Equation of motion

Canonical Commutation Rules

- Hermitian coordinate and momentum operators are postulated to obey the following canonical commutation rules

$$\left[q_i, p_j\right] = i\hbar\delta_{ij}$$

$$\left[q_i, q_j\right] = \left[p_i, p_j\right] = 0$$

- Because all the *q*'s commute, they can be diagonalized simultaneously; the same goes for the *p*'s.

$$\left|q_1', q_2' \cdots, q_{3N}'\right\rangle = \left|q_1'\right\rangle \otimes \left|q_2'\right\rangle \cdots \otimes \left|q_{3N}'\right\rangle$$

$$\left|p_1', p_2' \cdots, p_{3N}'\right\rangle = \left|p_1'\right\rangle \otimes \left|p_2'\right\rangle \cdots \otimes \left|p_{3N}'\right\rangle$$

generalization of commutation rules

- to examine one degree of freedom

$$[q, p] = i\hbar$$

$$[q, p^n] = in\hbar p^{n-1} \qquad [p, q^n] = -in\hbar q^{n-1}$$

- a generalization gives

$$[q, G(p)] = i\hbar \frac{\partial G}{\partial p} \qquad [p, F(q)] = -i\hbar \frac{\partial F}{\partial q}$$

spatial translation

- unitary operator

$$T(a) = e^{-\frac{iap}{\hbar}}$$

- *a* is any real number having the dimension of length. *T*(*a*) is unitary

$$\left[q, T(a)\right] = i\hbar \frac{\partial}{\partial p} = i\hbar \frac{-ia}{\hbar} T(a) = aT(a)$$

$$qT(a) = T(a)(q+a)$$

$$qT(a)|q'\rangle = T(a)(q+a)|q'\rangle = (q'+a)T(a)|q'\rangle$$

- $T(a)|q'\rangle$ is an eigenket of *q* with eigenvalue of (*q*+*a*)
- because *T* is unitary, it preserves norms

$$T(a)|q'\rangle = |q'+a\rangle$$

- the unitary transformation of the coordinate operator corresponding to a spatial translation.

$$qT(a) = T(a)(q+a)$$

$$T^{\dagger}(a)qT(a) = q+a$$

translation in momentum space

- the unitary operator

$$K(k) = e^{\frac{iqk}{\hbar}}$$

$$K^{\dagger}(k)\, pK(k) = p + k$$

$$K(k)|p'\rangle = |p' + k\rangle$$

- Translations in momentum space are often referred to as boosts.

time-energy commutator

- put time on the same footing as the spatial coordinates by generalizing the commutation rule to one between 4-vectors for position and momentum.

$$[t, H] = -i\hbar$$

- if *t* is to have a continuous spectrum like the coordinates, then so must *H*; i.e., there could be no lower bound to energies and no bound states with discrete energies!

Schrodinger Wave Functions

- Schrodinger wave function is the scalar product

$$\langle q_1' \cdots | \psi \rangle$$

- transformation function between the coordinate and momentum

$$\langle q' | p' \rangle = \langle q' = 0 | T^\dagger(q') | p' \rangle = e^{\frac{ip'q'}{\hbar}} \langle q' = 0 | p' \rangle$$

$$= e^{\frac{ip'q'}{\hbar}} \langle q' = 0 | K(p') | p' = 0 \rangle$$

$$= e^{\frac{ip'q'}{\hbar}} \langle q' = 0 | p' = 0 \rangle$$

- The constant is determined by requiring

$$\langle q'|q''\rangle = \int dp' \langle q'|p'\rangle\langle p'|q''\rangle = \delta(q'-q'')$$
$$= \int dp' e^{\frac{ip'(q'-q'')}{\hbar}} \left|\langle q'=0|p'=0\rangle\right|^2$$

- the Fourier representation of the delta function:

$$\delta(q') = \int \frac{dp'}{2\pi\hbar} e^{\frac{ip'q'}{\hbar}}$$

$$\left|\langle q'=0|p'=0\rangle\right|^2 = (2\pi\hbar)^{-1}$$

$$\langle q'|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ip'q'}{\hbar}}$$

momentum space wave functions

- Configuration and wave functions

$$\varphi(q') = \langle q' | \psi \rangle$$

- momentum space wave functions

$$\begin{aligned}
\phi(p') &= \langle p' | \psi \rangle \\
&= \int dq' \langle p' | q' \rangle \langle q' | \psi \rangle \\
&= \int \frac{dq'}{\sqrt{2\pi\hbar}} e^{-\frac{ip'q'}{\hbar}} \langle q' | \psi \rangle = \int \frac{dq'}{\sqrt{2\pi\hbar}} e^{-\frac{ip'q'}{\hbar}} \varphi(q')
\end{aligned}$$

$$\varphi(q') = \int \frac{dp'}{\sqrt{2\pi\hbar}} e^{\frac{ip'q'}{\hbar}} \phi(p')$$

The density matrix

$$\langle q'|\rho|q''\rangle = \varphi^*(q')\varphi(q'') \qquad \langle p'|\rho|p''\rangle = \phi^*(p')\phi(p'')$$

$$\langle p'|\rho|p''\rangle = \int dq'\,dq''\,\langle p'|q'\rangle\langle q'|\rho|q''\rangle\langle q''|p''\rangle$$

$$= \int \frac{dq'dq''}{2\pi\hbar} e^{\frac{-ip'q'}{\hbar}} e^{\frac{ip''q''}{\hbar}} \langle q'|\rho|q''\rangle$$

- to compute the momentum distribution one must know the off- diagonal elements of p in the coordinate representation.
- the probability distribution for a complete set of compatible observables does not determine the probability distribution for an incompatible observable.

action of the momentum operator

- action of the momentum operator on configuration space wave functions

$$\langle q' | p^n | q'' \rangle = \int dp' \langle q' | p' \rangle (p')^n \langle p' | q'' \rangle$$

$$= \int \frac{dp'}{2\pi\hbar} (p')^n e^{\frac{ip'(q'-q'')}{\hbar}}$$

- n-th derivative of a delta function:

$$\delta(x) = \int dk e^{ikx} \qquad \frac{d^n \delta(x)}{dx} = \delta^{(n)}(x) = \int dk (ik)^n e^{ikx}$$

$$\int \delta^{(n)}(x - x') f(x') dx' = \frac{d^n f(x)}{dx^n}$$

$$\langle q'|q''\rangle = \delta(q' - q'')$$

$$\langle q'|p^n|q''\rangle = \int \frac{dp'}{2\pi\hbar}(p')^n e^{\frac{ip'(q'-q'')}{\hbar}}$$

$$= \left(\frac{\hbar}{i}\right)^n \delta^{(n)}(q' - q'')$$

$$\langle q'|p^n|\psi\rangle = \int dq'' \langle q'|p^n|q''\rangle\langle q''|\psi\rangle$$

$$= \left(\frac{\hbar}{i}\right)^n \int dq'' \delta^{(n)}(q' - q'')\varphi(q'')$$

$$= \left(\frac{\hbar}{i}\right)^n \frac{d^n\varphi(q')}{dq'^n} = \left(\frac{\hbar}{i}\frac{\partial}{\partial q'}\right)^n \varphi(q')$$

Also $\langle p'|q^n|\psi\rangle = \left(i\hbar\frac{\partial}{\partial p'}\right)^n \phi(p')$

in higher degree freedoms

- The displacement by the 3-vector a is to be produced by a unitary operator *T*(*a*) that

$$T^{\dagger}(\mathbf{a})\mathbf{x}_n T(\mathbf{a}) = \mathbf{x}_n + \mathbf{a}$$

n: particle index

$$T(\mathbf{a}) = \prod_{n=1}^{N} e^{-\frac{i\mathbf{p}_n \cdot \mathbf{a}}{\hbar}}$$

$$= \exp\left(\sum_n -\frac{i\mathbf{p}_n \cdot \mathbf{a}}{\hbar}\right)$$

$$= e^{-\frac{i\mathbf{P}\cdot\mathbf{a}}{\hbar}}$$

total momentum $\mathbf{P} = \sum_n \mathbf{p}_n$

uncertainty

- a precise definition of the uncertainty is the root-mean- square dispersion

$$\Delta A = \sqrt{\left\langle A - \langle A \rangle \right\rangle} = \sqrt{\left\langle A^2 \right\rangle - \langle A \rangle^2}$$

- the second moment of the probability distribution

$$\Delta A = \sum_a \left(a^2 - \langle A \rangle \right) \left| \langle a | \phi \rangle \right|^2$$

uncertainty relation

- Let *B* be an observable that does not commute with *A*.

$$\bar{A} = A - \langle A \rangle \qquad \bar{A}|\phi\rangle = |\phi_A\rangle$$

$$\bar{B} = B - \langle B \rangle \qquad \bar{B}|\phi\rangle = |\phi_B\rangle$$

$$(\Delta A \Delta B)^2 = \langle \bar{A}^2 \rangle \langle \bar{B}^2 \rangle = \langle \phi_A | \phi_A \rangle \langle \phi_B | \phi_B \rangle$$

- Schwartz inequality

$$(\Delta A \Delta B)^2 = \langle \bar{A}^2 \rangle \langle \bar{B}^2 \rangle \geq \left| \langle \bar{A}\bar{B} \rangle \right|^2$$

- Decompose

$$\bar{A}\bar{B} = \frac{1}{2}\left[\bar{A},\bar{B}\right] + \frac{1}{2}\left\{\bar{A},\bar{B}\right\}$$
$$= \frac{1}{2}[A,B] + \frac{1}{2}\left\{\bar{A},\bar{B}\right\} \qquad\qquad [A,B] = iC$$

- Because *C* and $\left\{\bar{A},\bar{B}\right\}$ are Hermitians, the average value of *C* and $\left\{\bar{A},\bar{B}\right\}$ are real

$$\left\langle \bar{A}\bar{B} \right\rangle^2 = \frac{1}{4}\left|\left\langle\left\{\bar{A},\bar{B}\right\}\right\rangle + i\langle C\rangle\right|^2 = \frac{1}{4}\left[\left\langle\left\{\bar{A},\bar{B}\right\}\right\rangle^2 + \langle C\rangle^2\right]$$

- the general form of Heisenberg's uncertainty relation.

$$\Delta A \Delta B \geq \frac{1}{2}\left|\left\langle [A, B] \right\rangle\right|$$

- For the canonical variables

$$\Delta p_i \Delta q_j \geq \frac{1}{2}\hbar \delta_{ij}$$

- remark:

$$\left\langle \left\{ \overline{A}, \overline{B} \right\} \right\rangle = 0$$

if $\quad \left|\phi_A\right\rangle \propto \left|\phi_B\right\rangle$

$$\left\langle \overline{A}^2 \right\rangle \left\langle \overline{B}^2 \right\rangle = \left|\left\langle \overline{A}\overline{B} \right\rangle\right|^2$$

The Schrodinger Picture

- The basic assumption will be that time evolution is represented by a unitary transformation parametrized by a continuous parameter *t*
- if $|\varphi;0>$ is some state of a system at $t = 0$, then at a later time $|\varphi; t> = L_t|\varphi; 0>$, where L_t is a linear operator.

- For some time-independent observable, A, its expectation value as a function of time

$$\langle \phi;t | A | \phi;t \rangle = \sum_a a \left| \langle a | \phi;t \rangle \right|^2$$

- the probabilities for the various eigenvalues will change with time, but by hypothesis, not the eigenvalues themselves.

$$\langle \phi;0 | L_t^\dagger A L_t | \phi;0 \rangle = \sum_{a_t} a_t \left| \langle a_t | \phi;0 \rangle \right|^2$$

Here a_t are the eigenvalues of $L_t^\dagger A L_t$

$|a_t\rangle$ are the eigenvectors of

- any unitary transformation of a Hermitian operator leave its spectrum invariant. L_t is a unitary operator.
- The unitary operators must only depend on time differences

$$|\phi;t\rangle = U(t-t')|\phi;t'\rangle$$

- and satisfy the following composition law:

$$U(t_1)U(t_2) = U(t_1+t_2)$$

$$U(t) = \left[U(t/N)\right]^N$$

infinitesimal time

- When $\delta t \to 0$ $U(\delta t) \to 1$
- The possible unitary matrix

$$U(\delta t) = 1 + i\Delta(\delta t)$$

- $\Delta(\delta t)$ must be an infinitesimal Hermitian operator to first order (but why?)
- The composition law implies that Δ is linear in *t*

$$\Delta(\delta t_1) + \Delta(\delta t_2) = \Delta(\delta t_1 + \delta t_2)$$

$$\Delta(\delta t) \propto \delta t$$

- The result can be expressed as

$$U(\delta t) = 1 - \frac{i}{\hbar}\delta t H$$

- The operator *H* has the dimension of energy. it is Hamiltonian of the system in question.

- For finite time differences,

$$U(t) = \left[U(t/N)\right]^N = \lim_{N\to\infty}\left(1 - \frac{i}{\hbar}\frac{Ht}{N}\right)^N$$

$$= \exp\left(-\frac{i}{\hbar}Ht\right)$$

- the time derivative of U is

$$U(\delta t+t)-U(t)=\left[U(\delta t)-1\right]U(t)=\left(1-\frac{i}{\hbar}\delta tH\right)U(t)$$

$$\frac{\partial U}{\partial t}=\frac{U(\delta t+t)-U(t)}{\delta t}=-\frac{i}{\hbar}HU(t)$$

- The solution for initial condition that $U(0)=1$

$$U(t)=\exp\left(-\frac{i}{\hbar}Ht\right)$$

Schrodinger equation

- The Schrodinger equation

$$|\phi;t\rangle = U(t-t')|\phi;t'\rangle$$

$$i\hbar\frac{\partial}{\partial t}|\phi;t\rangle = i\hbar\frac{\partial}{\partial t}U(t)|\phi;0\rangle = HU(t)|\phi;0\rangle = H|\phi;t\rangle$$

- a ket $|\psi_E;t\rangle$ energy eigenstates satisfies time independent Schrodinger eq. $(H-E)|\psi_E;t\rangle = 0$

$$|\psi_E;t\rangle = e^{-\frac{i}{\hbar}Et}|\psi_E;0\rangle$$

- stationary states because they do not change in time aside from a phase factor.

- the matrix elements of any time-independent observable A between stationary states also have a time dependence that is merely a phase:

$$\langle \psi_E ; t | A | \psi_{E'} ; t \rangle = e^{\frac{i}{\hbar}(E-E')t} \langle \psi_E ; 0 | A | \psi_{E'} ; 0 \rangle$$

- for any operator

$$\langle \psi_E | [A, H] | \psi_E \rangle = 0$$

the coordinate representation

- N-particle hamiltonian

$$H = \sum_n \frac{p_n^2}{2m_n} + V(x_1, x_2 \cdots, x_N)$$

- denote a coordinate eigenket $|r_1, r_2 \cdots, r_N\rangle$

$$\langle r_1, r_2 \cdots, r_N | p_n | \phi; t\rangle = \frac{\hbar}{i} \frac{\partial}{\partial x_n} \phi(r_1, r_2 \cdots, r_N; t)$$

- Schrodinger equation in the coordinate representation:

$$i\hbar \frac{\partial}{\partial t} |\phi; t\rangle = H |\phi; t\rangle$$

$$i\hbar \frac{\partial}{\partial t} \phi(t) = \left[\sum_n \frac{1}{2m_n} \left(\frac{\hbar}{i} \frac{\partial}{\partial x_n} \right)^2 + V \right] \phi(t)$$

- the scalar product of any two solutions of the time-dependent Schrodinger equation is independent of time.

Probability distribution

- the coordinate space probability distribution,

$$w\left(r_1, r_2 \cdots, r_N; t\right) = \left|\phi\left(r_1, r_2 \cdots, r_N; t\right)\right|^2$$

- constancy of the norm

$$\frac{\partial}{\partial t} \int d^3 r_1 d^3 r_2 \cdots d^3 r_N w\left(r_1, r_2 \cdots, r_N; t\right) = 0$$

continuity equation

- in any infinitesimal region of configuration space,

$$\frac{\partial}{\partial t} w\left(r_1, r_2 \cdots, r_N; t\right) + \sum_n \frac{\partial}{\partial r_n} \cdot \mathbf{i}_n\left(r_1, r_2 \cdots, r_N; t\right) = 0$$

- probability flow

$$\mathbf{i}_n\left(r_1, r_2 \cdots, r_N; t\right) = \frac{\hbar}{2 m_n i}\left(\phi^* \frac{\partial \phi}{\partial r_n} - \phi \frac{\partial \phi^*}{\partial r_n}\right)$$

Derivation

$$i\hbar \frac{\partial}{\partial t}\left|\phi;t\right\rangle = H\left|\phi;t\right\rangle \qquad -i\hbar \frac{\partial}{\partial t}\left\langle\phi;t\right| = \left\langle\phi;t\right|H$$

$$i\hbar \frac{\partial}{\partial t}\left|\phi(r)\right|^2 = i\hbar \frac{\partial}{\partial t}\left|\left\langle\phi;t|r\right\rangle\right|^2 = \left\langle\phi;t|r\right\rangle\left\langle r\right|H\left|\phi;t\right\rangle - \left\langle\phi;t\right|H\left|r\right\rangle\left\langle r|\phi;t\right\rangle$$

- potential V is diagonal in the coordinate representation

$$\left\langle\phi;t|r\right\rangle\left\langle r\right|V\left|\phi;t\right\rangle - \left\langle\phi;t\right|V\left|r\right\rangle\left\langle r|\phi;t\right\rangle = 0$$

Derivation

- Kinetic energy part

$$\langle \phi;t|r\rangle\langle r|K|\phi;t\rangle - \langle \phi;t|K|r\rangle\langle r|\phi;t\rangle$$

$$= -\frac{\hbar^2}{2m}\left[\phi^*(r)\frac{\partial^2}{\partial r^2}\phi(r) - \phi(r)\frac{\partial^2}{\partial r^2}\phi^*(r)\right]$$

$$= -\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\cdot\left(\phi^*(r)\frac{\partial \phi(r)}{\partial r} - \phi(r)\frac{\partial \phi^*(r)}{\partial r}\right)$$

charged particles

- charge density

$$\rho(r,t)=\sum_n e_n \int d^3r_1 d^3r_2 \cdots d^3r_N \delta(r-r_n) w(r_1,r_2\cdots,r_N;t)$$

- current density

$$\mathbf{j}(r,t)=\sum_n e_n \int d^3r_1 d^3r_2 \cdots d^3r_N \delta(r-r_n) \mathbf{i}_n(r_1,r_2\cdots,r_N;t)$$

Density matrix

- Let {|a>} be a basis that diagonalizes the density matrix

$$\rho(0) = \sum_a |a\rangle p_a \langle a|$$

- At time t $\quad |a\rangle \to \exp(-iHt/\hbar)|a\rangle$

$$\rho(t) = e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}$$

- The equation of motion for the density matrix

$$i\hbar\frac{d}{dt}\rho(t) = i\hbar\frac{d}{dt}\left[e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}\right]$$

$$= He^{-iHt/\hbar}\rho(0)e^{iHt/\hbar} - e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}H$$

$$= \left[H, \rho(t)\right]$$

time-dependent hamiltonian

- unitary time evolution operator U(t,t') depends on both of its arguments
- infinitesimal time transformations

$$U(t+\delta_1+\delta_2, t+\delta_1)U(t+\delta_1, t) = U(t+\delta_1+\delta_2, t)$$

$$U(t+\delta_1, t) = 1 + iF(t, \delta)$$

- F should be proportional to δ

$$F(t,\delta_1) + F(t,\delta_2) = F(t, \delta_1+\delta_2) \qquad F(t,\delta t) = H(t)\delta t/\hbar$$

$$U(t+\delta t, t') = U(t+\delta t, t)U(t,t') = U(t,t') - iH(t)\delta t U(t,t')/\hbar$$

$$i\hbar\frac{\partial}{\partial t}U(t,t') = H(t)U(t,t')$$

Heisenberg picture

- The Heisenberg picture is better suited to bringing out fundamental features, such as symmetries and conservation laws, and it is indispensable in systems with many degrees of freedom,
- The matrix elements of a time-independent observable A in the moving basis are

$$\langle \psi_b ; t | A | \psi_{b'} ; t \rangle = \langle \psi_b ; 0 | e^{iHt/\hbar} A e^{-iHt/\hbar} | \psi_{b'} ; 0 \rangle$$

- In the Heisenberg picture, kets that describe the time evolution of pure states are fixed in the Hilbert space, and observables A that are time-independent in the Schrodinger picture are replaced by operators A(t) that evolve with the unitary transformation

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar}$$

- equation of motion

$$i\hbar \frac{d}{dt} A(t) = \left[A(t), H \right]$$

- Observables that commute with the Hamiltonian are constants of motion.
- Anyone constant of motion can be diagonalized simultaneously with the Hamiltonian, i.e, they possess simultaneous eigenstates. The Hamiltonian and a set of constants of motion can be diagonalized simultaneously provided that all these constants of motion commute with each other.
- The density matrix does not move in the Heisenberg picture

- if an observable Bs(t) is explicitly time-dependent in the Schrodinger picture,

$$i\hbar\frac{d}{dt}B_H(t)=i\hbar\frac{\partial}{\partial t}B_H(t)+\left[B_H(t),H\right]$$

- the Hamiltonian Hs(t) itself be time-dependent in the Schrodinger picture

$$A_H(t',t)=U^\dagger(t',t)A_S U(t',t)$$

$$i\hbar\frac{\partial}{\partial t}A_H(t,t')=\left[A(t,t'),H_H(t,t')\right]$$

time-energy uncertainty relation

- start at t=0 with a system in a non-stationary state |Φ>
- the probability that the evolving system is still in |Φ> at time t

$$P(t) = \left|\langle\Phi|\, e^{-iHt/\hbar}\, |\Phi\rangle\right|^2 = \left|\int_0^\infty dE e^{-iEt/\hbar} w_\Phi(E)\right|^2$$

$$w_\Phi(E) = \sum_a \left|\langle Ea|\Phi\rangle\right|^2$$

- The general uncertainty relation for non-commuting observables

$$P(t)\Delta E \geq \frac{1}{2}\left|\left\langle\left[P(t),H\right]\right\rangle\right| \geq \frac{1}{2}\hbar\left\langle\frac{dP(t)}{dt}\right\rangle$$

- define the function $\tau(t)=\frac{P(t)}{dP(t)/t}$

$$\langle\tau(t)\rangle\Delta E \geq \frac{\hbar}{2}$$

lifetime

- the exponential decay law when τ is time-independent:

$$P(t) = e^{-t/\tau}$$

- The spectral density to the exponential decay law

$$w_{\Phi}(E) = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma}{\left(E - E_0\right)^2 + \frac{1}{4}\Gamma^2}$$

- Γ is the width of the decaying state.

$$\Gamma = \frac{\hbar}{\tau}$$