I.5 The Schrödinger Equation

I.5.1 Free Particles

* We have characterized free-particle solutions of a quantum mechanical equation of motion, but we don't have the equation itself yet.

* We already know this EOM has to be
  - linear (superposition principle)
  - homogeneous (need freedom to normalize $|\psi|^2$ to be a probability density)
  - first order in time (one initial condition, $\psi(\vec{r},0)$ or $\phi(\vec{k})$, are sufficient to completely determine a system, no derivatives needed)

* The dispersion relation $\omega = \frac{\hbar}{2m}k^2$ then dictates that for a free-particle wave fct. $\psi(\vec{r},t)$

$$\boxed{-i\hbar \frac{\partial \psi}{\partial t} = \frac{\hbar^2}{2m}\Delta\psi}$$

$\Delta = \nabla\nabla$ is the Laplace operator

Why?

$$\frac{\hbar^2}{2m}\Delta \frac{1}{(2\pi)^{3/2}}\int d^3k\, \phi(\vec{k})\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} = \frac{\hbar^2}{2m}\frac{1}{(2\pi)^{3/2}}\int d^3k\, \phi(\vec{k})(i\vec{k})^2 e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

$$= -\frac{\hbar^2 k^2}{2m}\psi(\vec{r},t)$$

$$-i\hbar\frac{\partial}{\partial t}\frac{1}{(2\pi)^{3/2}}\int d^3k\, \phi(\vec{k})\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} = -i\hbar\frac{1}{(2\pi)^{3/2}}\int d^3k\, \phi(\vec{k})(-i\omega)e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

$$= -\hbar\omega\, \psi(\vec{r},t)$$

$\square$

* This equation is called the free (time-dependent) Schrödinger equation.

It is of diffusion-type except for the imaginary unit "i" appearing which makes its solutions manifestly complex-valued.

* We could expand this equation by analogy to particles in a potential $V(\vec{r},t)$ by postulating $\underbrace{\hbar\omega}_{E} = \underbrace{\frac{\hbar^2}{2m} k^2}_{T} + V$

I.5.2 Action Waves and Hamilton-Jacobi as a Classical Limit

* We still would like to make a firm connection with classical mechanics. The SE (Schrödinger equation) doesn't look as if there is a cl. mechanics limit. Hmm...

Is there a description of cl. mechanics of point particles based on waves? Yes! Hamilton-Jacobi theory.

* Recall

$$\boxed{\frac{\partial S}{\partial t} + H(q_1, \ldots, q_s; p_1, \ldots, p_s, t) = 0}$$

with $p_i = \frac{\partial S}{\partial q_i}$ is a non-linear, first order partial diff. equation for S. $s = 1, \ldots, n$ = # of degrees of freedom

Here $S(q_1, \ldots, q_s, t)$ is the Hamilton principle action or action with variable endpoint $\overset{q}{\overset{\shortparallel}{(q_i)_{i=1}^s}}$; the q_i are generalized coordinates:

$$S(q,t) = \int_{t_0}^{t} L(Q, \dot{Q}, T)\, dT$$

L = Lagrange fct. of the system and $\underset{(Q_i(T))_{i=1}^s}{\overset{\shortparallel}{Q(T)}}$ is the motion of the system from a fixed $\underset{\text{initial}}{\text{point}}$ $q_0 = Q(t_0)$ at a fixed time t_0 to a variable $\overset{\text{end}}{\text{point}}$ $q = Q(t)$ at a variable time t.

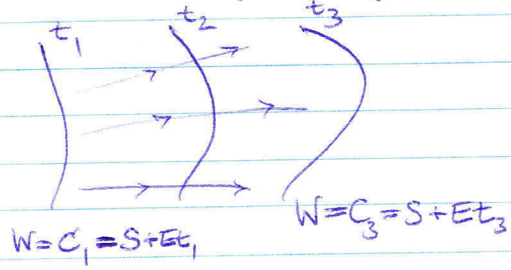
$$H = \sum_{i=1}^{s} \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L$$ is the Hamilton fct. of the system.

* Recall: For systems with constant energy E we can separate time t and coordinates q: $S(q,t) = W(q) - Et$

From now on let $q = \vec{r}$ be point in $\mathbb{R}^3$, i.e. cartesian coord.

W = const. defines a hypersurface in coord. space $\mathbb{R}^3$

$\Rightarrow S$ = const. defines surfaces W = const. moving as a fct. of time



can be interpreted as moving wave fronts.

* Recall: velocity of the action waves $\vec{u} = \frac{E}{p}\hat{p}$ where $\vec{p} = \nabla S = \nabla W$ is the particle momentum. This is different from the particle velocity $\vec{v} = \frac{\vec{p}}{m}$ but in fact it is the same as the phase velocity of a wave packet! So S is a candidate for a classical quantity

to relate to ψ.

* Recall: $S(q,t)$ has all the information about the classical system.

Simple example: 1-D free particle; H-J equation: $\frac{1}{2m}\left(\frac{\partial S}{\partial q}\right)^2 = -\frac{\partial S}{\partial t}$

separation ansatz $S = W(q) - Et \Rightarrow \left(\frac{\partial W}{\partial q}\right)^2 = \alpha^2 = \text{const.}$

and $-2mE = \alpha^2 \quad \Rightarrow S = \alpha q - \frac{\alpha^2}{2m} t + \text{const.}$

(and $E = \frac{\alpha^2}{2m}$)

We can reconstruct the motion through $\frac{\partial S}{\partial \alpha} = \beta = \text{const}$

$\Rightarrow q - \frac{\alpha}{m} t = \text{const.}$; const. and α fixed by initial conditions $q(0) = q_0$, $\dot{q}(0) = \frac{p_0}{m}$

$\Rightarrow q = q_0 + \frac{p_0}{m} t$

More examples maybe in the HW.

* Since $S = \vec{r}\cdot\vec{p} - Et$ for free particle a plane wave can be written as $\sim e^{i(\vec{k}\cdot\vec{r} - \omega t)} = e^{\frac{i}{\hbar} S}$. We postulate therefore that the QM equation of motion reduce in the classical limit to the Hamilton-Jacobi equation for the "phase" $S(\vec{r},t)$.

This is similar to the eikonal approximation in optics:

wave optics $\xrightarrow[\text{appr.}]{\text{eikonal}}$ geometric optics.

I.5.3 Constraints from the Probabilistic Interpretation.

* For a conserved quantity with spatial density $\varsigma(\vec{r})$ the conservation law $\frac{d}{dt}\int_V \varsigma \, d^3r = 0$ for a static ~~ca~~ distribution implies the general conservation law

$$\boxed{\frac{\partial \varsigma}{\partial t} + \nabla \vec{j} = 0} \qquad (\text{II}) \quad \text{"Continuity Equation"}$$

where $\vec{j}$ is the current associated with the density.

Example: $\varsigma \overset{el.}{\vee}$ charge density, $\vec{j}$ = el. current density

* If ς is a density associated with a distribution of particles (their number or el. charge etc.) then the current density is

$$\vec{j}(\vec{r},t) = \varsigma(\vec{r},t)\, \vec{v}(\vec{r},t)$$

where $\vec{v}$ is the velocity field of the particles.

Why? HW2

* In particular, for systems of particles the continuity equation is

$$\boxed{\frac{\partial \varsigma}{\partial t} + \varsigma \nabla \vec{v} + (\nabla \varsigma) \cdot \vec{v} = 0} \qquad (*)$$

* We postulate that the QM equation of motion should permit the existence of a current $\vec{j}$ associated with wave functions $\psi(\vec{r},t)$ such that the continuity equation ($\square$) holds for $\rho = |\psi|^2$. Moreover in the classical limit it should reproduce (*), the continuity equation for particles.

I.5.4 Derivation of the Schrödinger Equation

* The general ansatz for a linear, homogeneous, 1st order in time wave equation is

We will often use Einstein's sum convention from here on: indices occuring twice have to be summed over

$$\left(a + b_0 \frac{\partial}{\partial t} + b_k \frac{\partial}{\partial r_k} + c_{0k} \frac{\partial^2}{\partial t \partial r_k} + c_{jk} \frac{\partial^2}{\partial r_j \partial r_k} + \dots \right) \psi = 0$$

Because we look for the simplest possible equation of motion we won't consider higher order terms.

Coefficients can be complex, i.e.

$$a = a' + i a'' \qquad c_{0k} = c'_{0k} + i c''_{0k}$$

$$b_0 = b_0' + i b'' \qquad c_{jk} = c'_{jk} + c''_{jk}$$

$$b_j = b_j' + i b_j''$$

Where alle $(\,)'$ and $(\,)''$ coefficients are now real.

* We can write any solution ψ in terms of amplitude and phase:

$$\psi(\vec{r},t) = A(\vec{r},t)\, e^{\frac{i}{\hbar} S(\vec{r},t)}$$

where A and S are real-valued functions.

Using this in our general equation:

$$a + \frac{i}{\hbar} b_0 \frac{\partial S}{\partial t} + b_0 \frac{1}{A}\frac{\partial A}{\partial t} + \frac{i}{\hbar} b_k \frac{\partial S}{\partial r_k} + \frac{1}{A} b_k \frac{\partial A}{\partial r_k}$$

$$+ \frac{i}{\hbar} c_{jk} \frac{\partial^2 S}{\partial r_j \partial r_k} - \frac{1}{\hbar^2} c_{jk} \frac{\partial S}{\partial r_j}\frac{\partial S}{\partial r_k} + \frac{2i}{\hbar A} c_{jk} \frac{\partial A}{\partial r_j}\frac{\partial S}{\partial r_k} + \frac{1}{A} c_{jk} \frac{\partial^2 A}{\partial r_j \partial r_k} = 0$$

We haven't written terms $\frac{\partial^2 \psi}{\partial t \partial r_j}$ which will turn out to ~~have~~ disappear.

Separating imaginary and real part:

$$(\mathcal{I}) \quad a' + b_0' \frac{1}{A}\frac{\partial A}{\partial t} + \frac{1}{A} b_k' \frac{\partial A}{\partial r_k} + \frac{1}{A} c_{jk}' \frac{\partial^2 A}{\partial r_j \partial r_k}$$

$$- \frac{2}{\hbar A} c_{jk}'' \frac{\partial A}{\partial r_j}\frac{\partial S}{\partial r_k} - \frac{1}{\hbar} b_0'' \frac{\partial S}{\partial t} - \frac{1}{\hbar} b_k'' \frac{\partial S}{\partial r_k} - \frac{1}{\hbar} c_{jk}'' \frac{\partial^2 S}{\partial r_j \partial r_k} - \frac{1}{\hbar^2} c_{jk}' \frac{\partial S}{\partial r_j}\frac{\partial S}{\partial r_k} = 0$$

$$(\mathcal{R}) \quad a'' + \frac{1}{\hbar} b_0' \frac{\partial S}{\partial t} + \frac{1}{\hbar} b_k' \frac{\partial S}{\partial r_k} + \frac{1}{\hbar} c_{jk}' \frac{\partial^2 S}{\partial r_j \partial r_k} - \frac{1}{\hbar^2} c_{jk}'' \frac{\partial S}{\partial r_j}\frac{\partial S}{\partial r_k}$$

$$+ \frac{2}{\hbar A} c_{jk}' \frac{\partial A}{\partial r_j}\frac{\partial S}{\partial r_k} + b_0'' \frac{1}{A}\frac{\partial A}{\partial t} + \frac{1}{A} b_k'' \frac{\partial A}{\partial r_k} + \frac{1}{A} c_{jk}'' \frac{\partial^2 A}{\partial r_j \partial r_k} = 0$$

Two coupled diff. equations for phase and amplitude.

* The H-J equation for a real-valued potential energy $V(\vec{r},t)$ for a particle of mass m is

$$\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\frac{\partial S}{\partial r_j}\right)\left(\frac{\partial S}{\partial r_j}\right) + V(\vec{r},t) = 0$$

Comparing coefficients with ($\mathcal{S}$) would suggest

$$a' = V \quad , \quad b_0' = 0 \quad , \quad b_k' = 0 \qquad \forall K = 1,2,3$$

$$c_{jk}'' = 0 \qquad \forall j,k = 1,2,3 \quad , \quad b_0'' = -\hbar \quad , \quad b_k'' = 0 \qquad \forall k$$

$$c_{jk}' = -\frac{\hbar^2}{2m}\delta_{jk}$$

$$(\mathcal{S}) \Rightarrow \quad \frac{\partial S}{\partial t} + \frac{1}{2m}\left((\nabla S)^2 - \frac{\hbar^2 \Delta A}{A}\right) + V = 0$$

This is still a quantum equation. In the limit $\hbar \to 0$ we can identify S with the classical action and ($\mathcal{S}$) $\to$ Hamilton-Jacobi.

In more detail: classically $\nabla S = \vec{p}$, i.e. the approximation $\hbar \to 0$ means

$$p^2 \gg \frac{\hbar^2 \Delta A}{A} \quad \text{or} \quad \frac{\Delta A}{A} \ll k^2 ;$$

variations of A have to be small on the scale of typical wave lengths $\lambda \sim \frac{1}{k}$

* With the set of coefficients above ($\mathcal{A}$) becomes

$$a'' - \frac{\hbar}{2m}\Delta S - \frac{1}{A}\frac{2\hbar}{2m}(\nabla A)\cdot(\nabla S) - \frac{\hbar}{A}\frac{\partial A}{\partial t} = 0$$

On the other hand the continuity equation (*) for $\rho = A^2$ is $(\vec{p} = \nabla S)$

$$\frac{\partial A}{\partial t} + \frac{A}{2m}\Delta S + \frac{1}{m}(\nabla A)\cdot(\nabla S) = 0 \qquad (**)$$

Comparing coefficients: $a'' = 0$

Then ($\mathcal{A}$) coincides with (**) for $\nabla S \to \vec{p}$

* Plugging all coefficients into our ansatz gives

$$\boxed{\left(-i\hbar\frac{\partial}{\partial t} - \frac{\hbar^2}{2m}\Delta + V\right)\psi = 0}$$

Time-dependent Schrödinger equation (SE) for particles with forces acting.

This is the generalization of the free-particle result from I.5.1 for real-valued potentials $V(\vec{r},t)$

* Our construction ensures that in the classical limit the t-dep. SE recovers H-J and the classical continuity equation.

* Complex valued potentials are sometimes used in the SE. The imaginary part describes absorption or creation of particles and the continuity equation needs to be modified.

* Instead of a decomposition $\psi(\vec{r},t) = A(\vec{r},t)\, e^{\frac{i}{\hbar}S(\vec{r},t)}$ with real-valued A, S sometimes one uses $\psi(\vec{r},t) = C\, e^{\frac{i}{\hbar}S_{qu}(\vec{r},t)}$ with a $\mathbb{C}$-valued "quantum action" S_{qu}. One can easily check that it fulfills a "quantum" Hamilton-Jacobi equation analogous to $(\mathcal{S})$.

$$(\mathcal{S}') \qquad \frac{\partial S_{qu}}{\partial t} + \frac{1}{2m}\left((\nabla S_{qu})^2 - i\hbar\Delta S_{qu}\right) + V = 0$$

I.5.5 Momentum Space Representation

* In the general case the time evolution from $\psi(\vec{r},0)$ to $\psi(\vec{r},t)$ for arbitrary t might not be as simple as in the free particle case. However we can take a Fourier transformation for any $\psi(\vec{r},t)$ to arrive at a FT wave fct. $\phi(\vec{k},t)$.

It will be more convenient to switch from $\phi(\vec{k},t)$ to a modified $\phi(\vec{p},t)$ in terms of momentum $\vec{p} = \hbar\vec{k}$.

* Using the substitutions $\vec{p} \longleftrightarrow \hbar\vec{k}$, $d^3p \longleftrightarrow \hbar^3 d^3k$ $\phi(\vec{p}) \longleftrightarrow \hbar^{-3/2}\phi(\vec{k})$ the FT relations between $\vec{r}$ and $\vec{k}$ can be rewritten between $\vec{r}$ and $\vec{p}$ as

$$\boxed{\begin{aligned} \psi(\vec{r},t) &= \frac{1}{(2\pi\hbar)^{3/2}} \int_{\mathbb{R}^3} \phi(\vec{p},t)\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\, d^3p \\ \phi(\vec{p},t) &= \frac{1}{(2\pi\hbar)^{3/2}} \int_{\mathbb{R}^3} \psi(\vec{r},t)\, e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\, d^3r \end{aligned}}$$

if the Fourier integrals exist. $\phi(\vec{p},t)$ is the (time-dep.) wave fct. in momentum space.

* Example: for a free particle

$$\phi(\vec{p},t) = \phi(\vec{p},0)\, e^{-i\omega(\vec{p})t} = \phi(\vec{p},0)\, e^{-\frac{i}{\hbar}E(\vec{p})t}$$

Why? cf. I.4.3

* From the Schrödinger equation in coordinate space one can derive an equation of motion for $\phi(\vec{p},t)$:

$$\boxed{i\hbar \frac{\partial}{\partial t} \phi(\vec{p},t) = \frac{p^2}{2m} \phi(\vec{p},t) + V(i\hbar \nabla_p)\, \phi(p,t)}$$

"Momentum space Schrödinger equation"

where $V(i\hbar \nabla_p)$ is the potential $V(\vec{r})$ in momentum space. Note that $\vec{p}$-space S.E. follows from $\vec{r}$-space S.E. from the simple translation rules

(cf. I.4.1) $\quad \vec{r} \longleftrightarrow i\hbar \nabla_p \quad ; \quad \vec{p} \longleftrightarrow -i\hbar \nabla_r$

Explicit proof: HW 3

* We say: $\psi(\vec{r},t)$ and its FT $\phi(\vec{p},t)$ describe the same "state" of a physical system.

I.6 Probabilities and Expectation Values

* By construction solutions $\psi(\vec{r},t)$ of the S.E. lead to a probability density $\rho = |\psi|^2 = \psi^* \psi$ which satisfies a continuity equation

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

where $\boxed{\vec{j} = \frac{\hbar}{2mi}\left[\psi^* \nabla \psi - (\nabla \psi)^* \psi\right]}$

is the current density of the wave function ψ

Why? HW I [2]

In the classical limit $\vec{j} \longrightarrow \vec{j}_{cl} = \rho \vec{v}$

* For square-integrable fcts. ψ (i.e. $\int_{\mathbb{R}^3} |\psi|^2 d^3r$ exists) we agree to normalize the total probability to unity, i.e.

$$\int_{\mathbb{R}^3} |\psi|^2 d^3r = 1$$

Then $|\psi(\vec{r},t)|^2 d^3r$ is the probability to find a particle at time t in a volume d^3r at $\vec{r}$.

* Because of Plancherel's theorem we can interpret $|\phi(\vec{p})|^2$ as a probability density to find particles at a momentum $\vec{p}$.

For square-integrable fcts. $\int |\psi|^2 d^3r = 1 = \int |\phi|^2 d^3p$.

* With probability densities we can calculate expectation values *

E.g. $$\langle \vec{r} \rangle = \int_{\mathbb{R}^3} \vec{r}\, |\psi(\vec{r},t)|^2 d^3r = \int_{\mathbb{R}^3} \psi^*(\vec{r},t)\, \vec{r}\, \psi(\vec{r},t) d^3r$$

*if these integrals exist.

"Average particle position"

we will often prefer this "bra-ket" like notation for expectation values

$$\langle (\vec{r} - \langle \vec{r} \rangle)^2 \rangle = \int_{\mathbb{R}^3} \psi^* \, (\vec{r} - \langle \vec{r} \rangle)^2 \, \psi \, d^3r$$

variance of position around the mean

etc.

Generally for any observable $F(\vec{r})$ (which does not depend on $\vec{p}$)

$$\boxed{\langle F \rangle = \int_{\mathbb{R}^3} \psi^*(\vec{r},t)\, F(\vec{r})\, \psi(\vec{r},t)\, d^3r}$$

* Similarly $$\langle \vec{p} \rangle = \int_{\mathbb{R}^3} \vec{p}\, |\phi(\vec{p},t)|^2 d^3p = \int_{\mathbb{R}^3} \phi^*(\vec{p},t)\, \vec{p}\, \phi(\vec{p},t)\, d^3p$$

average momentum

Average kinetic energy $\langle T \rangle = \int_{\mathbb{R}^3} \phi^* \frac{p^2}{2m} \phi \, d^3p$

etc.

For any observable $F(\vec{p})$ (which does not depend on $\vec{r}$)

$$\boxed{\langle F \rangle = \int_{\mathbb{R}} \phi^*(\vec{p},t)\, F(\vec{p})\, \phi(\vec{p},t)\, d^3p}$$

* We can express expectation values of quantities $F(\vec{r})$ in momentum space via Fourier transform:

$$\langle \vec{r} \rangle = \int \psi^*(\vec{r},t)\, \vec{r}\, \psi(\vec{r},t)\, d^3r =$$

$$= \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3p' \int d^3r\; \phi^*(\vec{p}',t)\, e^{-\frac{i}{\hbar}\vec{p}'\cdot\vec{r}} \left[-i\hbar \nabla_p\; e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}} \right] \phi(\vec{p},t)$$

$$\underset{\text{p.I.}}{=} \frac{1}{(2\pi\hbar)^3} \int d^3p\, d^3p'\; \phi^*(\vec{p}',t) \left[+i\hbar \nabla_p\; \phi(\vec{p},t) \right] \underbrace{e^{-\frac{i}{\hbar}\vec{r}(\vec{p}'-\vec{p})}}_{\substack{(2\pi)^3 \delta^{(3)}\left(\frac{i}{\hbar}(\vec{p}'-\vec{p})\right) \\ =(2\pi\hbar)^3 \delta^{(3)}(\vec{p}'-\vec{p})}} + \text{boundary terms}$$

assume $\phi(\vec{p},t)$ falling off sufficiently fast

$$= \int d^3p\; \phi^*(\vec{p},t)\, \underbrace{i\hbar \nabla_p}_{\substack{\text{representation} \\ \text{of } \vec{r} \text{ in momentum space} \\ \text{cf. I.4.1}}}\, \phi(\vec{p},t)$$

Generally for any observable $F(\vec{r})$

$$\langle F \rangle = \int_{\mathbb{R}^3} \phi^*(\vec{p},t)\, F(i\hbar\nabla_p)\, \phi(\vec{p},t)\, d^3p$$

Similarly for observables $F(\vec{p})$

$$\langle F \rangle = \int_{\mathbb{R}^3} \psi(\vec{r},t)\, F(-i\hbar\nabla_r)\, \psi(\vec{r},t)\, d^3r$$

In particular

$$\langle \vec{p} \rangle = \int_{\mathbb{R}^3} \psi^* (\underbrace{-i\hbar\nabla}_{\substack{\text{representation} \\ \text{of } \vec{p} \text{ in coord. space}}} \psi)\, d^3r$$

* In classical mechanics all the information on a system can be written in terms of $\vec{r}$ and $\vec{p}$. Thus consider a general observable $F(\vec{r},\vec{p})$

Our results so far seem to imply

$$\boxed{\begin{aligned}\langle F\rangle &= \int_{\mathbb{R}_3} \psi^*(\vec{r},t)\, F(\vec{r}, -i\hbar\nabla_r)\, \psi(\vec{r},t)\, d^3r \\ &= \int_{\mathbb{R}^3} \phi^*(\vec{p},t)\, F(i\hbar\nabla_p, \vec{p})\, \phi(\vec{p},t)\, d^3p\end{aligned}}$$

It is straightforward to prove this formula as long as pairs of conjugate variables (x, p_x), (y, p_y), (z, p_z) are separable, i.e. do not appear as products.

If they do there is an ambiguity as $\underbrace{x\frac{\partial}{\partial x}}_{\sim xp} \neq \underbrace{\frac{\partial}{\partial x}x}_{\sim px}$

This seems in accordance with the uncertainty relation: x and p_x can not be determined sharply at the same time.

Examples: $\vec{L} = \vec{r}\times\vec{p}$ has separable conjugate variables $\rightarrow$ $\langle \vec{L}\rangle$ calculable

action for free particle $S = \vec{r}\cdot\vec{p} - Et$: non-separable pairs ; $\langle S\rangle = ?$

I.7 Operators and Operator Algebra

I.7.1 Spaces of Functions and Operators

* We will organize possible wave functions ψ mathematically into spaces of functions. Because of the superposition principle we'll be interested in linear spaces or $\overbrace{\text{vector spaces}}^{\text{over } \mathbb{C}}$; i.e. if ψ_1 and ψ_2 are in the vector space then $\lambda\psi_1 + \psi_2$ is also an element of the same vector space for any $\lambda \in \mathbb{C}$. [I]

* Examples: $L^1(\mathbb{R}^n)$, $L^2(\mathbb{R}^n)$, $C^1(\mathbb{R}^n)$ i.e. the integrable, square-integrable, differentiable fcts. (complex-valued) over $\mathbb{R}^n$ are vector spaces of functions.

* Let $\mathcal{S}_1$ and $\mathcal{S}_2$ be two vector spaces of fcts. A map

$$F: \mathcal{S}_1 \to \mathcal{S}_2$$
$$f \mapsto g$$

is often called an operator.

An operator is called
$$\begin{cases} \text{linear if } & F(\lambda\psi_1 + \psi_2) = \lambda F(\psi_1) + F(\psi_2) \\ \text{anti-linear if } & F(\lambda\psi_1 + \psi_2) = \lambda^* F(\psi_1) + F(\psi_2) \end{cases}$$

Most operators we'll encounter in quantum mechanics will be linear.

* Examples: Multiplicative operators, e.g. $f(x) \mapsto x f(x)$, and derivatives, i.e. $f(x) \mapsto \frac{df}{dx}$ are examples of important linear operators between suitable functional vector spaces.

[I] The usual rules in vector spaces about adding vectors and multiplying them with scalars apply.

* For $f \in L^2(\mathbb{R}^3)$ and an operator $\mathcal{O}: L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ we define the expectation value of the operator $\mathcal{O}$ with respect to f as

$$\langle \mathcal{O} \rangle = \int_{\mathbb{R}^3} f^*(\vec{r})\, \underbrace{\mathcal{O}}_{\mathcal{O}\text{ acts on } f} f(\vec{r})\, d^3r \qquad \text{if the integral exists.}$$

* With these new definitions we can make the following identifications:

  - The physical states of a system can be identified with (normalized) vectors both in a vector space of coordinate space wave functions $\mathcal{S}_{\vec{r}}$ and a vector space of momentum space wave fcts $\mathcal{S}_{\vec{p}}$ (and both are related by FT)

  - Physical observables $\mathcal{O}$ that depend on position $\vec{r}$ and momentum $\vec{p}$ can be identified with operators $\mathcal{O}_{\vec{r}}: \mathcal{S}_{\vec{r}} \to \mathcal{S}_{\vec{r}}$ and operators $\mathcal{O}_{\vec{p}}: \mathcal{S}_{\vec{p}} \to \mathcal{S}_{\vec{p}}$ and the expectation value of $\mathcal{O}$ (in a state ψ) corresponds to the expectation value of either operator:

$$\langle \mathcal{O} \rangle = \int_{\mathbb{R}^3} \psi_{\vec{r}}^*(\vec{r})\, \mathcal{O}_{\vec{r}}\, \psi_{\vec{r}}(\vec{r})\, d^3r = \int_{\mathbb{R}^3} \psi_{\vec{p}}^*(\vec{p})\, \mathcal{O}_{\vec{p}}\, \psi_{\vec{p}}(\vec{p})\, d^3p$$

with the caveats discussed at the end of I.6.

* Note: we will usually drop the index on the operator and write $\mathcal{O}$ for both operators and observable. We will often use ψ and ϕ for $\psi_{\vec{r}}$ and $\psi_{\vec{p}}$.

* The vector spaces $\mathcal{S}_{\vec{r}}$ and $\mathcal{S}_{\vec{p}}$ of interest will usually contain L^2 but be larger than L^2 (to allow e.g. for plane waves).

* Important operators and their $\vec{r}$ and $\vec{p}$ representations:

	$\mathcal{O}$	$\mathcal{O}_{\vec{r}}$	$\mathcal{O}_{\vec{p}}$
position	$\vec{r}$	$\vec{r}$	$i\hbar\nabla_p$
momentum	$\vec{p}$	$-i\hbar\nabla_r$	$\vec{p}$
angular momentum	$\vec{L}$	$-i\hbar\,\vec{r}\times\nabla_r$	$i\hbar\,\nabla_p\times\vec{p}$
kinetic energy	T	$-\frac{\hbar^2}{2m}\Delta$	$\frac{p^2}{2m}$
pot. energy	V	$V(\vec{r})$	$V(i\hbar\nabla_p)$
energy/Hamilton fct.	E or H	$-\frac{\hbar^2}{2m}\Delta+V(\vec{r})$	$\frac{p^2}{2m}+V(i\hbar\nabla_p)$

* With the concept of a Hamilton operator both Schrödinger eqs. in $\vec{r}$-and $\vec{p}$-space can be written in short-hand notation

$$\boxed{i\hbar\frac{\partial\psi}{\partial t}=H\psi}$$

I.7.2 Products and Commutators

* Two operator $F, G: \mathcal{S}\to\mathcal{S}$ can be concatenated in the usual sense by applying them sequentially:

$$G\circ F:\mathcal{S}\to\mathcal{S}$$
$$f\mapsto G(F(f))$$

* We will just write GF instead of $G \circ F$, but be aware that this "product" is usually not commutative: $GF \neq FG$

E.g. $x \frac{d}{dx} \neq \frac{d}{dx} x$ in the operator sense since

$$x\left(\frac{d}{dx} f(x)\right) \neq \frac{d}{dx}\left(x f(x)\right)$$

* It is hence useful to define the commutator of two such operators F, G:

$$[F,G] = FG - GF$$

which is again an operator on the same space $\mathcal{S}$.

* We can establish the following properties for commutators of operators F, G, H:

$$[F,G] = -[G,F] \qquad \text{anti-symmetry}$$

$$\left.\begin{aligned} [F, \lambda G + H] &= \lambda [F,G] + [F,H] \\ [\lambda F + G, H] &= \lambda [F,H] + [G,H] \end{aligned}\right\} \text{bi-linearity}$$

for any $\lambda \in \mathbb{C}$

$$\left.\begin{aligned} [FG, H] &= F[G,H] + [F,H]G \\ [F, GH] &= [F,G]H + G[F,H] \end{aligned}\right\} \text{product rule} \qquad \text{(check!)}$$

$$[F,[G,H]] + [H,[F,G]] + [G,[H,F]] = 0 \qquad \text{Jacobi identity} \quad (\text{cf HW III, [2]})$$

These properties make the commutator a Lie product (or Lie bracket) on the algebra of operators over $\mathcal{S}$.

* In QM the commutators of pairs of conjugate variables are particularly important. They are typically of the type $\sim q, \sim \frac{\partial}{\partial q}$

For position and momentum in cartesian space:

$$[x, p_x] = i\hbar \, \mathbb{1}$$

where $\mathbb{1}$ is the identity operator on the functional vector space $\mathcal{S}$.

Why? In $\vec{r}$-space representation $[x, p_x] f = x\left(-i\hbar\frac{\partial}{\partial x}\right)f - \left(-i\hbar\frac{\partial}{\partial x}\right)(xf)$

$$= i\hbar f - i\hbar x\frac{\partial f}{\partial x} + i\hbar x\frac{\partial f}{\partial x} = i\hbar f \quad \text{for any fct. } f.$$

Generally $\boxed{[r_i, p_j] = i\hbar\,\delta_{ij}}$ (we often omit $\mathbb{1}$ for the identity op.)

We have used $\vec{r}$-space operators here, one can check that the result holds if $\vec{p}$-space operators are used: $[r_{\vec{r},i}, p_{\vec{r},j}] = i\hbar\,\delta_{ij} = [r_{\vec{p},i}, p_{\vec{p},j}]$

* Relation between $\vec{r}$- and $\vec{p}$-space commutators:

Let $F(\vec{r},\vec{p})$, $G(\vec{r},\vec{p})$ be two operators on a space $\mathcal{S}$ of sufficiently fast falling functions with the caveats mentioned in I.6 (pairs of conjugate variables separable) then the commutators of their representations in coordinate space and momentum space are related by Fourier transformation, i.e.

$$[F_{\vec{r}}, G_{\vec{r}}]\, f(\vec{r}) = (2\pi\hbar)^{-3/2} \int_{\mathbb{R}^3} [F_{\vec{p}}, G_{\vec{p}}]\, \hat{f}(\vec{p})\, e^{\frac{i}{\hbar}\vec{r}\cdot\vec{p}}\, d^3p$$

where $\hat{f}$ is the FT of f and f is any function in the space $\mathcal{S}$.

Why? HW

* In particular: if $[F_{\vec{r}}, G_{\vec{r}}] = \alpha \mathbb{1}$ where $\alpha \in \mathbb{C}$ constant then the commutators are equal: $[F_{\vec{p}}, G_{\vec{p}}] = \alpha \mathbb{1}$

Example: $[r_i, p_i]$

* We can define analytic functions of operators by formal power series. For example for any operator A

$$e^A = \mathbb{1} + A + \frac{1}{2!} A \circ A + \dots = \sum_{k=0}^{\infty} \frac{1}{k!} A^k$$

* Careful: since operators usually don't commute many well-known identities for analytic fcts. are much more complicated. Most famous example:

Baker–Campbell–Hausdorff formula:

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]+\frac{1}{12}[A,[A,B]]-\frac{1}{12}[B,[A,B]]-\frac{1}{24}[B,[A,[A,B]]]+\dots}$$

where ... are th order commutators and above (in general the sum is infinite)

Why? The special case that A, B commute with [A, B] is treated in HW3 [4]

* We note an analogy between the Poisson bracket for classical quantities and the commutators of the respective operators. However this analogy is not universal and breaks down for sufficiently complicated cases.

I.8 Dynamics of Expectation Values

I.8.1 Equation of Motion for Expectation Values

* We expect that expectation values of operators often have a classical interpretation and thus that they follow classical equations of motion.

Examples: Average position $\langle \vec{r} \rangle$ of a wave packet $\approx$ position of the classical particle it represents

$\langle \vec{p} \rangle$ of a wave packet $\approx$ momentum of the corresponding cl. particle.

* Let F be an operator acting on solutions $\psi(\vec{r},t)$ of a S.E. with mass m and pot. energy $V(\vec{r})$. Then

$$(\Delta) \qquad \boxed{i\hbar \frac{d}{dt}\langle F \rangle = \langle [F,H] \rangle + i\hbar \left\langle \frac{\partial F}{\partial t} \right\rangle}$$

for the expectation value of F with respect to any ψ which falls sufficiently fast.

Why?

$$i\hbar \frac{d}{dt}\langle F \rangle = i\hbar \int \psi^* F \frac{\partial \psi}{\partial t}\, d^3r + i\hbar \int \frac{\partial \psi^*}{\partial t} F \psi\, d^3r + i\hbar \int \psi^* \frac{\partial F}{\partial t} \psi\, d^3r$$

$$= \int \psi^* F H \psi\, d^3r - \int (H\psi)^* F\psi\, d^3r + i\hbar \left\langle \frac{\partial F}{\partial t} \right\rangle$$

$$= \langle FH \rangle - \int \underbrace{-\frac{\hbar^2}{2m}\Delta \psi^*}_{2\times \text{ partial integration}} F\psi\, d^3r - \int \psi^* V F\psi\, d^3r + i\hbar \left\langle \frac{\partial F}{\partial t} \right\rangle$$

$$= \langle FH \rangle - \langle HF \rangle + i\hbar \left\langle \frac{\partial F}{\partial t} \right\rangle$$

$\square$

* We note the formal correspondence with the equation

$$\frac{df}{dt} = \{f,H\} + \frac{\partial f}{\partial t}$$

for a classical quantity f where $\{\,,\}$ are the Poisson brackets.

I.e. $\langle F\rangle$ behaves like the classical quantity F if $\langle \underset{\text{operators}}{[F,H]}\rangle \approx \underset{\text{cl. quantities}}{\{F,H\}}$

* In particular, for any operator F that does not depend explicitly on time:

If $[F,H]=0$ we have $\langle F\rangle = \text{const.}$ for any state ψ. We call F a constant of motion in analogy to classical mechanics.

* Examples:

  - $[\vec{p}, T] = 0$ i.e. momentum is a constant of motion for free particles ($V = \text{const}$).

  - $[\vec{L}, T] = 0$ (cf. HW3, [3]), i.e. angular momentum is a constant of motion for free particles

  - $[H,H] = 0$ always, i.e. (average) energy is conserved always as long as $\frac{\partial H}{\partial t} = 0$.

* Equation (Δ) and everything here holds irrespective of whether $\vec{r}$ or $\vec{p}$-space is chosen for the calculation.

Why? Clear from invariance of expectation values and commutators.

I.8.2 Ehrenfest Theorem

* We will need the following important commutators:

– $[\vec{r}, H] = i\hbar \vec{p}$ Why? $[\vec{r}, H] = \underset{HW3[2]}{[\vec{r}, T]} = \frac{1}{m}\underbrace{[\vec{r}, p_k]}_{(i\hbar\delta_{kj})_{j=1}^{3}} p_k = i\hbar \frac{\vec{p}}{m}$

– $[\vec{p}, f(\vec{r})] = -i\hbar \nabla f$ Why? $-i\hbar[\nabla, f(\vec{r})] = -i\hbar \nabla f$

for any differentiable fct. f.

* Ehrenfest Theorem

For the expectation values of position $\vec{r}$ and momentum $\vec{p}$ we find for any state ψ obeying a S.E. with mass m and pot. energy $V(\vec{r})$:

$$m \frac{d\langle\vec{r}\rangle}{dt} = \langle\vec{p}\rangle$$

$$\frac{d\langle\vec{p}\rangle}{dt} = \langle\vec{F}\rangle$$

where $\vec{F} = -\nabla V$ as in cl. mechanics

Why? $\frac{d\langle\vec{r}\rangle}{dt} = \frac{1}{i\hbar}\langle[\vec{r}, H]\rangle = \frac{\langle\vec{p}\rangle}{m}$

$\frac{d\langle\vec{p}\rangle}{dt} = \frac{1}{i\hbar}\langle[\vec{p}, V]\rangle = -\langle\nabla V\rangle$

* Compare: The canonical equations for classical $\vec{r}_{cl}, \vec{p}_{cl}$ are

$$m \frac{d\vec{r}_{cl}}{dt} = \vec{p}_{cl}$$

$$\frac{d\vec{p}_{cl}}{dt} = -\nabla V(\vec{r}_{cl})$$

They match the eqs. for $\langle\vec{r}\rangle, \langle\vec{p}\rangle$ as long as $\langle\nabla V(\vec{r})\rangle \approx \nabla V(\langle\vec{r}\rangle)$