1.7 Probability Current

1. Consider the time-dependent Schrödinger Equation and its complex conjugate:

$$\imath\hbar\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\psi(x,t) \tag{1.7.55}$$

$$-\imath\hbar\frac{\partial}{\partial t}\psi^*(x,t) = H\psi^*(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\psi^*(x,t) \tag{1.7.56}$$

2. Multiply Eq. (1.7.55) by $\psi^*(x,t)$, and Eq. (1.7.56) by $\psi(x,t)$:

$$
\begin{aligned}
\psi^*(x,t)\imath\hbar\frac{\partial}{\partial t}\psi(x,t) &= \psi^*(x,t)H\psi(x,t) \\
&= \psi^*(x,t)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\psi(x,t)
\end{aligned}
\tag{1.7.57}
$$

$$
\begin{aligned}
-\psi(x,t)\imath\hbar\frac{\partial}{\partial t}\psi^*(x,t) &= \psi(x,t)H\psi^*(x,t) \\
&= \psi(x,t)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\psi^*(x,t)
\end{aligned}
\tag{1.7.58}
$$

3. The potential is assumed to be real and the Hamiltonian, Hermitian. Subtract the two equations to obtain (see that the terms involving V cancels out)

$$
\begin{aligned}
\imath\hbar\frac{\partial}{\partial t}\left[\psi(x,t)\psi^*(x,t)\right] &= -\frac{\hbar^2}{2m}\left[\psi^*(x,t)\frac{\partial^2}{\partial x^2}\psi(x,t)\right. \\
&\quad\left. - \psi(x,t)\frac{\partial^2}{\partial x^2}\psi^*(x,t)\right]
\end{aligned}
\tag{1.7.59}
$$

or

$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{\hbar}{2m\imath}\frac{\partial}{\partial x}\left[\psi^*(x,t)\frac{\partial}{\partial x}\psi(x,t) - \psi(x,t)\frac{\partial}{\partial x}\psi^*(x,t)\right] \tag{1.7.60}$$

4. If we make the variable substitution:

$$
\begin{aligned}
\mathcal{J} &= \frac{\hbar}{2m\imath}\left[\psi^*(x,t)\frac{\partial}{\partial x}\psi(x,t) - \psi(x,t)\frac{\partial}{\partial x}\psi^*(x,t)\right] \\
&= \frac{\hbar}{m}\mathcal{I}\left[\psi^*(x,t)\frac{\partial}{\partial x}\psi(x,t)\right]
\end{aligned}
\tag{1.7.61}
$$

(where $\mathcal{I}\left[\cdots\right]$ represents the imaginary part of the quantity in brackets) we obtain

$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{\partial}{\partial x}\mathcal{J} \tag{1.7.62}$$

or in three-dimensions

$$\frac{\partial}{\partial t}\rho(x,t) + \nabla\cdot\mathcal{J} = 0 \tag{1.7.63}$$

5. Equation (1.7.63) looks like the continuity equation of classical fluid provided $\mathcal{J}$ is the flux. In fact $\mathcal{J}$ is the flux associated with the probability density and is hence called the "probability current". (We will see later how this actually does correspond to a "classical-like" flux.)

6. Continuity equation of a classical fluid is basically the following: If you have a small volume element in a fluid. The change in density in that volume element is given by the amount of fluid coming into the volume element minus the amount going out. That is, flux in minus flux out. The mathematical form of this is Eq. (1.7.63). Hence the imaginary portion of the time-dependent Schrödinger Equation is a continuity equation. (Clear?)

7. **Homework**:

   (a) Prove that $\{\nabla \cdot \mathcal{J} = 0\}$ for a *stationary state*.

   (b) Calculate the probability current for the wavefunction

$$\psi = \frac{\exp\{\imath kx\}}{x} \tag{1.7.64}$$

1.8   Flux or probability current and its connections to magnetization

Let us evaluate the flux for a hydrogen atom wavefunction.

$$\mathcal{J} = \frac{\hbar}{\mu}\mathcal{I}\left[\psi^*(x,t)\nabla\psi(x,t)\right] \tag{1.8.65}$$

For ∇ in spherical coordinates we can use Eq. (1.6.24) and definitions in that same page to obtain:

$$\nabla = \vec{r_{e-N}}\frac{\partial}{\partial r_{e-N}} + \vec{\theta}\frac{\partial}{\partial\theta} + \frac{\vec{\phi}}{r_{e-N}\sin\theta}\frac{\partial}{\partial\phi} \tag{1.8.66}$$

Now its only the ϕ dependent part in Eq. (V.0.37) that has an imaginary term in it:

$$\begin{aligned}\psi_{n,l,m}(\rho,\theta,\phi;t) &\propto \exp\left[-\rho/2\right]\rho^l F(\rho)\mathcal{P}_{l,m}(\cos\theta)\exp\{\imath m\phi\}\\&\quad \exp\left[-\imath E_{\mu,n}t/\hbar\right]\end{aligned} \tag{1.8.67}$$

This leads to

$$\mathcal{J} = \vec{\phi}\frac{m\hbar}{\mu r_{e-N}\sin\theta}|\psi_{n,l,m}|^2 \tag{1.8.68}$$

proportional to the m quantum number. The fact that it is directed along $\vec{\phi}$ implies it is a *rotating wave*!!

Does it then make sense to you that the magnetic moment inside a small volume element is defined as:

$$d\vec{M} = \frac{1}{2}\vec{r} \times e\mathcal{J}\,dV \tag{1.8.69}$$

So, now you know where an orbital magnetic moment comes from, it comes from the flux. *Seems like Faraday's' law applies here too!!*

Using Eq. (1.8.69) and the definition of flux the orbital magnetic moment is:

$$M = -\frac{e}{2\mu} \langle \psi \,|\mathbf{L}|\, \psi \rangle \tag{1.8.70}$$

and the orbital magnetic moment operator is:

$$\mathbf{M} = -\frac{e}{2\mu}\mathbf{L} = \frac{g_e\beta}{\hbar}\mathbf{L} \tag{1.8.71}$$

where $\beta = \frac{e\hbar}{2\mu}$ is called the *Bohr magneton*, a unit of the magnetic moment. The orbital g-factor $g_e = 1$ for the hydrogen. This also means:

$$\mathbf{M_z} = -\frac{e}{2\mu}\mathbf{L_z} = \frac{g_e\beta}{\hbar}\mathbf{L_z} \tag{1.8.72}$$

Does this remind you of Eq. (2.1.2), very early!!

These can get you NMR chemical shifts in a complicated system!! Leads into Zeeman effect next.

The spin angular momentum also contains two operators, $\mathbf{S^2}$ and $\mathbf{S_z}$. There is a magnetization associated with these operators also that has a similar mathematical form as the equations above. We will use these ideas in the next section to learn more about the foundations of quantum mechanics.