \tag{45}$$

leads to the equations of motion

$$\frac{dx}{dt} = \frac{\partial H}{\partial p_x}; \qquad \frac{dp_x}{dt} = -\frac{\partial H}{\partial x} = -\frac{\partial V}{\partial x}. \tag{46}$$

Quantum mechanically the velocity of the particle no longer has a precise meaning, but we can ask: How does the expectation value of x change with time? Calculate $\frac{d\langle x\rangle}{dt}$:

$$\frac{d\langle x\rangle}{dt} = \int d\vec{r}\, x \frac{\partial}{\partial t}\Big(\Psi^*(\vec{r}, t)\Psi(\vec{r}, t)\Big). \tag{47}$$

(Note, in particular, the quantity x in the integrand is not a function of the time. It is merely the dummy integration variable, which weights the time-dependent function $\Psi^*\Psi$. It says we must weight all values of x from $-\infty$ to $+\infty$ with x and the probability density function to obtain $\langle x\rangle$.) Using the continuity equation, we can rewrite this as

$$\begin{aligned}
\frac{d\langle x\rangle}{dt} &= -\int d\vec{r}\;\; x\,\mathrm{div}\vec{S} = -\int d\vec{r}\;\; x\Big(\frac{\partial S_x}{\partial x} + \frac{\partial S_y}{\partial y} + \frac{\partial S_z}{\partial z}\Big) \\
&= -\int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \Big[x S_x\Big]_{x=-\infty}^{\infty} - \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dz \Big[x S_y\Big]_{y=-\infty}^{\infty} \\
&- \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \Big[x S_z\Big]_{z=-\infty}^{\infty} + \int d\vec{r}\;\; S_x \\
&= \frac{\hbar}{2mi} \int d\vec{r} \Big(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x}\Big) \\
&= \frac{1}{m} \int d\vec{r}\;\; \Psi^* \Big(\frac{\hbar}{i} \frac{\partial \Psi}{\partial x}\Big) = \frac{1}{m} \langle p_x\rangle,
\end{aligned} \tag{48}$$

where all integrated terms disappear, and we have done one more integration by parts on the $\Psi \frac{\partial \Psi^*}{\partial x}$ term in the last step. Therefore, we see

$$\frac{d\langle x\rangle}{dt} = \frac{1}{m}\langle p_x\rangle, \tag{49}$$

which is the first equation of motion, provided we replace x and p_x by their expectation values $\langle x\rangle$ and $\langle p_x\rangle$. In exactly the same fashion,

$$\begin{aligned}
\frac{d\langle p_x\rangle}{dt} &= \frac{d}{dt} \int d\vec{r} \Psi^* \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} \\
&= \int d\vec{r} \Big(\frac{\hbar}{i} \frac{\partial \Psi^*}{\partial t}\Big)\Big(\frac{\partial \Psi}{\partial x}\Big) + \int d\vec{r} \Psi^* \frac{\hbar}{i} \Big(\frac{\partial^2 \Psi}{\partial t \partial x}\Big) \\
&= \int d\vec{r} \Big(\frac{\hbar}{i} \frac{\partial \Psi^*}{\partial t}\Big)\Big(\frac{\partial \Psi}{\partial x}\Big) + \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \frac{\hbar}{i} \Psi^* \frac{\partial \Psi}{\partial t}\Big]_{x=-\infty}^{\infty}
\end{aligned}$$

$$
\begin{aligned}
&+\int d\vec{r}\frac{\partial\Psi^*}{\partial x}\left(-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}\right)\\
&=-\frac{\hbar^2}{2m}\int d\vec{r}\left[\nabla^2\Psi^*\frac{\partial\Psi}{\partial x}+\frac{\partial\Psi^*}{\partial x}\nabla^2\Psi\right]+\int d\vec{r}\left[\Psi^*V\frac{\partial\Psi}{\partial x}+\frac{\partial\Psi^*}{\partial x}V\Psi\right]\\
&=-\frac{\hbar^2}{2m}[\ 0\ ]+\int d\vec{r}\,V\frac{\partial(\Psi^*\Psi)}{\partial x}\\
&=\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz\Psi^*\Psi V\Big]_{x=-\infty}^{\infty}-\int d\vec{r}\,\Psi^*\Psi\left(\frac{\partial V}{\partial x}\right),
\end{aligned}
\tag{50}
$$

where the term with ∇^2 operators disappears via integrations by parts, similarly to the integrated terms shown explicitly. Thus,

$$
\frac{d\langle p_x\rangle}{dt}=-<\left(\frac{\partial V}{\partial x}\right)>, \tag{51}
$$

which is the quantum-mechanical analogue of the second classical equation of motion, where again the classical quantities, p_x, and, $\frac{\partial V}{\partial x}$, have been replaced with their quantum-mechanical expectation values.

F Operational Calculus, The Linear Operators of Quantum Mechanics, Hilbert Space

In the last few sections, we have met many operators acting on the Schrödinger Ψ. In this section, we want to make a more systematic study of the linear operators of quantum theory. The operator, O, is a command. Acting on a function, it produces another function, $(O\Psi(x))$. Examples include $O = f(x)$. Acting on the function $\Psi(x)$, it produces the new function, $f(x)\Psi(x)$. The command is: Multiply the old function by $f(x)$. The second common example is the operator $\frac{d}{dx}$. When acting on the function Ψ, it produces the new function

$$
\frac{d\Psi(x)}{dx}.
$$

The operators of quantum theory are linear operators. When acting on functions $\Psi(x)$, which are linear combinations of functions, $\Psi(x) = \lambda_1\Psi_1(x) + \lambda_2\Psi_2(x)$, where λ_1 and λ_2 are arbitrary complex numbers, the linear operator O yields

$$
(O\Psi(x)) = \lambda_1(O\Psi_1(x)) + \lambda_2(O\Psi_2(x)). \tag{52}
$$

Another type of operator is the parity or space-inversion operator, P. It is the command: Change x to $-x$, y to $-y$, and z to $-z$ in the function on which it acts

$$
P\Psi(x, y, z) = \Psi(-x, -y, -z).
$$

Products of operators are operators acting in succession on our functions:

$$
O_2O_1\Psi = O_2(O_1\Psi).
$$

Because we deal with wave functions and operators acting on wave functions, we need to define the function space on which the operators act. The wave functions of quantum mechanics are square-integrable in coordinate space.

$$\int d\vec{r}\Psi^*\Psi = \text{finite.} \tag{53}$$

The space of all square-integrable functions is known as a Hilbert space. It will be useful to define a Scalar Product of the functions Φ and Ψ by

$$\int d\vec{r}\Phi^*\Psi = < \Phi, \Psi > . \tag{54}$$

The functions Φ and Ψ are said to be orthogonal to each other if $< \Phi, \Psi >= 0$. Note, the scalar product has the property

$$< \Phi, \Psi >=< \Psi, \Phi >^* . \tag{55}$$

Note also, the scalar product is linear in Ψ,

$$< \Phi, \lambda_1\Psi_1 + \lambda_2\Psi_2 >= \lambda_1 < \Phi, \Psi_1 > +\lambda_2 < \Phi, \Psi_2 >, \tag{56}$$

but is antilinear in Φ,

$$< \lambda_1\Phi_1 + \lambda_2\Phi_2, \Psi >= \lambda_1^* < \Phi_1, \Psi > +\lambda_2^* < \Phi_2, \Psi > . \tag{57}$$

Eq. (56) follows from the linear character of the unit operator.

An important concept is the Adjoint of an Operator, written as $O^\dagger$.

$$\int d\vec{r}\Phi^*(O\Psi) = \int d\vec{r}(O^\dagger\Phi)^*\Psi \tag{58}$$

for any arbitrary pair of functions Φ and Ψ of our function space.

A Hermitian Operator, O, is a self-adjoint operator. If

$$O = O^\dagger, \quad \text{then } O \text{ is hermitian.} \tag{59}$$

Note, the operator

$$\frac{d}{dx} \quad \text{is not hermitian,}$$

but the operator

$$\frac{\hbar}{i}\frac{d}{dx} \quad \text{is hermitian,}$$

because

$$\begin{aligned}\int d\vec{r}\Psi^*\left(\frac{\hbar}{i}\frac{d\Phi}{dx}\right) &= \frac{\hbar}{i}\int\int dydz\Psi^*\Phi\Big]_{x=-\infty}^{\infty} - \frac{\hbar}{i}\int d\vec{r}\frac{d\Psi^*}{dx}\Phi \\ &= \int d\vec{r}\left(\frac{\hbar}{i}\frac{d\Psi}{dx}\right)^*\Phi,\end{aligned} \tag{60}$$

where the integrated term must be zero for square-integrable functions, Ψ and Φ. Note also, the operator $\frac{\hbar}{i}\frac{\partial}{\partial x}$ is the momentum operator, p_x, when acting on a

function of the coordinates.

$$(p_x)_{\text{op.}}\Psi(\vec{r}, t) = \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(\vec{r}, t). \tag{61}$$

The product of two hermitian operators is in general not hermitian,

$$\int d\vec{r}\Psi^* O_2 O_1 \Phi = \int d\vec{r}(O_2^\dagger \Psi)^* O_1 \Phi = \int d\vec{r}(O_1^\dagger O_2^\dagger \Psi)^* \Phi, \tag{62}$$

so

$$(O_2 O_1)^\dagger = O_1^\dagger O_2^\dagger. \tag{63}$$

The product of the two hermitian operators is hermitian only if the operators commute. In the general case (for noncommuting operators), if O_1 and O_2 are both hermitian,

$$(O_1 O_2 + O_2 O_1) \qquad \text{and} \qquad i(O_1 O_2 - O_2 O_1)$$

are hermitian.

The commutator of two operators is very important in quantum mechanics. It is defined as

$$[O_1, O_2] = (O_1 O_2 - O_2 O_1). \tag{64}$$

G The Heisenberg Commutation Relations

The commutator

$$[p_x, x] = \frac{\hbar}{i}. \tag{65}$$

This commutator relation follows from

$$(p_x x - x p_x)\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}(x\Psi) - x\frac{\hbar}{i}\frac{\partial}{\partial x}(\Psi) = \frac{\hbar}{i}\Psi \tag{66}$$

for *all* Ψ of the Hilbert space. Eq. (65) is known as the Heisenberg commutation relation. Although we have demonstrated it here with the use of the wave function, it was introduced into quantum theory by Heisenberg without the concept of a wave function (see chapter 6D). Similarly, again using the technique of eq. (66),

$$[p_x, F(x, y, z)] = \frac{\hbar}{i}\frac{\partial F}{\partial x}. \tag{67}$$

On the other hand,

$$[p_x, G(p_x, p_y, p_z)] = 0, \tag{68}$$

but

$$[G(p_x, p_y, p_z), x] = \frac{\hbar}{i}\frac{\partial G}{\partial p_x}. \tag{69}$$

In particular, if H is a Hamiltonian, a function of the operators, p_x, p_y, p_z, x, y, z,

$$[p_x, H] = \frac{\hbar}{i}\frac{\partial H}{\partial x}; \qquad [x, H] = -\frac{\hbar}{i}\frac{\partial H}{\partial p_x}. \tag{70}$$

Expectation values of Hermitian operators are real. If $O = O^\dagger$,

$$< \Psi, O\Psi >=< O^\dagger\Psi, \Psi >=< O\Psi, \Psi >=< \Psi, O\Psi >^*, \tag{71}$$

so $< O >=< O >^*$.

If $O = O(\vec{p}, \vec{r}, t)$,

$$\frac{\hbar}{i}\frac{d}{dt} < O >=< [H, O] > + \frac{\hbar}{i} < \frac{\partial O}{\partial t} >, \tag{72}$$

where H is the Hamiltonian of the system, a hermitian operator, $H = H^\dagger$.

$$\begin{aligned}
&\frac{d}{dt} < \Psi, O\Psi >= \left(< \frac{\partial \Psi}{\partial t}, O\Psi > + < \Psi, O\frac{\partial \Psi}{\partial t} > + < \Psi, \frac{\partial O}{\partial t}\Psi > \right) \\
&= \frac{i}{\hbar}[< H\Psi, O\Psi > + < \Psi, O(-H\Psi) >] + < \frac{\partial O}{\partial t} > \\
&= \frac{i}{\hbar} < \Psi, (H^\dagger O - OH)\Psi > + < \frac{\partial O}{\partial t} > \\
&= \frac{i}{\hbar} < \Psi, (HO - OH)\Psi > + < \frac{\partial O}{\partial t} > .
\end{aligned} \tag{73}$$

H Generalized Ehrenfest Theorem

In the above relation, let $O = q_s$, where q_s is a generalized coordinate, and the Hamiltonian of the system is expressed in terms of generalized coordinates, q_s, and their canonically conjugate momenta, p_s. Then,

$$\begin{aligned}
\frac{\hbar}{i}\frac{d}{dt} < q_s > &= < [H, q_s] >= \frac{\hbar}{i} < \frac{\partial H}{\partial p_s} > \\
\frac{\hbar}{i}\frac{d}{dt} < p_s > &= < [H, p_s] >= -\frac{\hbar}{i} < \frac{\partial H}{\partial q_s} > .
\end{aligned} \tag{74}$$

These relations are the quantum analogues of the Hamiltonian form of the equations of motion.

$$\begin{aligned}
\frac{d}{dt} < q_s > &= < \frac{\partial H}{\partial p_s} > \\
\frac{d}{dt} < p_s > &= - < \frac{\partial H}{\partial q_s} > .
\end{aligned} \tag{75}$$

I Conservation Theorems: Angular Momentum, Runge–Lenz Vector, Parity

In the last section, we showed

$$\frac{d}{dt} < O >= \frac{i}{\hbar} < [H, O] > + < \frac{\partial O}{\partial t} > . \tag{76}$$

Thus, if an operator, O, commutes with the Hamiltonian, H, and is not an explicit function of the time, the time derivative of its expectation value in any state, Ψ, is equal to zero. This operator is the quantum-mechanical analogue of a classical "integral" of the motion. The operator, O, is conserved.

The simplest example, as in classical physics, is the Hamiltonian operator itself, provided it is not an explicit function of the time. For such a Hamiltonian, the conserved value of H is the energy E, as in classical physics. As a second example, consider single-particle motion in a central force field, with

$$H = \frac{1}{2m}(\vec{p} \cdot \vec{p}) + V(r), \tag{77}$$

where the potential function is a function of the scalar r only, where $r^2 = x^2 + y^2 + z^2$. (Note, we could also have chosen the two-body system with a central interaction, provided we replace m by the reduced mass and $\vec{r}$ stands for the relative vector, $\vec{r}_1 - \vec{r}_2$; see the next section). In this case, the three components of the orbital angular momentum vector,

$$\vec{L} = [\vec{r} \times \vec{p}], \tag{78}$$

are conserved quantities. For example,

$$\begin{aligned}
&[H, L_x] = [H, (yp_z - zp_y)] = y[H, p_z] + [H, y]p_z - z[H, p_y] - [H, z]p_y \\
&= y[V, p_z] + \tfrac{1}{2m}[p_y^2, y]p_z - z[V, p_y] - \tfrac{1}{2m}[p_z^2, z]p_y \\
&= -\frac{\hbar}{i} y \frac{\partial V}{\partial z} + \frac{\hbar}{i}\frac{p_y}{m} p_z - z\left(-\frac{\hbar}{i}\frac{\partial V}{\partial y}\right) - \frac{\hbar}{i}\frac{p_z}{m} p_y \\
&= \frac{\hbar}{i}\left(-y\frac{dV}{dr}\frac{z}{r} + z\frac{dV}{dr}\frac{y}{r}\right) = 0.
\end{aligned} \tag{79}$$

Similarly,

$$[H, L_y] = [H, L_z] = 0. \tag{80}$$

In the above calculation, we have made use of the trivial but useful commutator identities

$$[A, BC] = B[A, C] + [A, B]C; \quad \text{also} \quad [AB, C] = A[B, C] + [A, C]B. \tag{81}$$

From the commutators, $[H, L_k] = 0$, we also have that H commutes with the operator $\vec{L}^2$

$$[H, \vec{L}^2] = \sum_{\alpha=x,y,z} L_\alpha[H, L_\alpha] + [H, L_\alpha]L_\alpha = 0. \tag{82}$$

As a third example, consider the hydrogen atom Hamiltonian

$$H = \frac{1}{2\mu}(\vec{p}\cdot\vec{p}) - \frac{e^2}{r}. \tag{83}$$

For the Hamiltonian with this $1/r$ potential, the three components of the Runge–Lenz vector, $\vec{\mathcal{R}}$, are conserved, where classically $\vec{\mathcal{R}} = \frac{1}{\mu}[\vec{p}\times\vec{L}] - \frac{e^2}{r}\vec{r}$. Quantum mechanically, we must convert this into a hermitian operator by using the symmetrized form of the first term. Remembering the interchange of the order of the two vectors in a vector product introduces a minus sign, the symmetrized form for $\vec{\mathcal{R}}$ is

$$\vec{\mathcal{R}} = \frac{1}{2\mu}\Big([\vec{p}\times\vec{L}] - [\vec{L}\times\vec{p}]\Big) - \frac{e^2}{r}\vec{r}. \tag{84}$$

Note,

$$\begin{aligned}\tfrac{1}{2}\big([\vec{p}\times\vec{L}]_x - [\vec{L}\times\vec{p}]_x\big) &= \tfrac{1}{2}\Big((p_yL_z - p_zL_y) - (L_yp_z - L_zp_y)\Big)\\ &= \tfrac{1}{2}\Big((p_yL_z + L_zp_y) - (p_zL_y + L_yp_z)\Big).\end{aligned} \tag{85}$$

Note, p_yL_z is not a hermitian operator, because p_y does not commute with $L_z = (xp_y - yp_x)$. The symmetrized form of this operator, $\frac{1}{2}(p_yL_z + L_zp_y)$, however, is hermitian. In making the transition from classical physics quantities to quantum-mechanical operators, the hermitian, symmetrized form of the classical quantities will often give the needed quantum-mechanical operators. The proof that $[H, \mathcal{R}_k] = 0$, where H is the hydrogen atom Hamiltonian, will be left as an exercise (part of problem 13).

As a final example of a conserved operator, consider the space inversion or parity operator, P, where

$$P\Psi(x, y, z, t) = \Psi(-x, -y, -z, t). \tag{86}$$

For a Hamiltonian,

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z), \qquad \text{with} \quad V(-x, -y, -z) = V(x, y, z), \tag{87}$$

that is, with a potential that is space-inversion invariant, we have

$$\begin{aligned}HP\Psi(\vec{r}, t) &= H\Big(\frac{\hbar}{i}\overrightarrow{\nabla}, \vec{r}\Big)\Psi(-\vec{r}, t)\\ PH\Psi(\vec{r}, t) &= H\Big(-\frac{\hbar}{i}\overrightarrow{\nabla}, -\vec{r}\Big)\Psi(-\vec{r}, t) = H\Big(\frac{\hbar}{i}\overrightarrow{\nabla}, \vec{r}\Big)\Psi(-\vec{r}, t),\end{aligned} \tag{88}$$

so

$$(HP - PH)\Psi(\vec{r}, t) = 0 \tag{89}$$

for all Ψ of our Hilbert space. Hence, $[H, P] = 0$, and P is a conserved quantity. Finally, note also, P is a hermitian operator, because

$$\int d\vec{r}\Psi^*(\vec{r}, t)P\Psi(\vec{r}, t) = \int d\vec{r}\Psi^*(\vec{r}, t)\Psi(-\vec{r}, t) = \int d\vec{r}\Psi^*(-\vec{r}, t)\Psi(\vec{r}, t)$$

$$= \int d\vec{r}\Big(P^{\dagger}\Psi(\vec{r},t)\Big)^{*}\Psi(\vec{r},t),$$

where we have made the change of variables, $x \to -x$, $y \to -y$, $z \to -z$, and have changed the order of the integration limits in the three integrals implied by our shorthand notation in the last step of the first line. We see $P^{\dagger} = P$. Therefore, the expectation value of the operator P must also be real. Finally, because

$$P^2\Psi(\vec{r},t) = \Psi(\vec{r}),$$

the operator P^2 has an expectation value of 1. The real expectation value of the operator P can thus be only either $+1$ or -1. The solutions of the Schrödinger equation for the space-inversion invariant Hamiltonian of eq. (87) must thus either be unchanged or change sign under the space-inversion operation. The wave function must have even or odd parity.

J Quantum-Mechanical Hamiltonians for More General Systems

As an example of a slightly more general system, consider a particle of mass, m, and charge, e, moving in an electromagnetic field derivable from a vector potential, $\vec{A}(\vec{r})$, and a scalar potential, $\Phi(\vec{r})$. The classical Hamiltonian is given by

$$H = \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} + e\Phi. \tag{90}$$

This relation can be written in the form

$$H = \frac{(\vec{p}\cdot\vec{p})}{2m} - \frac{e}{2mc}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A} + e\Phi. \tag{91}$$

Note, because in general $[p_x, A_x] \neq 0$, we have written the scalar product of $\vec{A}$ with $\vec{p}$ in symmetrized, hermitian form, so the Hamiltonian in the second form is a candidate for the quantum-mechanical Hamiltonian of this system. This relation is indeed the correct quantum-mechanical Hamiltonian. The predictions based on this form of the Hamiltonian are in agreement with the experiment! (We shall study this system in more detail later, where we will discuss the role of the gauge of the potentials, the gauge transformation, the Aharanov–Bohm effect, etc.) For more complicated systems, however, the simple process of symmetrization of a classical Hamiltonian may not be sufficient, particularly if the physically relevant coordinates are a set of complicated curvilinear coordinates, say, in the case of a many-body system in which some of the degrees of freedom are "frozen" or do not come into play at a region of low-energy excitations.

K The Schrödinger Equation for an n-particle System

For the general n-particle system, with the Hamiltonian

$$H = \sum_{k=1}^{n} \frac{(\vec{p}_k \cdot \vec{p}_k)}{2m_k} + V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n), \tag{92}$$

we are led (as in the case of the single-particle system) to the Schrödinger equation

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = -\sum_k \frac{\hbar^2}{2m_k}\nabla_k^2 \Psi + V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n)\Psi. \tag{93}$$

For the two-particle system with no external forces, in particular, it will be useful to make a transformation to relative and center of mass coordinates

$$\vec{r} = \vec{r}_1 - \vec{r}_2, \qquad \vec{R} = \frac{(m_1\vec{r}_1 + m_2\vec{r}_2)}{(m_1 + m_2)}, \tag{94}$$

and

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2(m_1 + m_2)}\nabla^2_{\text{C.M.}}\Psi - \frac{\hbar}{2\mu}\nabla^2_{\text{rel.}}\Psi + V(\vec{r})\Psi, \tag{95}$$

where μ is the reduced mass, $\mu = m_1 m_2/(m_1 + m_2)$ and the potential is a function of the relative $\vec{r}$ only (no external fields). In this case, the center of mass motion separates. With $\Psi(\vec{R}, \vec{r}, t) = \Psi_{\text{C.M.}}(\vec{R}, t)\Psi_{\text{rel.}}(\vec{r}, t)$, the center of mass term leads to a plane wave solution

$$\Psi_{\text{C.M.}}(\vec{R}, t) = Ae^{\frac{i}{\hbar}(\vec{P}\cdot\vec{R} - E_{\text{transl.}}t)}, \tag{96}$$

where $\vec{P}$ is the linear momentum associated with the center of mass motion of the system of mass $(m_1 + m_2)$ and $E_{\text{transl.}}$ is the translational energy associated with the center of mass motion, $E_{\text{transl.}} = P^2/2(m_1 + m_2)$. The Schrödinger equation is then effectively an equation equivalent to a single-particle equation, provided the mass is replaced by the reduced mass.

$$-\frac{\hbar}{i}\frac{\partial \Psi_{\text{rel.}}}{\partial t} = -\frac{\hbar^2}{2\mu}\nabla^2_{\text{rel.}}\Psi_{\text{rel.}}(\vec{r}, t) + V(\vec{r})\Psi_{\text{rel.}}(\vec{r}, t). \tag{97}$$

In n-particle systems, it will be useful to transform from the coordinates $x_1, \ldots, z_n$ to a set of generalized coordinates q_s. Often, some of these will not come into play. In a polyatomic molecule, e.g., the ammonia molecule, NH_3, we have a system with 4 atomic nuclei and 10 electrons, a 14-particle system with 42 degrees of freedom (assuming we can neglect the electron and nuclear spins). These coordinates could be chosen as the 3 center of mass coordinates, which merely describe the free-particle translation of the whole system in space: 3 angular coordinates, say, three Euler angles, ϕ, θ, χ, which describe the orientation of the molecule in space and describe the rotational motion of the molecule; 6 relative coordinates, which describe the relative motions of the atomic nuclei, that is, the vibrational motions of the molecule; and finally 3×10 electronic coordinates

(again ignoring for the moment the electron spins), which describe the electron motions of the molecule. At very low excitation energies, only the rotational degrees of freedom, ϕ, θ, χ, may need to be considered. Therefore, if we can transform the general $3n = 42$-dimensional Laplacian operator of this 14-particle system from the 3×14 Cartesian coordinates to the physically relevant 42 generalized coordinates, q_s, including ϕ, θ, χ, we arrive at the desired Schrödinger equation, if the variations with all q_s are neglected, except for the variations with the needed ϕ, θ, χ. Even for the 1-particle system, it will generally be useful to express the Schrödinger equation not in terms of the Cartesian coordinates x, y, z, but in terms of some set of curvilinear coordinates, e.g., spherical coordinates r, θ, ϕ.

L The Schrödinger Equation in Curvilinear Coordinates

If we transform from the 3n Cartesian coordinates $x_1, \ldots, z_n$ to a new set of 3n generalized coordinates q_s, with $s = 1, \ldots, 3n$, through

$$x_1 = f_1(q_1, q_2, \ldots, q_{3n}), \quad \cdots, \quad \cdots, \quad z_n = f_{3n}(q_1, q_2, \ldots, q_{3n}) \tag{98}$$

the classical kinetic energy expression can be written as a homogeneous quadratic function of the $\dot{q}_i$,

$$T = \tfrac{1}{2} \sum_{i,j} g_{ij} \dot{q}_i \dot{q}_j, \tag{99}$$

where the g_{ij} are in general functions of the q_s. The classical Hamiltonian expressed in the generalized momenta, p_s, canonically conjugate to these q_s, can then be written as

$$H_{\text{class.}} = \tfrac{1}{2} \sum_{ij} g^{ij} p_i p_j + V(q_1, q_2, \ldots, q_{3n}), \tag{100}$$

where the g^{ij} matrix, that is, the superscripted g-matrix, is the inverse of the g_{ij} matrix, that is, the subscripted g-matrix

$$\sum_{\alpha} g_{i\alpha} g^{\alpha j} = \delta_i^j, \qquad \text{and} \qquad \sum_{\alpha} g^{i\alpha} g_{\alpha j} = \delta_j^i. \tag{101}$$

Note, the g^{ij} are in general complicated functions of the q_s and do not commute with the p_s. A large number of ways would exist of making the kinetic energy term hermitian, so the hermiticity requirement alone does not lead to the correct quantum-mechanical Hamiltonian. We know, however, how to transform the 3n-dimensional Laplacian operator from its Cartesian form to the form involving partial derivatives with respect to the new generalized q_s. Therefore, we can write the proper Schrödinger equation. We need, in addition to the g^{ij}, the function g, given by the determinant of the subscripted g-matrix,

$$g = |g_{ij}| = \det(g_{ij}). \tag{102}$$

Writing the 3n-dimensional Laplacian ∇^2 in the curvilinear coordinates, we arrive at the Schrödinger equation

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2}\sum_{ij}\frac{1}{\sqrt{g}}\frac{\partial}{\partial q_i}\left(g^{ij}\sqrt{g}\frac{\partial \Psi}{\partial q_j}\right) + V\Psi. \tag{103}$$

If Ψ is assumed to be a function of only a few of the q_i, the equation will simplify.

Problems

1. A free particle moving in the x-direction, (1-D motion) has a momentum distribution given by

$$\phi(p,t) = \sqrt{\frac{1}{\alpha\sqrt{\pi}}}e^{-\frac{1}{2}\frac{(p-p_0)^2}{\alpha^2}}e^{-\frac{i}{\hbar}\frac{p^2}{2m}t}$$

$$\phi(p,t) = \sqrt{\frac{4}{3\alpha^5\sqrt{\pi}}}(p-p_0)^2 e^{-\frac{1}{2}\frac{(p-p_0)^2}{\alpha^2}}e^{-\frac{i}{\hbar}\frac{p^2}{2m}t}.$$

For both cases, calculate the spatial probability density amplitude function, $\Psi(x,t)$, for this particle. Calculate $< p >$, $< p^2 >$, $< \Delta p >$, $\langle x \rangle$, $< x^2 >$, and $< \Delta x >$, and verify the uncertainty principle. Give an interpretation of Δx, in the limit $\hbar \to 0$, in classical terms.

2. From the "dispersion law,"

$$\frac{E^2}{c^2} - (\vec{p}\cdot\vec{p}) = m_0^2 c^2$$

for a relativistic free particle, derive a wave equation. (This equation is known as the Klein–Gordon equation.) If the probability density current is to have the form

$$\vec{S} = \frac{\hbar}{2mi}\left(\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*\right)$$

with

$$div\vec{S} + \frac{\partial W}{\partial t} = 0$$

to preserve conservation of probability, show how the probability density, W, must be related to Ψ, $\frac{\partial \Psi}{\partial t}$, Ψ^*, $\frac{\partial \Psi^*}{\partial t}$. Is this an acceptable W? Is $W \geq 0$ everywhere, for all t?

3. A particle of charge, e, and mass, m, in an electromagnetic field, derivable from vector and scalar potentials, $\vec{A}$, Φ, has a Hamiltonian

$$H = \frac{\vec{p}^2}{2m} - \frac{e}{2mc}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{e^2}{2mc^2}\vec{A}^2 + e\Phi.$$

(Note the symmetrized form of the second term.) Write the Schrödinger equation for this case. Find an expression for the probability density current, $\vec{S}$, with $W = \Psi^*\Psi$. Calculate

$$\frac{d\langle x\rangle}{dt}, \quad \text{and} \quad \frac{d\langle p_x\rangle}{dt},$$

and show how these are related to the classical equations of motion.

Also, show the wave equation is gauge invariant, and under the transformation

$$\vec{A} \to \vec{A}' = \vec{A} + \vec{\nabla}\chi, \qquad \Phi \to \Phi' - \frac{1}{c}\frac{\partial \chi}{\partial t},$$

where $\chi = \chi(x, y, z; t)$, the wave equation remains unchanged, provided

$$\Psi \to \Psi' = \Psi e^{\frac{ie}{\hbar c}\chi(x,y,z;t)}.$$

4. In describing scattering processes of complex projectiles from nuclei, it is sometimes useful to use a fictitious complex potential

$$V = V_1 + iV_2,$$

where V_1 and V_2 are both real. Assume V_2 = constant = W, inside a sphere of radius, $r_0 = 10^{-12}$ cm, and $V_2 = 0$ for $r > r_0$. Determine, W, magnitude in eV and sign, so the probability is 0.1 per 10^{-21} seconds for the *loss* of flux of incoming projectile particles. (Incoming α particles, e.g., can be "lost" by conversion to ^{3}He and neutrons, etc. Note, 10^{-21} seconds is a typical traversal time for a fast but nonrelativistic nuclear particle through a heavy nucleus.)

5. The classical kinetic energy for a rigid rotator, e.g., a polyatomic molecule such as H_2O to very good approximation, is given in terms of the three Euler angles, ϕ, θ, χ, and the three principal moments of inertia, A, B, C, by

$$2T = A(\dot{\theta}\cos\chi + \dot{\phi}\sin\theta\sin\chi)^2 + B(-\dot{\theta}\sin\chi + \dot{\phi}\sin\theta\cos\chi)^2 + C(\dot{\chi} + \dot{\phi}\cos\theta)^2.$$

Assuming other degrees of freedom, such as vibrational, translational, and electronic, in the case of the polyatomic molecule, can be neglected, then $V = 0$. Write the Schrödinger equation for the rigid rotator (asymmetric case, $A \neq B \neq C$). For the symmetric rotator, with $A = B$, show the time-independent wave function separates via the Ansatz

$$\psi(\phi, \theta, \chi) = \frac{1}{2\pi} e^{iM\phi} e^{iK\chi} \Theta(\theta),$$

and write the differential equation for $\Theta(\theta)$. (For the asymmetric case, the differential equation approach may not be the best way to solve this problem.)

6. Transpose the Schrödinger equation for the hydrogenic atom, with

$$H = \frac{\vec{p}\cdot\vec{p}}{2\mu} - \frac{Ze^2}{r},$$

where the above $\vec{p}$ and $\vec{r}$, which are $\vec{p}_{\text{physical}}$, and $\vec{r}_{\text{physical}}$ are transcribed into dimensionless $\vec{p}$ and $\vec{r}$ via

$$\vec{r}_{\text{phys.}} = a_0 \vec{r}, \quad \vec{p}_{\text{phys.}} = \frac{\hbar}{a_0}\vec{p}, \qquad \text{with } a_0 = \frac{\hbar^2}{\mu e^2 Z},$$

$$H_{\text{phys.}} = \frac{\mu Z^2 e^4}{\hbar^2} H, \qquad E_{\text{phys.}} = \frac{\mu Z^2 e^4}{\hbar^2}\epsilon.$$

Transpose the Schrödinger equation for the hydrogenic atom, further, into an equation written in terms of "stretched parabolic coordinates," μ, ν, ϕ, defined in terms of the dimensionless $\vec{r} = (x, y, z)$ by

$$\mu = \sqrt{(r+z)}[-2\epsilon]^{\frac{1}{4}}, \qquad \nu = \sqrt{(r-z)}[-2\epsilon]^{\frac{1}{4}}, \qquad \phi = \tan^{-1}\left(\frac{y}{x}\right),$$

where $r = \sqrt{x^2 + y^2 + z^2}$, and $\epsilon = E/(\mu Z^2 e^4/\hbar^2)$, or

$$x = \frac{\mu\nu}{[-2\epsilon]^{\frac{1}{2}}}\cos\phi, \qquad y = \frac{\mu\nu}{[-2\epsilon]^{\frac{1}{2}}}\sin\phi, \qquad z = \frac{(\mu^2 - \nu^2)}{2[-2\epsilon]^{\frac{1}{2}}},$$

where this transformation is useful for bound states, with $\epsilon < 0$. Transform the Laplacian into these stretched parabolic coordinates.

Another set of useful coordinates for the hydrogenic atom are the conventional parabolic coordinates, defined in terms of the dimensionless $\vec{r} = (x, y, z)$, by

$$\xi = r - z, \qquad \eta = r + z, \qquad \phi = \tan^{-1}\left(\frac{y}{x}\right),$$

$$x = \sqrt{\xi\eta}\cos\phi, \qquad y = \sqrt{\xi\eta}\sin\phi, \qquad z = \tfrac{1}{2}(\eta - \xi).$$

Transform the Laplacian into these curvilinear coordinates, and write the Schrödinger equation for the hydrogenic atom in these parabolic coordinates.