

PHYS 621 – Quantum Mechanics Study Notes

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CHAPTER 1

The Failure of Classical Physics

The following is a quick summary of some of the phenomena which classical mechanics and electromagnetic theory could not properly model and explain.

1.1 Black-body radiation

The primary quantity of interest here is the energy density of some box which is kept at temperature T , denoted as $u(\nu, T)$. The total energy that strikes an area A of the wall of the box in time t is

$$\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \theta \int_0^{ct} r^2 \frac{A \cos \theta}{4\pi r^2} u(\nu, T) d\nu = \frac{ctA}{4} u(\nu, T) d\nu. \quad (1.1)$$

If the box absorbs some fraction $f(\nu, T)$ of this energy, then the total energy absorbed by the box at temperature T from light at frequency ν is

$$E(\nu, T) = \frac{c}{4} f(\nu, T) u(\nu, T). \quad (1.2)$$

A body is called “black” if $f \equiv 1$, meaning that all light is perfectly absorbed.

1.1.1 Classical treatment

We can solve Maxwell’s equations (no sources!) inside the box with periodic boundary conditions, which gives

$$\frac{\partial^2 \tilde{\mathbf{E}}}{\partial t^2} + c^2 k^2 \tilde{\mathbf{E}} = 0, \quad (1.3)$$

where $\tilde{\mathbf{E}}(\mathbf{k})$ are the Fourier expansion coefficients of the electric field such that

$$\vec{E} = \sum_{\mathbf{k}} e^{i\vec{k} \cdot \vec{r}} \tilde{\mathbf{E}}(\mathbf{k}). \quad (1.4)$$

A similar equation holds for the magnetic field. We can thus model the electromagnetic (EM) radiation by an infinite set of uncoupled harmonic oscillators.

Next, we find the number of modes in a small volume of the reciprocal space to be

$$\rho(\vec{k}) d^3\vec{k} = 2 \frac{V}{(2\pi)^3} d\vec{k}. \quad (1.5)$$

The factor of two comes from the fact that there are two independent components in \vec{E} (in solving MEs, there is a condition that \vec{E} be perpendicular to \vec{k}), and the second factor comes from the volume per mode in the reciprocal space.

Using the equipartition theorem (which states that $U = \frac{1}{2}k_B T$ is the energy contribution from each quadratic degree of freedom in the Hamiltonian – of which there are two for a given harmonic oscillator), the relation $d^3\vec{k} = 4\pi k^2 dk$ (assuming angular symmetry), and the dispersion relation $c = \nu\lambda$ ($k = 2\pi/\lambda$), we recover the Rayleigh-Jeans law for the energy density of a blackbody:

$$\boxed{\frac{(k_B T/2)\rho(k) dk}{V} = 8\pi \underbrace{\frac{k_B T}{c^3}}_{u(\nu, T)} \nu^2 d\nu}, \quad (1.6)$$

Clearly the energy density diverges to ∞ for more energetic light (which is where the term “ultraviolet catastrophe” originates).

1.1.2 Quantum treatment

The quantum nature comes from using Einstein’s formula for the energy of a photon of light at frequency ν : $E = nh\nu$ ($n = 0, 1, 2, \dots$). We can use the partition function to derive the fact that the average energy of a harmonic oscillator is

$$\langle E \rangle = \frac{h\nu}{e^{\beta h\nu} - 1}, \quad (1.7)$$

where $\beta = 1/k_B T$. Using this fact instead of the equipartition theorem, we find

$$\boxed{u(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\beta h\nu} - 1}}. \quad (1.8)$$

Notice that this resolves the ultraviolet catastrophe since the energy density now is bounded at all frequencies of light, peaking at some ν_0 (is there a well-known formula for this?).

1.2 Photo-electric effect

The photo-electric effect is the phenomenon that if light is shined on a metal and set up a potential difference between the metal and some other metallic plate, say, that there is a current between the plates (in some circumstances).

1.2.1 Classical Treatment

We can treat an electron at the surface of the metal, which absorbs the light, to be a harmonic oscillator driven by the light (i.e. the force that the electric field of the light wave exerts on the electron). That is,

$$m\ddot{x}(t) + kx(t) = -e\mathcal{E}_0 \cos(\omega t). \quad (1.9)$$

Solving gives,

$$x(t) = x_0 \cos(\omega_0 t + \phi_0) - \frac{e\mathcal{E}_0}{m} \frac{\cos(\omega t)}{\omega_0^2 - \omega^2}, \quad (1.10)$$

where $\omega_0^2 = k/m$, which depends on the metal in consideration. The first term is just the homogeneous solution of the equation with x_0 and ϕ_0 determined by initial conditions. Notice that the energy of the electron is (considering only the contribution associated with the transient term – i.e. that from the driving force)

$$E(t) = \frac{1}{2}m\dot{x}^2 + \frac{k}{2}x \approx \frac{e^2\mathcal{E}_0^2}{2m} \frac{1}{(\omega_0^2 - \omega^2)^2} [\omega^2 \sin^2(\omega t) + \omega_0^2 \cos^2(\omega t)]. \quad (1.11)$$

The average energy over one period of oscillation $T = 2\pi/\omega$ is just

$$\langle E \rangle = \frac{e^2\mathcal{E}_0^2}{4m} \frac{\omega_0^2 + \omega^2}{(\omega_0^2 - \omega^2)^2}. \quad (1.12)$$

Recall that the intensity of light is proportional to \mathcal{E}_0^2 , so the average energy of the electron is predicted to be proportional to the intensity of the light shone on the metal. Above some threshold energy, we should observe a current, and by increasing the intensity of the light, we would expect classically that the current is proportional in some way (would have to work out the proportionality) to the intensity. In fact, for any color of light, we could observe a current if we have intense enough light.

1.2.2 Quantum Treatment

The classical treatment is inconsistent with experimental observations. In reality, it is found that no matter how intense we make the light, some wavelengths are simply incapable of generating any current. Again, in this case, we quantize the energy of a photon as $E = h\nu$. For a metal with work function $W = h\nu_0$, where ν_0 is a convenient parameter with which to compare the frequency of the light, the kinetic energy of an electron which is freed from the metal by this photon is

$$K = E - W = h(\nu - \nu_0). \quad (1.13)$$

Clearly then, we have to have $\nu > \nu_0$ at the very least to observe a current. If we satisfy this condition, then increasing the intensity of light – which corresponds to increasing the number of photons – does in fact lead to larger observed currents.

1.3 Compton scattering

In classical mechanics, treating light as a wave, if we shine light on a charged particle, say an electron, we would find that the electron is excited by the light similar to the above argument. In quantum mechanics, however, treating the photon as a particle, the light has momentum proportional to $p = h/\lambda = h\nu/c$, and the photon interacts “concretely” with the electron by exchanging momentum and scattering at some angle θ relative to the axis of the incoming light. Quantitatively, we have the Compton relation

$$\Delta\lambda = \frac{h}{mc}(1 - \cos\theta). \quad (1.14)$$

Note that h/mc is known as the Compton wavelength of the electron.

We can derive this relation as follows. First, let us work in the rest frame of the electron, and the photon approach the electron with momentum $\vec{p}_\gamma = h/\lambda\hat{x}$. After the collision, the photon has momentum $\vec{p}'_\gamma = \frac{h}{\lambda'}[\sin\theta\hat{x} + \cos\theta\hat{y}]$ while the electron has momentum \vec{p}'_e . Note that energy conservation gives

$$p_\gamma c + mc^2 = p'_\gamma c + \sqrt{m^2 c^4 + p_e'^2 c^2}. \quad (1.15)$$

If we subtract $p'_\gamma c$ from both sides and square, we have

$$\begin{aligned} [(p_\gamma - p'_\gamma)c + mc^2]^2 &= m^2 c^4 + |\vec{p}'_\gamma - \vec{p}_\gamma|^2 c^2 \\ (p'_\gamma - p_\gamma)^2 + 2(p_\gamma - p'_\gamma)mc &= p_\gamma'^2 + p_\gamma^2 - 2p'_\gamma p_\gamma \cos\theta \\ \frac{1}{p'_\gamma} - \frac{1}{p_\gamma} &= \frac{1 - \cos\theta}{mc} \\ \lambda' - \lambda = \Delta\lambda &= \frac{h}{mc}(1 - \cos\theta). \end{aligned} \quad (1.16)$$

1.4 Atom stability and spectral lines

In the homework, we completed a problem showing that based on classical mechanics an electron should collapse into the nucleus of an atom very quickly (because of the EM radiation from its acceleration). Clearly this is in contrast with the stability of the universe in general, and can be broached with the introduction of a few different models, although the Schrödinger equation is the most correct treatment and is the subject of much of the topic of non-relativistic QM.

There is also the issue of the spectral lines from atoms, which are distinct wavelengths of light emitted and absorbed by atoms. Note that the emission and absorption spectra are identical (corresponding to the energy levels of an atom). This observation is in stark contradiction to the classical expectation, which is that the spectra are continuous. For emission, the electron radiates light of all frequencies within a certain range, given by its acceleration at any time. On the other hand, there is no classical restriction on which frequencies an electron is permitted to interact with, so it absorbs any light happily.

CHAPTER 2

Wave-Particle Duality and Wave Mechanics

In the previous chapter, we have observed that light can be treated as both a particle in some instances and a wave in others. It is natural then to extend this to matter particles such as electrons, which have in some instances as wave-like properties. De Broglie introduced the wavelength of a particle as $\lambda = h/p$, and from this formula, we can reproduce the different observations which corroborate this wave-particle duality of matter. For instance, a couple well known results are the two-slit experiment and Bragg reflection, both of which give interference patterns that can only be attributed to the wave nature of particles.

2.1 Wave packets

A particle's wave-function can be written

$$\Psi(\vec{r}, t) = \int \frac{d^3\vec{k}'}{(2\pi)^{3/2}} g(\vec{k}') e^{i[\vec{k}' \cdot \vec{r} - \omega(\vec{k}')t]}, \quad (2.1)$$

where g is some complex profile function whose magnitude $|g|$ is strongly localized around \vec{k} . This is a superposition of plane waves corresponding to different momenta (we will see later that we cannot consider a particle with definite momentum $\vec{p} = \hbar\vec{k}$) with time dependence given by a phase with $\omega = E/\hbar = \hbar k'^2/2m$.

We can analyze this wave-packet using the method of stationary phase. Defining $\phi(\vec{k}') = \vec{k}' \cdot \vec{r} - \omega t$, we expand around the peak of $|g|$, which gives

$$\phi(\vec{k}') \approx \phi(\vec{k}) + (\vec{k}' - \vec{k}) \cdot \vec{\nabla}_{\vec{k}'} \phi(\vec{k}')|_{\vec{k}'=\vec{k}} + \dots \quad (2.2)$$

Putting this into Eq. (2.1), we have

$$\Psi(\vec{r}, t) \approx e^{i[\vec{k} \cdot \vec{r} - \omega(\vec{k})t]} \int \frac{d^3\vec{k}'}{(2\pi)^{3/2}} g(\vec{k}') e^{i[\vec{r} - \frac{\hbar\vec{k}}{m}t] \cdot [\vec{k}' - \vec{k}]}. \quad (2.3)$$

Notice that the first factor is just a phase factor, and the line of constant phase $\phi = \phi_0$ is given by

$$x_i = \frac{\phi_0}{k_i} + \frac{\omega(\vec{k})}{k_i} t. \quad (2.4)$$

The coefficient in front of the second term is called the phase velocity.

Now, turning to the phase factor inside the integral, we have some argument that depends on the distance between \vec{r} and $\vec{r}_0 = (\hbar\vec{k}/m)t$. We can identify \vec{r}_0 with the “center” of the wave-packet since for \vec{r} far from \vec{r}_0 , the exponential is very oscillatory and hence damps the amplitude of Ψ , but for $\vec{r} \approx \vec{r}_0$, there are no such cancellations and a peak at $\vec{r} = \vec{r}_0$. It is clear then that the wave-packet moves globally with this center at the group velocity $\vec{v}_{\text{group}} = \hbar\vec{k}/m$.

2.2 Mathematical Digression: δ -Function Definition and Properties

In the hand-wavey approach, we can regard delta-functions as the limit of a sequence of functions $\delta(x) = \lim_{n \rightarrow \infty} f_n(x)$ such that $\delta(x) = 0$ for all $x \neq 0$ and

$$\int_{-\infty}^{\infty} \phi(x) \delta(x) dx = \phi(0). \quad (2.5)$$

A few examples (certainly not exhaustive) of (f_n) include

- $f_n(x) = \begin{cases} n & |x| < 1/2n \\ 0 & |x| > 1/2n \end{cases}$
- $f_n(x) = \frac{n}{2} e^{-n|x|}$
- $f_n(x) = \frac{n}{\pi} \frac{1}{(nx)^2 + 1}$
- $f_n(x) = \frac{n}{\sqrt{\pi}} e^{-(nx)^2}$
- $f_n(x) = \frac{1}{\pi} \frac{\sin(nx)}{x}$
- $f_n(x) = \frac{1}{n\pi} \frac{\sin^2(nx)}{x^2}$

There are a couple of properties of δ -functions that should be enumerated¹

1. The δ -function is even: $\delta(x) = \delta(-x)$, which can be easily shown by a substitution $x \rightarrow -x$.
2. $\delta(cx) = \delta(x)/|c|$ for $c \in \mathbb{R}$ (substitute $u = cx$ and consider $c > 0$ and $c < 0$ separately).

¹Note that by equality of two dirac functions D_1 and D_2 , we really mean that $\int dx \phi(x) D_1(x) = \int dx \phi(x) D_2(x)$.

2.3. MATHEMATICAL DIGRESSION: FOURIER TRANSFORM DEFINITION AND PROPERTIES⁷

3. For a function $f(x)$ with simple roots $\{x_i : f(x_i) = 0\}$, $\delta(f(x)) = \sum_i \delta(x - x_i)/|f'(x_i)|$ (Break the integral into small pieces around each x_i and Taylor expand $f(x)$ about x_i).

Generalizing to n dimensions, we can define $\delta^{(n)}(\vec{x}) = 0$ for all $\vec{x} \neq 0$ and

$$\int_{\mathcal{D}} \phi(\vec{x}) \delta(\vec{x} - \vec{x}_0) dx = \begin{cases} \phi(\vec{x}_0) & \vec{x}_0 \in \mathcal{D} \\ 0 & \vec{x}_0 \notin \mathcal{D} \end{cases}. \quad (2.6)$$

Focusing on three dimensions, we have

$$\delta^{(3)}(\vec{r}) = \delta(x)\delta(y)\delta(z). \quad (2.7)$$

If we want to change to curvilinear coordinates (u, v, w) , then

$$\delta^{(3)}(\vec{r}) = |\text{Jac}[(x, y, z) \rightarrow (u, v, w)]| \delta(u)\delta(v)\delta(w). \quad (2.8)$$

For example, changing from Cartesian to spherical, we have

$$\delta^{(3)}(\vec{r} - \vec{r}_0) = \frac{1}{r^2} \delta(r - r_0) \delta(\cos \theta - \cos \theta_0) \delta(\phi - \phi_0). \quad (2.9)$$

2.3 Mathematical Digression: Fourier Transform Definition and Properties

Generically, an integral transform is of the form

$$\tilde{f}(y) = \int_a^b dx K(x, y) f(x). \quad (2.10)$$

The function K is called the kernel of the transform.

The Fourier transform is defined with $K(x, y) = e^{-iyx}/\sqrt{2\pi}$ such that

$$\tilde{f}(y) = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}} e^{-iyx} f(x). \quad (2.11)$$

Note that only functions f which are square integrable² have a fourier transform.

If we know the transform of f , we can invert the Fourier transform as follows to obtain

$$f(x) = \int_{-\infty}^{\infty} \frac{dy}{\sqrt{2\pi}} e^{iyx} \tilde{f}(y). \quad (2.12)$$

There are a few properties that are useful to enumerate:

1. Parseval's identity: $\int_{-\infty}^{\infty} |f(x)|^2 dx = \int_{-\infty}^{\infty} |\tilde{f}(y)|^2 dy$
2. $\mathcal{F}\left\{\frac{d^n f}{dx^n}\right\}(y) = (iy)^n \tilde{f}(y).$

² $\int_{-\infty}^{\infty} |f(x)|^2 dx \in \mathbb{R}$

3. The Fourier transform of $h(x) = \int_{-\infty}^{\infty} dx' f(x-x')g(x')$ (called a convolution) is just the product of the transforms of f and g separately: $\tilde{h}(y) = \sqrt{2\pi} \tilde{f}(y)\tilde{g}(y)$.

One more useful result to have in our back pocket is the Fourier transform of the δ -function³:

$$\tilde{\delta}(y) = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}} e^{-iyx} \delta(x-x_0) = \frac{e^{-ix_0y}}{\sqrt{2\pi}}. \quad (2.13)$$

From this we can also derive the integral representation of the δ -function by taking the inverse Fourier transform of Eq. (2.13)

$$\delta(x-x_0) = \int_{-\infty}^{\infty} \frac{dy}{\sqrt{2\pi}} e^{iyx} \tilde{\delta}(y) = \int_{-\infty}^{\infty} \frac{e^{-i(x-x_0)y}}{2\pi} dx. \quad (2.14)$$

Finally, we can extend the notion of this one-dimensional Fourier transform to three dimensions by taking successive Fourier transforms in each coordinate direction:

$$\tilde{f}(\vec{k}) = \int \frac{d^3\vec{r}}{(2\pi)^{3/2}} e^{-i\vec{k}\cdot\vec{r}} f(\vec{r}). \quad (2.15)$$

2.4 Wave mechanics

Recall that a wave packet is defined by

$$\Psi(\vec{r}, t) = \int \frac{d^3\vec{k}'}{(2\pi)^{3/2}} g(k') e^{i[\vec{k}'\cdot\vec{r} - \omega(\vec{k}')t]}. \quad (2.16)$$

Notice that this wave-function satisfies what we will call the free-particle Schrödinger equation (S.E.):

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t). \quad (2.17)$$

Acting on the wave-packet explicitly reproduces the dispersion relation $E = \hbar\omega = \hbar^2 k^2 / 2m$.

At this point, we introduce the Born interpretation of the wave function, which is that $\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$ is the spatial probability density for the particle which is describes. Note that these wave-functions must be normalized in the sense that

$$\int_{-\infty}^{\infty} \rho(\vec{r}, t) d^3\vec{r} = 1 \quad (2.18)$$

since measurement of the particle's position is certain to return some value.

Observe that this normalization is independent of time:

$$\frac{d}{dt} \int_{-\infty}^{\infty} |\Psi|^2 d^3\vec{r} = 0, \quad (2.19)$$

³We will skirt the problem of the existence of such a Fourier transform which requires that the δ -function is square integrable but is not well defined at this point

This implies that

$$\begin{aligned}
\int d^3\vec{r} \left[\Psi^* \frac{\partial \Psi}{\partial t} + \text{c.c.} \right] &= \int d^3\vec{r} \left[\Psi^* \left(-\frac{\hbar}{2mi} \nabla^2 \Psi \right) + \text{c.c.} \right] = 0 \\
- \int d^3\vec{r} \frac{\hbar}{2mi} \left[\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^* \right] &= - \int d^3\vec{r} \vec{\nabla} \cdot \frac{\hbar}{2mi} \left[\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^* \right] = 0 \\
- \int dS_\infty \underbrace{\frac{\hbar}{2mi} \left[\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^* \right]}_{\vec{j}(\vec{r}, t)} &= 0, \tag{2.20}
\end{aligned}$$

where \vec{j} is interpreted the probability current density. It should be clear that $\vec{j}(\vec{r}, t)|_{S_\infty} = 0$ since $\Psi \rightarrow 0$ as $|\vec{r}| \rightarrow \infty$. Here we have proven a continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0, \tag{2.21}$$

which is a local probability conservation result.

Once we have the wave-function, we can calculate the average of a function $f(\vec{r})$ is

$$\langle f(\vec{r}) \rangle(t) = \int d^3\vec{r} f(\vec{r}) \rho(\vec{r}, t). \tag{2.22}$$

In particular, the average position of a particle is

$$\langle \vec{r}(t) \rangle = \int d^3\vec{r} \vec{r} |\Psi(\vec{r}, t)|^2. \tag{2.23}$$

Now, we turn our attention to the calculation of the average momentum. We can define a momentum space wave-function by taking the Fourier transform of the coordinate wave-function:

$$\begin{aligned}
\tilde{\Psi}(\vec{p}, t) &= \int \frac{d^3\vec{r}}{(2\pi)^{3/2}} e^{-i\vec{k} \cdot \vec{r}} \Psi(\vec{r}, t) \\
&= \int \frac{d^3\vec{r}}{(2\pi\hbar)^{3/2}} e^{-i\vec{p} \cdot \vec{r}/\hbar} \left[\int \frac{d^3\vec{p}'}{(2\pi\hbar)^{3/2}} g(\vec{p}'/\hbar) e^{-i} e^{i[\vec{p}' \cdot \vec{r} - Et]/\hbar} \right] \\
&= e^{-iEt/\hbar} g(\vec{p}). \tag{2.24}
\end{aligned}$$

From this, it is trivial to see that the average momentum is

$$\langle \vec{p}(t) \rangle = \int d^3\vec{p} \vec{p} |\tilde{\Psi}(\vec{p}, t)|^2. \tag{2.25}$$

Less trivially, in terms of the coordinate space wave-function:

$$\begin{aligned}
\langle \vec{p}(t) \rangle &= \int \frac{d^3 \vec{p}}{(2\pi\hbar)^{3/2}} \vec{p} \tilde{\Psi}^*(\vec{p}, t) \tilde{\Psi}(\vec{p}, t) \\
&= \int \frac{d^3 \vec{p}}{(2\pi\hbar)^{3/2}} \vec{p} \left[\int \frac{d^3 \vec{r}'}{(2\pi\hbar)^{3/2}} e^{-i\vec{p} \cdot \vec{r}' / \hbar} \Psi^*(\vec{r}', t) \right] \left[\int \frac{d^3 \vec{r}}{(2\pi\hbar)^{3/2}} e^{i\vec{p} \cdot \vec{r} / \hbar} \Psi(\vec{r}, t) \right] \\
&= \int \frac{d^3 \vec{p}}{(2\pi\hbar)^{3/2}} \left[\int \frac{d^3 \vec{r}'}{(2\pi\hbar)^{3/2}} e^{-i\vec{p} \cdot \vec{r}' / \hbar} \Psi^*(\vec{r}', t) \right] \left[\int \frac{d^3 \vec{r}}{(2\pi\hbar)^{3/2}} \left(i\hbar \vec{\nabla} e^{i\vec{p} \cdot \vec{r} / \hbar} \right) \Psi(\vec{r}, t) \right] \quad (2.26) \\
&= \int \frac{d^3 \vec{p}}{(2\pi\hbar)^{3/2}} \left[\int \frac{d^3 \vec{r}'}{(2\pi\hbar)^{3/2}} e^{-i\vec{p} \cdot \vec{r}' / \hbar} \Psi^*(\vec{r}', t) \right] \left[\int \frac{d^3 \vec{r}}{(2\pi\hbar)^{3/2}} e^{i\vec{p} \cdot \vec{r} / \hbar} \left(-i\hbar \vec{\nabla} \Psi(\vec{r}, t) \right) \right] \\
&= \int \frac{d^3 \vec{r}}{(2\pi\hbar)^{3/2}} \Psi^*(\vec{r}, t) \left(-i\hbar \vec{\nabla} \right) \Psi(\vec{r}, t).
\end{aligned}$$

From this, we may define the coordinate space momentum operator $\vec{p} = -i\hbar \vec{\nabla}$.

We could actually reverse the argument for $\langle \vec{r}(t) \rangle$, which would give

$$\langle \vec{r}(t) \rangle = \int \frac{d^3 \vec{p}}{(2\pi\hbar)^{3/2}} \tilde{\Psi}^*(\vec{p}, t) \left(i\hbar \vec{\nabla}_p \right) \tilde{\Psi}(\vec{p}, t). \quad (2.27)$$

From this, the momentum space position operator is given as $\vec{r} = i\hbar \vec{\nabla}_p$, which is quite similar to the momentum operator. This is one of the first hints of the intimate connection between position and momentum.

CHAPTER 3

Schrödinger Equation; Uncertainty Relations

3.1 Time-dependent Schrödinger Equation

In the last section, we derived the governing equation for the wave-function of a free particle

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t). \quad (3.1)$$

We can add in interactions through the potential $V(\vec{r})$ as

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r}, t) = H\Psi, \quad (3.2)$$

where we define the Hamiltonian operator $H = \vec{p}^2/2m + V(\vec{r})$.

Note that we still retain the Born interpretation of the wave-function, which is that $\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$ is the spatial probability density, and furthermore, we could repeat the manipulations to derive the probability density current and arrive at the exact same answer (worked out in a homework problem):

$$\vec{j}(\vec{r}, t) = \frac{\hbar}{2mi} \left[\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^* \right]. \quad (3.3)$$

Furthermore, we still have the local continuity equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0, \quad (3.4)$$

which follows from the normalization of the wave-function

$$\int_{-\infty}^{\infty} |\Psi(\vec{r}, t)|^2 = 1. \quad (3.5)$$

Working toward a solution, we use separation of variables and write $\Psi(\vec{r}, t) = f(t)\psi(\vec{r})$ and obtain

$$\frac{1}{f(t)} \left(i\hbar \frac{df}{dt} \right) = \frac{1}{\psi(\vec{r})} \left[-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) \right] = E. \quad (3.6)$$

Thus, we have two separate equations for the time and spatial dependence. The time-dependence has a trivial solution

$$f(t) = e^{-iEt/\hbar}. \quad (3.7)$$

3.2 Time-independent Schrödinger Equation

Continuing with our separable solution, we see the spatial differential equation does not quite have such a trivial solution

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = H\psi(\vec{r}) = E\psi(\vec{r}). \quad (3.8)$$

This is called the time-independent S.E. typically. It is also an energy eigenvalue equation, where E and ψ are the energy eigenvalue and eigenfunction, respectively, of the Hamiltonian operator. Generally, we can only say a few things about E and ψ without an explicit form for the potential.

- For a separable wave-function: $\langle H \rangle = \int d^3\vec{r} e^{iEt/\hbar} \psi^*(\vec{r}) H e^{-iEt/\hbar} \psi(\vec{r}) = E$
- The energy spectrum is strictly real: H is a hermitian operator¹, so $\langle H \rangle = E = \int d^3\vec{r} [H\psi(\vec{r})]^* \psi(\vec{r}) = E^*$
- The set of energy eigenfunctions is orthogonal: Notice that $\int d^3\vec{r} \psi_m^* H \psi_n = E_n \int d^3\vec{r} \psi_m^* \psi_n = E_m \int d^3\vec{r} \psi_m^* \psi_n$ exploiting the hermiticity of H . Subtracting the two equations, we have $(E_n - E_m) \int d^3\vec{r} \psi_m^* \psi_n = 0$, and since $E_n - E_m \neq 0$, ψ_m and ψ_n must be orthogonal.
- The eigenfunctions of H form a complete basis such that any square-integrable function $\phi(\vec{r}) = \sum_n c_n \psi_n(\vec{r})$ with $c_n = \int d^3\vec{r} \psi_n^*(\vec{r}) \phi(\vec{r})$.

3.3 General Solution of the Time-dependent Schrödinger Equation

We worked with separable solutions above, but in general, a solution $\Psi(\vec{r}, t)$ of the S.E. need not be separable. However, any solution can be expanded in the basis of energy eigenfunctions as in the bullet point of the last bullet point:

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}) e^{-iE_n t/\hbar}. \quad (3.9)$$

Note that $\Psi(\vec{r}, t)$ must satisfy the relevant boundary conditions (BCs)². Additionally, for bound states, Ψ must be normalizable as well.

¹ $\int d^3\vec{r} f^*(\vec{r}) H g(\vec{r}) = \int d^3\vec{r} [H f(\vec{r})]^* g(\vec{r})$

² ψ and $\vec{\nabla}\psi$ must be continuous – except perhaps in the case where $V(\vec{r})$ contains a δ -function

3.4 Heisenberg's uncertainty relations

The commutator of two operators A and B is $[A, B] = AB - BA$. For the position and momentum operators

$$[x, p]f(x) = -i\hbar[x, \frac{\partial}{\partial x}]f(x) = -i\hbar\left[x\frac{\partial f}{\partial x} - \frac{\partial}{\partial x}xf(x)\right] = i\hbar f(x) \quad (3.10)$$

$$\Rightarrow [x, p] = i\hbar. \quad (3.11)$$

Generally, $[x_i, p_j] = i\hbar\delta_{ij}$.

Let us also define the uncertainty in the observable A corresponding to the operator A as

$$\Delta A^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2. \quad (3.12)$$

Note that ΔA is not some measurement error. It is an intrinsic uncertainty in the quantity A imposed by the fact that the wave-function is not necessarily an eigenstate of A . We can derive a lower bound on $\Delta A \Delta B$ that depends on the commutator $[A, B]$.

For any square-integrable functions f and g we have the Cauchy-Schwarz inequality

$$\left(\int d^3\vec{r} |f(\vec{r})|^2 \right) \left(\int d^3\vec{r} |g(\vec{r})|^2 \right) \geq \left| \int d^3\vec{r} g^*(\vec{r}) f(\vec{r}) \right|^2. \quad (3.13)$$

Note that the roles of f and g are interchangeable, so we can also write

$$\left(\int d^3\vec{r} |f(\vec{r})|^2 \right) \left(\int d^3\vec{r} |g(\vec{r})|^2 \right) \geq \frac{1}{2} \left[\left| \int d^3\vec{r} g^*(\vec{r}) f(\vec{r}) \right|^2 + \left| \int d^3\vec{r} f^*(\vec{r}) g(\vec{r}) \right|^2 \right] \quad (3.14)$$

Observe

$$\Delta A^2 \Delta B^2 = \left(\int d^3\vec{r} \Psi^* (A - \langle A \rangle)^2 \Psi \right) \left(\int d^3\vec{r} (B - \langle B \rangle)^2 \right). \quad (3.15)$$

Since we are interested in observables A and B , we assume that A and B are hermitian such that if we define $f = (A - \langle A \rangle)\Psi$ and $g = (B - \langle B \rangle)\Psi$ then

$$\begin{aligned} \Delta A^2 \Delta B^2 &= \left(\int d^3\vec{r} |f(\vec{r})|^2 \right) \left(\int d^3\vec{r} |g(\vec{r})|^2 \right) \\ &\geq \frac{1}{2} \left[\left| \int d^3\vec{r} \Psi^* (B - \langle B \rangle) (A - \langle A \rangle) \Psi \right|^2 \right. \\ &\quad \left. + \left| \int d^3\vec{r} \Psi^* (A - \langle A \rangle) (B - \langle B \rangle) \Psi \right|^2 \right] \\ &\geq \frac{1}{4} \left| \int d^3\vec{r} \Psi^* [A, B] \Psi \right|^2 = \frac{1}{4} |\langle [A, B] \rangle|^2. \end{aligned} \quad (3.16)$$

From this, we can write down the Heisenberg uncertainty relation

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \quad (3.17)$$

