01 - Review of Quantum Mechanics

- Aim of Section:
  - Brief reminder of principles of quantum mechanics presented in previous course (PHY 373).

Wavefunction

- In quantum mechanics, instantaneous state of single point particle (e.g., electron) moving in three dimensions specified by wavefunction:
$$\psi(\mathbf{x}, t).$$
- Wavefunction is complex function of position, $\mathbf{x}$, and time, t.
- Interpretation of wavefunction is that probability of measurement of particle's position at time t finding that particle lies in small volume $d^3\mathbf{x}$, centered at position vector $\mathbf{x}$, is proportional to
$$|\psi(\mathbf{x}, t)|^2 \, d^3\mathbf{x}.$$

Normalization of Wavefunction - I

- By analogy, probability of particle being found anywhere in space is
$$\int |\psi(\mathbf{x},t)|^2\, d^3\mathbf{x},$$
where integral is over all space.
- However, particle is bound to be found somewhere in space, so previous probability should be unity.
- Consequently, a properly normalized wavefunction satisfies normalization condition:
$$\int |\psi(\mathbf{x},t)|^2\, d^3\mathbf{x} = 1.$$
- From now on, all wavefunctions are assumed to be properly normalized, unless stated otherwise.

Normalization of Wavefunction - II

- For properly normalized wavefunction, probability of measurement of particle's position at time t finding that particle lies in small volume $d^3\mathbf{x}$, centered at position vector $\mathbf{x}$, is equal to

$$|\psi(\mathbf{x},t)|^2 \, d^3\mathbf{x}.$$

Operators

- In quantum mechanics, dynamical variables (e.g., position, momentum, angular momentum, energy) are represented by complex algebraic/differential operators that act on wavefunction.
- Incidentally, an operator is merely something that acts on a wavefunction, and thereby converts it into a different (in general) wavefunction.
- For example, three Cartesian components of a point particle's position are represented by real algebraic operators, x, y, and z.

Expectation Value

- Suppose we make large number of independent measurements of x-component of particle's position, and average results.
- From probabilistic interpretation of wavefunction, and fact that x-component of position represented by algebraic operator x, average value of measurements, which is known as expectation value, given by

$$\langle x\rangle = \int x\,|\psi(\mathbf{x},t)|^2\,d^3\mathbf{x} \equiv \int \psi^*(\mathbf{x},t)\,x\,\psi(\mathbf{x},t)\,d^3\mathbf{x}.$$

- By analogy, if a general dynamical variable is represented by operator A then expectation value of A is

$$\langle A\rangle = \int \psi^*(\mathbf{x},t)\,A\,\psi(\mathbf{x},t)\,d^3\mathbf{x}. \tag{1}$$

Variance and Standard Deviation

- In general, each measurement of variable corresponding to A will yield a different result. Mean value of measurements is $\langle A\rangle$.
- Scatter about mean value characterized by variance:

$$\begin{aligned}\sigma_A^2 &= \langle (A-\langle A\rangle)^2\rangle = \langle (A^2 - 2\,A\,\langle A\rangle + \langle A\rangle^2\rangle \\ &= \langle A^2\rangle - \langle A\rangle^2. \end{aligned} \tag{2}$$

- Measurement of variable corresponding to A likely to yield result in range $\langle A\rangle \pm 3\,\sigma_A$ (assuming Gaussian distribution), and very unlikely to yield result outside this range.
- σ_A (which is square root of variance) is termed standard deviation.

Eigenstates and Eigenvalues - I

- An eigenstate of operator A corresponding to eigenvalue a (where, a is, in general, a complex number) is such that

$$A\,\psi = a\,\psi.$$

- Convenient to label eigenstate using corresponding eigenvalue. So, previous equation becomes

$$A\,\psi_a = a\,\psi_a.$$

Eigenstates and Eigenvalues - II

- Expectation value of A when $\psi = \psi_a$ is

$$\langle A\rangle = \int \psi_a^*\, A\, \psi_a\, d^3\mathbf{x} = \int \psi_a^*\, a\, \psi_a\, d^3\mathbf{x} = a \int \psi_a^*\, \psi_a\, d^3\mathbf{x} = a.$$

- Likewise,

$$\begin{aligned}\langle A^2\rangle &= \int \psi_a^*\, A^2\, \psi_a\, d^3\mathbf{x} = \int \psi_a^*\, A\, a\, \psi_a\, d^3\mathbf{x} \\ &= \int \psi_a^*\, a^2\, \psi_a\, d^3\mathbf{x} = a^2 \int \psi_a^*\, \psi_a\, d^3\mathbf{x} = a^2.\end{aligned}$$

- Hence,

$$\sigma_A^2 = \langle A^2\rangle - \langle A\rangle^2 = 0.$$

Eigenstates and Eigenvalues - III

- Conclude that if $\psi = \psi_a$ then measurement of A is bound to give result a.
- In other words, eigenstate of A, corresponding to eigenvalue a, represents quantum state in which measurement of variable corresponding to A bound to give result a.

Hermitian Operators - I

- Expectation value of measurement of dynamical variable represented by operator A is

$$\langle A\rangle = \int \psi^*\, A\,\psi\, d^3\mathbf{x}.$$

- However, if variable is physical quantity (e.g., position, momentum) then expectation value must be real (no physical measurement yields a complex result).
- Now,

$$\langle A\rangle^* = \int \psi\,(A\,\psi)^*\, d^3\mathbf{x}.$$

Hermitian Operators - II

- We require

  $$\langle A\rangle^* = \langle A\rangle,$$

  which implies that

  $$\int (A\,\psi)^*\,\psi\,d^3\mathbf{x} = \int \psi^*\,(A\,\psi)\,d^3\mathbf{x} \tag{3}$$

  (brackets indicate which wavefunction A acts on).
- Any operator that satisfies previous condition is termed Hermitian.
- Conclude that all operators that represent physical (i.e., measurable) variables in quantum mechanics must be Hermitian operators.
- Obvious that real algebraic operators (e.g., x) are Hermitian.

Hermitian Operators - III

- Possible to prove number of important theorems regarding Hermitian operators:
  1. Eigenvalues of Hermitian operator are all real. (Hw. 1, Q. 1).
  2. Eigenstates of Hermitian operator corresponding to different eigenvalues, a and a', are mutually orthogonal: i.e.,

     $$\int \psi_a^* \, \psi_{a'} \, d^3\mathbf{x} = 0.$$

     (Hw. 1, Q. 2).
  3. Eigenstates of Hermitian operator corresponding to same eigenvalue can be chosen so as to be mutually orthogonal. (Hw. 1, Q. 3).
  4. Eigenstates form a complete set: i.e., a general wavefunction can be represented as a linear superposition of eigenstates. (Hard to prove, leave to mathematicians).

Orthonormality Constraint

- Assume that eigenstates of A are properly normalized, and that any eigenstates corresponding to same eigenvalue have been chosen so as to be mutually orthogonal.
- Index different eigenstates by integer i that runs from 1 to ∞. (There must be an infinite number of eigenstates, otherwise states could never form a complete set.)
- Eigenstates satisfy orthonormality constraint:

$$\int \psi_i^{*}\,\psi_j\,d^3\mathbf{x} = \delta_{ij}.$$

- Previous expression merely states that eigenstates are both mutually orthogonal and properly normalized.

Expansion of Wavefunction

- A general wavefunction can be expressed as a linear superposition of the ψ_i:

  $$\psi = \sum_{i=1,\infty} c_i\,\psi_i, \tag{4}$$

  where the c_i are complex numbers.

- Easily demonstrated that (Hw. 1, Q. 4)

  $$c_i = \int \psi_i^{\,*}\,\psi\,d^3\mathbf{x}.$$

- If ψ is properly normalized then (Hw. 1, Q. 5)

  $$\sum_{i=1,\infty} |c_i|^{\,2} = 1. \tag{5}$$

Measurement - I

- Easily demonstrated that (Hw. 1, Q. 6)

  $$\langle A\rangle = \sum_{i=1,\infty} |c_i|^2\, a_i,$$

  where a_i is eigenvalue corresponding to ith eigenstate.
- Interpret previous equation in probabilistic sense. $|c_i|^2$ is probability that measurement of dynamical variable corresponding to A yields result a_i.
- (5) ensures that sum of probabilities is unity (as must be case).
- Can see that eigenvalues of A can be interpreted as various possible results of measurement of dynamical variable corresponding to A.

Measurement - II

- Can now appreciate why eigenvalues of A must be real.
- Immediately after measurement of dynamical variable corresonding to A yields result a_i, system must be in state in which measurement of variable bound to yield result a_i. (Because second measurement made immediately after first must give same answer.)
- Have seen that such a state is ψ_i.
- Hence, measurement of variable yielding result a_i causes wavefunction (4) to collapse to ψ_i. In other words, system is left in state for which $|c_j|^2 = \delta_{ij}$.

Commuting Operators

- Let A and B be Hermitian operators.
- Suppose that

$$A\,B\,\psi = B\,A\,\psi$$

  for all wavefunctions.
- Follows that

$$(A\,B - B\,A)\,\psi = 0.$$

- Can take general wavefunction as read, and write

$$A\,B - B\,A = 0.$$

- Two operators that satisfy previous equation are said to commute with one another.
- Note that complex numbers commute with all operators.

Simultaneous Eigenstates - I

- Suppose that A and B are commuting Hermitian operators.
- Let ψ_a be an eigenstate of A corresponding to eigenvalue a. Follows that
$$A\,\psi_a = a\,\psi_a.$$
- Now,
$$B\,A\,\psi_a = B\,a\,\psi_a,$$
or
$$A\,(B\,\psi_a) = a\,(B\,\psi_a).$$
- We deduce that $B\,\psi_a$ is an eigenstate of A corresponding to eigenvalue a.

Simultaneous Eigenstates - II

- Follows that $B\,\psi_a \propto \psi_a$. Let constant of proportionality be b.
- Hence,

$$B\,\psi_a = b\,\psi_a.$$

- Deduce that ψ_a is eigenstate of B corresponding to eigenvalue b.
- In other words, if A and B are commuting operators then every eigenstate of A is also an eigenstate of B. That is, A and B possess simultaneous eigenstates.

Simultaneous Eigenstates - III

- A simultaneous eigenstate of A and B corresponding to eigenvalues a and b is denoted $\psi_{a,b}$, where

$$A\,\psi_{a,b} = a\,\psi_{a,b},$$
$$B\,\psi_{a,b} = b\,\psi_{a,b},$$

- $\psi_{a,b}$ is a state in which a measurement of dynamical variable corresponding to A is bound to give result a, and a measurement of dynamical variable corresponding to B is bound to give result b.
- After each measurement, wavefunction remains $\psi_{a,b}$ so measurement of A does not affect value of subsequent meaurement of B, and vice versa.
- Conclude that if A and B commute then corresponding dynamical variables can be measured 'simultaneously'.

Simultaneous Eigenstates - IV

- Suppose that we wish to uniquely label eigenstates of A by corresponding eigenvalues. If A possesses degenerate eigenstates (i.e., eigenstates with same eigenvalue) then this scheme is frustrated.
- However, if B commutes with A then eigenstates of A are also eigenstates of B. Simultaneous eigenstates of A and B with same eigenvalue of A do not necessarily have same eigenvalue of B. Thus, possible to uniquely label simultaneous eigenstates of A and B via corresponding eigenvalues.
- Scheme could only be frustrated if A and B possess doubly degenerate eigenstates (i.e., different eigenstates that possess same eigenvalues of both A and B).

Simultaneous Eigenstates - V

- In this case, search for third dynamical variable whose corresponding operator, C, commutes with both A and B. Hopefully, A, B, and C do not possess triply degenerate eigenstates.
- If they do then search for fourth dynamical variable whose corresponding operator, D, commutes with both A, B, and C.
- Continue this process until obtain complete set of commuting operators whose simultaneous eigenstates are each labelled by a unique set of eigenvalues.

Simultaneous Eigenstates - VI

- As an example, energy eigenstates of hydrogen atom are highly degenerate. In fact, ith energy eigenvalue corresponds to i^2 different eigenstates (neglecting spin).
- Clearly, cannot uniquely label energy eigenstates by energy eigenvalues.
- However, operator corresponding to energy, H, commutes with operators corresponding to square of total angular momentum, L^2, and projection of angular momentum along z-axis (say), L_z.
- So, H, L^2, and L_z possess simultaneous eigenstates. Each eigenstate possesses different set of eigenvalues of three operators. Thus, possible to uniquely label energy eigenstates of hydrogen atom in terms of eigenvalues of H, L^2, and L_z.

Noncommuting Operators - I

- Have seen that if A and B are commuting Hermitian operators then corresponding dynamical variables can be simultaneously measured. In other words, quantum state corresponding to definite result of measurement of first variable also corresponds to definite result of measurement of second variable.
- Stands to reason that if A and B do not commute then corresponding variables cannot be simultaneously measured. That is, quantum state corresponding to definite result of measurement of first variable corresponds to range of different results of measurement of second variable.
- Let us try to quantify this effect.

Noncommuting Operators - II

- A straightforward generalization of (3) yields

$$\int (A\,\psi_1)^*\,\psi_2\,d^3\mathbf{x} = \int \psi_1^*\,(A\,\psi_2)\,d^3\mathbf{x}, \tag{6}$$

  for an Hermitian operator A. Here, ψ_1 and ψ_2 are general wavefunctions.
- Let $f = (A - \langle A\rangle)\,\psi$, where ψ is a general wavefunction.
- Follows that

$$\int |f|^2\,d^3\mathbf{x} = \int f^*\,f\,d^3\mathbf{x} = \int [(A - \langle A\rangle)\,\psi]^*\,[(A - \langle A\rangle)\,\psi]\,d^3\mathbf{x}.$$

- Making use of (1), (2) and (6), we obtain

$$\int |f|^2\,d^3\mathbf{x} = \int \psi^*\,(A - \langle A\rangle)^2\,\psi\,d^3\mathbf{x} = \langle (A - \langle A\rangle)^2\rangle = \sigma_A^2.$$

Noncommuting Operators - III

- Likewise, if $g = (B - \langle B\rangle)\,\psi$ then

$$\int |g|^2\, d^3\mathbf{x} = \sigma_B^2.$$

- According to Schwarz inequality,

$$\left|\int f^*\, g\, d^3\mathbf{x}\right|^2 \leq \int |f|^2\, d^3\mathbf{x} \int |g|^2\, d^3\mathbf{x}.$$

- If z is a complex number then

$$|z|^2 = [\mathrm{Re}(z)]^2 + [\mathrm{Im}(z)]^2 \geq [\mathrm{Im}(\mathrm{z})]^2 = \left[\frac{1}{2\,\mathrm{i}}\,(z - z^*)\right]^2.$$

Noncommuting Operators - IV

- If $z = \int f^{*}\, g\, d^{3}\mathbf{x}$ then previous four equations imply that

$$\sigma_A^2\, \sigma_B^2 \geq \left[\frac{1}{2\,\mathrm{i}}\,(z - z^{*})\right]^2.$$

- Have

$$z = \int [(A - \langle A\rangle)\,\psi]^{*}\, [(B - \langle B\rangle)\,\psi]\, d^{3}\mathbf{x}$$

$$= \int \psi^{*}\,(A - \langle A\rangle)\,(B - \langle B\rangle)\,\psi\, d^{3}\mathbf{x} = \langle (A - \langle A\rangle)\,(B - \langle B\rangle)\rangle,$$

where use has been made of (1) and (6).

- Easily seen that

$$\langle (A - \langle A\rangle)\,(B - \langle B\rangle)\rangle = \langle A\, B\rangle - \langle A\rangle\, \langle B\rangle.$$

Noncommuting Operators - V

- Likewise

$$\begin{aligned} z^* &= \int [(B - \langle B\rangle)\,\psi]^*\,[(A - \langle A\rangle)\,\psi]\,d^3\mathbf{x} \\ &= \int \psi^*\,(B - \langle B\rangle)\,(A - \langle A\rangle)\,\psi\,d^3\mathbf{x} = \langle (B - \langle B\rangle)\,(A - \langle A\rangle)\rangle. \end{aligned}$$

- Easily seen that

$$\langle (B - \langle B\rangle)\,(A - \langle A\rangle)\rangle = \langle B\,A\rangle - \langle A\rangle\,\langle B\rangle.$$

- Previous five equations yield

$$\sigma_A^2\,\sigma_B^2 \geq \left(\frac{1}{2\,\mathrm{i}}\,\langle [A, B]\rangle\right)^2, \tag{7}$$

where

$$[A, B] \equiv A\,B - B\,A$$

is termed commutator of operators A and B.

Heisenberg Uncertainty Principle

- Clear from previous equation that if $[A, B] \neq 0$ then state in which measurement of dynamical variable corresponding to A yields definite result (i.e., $\sigma_A = 0$) corresponds to state in which measurement of dynamical variable corresponding to B could yield all possible results (i.e., $\sigma_B = \infty$.)
- In other words, exact knowledge of value of dynamical variable corresponding to A corresponds to complete lack of knowledge of value of dynamical variable corresponding to B.
- This proposition is known as Heisenberg's uncertainty principle. It only applies to dynamical variables corresponding to noncommuting operators.

Position

- Three Cartesian components of particle's position represented by algrebraic operators x, y, and z.
- Algebraic operators commute with one another. In other words,

  $$x\,y = y\,x,$$

  et ceteta.
- Conclude that three Cartesian components of particle's position can be simultaneously measured.

Linear Momentum - I

- Three Cartesian components of particle's linear momentum represented by differential operators

  $$p_x \equiv -\mathrm{i}\,\hbar\,\frac{\partial}{\partial x},$$

  $$p_y \equiv -\mathrm{i}\,\hbar\,\frac{\partial}{\partial y},$$

  $$p_z \equiv -\mathrm{i}\,\hbar\,\frac{\partial}{\partial z},$$

  where $\hbar$ is Planck's constant divided by 2π.

- Partial derivatives commute with one another:

  $$\frac{\partial}{\partial x}\,\frac{\partial}{\partial y} = \frac{\partial}{\partial y}\,\frac{\partial}{\partial x},$$

  et cetara.

Linear Momentum - II

- Conclude that three Cartesian components of particle's linear momentum can be simultaneously measured.

Position and Linear Momentum - I

- Operators representing x-components of position and momentum do not commute: in fact (Hw. 1, Q. 7)

$$[x, p_x] = \mathrm{i}\,\hbar.$$

- Follows from (7) that

$$\sigma_x\,\sigma_{p_x} \geq \hbar.$$

  This is original form of Heisenberg uncertainty principle. (It was subsequently generalized to all noncommuting operators.)

- Previous equation states that is impossible to simultaneously measure x-components of particle's position and linear momentum. Exact knowledge of value of one implies complete uncertainty in value of other.

Position and Linear Momentum - II

- Let $x_1 \equiv x$, $x_2 \equiv y$, et cetera, and let $p_1 \equiv p_x$, et cetera.
- It is easily seen that the x_i and the p_i satisfy commutation relations

$$[x_i, x_j] = 0, \tag{8}$$

$$[p_i, p_j] = 0, \tag{9}$$

$$[x_i, p_j] = \mathrm{i}\,\hbar\,\delta_{ij}. \tag{10}$$

- Clear that we can only exactly measure one of each x_i, p_i pair. In other words, we can simultaneously measure (x_1, x_2, x_3), (p_1, x_2, x_3), (x_1, p_2, x_3), $\cdots$, (p_1, p_2, p_3).

Schrödinger's Equation - I

- When system is not being observed, its wavefunction evolves in time according to Schrödinger's equation:

  $$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t} = H\,\psi, \tag{11}$$

  where H is an Hermitian operator, known as Hamiltonian, that represents energy of system.

Schrödinger's Equation - II

- Schrödinger's equation must conserve $\int |\psi|^2 \, d^3\mathbf{x}$, otherwise properly normalized wavefunction would not remain properly normalized as it evolves in time, which would not make any sense.
- Multiplying (11) by ψ^*, we obtain

$$\mathrm{i}\,\hbar\,\frac{\partial\psi}{\partial t}\,\psi^* = \psi^*\,H\,\psi.$$

- Multiplying complex conjugate of (11) by ψ, we obtain

$$\mathrm{i}\,\hbar\,\frac{\partial\psi^*}{\partial t}\,\psi = -(H\,\psi)^*\,\psi.$$

Schrödinger's Equation - III

- Adding previous two equations yields

$$\mathrm{i}\,\hbar\,\frac{\partial|\psi|^2}{\partial t} = \psi^*\,H\,\psi - (H\,\psi)^*\,\psi.$$

- Integration over all space gives

$$\mathrm{i}\,\hbar\,\frac{d}{dt}\int|\psi|^2\,d^3\mathbf{x} = \int\psi^*\,H\,\psi\,d^3\mathbf{x} - \int(H\,\psi)^*\,\psi\,d^3\mathbf{x}.$$

- However, because H is an Hermitian operator

$$\int(H\,\psi)^*\,\psi\,d^3\mathbf{x} = \int\psi^*\,H\,\psi\,d^3\mathbf{x}.$$

Schrödinger's Equation - IV

- Hence, we deduce that

$$\frac{d}{dt}\int |\psi|^2 \, d^3\mathbf{x} = 0.$$

- In other words, if

$$\int |\psi|^2 \, d^3\mathbf{x} = 1$$

  at time $t = 0$ then $\int |\psi|^2 \, d^3\mathbf{x} = 1$ at all subsequent times, as wavefunction evolves according to Schrödinger's equation.
- This important conservation law is guaranteed as long as Hamiltonian is Hermitian (which is another way of saying that Hamiltonian has to be Hermitian).

Time Evolution - I

- Consider dynamical variable represented by Hermitian operator A.
- Expectation value of measurement of variable is

$$\langle A\rangle = \int \psi^*\, A\, \psi\, d^3\mathbf{x}.$$

- Follows that

$$\frac{d\langle A\rangle}{dt} = \int \frac{\partial\psi^*}{\partial t}\, A\, \psi\, d^3\mathbf{x} + \int \psi^*\, A\, \frac{\partial\psi}{\partial t}\, d^3\mathbf{x}.$$

- Here, we are assuming that A does not depend explicitly on time. (This is certainly case for operators that represent position and momentum.)

Time Evolution - II

- Making use of (11), we obtain

  $$\frac{d\langle A\rangle}{dt} = -\frac{1}{\mathrm{i}\,\hbar}\int (H\,\psi)^*\,A\,\psi\,d^3\mathbf{x} + \frac{1}{\mathrm{i}\,\hbar}\int \psi\,A\,(H\,\psi)\,d^3\mathbf{x}$$
  $$= -\frac{1}{\mathrm{i}\,\hbar}\int \psi^*\,H\,A\,\psi\,d^3\mathbf{x} + \frac{1}{\mathrm{i}\,\hbar}\int \psi\,A\,H\,\psi\,d^3\mathbf{x},$$

  where use has been made of fact that H is Hermitian.
- Follows that

  $$\frac{d\langle A\rangle}{dt} = \frac{1}{\mathrm{i}\,\hbar}\,\langle[A, H]\rangle. \tag{12}$$
- Conclude that dynamical variables whose corresponding operators commute with Hamiltonian have expectation values that are constant in time.

Ehrenfest Theorem - I

- By analogy with classical physics, Hamiltonian of point particle of mass m moving in potential $V(\mathbf{x})$ is

$$H = \sum_{i=1,3} \frac{p_i^2}{2m} + V(\mathbf{x}).$$

- According to (12),

$$\frac{d\langle x_i\rangle}{dt} = \frac{1}{\mathrm{i}\,h}\,\langle[x_i, H]\rangle = \frac{1}{\mathrm{i}\,\hbar\,2m}\,\langle\left[x_i, p_i^2\right]\rangle,$$
$$\frac{d\langle p_i\rangle}{dt} = \frac{1}{\mathrm{i}\,h}\,\langle[p_i, H]\rangle = \frac{1}{\mathrm{i}\,\hbar}\,\langle[p_i, V(\mathbf{x})]\rangle,$$

where use has been made of (8)–(10).

Ehrenfest Theorem - II

- However (Hw. 1, Q. 8),

$$\left[x_i, p_i^2\right] = 2\,\mathrm{i}\,\hbar\,p_i,$$

$$[p_i, V(\mathbf{x})] = -\mathrm{i}\,\hbar\,\frac{\partial V}{\partial x_i}.$$

- Hence, we obtain Ehrenfest's theorem:

$$\frac{d\langle x_i\rangle}{dt} = \frac{\langle p_i\rangle}{m},$$

$$\frac{d\langle p_i\rangle}{dt} = -\left\langle\frac{\partial V}{\partial x_i}\right\rangle.$$

Ehrenfest Theorem - III

- According to Ehrefest's theorem, expectation values of x_i and p_i evolve in time in analogous fashion to that predicted by classical physics.
- Ehrenfest's theorem ensures that quantum mechanics is consistent with classical mechanics. This is important, because we know that classical physics is valid on large lengthscales.
- Clear that classical limit corresponds to case in which we can replace $\langle x_i \rangle$ by x_i, et cetera. This is possible on lengthscales much larger than de Broglie wavelength.

Stationary States - I

- Consider eigenstate of Hamiltonian corresponding to eigenvalue E:

$$H\,\psi_E = E\,\psi_E.$$

- This state corresponds to quantum state of definite energy E.
- According to (11),

$$\mathrm{i}\,\hbar\,\frac{\partial\psi_E}{\partial t} = H\,\psi_E = E\,\psi_E. \tag{13}$$

- Let us write ψ_E in separable form

$$\psi_E(\mathbf{x},t) = F(t)\,\Psi_E(\mathbf{x}).$$

Stationary States - II

- (13) yields
  $$\mathrm{i}\,\hbar\,\frac{dF}{dt}\,\Psi_E(\mathbf{x}) = E\,F(t)\,\Psi_E(\mathbf{x}).$$
- Follows that
  $$\mathrm{i}\,\hbar\,\frac{dF}{dt} = E\,F,$$
  which gives
  $$F(t) = a\,\exp\left(\frac{-\mathrm{i}\,E\,t}{\hbar}\right),$$
  where a is arbitrary constant.

Stationary States - III

- Conclude that properly normalized eigenstate of Hamiltonian corresponding to eigenvalue E can be written

$$\psi_E(\mathbf{x},t) = \Psi_E(\mathbf{x})\,\exp\left(\frac{-\mathrm{i}\,E\,t}{\hbar}\right), \tag{14}$$

where

$$\int \Psi_E^*\,\Psi_E\,d^3\mathbf{x} = 1,$$

and

$$H\,\Psi_E = E\,\Psi_E. \tag{15}$$

Stationary States - IV

- Quantum state corresponding to wavefunction (14) is known as stationary state. (Because expectation value of energy does not evolve in time.)
- (15) is known as time independent Schrödinger equation. We shall spend most of course solving this equation for various atomic and molecular systems.