Quantum Mechanics **NAME:**

Homework 2a: Solving the Schrödinger's Equation: Homeworks are not handed in or marked. But you get a mark for reporting that you have done them. Once you've reported completion, you may look at the already posted supposedly super-perfect solutions.

Answer Table for the Multiple-Choice Questions

	a	b	c	d	e		a	b	c	d	e
1.	O	O	O	O	O	16.	O	O	O	O	O
2.	O	O	O	O	O	17.	O	O	O	O	O
3.	O	O	O	O	O	18.	O	O	O	O	O
4.	O	O	O	O	O	19.	O	O	O	O	O
5.	O	O	O	O	O	20.	O	O	O	O	O
6.	O	O	O	O	O	21.	O	O	O	O	O
7.	O	O	O	O	O	22.	O	O	O	O	O
8.	O	O	O	O	O	23.	O	O	O	O	O
9.	O	O	O	O	O	24.	O	O	O	O	O
10.	O	O	O	O	O	25.	O	O	O	O	O
11.	O	O	O	O	O	26.	O	O	O	O	O
12.	O	O	O	O	O	27.	O	O	O	O	O
13.	O	O	O	O	O	28.	O	O	O	O	O
14.	O	O	O	O	O	29.	O	O	O	O	O
15.	O	O	O	O	O	30.	O	O	O	O	O

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002 qmult 00700 1 1 4 easy memory: Schr. eqn. separation of variables

1. The time-independent Schrödinger equation is obtained from the full Schrödinger equation by:

   a) colloquialism. b) solution for eigenfunctions. c) separation of the x and y variables.
   d) separation of the space and time variables. e) expansion.

   SUGGESTED ANSWER: (d)

   Wrong Answers:
   a) Huh?

   Redaction: Jeffery, 2001jan01

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002 qmult 00720 1 1 1 easy memory: stationary state

2. A system in a stationary state will:

   a) not evolve in time. b) evolve in time. c) both evolve and not evolve in time.
   d) occasionally evolve in time. e) violate the Heisenberg uncertainty principle.

   SUGGESTED ANSWER: (a) The wave function itself will have the time oscillation factor $e^{i\omega t}$, but that is not considered time evolution of the state.

   Wrong answers:
   b) Exactly wrong.

   Redaction: Jeffery, 2001jan01

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002 qmult 00800 1 4 2 easy deducto-memory: orthogonality property

3. For a Hermitian operator eigenproblem, one can always find (subject to some qualitifications perhaps—but which are just mathemtical hemming and hawwing) a complete set (or basis) of eigenfunctions that are:

   a) independent of the x-coordinate. b) orthonormal. c) collinear. d) pathological.
   e) righteous.

   SUGGESTED ANSWER: (b)

   Wrong Answers:
   e) Not the best answer in this context anyway.

   Redaction: Jeffery, 2001jan01

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002 qmult 00810 1 4 2 easy deducto-memory: basis expansion

Extra keywords: mathematical physics

4. "Let's play *Jeopardy*! For $100, the answer is: If it shares the same same range as a basis set of functions and is at least piecewise continuous, then it can be expanded in the basis with a vanishing limit of the mean square error between it and the expansion."

   What is a/an _____, Alex?

   a) equation b) function c) triangle d) deduction e) tax deduction

   SUGGESTED ANSWER: (b) See WA-510.

   Wrong answers:
   e) Sounds plausible.

   Redaction: Jeffery, 2008jan01

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002 qmult 00820 1 4 5 easy deducto-memory: general Born postulate

Extra keywords: mathematical physics

5. "Let's play *Jeopardy*! For $100, the answer is: The postulate that expansion coefficients of a wave function in the eigenstates of an observable are the probability amplitudes for wave function collapse to eigenstates of that observable."

   What is _____, Alex?

a) the special Born postulate b) the very special Born postulate c) normalizability
d) the mass-energy equivalence e) the general Born postulate

SUGGESTED ANSWER: (e)

Wrong answers:
b) As Lurch would say AAAARGH.

Redaction: Jeffery, 2008jan01

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002 qmult 00830 1 1 4 easy memory: basis expansion physics

6. The expansion of a wave function in an observable's basis (or complete set of eigenstates) is

a) just a mathematical decomposition. b) useless in quantum mechanics.
c) irrelevant in quantum mechanics. d) not just a mathematical decomposition since the expansion coefficients are probability amplitudes. e) just.

SUGGESTED ANSWER: (d)

Wrong answers:
a) A nonsense answer.

Redaction: Jeffery, 2008jan01

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002 qmult 00900 1 4 1 easy deducto-memory: macro object in stationary state

7. "Let's play *Jeopardy*! For $100, the answer is: A state that no macroscopic system can be in except arguably for states of Bose-Einstein condensates, superconductors, superfluids and maybe others sort of."

What is a/an _____, Alex?

a) stationary state b) accelerating state c) state of the Union d) state of being
e) state of mind

SUGGESTED ANSWER: (a)

Wrong answers:
b) Clearly wrong.
c) Well we-all are in a state of the Union.
d) Lots of macroscopic objects are real things without being Bose-Einstein condensates either.
e) I'm a macroscopic object and I'm occasionally in a state of mind, but never noticeably in a Bose-Einstein condensate.

Redaction: Jeffery, 2001jan01

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002 qmult 01000 1 1 5 easy memory: stationary state is radical

8. A stationary state is:

a) just a special kind of classical state. b) more or less a kind of classical state.
c) voluntarily a classical state. d) was originally not a classical state, but grew into one.
e) radically unlike a classical state.

SUGGESTED ANSWER: (e)

Wrong Answers:
c) Nonsense answer.
d) Nonsense answer.

Redaction: Jeffery, 2001jan01

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002 qmult 01100 1 1 4 easy memory: macro system in a stationary state

9. Except arguably for certain special cases (superconductors, superfluids, and Bose-Einstein condensates), no macroscopic system can be in a:

a) mixed state. b) vastly mixed state. c) classical state. d) stationary state.
e) state of the union.

SUGGESTED ANSWER: (d)

Wrong answers:
b) Exactly wrong.
c) Exactly wrong too.
e) Macroscopic systems are frequently found in all 50 states of the Union and the commonwealth of Puerto Rico too.

Redaction: Jeffery, 2001jan01

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002 qmult 01400 1 4 4 easy deducto-memory: operators and Sch. eqn.

10. "Let's play *Jeopardy*! For $100, the answer is: An equation that must hold in order for the non-relativistic Hamiltonian operator and the operator $i\hbar\partial/\partial t$ to both yield an energy expectation value for a wave function $\Psi(x,t)$."

What is _____, Alex?

a) the continuity equation b) the Laplace equation c) Newton's 2nd law
d) Schrödinger's equation e) Hamiton's equation

SUGGESTED ANSWER: (d)

Wrong answers:
c) Schrödinger's equation is the analog to Newton's law for quantum mechanics.
e) The two Hamilton's equations together are equations of motion in classical mechanics that can be used instead of Newton's law in advanced treatments.

Redaction: Jeffery, 2001jan01

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002 qmult 02000 2 1 4 moderate memory: does gravity quantize

Extra keywords: reference: Nesvizhevsky et al. 2002, Nature, 413, 297

11. Can the gravitational potential cause quantization of energy states?

a) No. b) It is completely uncertain. c) Theoretically yes, but experimentally no.
d) Experimental evidence to date (post-2001) suggests it can.
e) In principle there is no way of telling.

SUGGESTED ANSWER: (d)

Wrong Answers:
b) This used to be the right answer.
c) If so then either theory or experiment is wrong.
e) Experiments can address the issue.

Redaction: Jeffery, 2001jan01

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002 qfull 00320 3 5 0 tough thinking: general time evolution equation

12. It follows from the general Born postulate that the expectation value of an observable Q is given by

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^* Q \Psi \, dx \ .$$

It's weird to call an operator an observable, but that is the convention (Co-137).

a) Write down the explicit expression for

$$\frac{d\langle Q \rangle}{dt} \ .$$

Recall Q in general can depend on time too.

b) Now use the Schrödinger equation

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

to eliminate partial time derivatives where possible in the expression for $d\langle Q \rangle/dt$. Remember how complex values behave when complex conjugated. You should use the angle bracket form for expectation values to simplify the expression where possible.

c) The commutator of two operators A and B is defined by

$$[A, B] = AB - BA \ ,$$

where it is always understood that the commutator and operators are acting on an implicit general function to the right. If you have trouble initially remembering the understood condition, you can write

$$[A, B]f = (AB - BA)f \ ,$$

where f is an explicit general function. Operators don't in general commute: i.e., $[A, B] = AB - BA \neq 0$ in general. Prove

$$\left[\sum_i A_i, \sum_j B_j\right] = \sum_{i,j} [A_i, B_j] \ .$$

d) Now show that $d\langle Q\rangle/dt$ can be written in terms of $\langle i[H, Q]\rangle$. The resulting important expression oddly enough doesn't seem to have a common name. I just call it the general time evolution formula. **HINTS:** First, V and Ψ^* do commute. Second, the other part of the Hamiltonian operator

$$T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

can be put in the right place using integration by parts and the normalization condition on the wave function. Note T turns out to be the kinetic energy operator.

e) If $d\langle Q\rangle/dt = 0$, then Q is a quantum mechanical constant of the motion. It's weird to call an observable (which is a operator) a constant of the motion, but that is the convention (Co-247). Show that the operator $Q = 1$ (i.e., the unit operator) is a constant of the motion. What is $\langle 1\rangle$?

f) Find the expression for $d\langle x\rangle/dt$ in terms of what we are led to postulate as the momentum operator

$$p = \frac{\hbar}{i}\frac{\partial}{\partial x} \ .$$

The position operator x should be eliminated from the expression. **HINTS:** Note V and x commute, but T and x do not. Leibniz's formula (Ar-558) might be of use in evaluating the commutator $[T, x]$. The formula is

$$\frac{d^n(fg)}{dx^n} = \sum_{k=0}^{n} \binom{n}{k} \frac{d^k f}{dx^k}\frac{d^{n-k} g}{dx^{n-k}} \ .$$

SUGGESTED ANSWER:

a) Behold:

$$\frac{d\langle Q\rangle}{dt} = \int_{-\infty}^{\infty} \left[\frac{\partial \Psi^*}{\partial t} Q\Psi + \Psi^* \left(\frac{\partial Q}{\partial t}\right)\Psi + \Psi^* Q \frac{\partial \Psi}{\partial t}\right] dx \ ,$$

where the brackets about $\partial Q/\partial t$ are to emphasis that $\partial Q/\partial t$ is the operator acting on Ψ and one doesn't have $\partial/\partial t$ acting on $Q\Psi$.

b) Behold:

$$\begin{aligned}\frac{d\langle Q\rangle}{dt} &= -\frac{1}{i\hbar}\int_{-\infty}^{\infty} H\Psi^* Q\Psi \, dx + \frac{1}{i\hbar}\int_{-\infty}^{\infty} \Psi^* Q H\Psi \, dx + \left\langle \frac{\partial Q}{\partial t}\right\rangle \\ &= -\frac{1}{i\hbar}\int_{-\infty}^{\infty} H\Psi^* Q\Psi \, dx + \frac{1}{i\hbar}\langle QH\rangle + \left\langle \frac{\partial Q}{\partial t}\right\rangle \ .\end{aligned}$$

c) Behold:

$$\left[\sum_i A_i, \sum_j B_j\right] = \sum_{i,j} A_i B_j - \sum_{i,j} B_j A_i = \sum_{i,j} [A_i, B_j] \ .$$

d) Well the hints practically give the game away. Commuting V with Ψ^* and using integration by parts twice with the boundary terms at infinity vanishing by normalizability gives

$$\frac{d\langle Q\rangle}{dt} = -\frac{1}{i\hbar}\int_{-\infty}^{\infty} \Psi^* H Q \Psi \, dx + \frac{1}{i\hbar}\langle QH\rangle + \left\langle \frac{\partial Q}{\partial t} \right\rangle = \frac{1}{\hbar}\langle i[H,Q]\rangle + \left\langle \frac{\partial Q}{\partial t} \right\rangle \ .$$

The fact that we can do this trick with H means that H is what is called a Hermitian operator. The reason for sticking the i inside the angle brackets is that $i[H,Q]$ is a Hermitian operator for Q Hermitian, but $[H,Q]$ is not (e.g., Mo-451). It's just nice to get the expression for $d\langle Q\rangle/dt$ in terms of Hermitian operators where possible.

e) Since 1 has no explicit time dependence and obviously commutes with H, it follows from the general time evolution expression that

$$\frac{d\langle 1\rangle}{dt} = 0 \ ,$$

and so $Q = 1$ is a quantum mechanical constant of the motion The expectation value $\langle 1\rangle$ is just the total probability of finding the particle anywhere: for a normalized wave function $\langle 1\rangle = 1$. Since the total probability is a constant of the motion, a normalized wave function stays normalized.

f) Well x doesn't explicitly depend on t, and so $\partial x/\partial t = 0$ and $\langle \partial x/\partial t\rangle = 0$. Now

$$[H,x] = [T,x] = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}x - x\frac{\partial^2}{\partial x^2}\right) = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} \ ,$$

where we have used Leibniz's formula (Ar-558). It now follows that

$$\frac{d\langle x\rangle}{dt} = \frac{\hbar}{im}\left\langle \frac{\partial}{\partial x}\right\rangle = \frac{1}{m}\langle p\rangle \ ,$$

where

$$p = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

is the momentum operator by postulate sort of.

Redaction: Jeffery, 2001jan01

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002 qfull 00330 3 5 0 tough thinking: Ehrenfest's theorem

Extra keywords: (Gr-17:1.12) Ehrenfest formulae

13. In one dimension, Ehrenfest's theorem in quantum mechanics is usually taken to consist of two formulae:

$$\frac{d\langle x\rangle}{dt} = \frac{1}{m}\langle p\rangle$$

and

$$\frac{d\langle p\rangle}{dt} = -\left\langle \frac{\partial V}{\partial x}\right\rangle \ ,$$

where the angle brackets indicate expectation values as usual.

a) From the general time evolution formula prove the 1st Ehrenfest formula. **HINTS:** Recall the general time evolution formula in non-relativistic quantum mechanics is

$$\frac{d\langle Q\rangle}{dt} = \left\langle \frac{\partial Q}{\partial t}\right\rangle + \frac{1}{\hbar}\langle i[H,Q]\rangle \ ,$$

where Q is any observable and H is the Hamiltonian:

$$H = T + V(x) \ .$$

Also recall that quantum mechanical momentum operator and kinetic energy operator are given by

$$p = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad \text{and} \qquad T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \ ,$$

respectively. Leibniz's formula (Ar-558) might be of use in evaluating some of the commutators:

$$\frac{d^n(fg)}{dx^n} = \sum_{k=0}^{n} \binom{n}{k} \frac{d^k f}{dx^k}\frac{d^{n-k} g}{dx^{n-k}} \ .$$

b) From the general time evolution formula prove the 2nd Ehrenfest formula.

c) In the macroscopic limit, the expectation values become the classical dynamical variables by the correspondence principle (which is an auxiliary principle of quantum mechanics enunciated by Bohr in 1920 (Wikipedia: Correspondance principle)): i.e., $\langle x \rangle$ becomes x, etc. (Note we are allowing a common ambiguity in notation: x and p are both coordinates and, in the classical formalism, the dynamical variables describing the particle. Everybody does this: who are we do disagree.) Find the macroscopic limits of the Ehrenfest formulae and identify the macroscopic limits in the terminology of classical physics.

d) If you **ARE** writing a **TEST**, omit this part.

If one combines the two Ehrenfest formulae, one gets

$$m\frac{d^2\langle x \rangle}{dt^2} = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

which looks very like Newton's 2nd law in its $F = ma$ form for a force given by a potential. Using the correspondence priniciple, it does become the 2nd law in the macroscopic limit. However, an interesting question arises—well maybe not all that interesing—does the $\langle x \rangle$ (which we could call the center of the wave packet) actually obey the 2nd law-like expression

$$m\frac{d^2\langle x \rangle}{dt^2} = -\frac{\partial V(\langle x \rangle)}{\partial \langle x \rangle} \ ?$$

To disprove a general statement, all you need to do is find one counterexample. Consider a potential of the form $V(x) = Ax^\lambda$, and show that in general the $\langle x \rangle$ doesn't obey 2nd law-like expression given above. Then show that it does in three special cases of λ.

SUGGESTED ANSWER:

a) Well x doesn't explicitly depend on t, and so $\partial x/\partial t = 0$ and $\langle \partial x/\partial t \rangle = 0$. Now

$$[H, x] = [T, x] = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}x - x\frac{\partial^2}{\partial x^2}\right) = -\frac{\hbar^2}{m}\frac{\partial}{\partial x} \ ,$$

where we have used Leibniz's formula (Ar-558) to find that

$$\frac{\partial^2}{\partial x^2}x = 0 + i\frac{\partial}{\partial x} + x\frac{\partial^2}{\partial x^2} \ .$$

It now follows that

$$\frac{d\langle x \rangle}{dt} = \frac{\hbar}{im}\left\langle \frac{\partial}{\partial x} \right\rangle = \frac{1}{m}\langle p \rangle \ ,$$

where

$$p = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

is the momentum operator.

b) Behold:

$$\frac{d\langle p \rangle}{dt} = \frac{1}{\hbar}\langle i[H, p] \rangle = \frac{1}{\hbar}\langle i[V, p] \rangle = \left\langle \left[V, \frac{\partial}{\partial x}\right] \right\rangle = \left\langle \left(V\frac{\partial}{\partial x} - \frac{\partial V}{\partial x}\right) \right\rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle \ .$$

c) Using the correspondence principle, the macroscopic limits of the Ehrenfest formulae are

$$\frac{dx}{dt}v = \frac{p}{m} \qquad \text{or} \qquad p = mv$$

and

$$\frac{dp}{dt} = -\frac{\partial V}{\partial x} = F \ .$$

The first formula is just the kinematic formula for instantaneous velocity and the second, the classical Newton's 2nd law formula for the case that the force F is derivable from a potential. These results imply that the macroscopic limit of quantum mechanics is classical mechanics.

Ehrenfest's theorem allows a partial demonstration of how classical dynamics emerges from quantum mechanics. But it's the easy part. The hard part is the theory of wave function collapse for which no consensus theory yet exists.

d) Actually, one would guess

$$\left\langle \frac{\partial V}{\partial x} \right\rangle \neq \frac{\partial V(\langle x \rangle)}{\partial \langle x \rangle}$$

in general since there is no obvious reason why the equality should hold in general. Thus the expectation value $\langle x \rangle$ (or center of the wave packet) doesn't obey the 2nd law-like expression. So in this respect, there is no classical correspondence. Classical correspondence in general only happens when we scrunch up the particle (or center of mass) wave function into in a Dirac delta function.

To prove concretely that there is no equality in general, all one needs is a single counterexample. Consider

$$V(x) = Ax^{\lambda} \ .$$

In this case

$$\left\langle \frac{\partial V}{\partial x} \right\rangle = \begin{cases} A\lambda \langle x^{\lambda-1} \rangle & \text{for } \lambda \neq 0; \\ 0 & \text{for } \lambda = 0 \end{cases}$$

and

$$\frac{\partial V(\langle x \rangle)}{\partial \langle x \rangle} = \begin{cases} A\lambda \langle x \rangle^{\lambda-1} & \text{for } \lambda \neq 0; \\ 0 & \text{for } \lambda = 0. \end{cases}$$

Clearly the two derivative-of-potential expressions are not equal in general since $\langle x^{\lambda-1} \rangle \neq \langle x \rangle^{\lambda-1}$ in general. However, in the special cases of $\lambda = 0$, $\lambda = 1$, and $\lambda = 2$, they are equal. Thus in these cases the expectation value $\langle x \rangle$ does obey the 2nd law-like expression.

The $\lambda = 2$ case is noteworthy since it is the simple harmonic oscillator potential. But for stationary states, $\langle x \rangle = 0$. So only for mixed states would one get a non-trivial case where $\langle x \rangle$ evolves in time like a classical object in simple harmonic oscillator potential.

Redaction: Jeffery, 2001jan01

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002 qfull 00400 2 3 0 moderate math: orthonormality leads to mean energy

Extra keywords: (Gr-30:2.10)

14. You are given a complete set of orthonormal stationary states (i.e., energy eigenfunctions) $\{\psi_n\}$ and a general wave equation $\Psi(x,t)$ that is for the same system as $\{\psi_n\}$: i.e., $\Psi(x,t)$ is detemined by the same Hamiltonian as $\{\psi_n\}$. The set of eigen-energies of $\{\psi_n\}$ are $\{E_n\}$. The system is bounded in space by $x = -\infty$ and $x = \infty$.

    a) Give the formal expansion expression of $\Psi(x,0)$ (i.e., $\Psi(x,t)$ at time zero) in terms of $\{\psi_n\}$. Also give the formal expression for the coefficients of expansion c_n.

    b) Now give the formal expansion for $\Psi(x,t)$ remembering that $\omega_n = E_n/\hbar$. Justify that this is the solution of the Schrödinger equation for the initial conditions $\Psi(x,0)$.

    c) Find the general expression, simplified as far as possible, for expectation value $\langle H^{\ell} \rangle$ in terms of the expansion coefficients, where ℓ is any positive (or zero) integer. Are these values time dependent?

    d) Give the special cases for $\ell = 0$, 1, and 2, and the expression for the standard deviation for energy σ_E. **HINTS:** This should be a very short answer: 3 or 4 lines.

SUGGESTED ANSWER:

a) Behold:

$$\Psi(x,0) = \sum_n c_n \psi_n(x) \ ,$$

where

$$c_n = \int_{-\infty}^{\infty} \psi_n(x)^* \Psi(x,0)\, dx \ .$$

b) Behold:

$$\Psi(x,t) = \sum_n c_n e^{-i\omega_n t} \psi_n(x) \ .$$

This solution is a sum of solutions for the Schrödinger equation for the system Hamiltonian, and thus it is a solution too. Since it matches the initial conditions, it is the solution for those initial conditions.

c) Behold:

$$\begin{aligned}
\langle H^\ell \rangle &= \int_{-\infty}^{\infty} \Psi(x,t)^* H^\ell \Psi(x,t)\, dx \\
&= \sum_{m,n} c_m^* c_n e^{-i(\omega_n - \omega_m)t} \int_{-\infty}^{\infty} \psi_m(x)^* H^\ell \psi_n(x)\, dx \\
&= \sum_{m,n} c_m^* c_n e^{-i(\omega_n - \omega_m)t} E_n^\ell \int_{-\infty}^{\infty} \Psi_m(x)^* \Psi_n(x)\, dx \\
&= \sum_{m,n} c_m^* c_n e^{-i(\omega_n - \omega_m)t} E_n^\ell \delta_{m,n} \\
&= \sum_n |c_n|^2 E_n^\ell \ ,
\end{aligned}$$

where we used expansion and orthonormality. The time dependence has vanished for all cases of ℓ.

d) The most interesting special cases are for normalization, energy expectation value, and second moment of the distribution:

$$\langle H^0 \rangle = \sum_n |c_n|^2 = 1 \ , \qquad \langle H \rangle = \sum_n |c_n|^2 E_n \ , \qquad \langle H^2 \rangle = \sum_n |c_n|^2 E_n^2 \ .$$

The energy standard deviation is given by

$$\sigma_E = \sqrt{\langle H^2 \rangle - \langle H \rangle^2} \ .$$

In fact, on any ideal measurement of energy (or ℓth power of energy) one obtains a value E_n (or E_n^ℓ) with a probability of $|c_n|^2$. Sometimes one hears $|c_n|^2$ called the probability of the system being in stationary state n. This is actually a bit careless. In the standard interpretation, the system isn't in any particular stationary state (unless the expansion contains only one term) before the measurement. The system is in a superposition of stationary states: i.e., it's partially in some number of stationary states. An ideal measurement projects the system into (or collapses the wave function to) a particular stationary state. Actually take an ensemble and measure any dynamical quantity (governed by some observable) and you project the system into an eigenstate for that observable. But energy eigenstates (stationary states) and other kinds of eigenstates do not necessarily form the same set. So how can the system be in a stationary state and an eigenstate for some other observable at the same time? It can be (but not necessarily is) if the Hamiltonian and the other observable commute. But in general, they won't.

Redaction: Jeffery, 2001jan01

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002 qfull 01000 2 5 0 moderate thinking: energy and normalization

Extra keywords: (Gr-24:2.2) zero-point energy

15. Classically $E \geq V_{\min}$ for a particle in a conservative system.

    a) Show that this classical result must be so. **HINT:** This shouldn't be a from-first-principles proof: it should be about one line.

    b) The quantum mechanical analog is almost the same: $\bar{E} = \langle H \rangle > V_{\min}$ for any normalizable state of the system considered. Note the equality $\bar{E} = \langle H \rangle = V_{\min}$ never holds quantum mechanically. (There is an over-idealized exception, which we consider in part (e).) Prove the inequality. **HINTS:** The key point is to show that $\langle T \rangle > 0$ for all physically allowed states. Use integration by parts.

    c) Now show that result $\bar{E} > V_{\min}$ implies $E > V_{\min}$, where E is any eigen-energy of the system considered. Note the equality $E = V_{\min}$ never holds quantum mechanically (except for the over-idealized system considered in part (e)). In a sense, there is no rest state for quantum mechanical particle. This lowest energy is called the zero-point energy.

    d) The $E > V_{\min}$ result for an eigen-energy in turn implies a 3rd result: any ideal measurement always yields an energy greater than $V_{\min}$ Prove this by reference to a quantum mechanical postulate.

    e) This part is **NOT** to be done on **EXAMS**: it's just too much (for the grader). There is actually an exception to $E > V_{\min}$ result for an eigen-energy where $E = V_{\min}$ occurs. The exception is for quantum mechanical systems with periodic boundary conditions and a constant potential. In ordinary 3-dimensional Euclidean space, the periodic boundary conditions can only occur for rings (1-dimensional systems) and sphere surfaces (2-dimensional systems) I believe. Since any real system must have a finite size in all 3 spatial dimensions, one cannot have real systems with only periodic boundary conditions. Thus, the exception to the $E > V_{\min}$ result is for unrealistic over-idealized systems. Let us consider the idealized ring system as an example case. The Hamiltonian for a 1-dimensional ring with a constant potential is

$$H = -\frac{\hbar^2}{2mr^2}\frac{\partial^2}{\partial\phi^2} + V \ ,$$

    where r is the ring radius, ϕ is the azimuthal angle, and V is the constant potential. Find the eigen-functions and eigen-energies for the Schrödinger equation for the ring system with periodic boundary conditions imposed. Why must one impose periodic boundary conditions on the solutions? What solution has eigen-energy $E = V_{\min}$?

SUGGESTED ANSWER:

a) Classically, for a conservative system $E = T + V$ is a constant: T is kinetic energy and V is potential energy: and $T = (1/2)mv^2 \geq 0$ always, of course. Thus $E \geq V \geq V_{\min}$. If $E = V_{\min}$, the system is in static equilibrium since $T = 0$ and $F = -dV/dx = 0$ for $V = V_{\min}$. Of course, a system with $T > 0$ can be instantaneously at the point where $V = V_{\min}$: the particle in this case is just passing through the equilibrium point where its acceleration is instantaneously zero.

b) In quantum mechanics the expectation value of the kinetic energy for any wave function is given by

$$\begin{aligned}\langle T \rangle &= \int_{-\infty}^{\infty} \Psi^* T \Psi \, dx = \frac{1}{2m}\int_{-\infty}^{\infty} \Psi^* p^2 \Psi \, dx = \frac{-1}{2m}\int_{-\infty}^{\infty} p\Psi^* p\Psi \, dx \\ &= \frac{1}{2m}\int_{-\infty}^{\infty} (p\Psi)^* p\Psi \, dx \\ &\geq 0 \ ,\end{aligned}$$

where we have used integration by parts, the vanishing of the boundary terms, and the fact that integrand of the penultimate line is evidently always greater than or equal to zero. Note the above derivation demands that the boundary terms vanish and that the function is sufficiently differentiable. The requirement of normalization and the fact that in reality all physical systems show no discontinuities or infinities guarantees conditions of the derivation. If discontinuities are introduced as a mathemetical idealization, then they must be treated so as to yield the same derivation in order to be valid. For instance, the infinite square well has a discontinuity in $\partial\psi/\partial x$ at the well walls. However, since the wave function is zero outside of the well and at the well walls, we derive the same result as above: $\langle T \rangle \geq 0$.

The only way $\langle T \rangle$ can be zero is if the derivative of the wave function were everywhere zero which requires that the wave function be a constant. A constant wave function cannot be normalized, and so is not a physically allowed wave function (except for the over-idealized systems considered in part (e).) Ergo

$$\langle T \rangle > 0$$

always. Ergo all over again

$$\bar{E} = \langle H \rangle > \langle V \rangle \geq V_{\min}$$

or

$$\bar{E} = \langle H \rangle > V_{\min}$$

which is the result we wanted to show.

c) For a stationary state, the expectation value of the Hamiltonian is just the eigen-energy:

$$E = \langle H \rangle \ .$$

Thus for a stationary state of eigen-energy E it follows that

$$E > V_{\min} \ .$$

d) Now for an Aristotelian syllogism:

Major premise: By quantum mechanical postulate the result of any ideal measurment of an observable is an eigenvalue of the observable for that system. Well if the eigenvalues form a continuum then it seems that an even ideal measurement must always be some average of a finite range of eigenvalues. But if the measurement is ideal it must be a very small range. The point is not cleared up in my sources.

Minor premise: All eigenvalues E obey $E > V_{\min}$.

Conclusion: All ideal measurements of energy of a quantum mechanical system yield an energy $E_{\text{measured}} > V_{\min}$.

Further Considerations:

What if the potential is time-varying? I guess the argument then is that at any instant the potential can be treated as a constant with instant-existing eigenstates. Then again any expectation or eigen-energy is greater than $V_{\min}$ always.

Further insight into our results come from a reasoning argument. Physical states are described by wave functions. To be physical, a wave function must be normalizable. To be normalizable function must have some curvature. Curvature gives rise to a kinetic energy contribution to energy expectation value unless somehow a pathological wave function can be found where the kinetic energy contributions all cancel out. The proof done above shows that no such pathological wave function can be found. We can further note that the classical state of rest doesn't exist in quantum mechanics. A stationary state may correspond to rest in some respects, but it is radically different in other respects.

Yet more further insight into our results can come from considering the time-independent Schrödinger equation in the form

$$\psi'' = \frac{2m}{\hbar^2}[V(x) - E]\psi \ .$$

For simplicity let ψ be a pure real stationary state as we are always free to arrange. Any normalizable wave function must "turn over" at least once somewhere: i.e., it's absolute value must have a global maximum (or maybe more than one equal global maxima). Now if ψ'' and ψ always have the same sign and are well defined, then for $\psi > 0$ there can only be a minimum and for $\psi < 0$ there can only be a maximum. Thus the absolute value can never have a global maximum and the wave function cannot be normalized.

This argument gives insight, but I don't think it is a fully convincing proof. One has to wonder couldn't $\psi' = \psi'' = \psi''' = 0$ and the nature of the stationary point be determined by

the fourth order derivative $\psi^{(4)}$? Also what if ψ'' is undefined at maximum or minimum which is a cusp: this happens for the wave function of a Dirac Delta function (see Gr-54). Clearly, a wave function that somehow was normalizable with $E \leq V_{\rm min}$ would be pathological, but more intricate argument is needed to show that it was impossible.

And also one can always imagine a normalizable wave function that is made of piecewise regions that have ψ and ψ'' always of the same sign. Maybe such wave functions can't be physical, but it would be tedious to argue generally enough to exclude them.

To investigate just a bit further let us consider a concrete example where $V(x)$ goes to a asymptotic constant $V_{\rm asy}$ for $|x|$ large. If $E < V_{\rm asy}$ in this asymptotic limit, then

$$\psi(x)_{\rm asy} = Ce^{\pm kx} \ ,$$

where C is some constant and

$$k = \sqrt{\frac{2m}{\hbar^2}[V_{\rm asy} - E]} \ .$$

The asymptotic wave functions if they applied everywhere are clearly not normalizable. They are allowed as the wave functions in some regimes: e.g., for x positive, Ce^{-kx} is allowed and for x negative, Ce^{kx}.

e) The time-independent Schrödinger equation in this case is

$$-\frac{\hbar^2}{2mr^2}\frac{\partial^2\psi}{\partial\phi^2} + V\psi = E\psi$$

which we can rewrite as

$$\frac{\partial^2}{\partial\phi^2} = -k^2\psi \ ,$$

where

$$k = \pm\sqrt{\frac{2mr^2}{\hbar^2}(E-V)}$$

with $E \geq V$ asssumed. The normalized solutions are

$$\psi = \frac{e^{ik\phi}}{\sqrt{2\pi}} \ ,$$

where we've just taken the azimuthal angle ϕ as the coordinate and not $r\phi$ (which would require a normalization constant $1/\sqrt{2\pi r}$. In order to be single-valued (which is a necessary condition on wave functions), we must have an integer k. Let us write k as m since n is more integerish: n is the quantum number for the eigenstates and eigenvalues. Thus

$$n = 0, \pm1, \pm2, \pm3, \ldots$$

and the quantized eigen-energies are given by

$$E = V + \frac{\hbar^2}{2mr^2}n^2 \ .$$

Requiring single-valuedness amounts to the same thing as requiring periodic boundary conditions for the ring since one can choose any point on the ring as a conventional boundary. Thus, periodic boundary conditions are required.

In the ring system, nothing forbids the $n = 0$. This means that we have valid eigenstate $\psi = 1/\sqrt{2\pi}$ which is a constant and the lowest eigen-energy is

$$E = V \ .$$

Since the potential is a constant, $V = V_{\rm min}$, and thus the lowest eigen-energy E equals $V_{\rm min}$. This is an exception to our usual rule that the eigen-energies obey $E > V_{\rm min}$, but it is for an over-idealized case.

Note that there are solutions that are ruled out. If $E - V = 0$, we have the linear solution

$$\psi = a\phi + b \ ,$$

where a and b are constants. The solution with $a = 0$ is just the $n = 0$ solution which is allowed. But if $a \neq 0$, the linear solution is not single-valued nor normalizable and must be ruled out.

If $E - V < 0$, we have exponential solutions

$$\psi = e^{\pm \kappa x} \ ,$$

where

$$\kappa = \sqrt{\frac{2mr^2}{\hbar^2}(V - E)} \ .$$

These solutions are not single-valued nor normalizable and must be ruled out.

Redaction: Jeffery, 2001jan01

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002 qfull 00110 2 5 0 moderate thinking: beyond the classical turning points

16. The constant energy of a classical particle in a conservative system is given by

$$E = T + V \ .$$

Since classically $T \geq 0$ always, a bound particle is confined by surface defined by $T = 0$ or $E = V(\vec{r})$. The points constituting this surface are called the turning points: a name which makes most sense in one dimension. Except for static cases where the turning point is trivially the rest point (and maybe some other weird cases), the particle comes to rest only for an instant at a turning point since the forces are unbalanced there. So it's a place where a particle "ponders for an instant before deciding where to go next". The region with $V > E$ is classically forbidden. Now for most quantum mechanical potential wells, the wave function extends beyond the classical turning point surface into the classical forbidden zone and, in fact, usually goes to zero only at infinity. If the potential becomes infinite somewhere (which is an idealization of course), the wave function goes to zero: this happens for the infinite square well for instance.

Let's write the 1-dimensional time-independent Schrödinger equation in the form

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{2m}{\hbar^2}(V - E)\psi \ .$$

a) Now solve for ψ for the region with $V > E$ with simplifying the assumption that V is constant in this region.

b) Can the solutions be normalized?

c) Can the solutions constitute an entire wave function? Can they be part of a wave function? In which regions?

d) Although we assumed constant V, what crudely is the behavior of the wave function likely to be like the regions with $V > E$.

e) For typical potentials considered at our level, qualitatively what is the likelihood of finding the particle in the classically forbidden region? Why?

SUGGESTED ANSWER:

a) Let

$$k^2 = \frac{2m}{\hbar^2}(V - E) \ ,$$

where we take k to be positive. Then

$$\frac{\partial^2 \psi}{\partial x^2} = k^2 \psi \ .$$

The solutions are

$$\psi = e^{\pm kx} \ .$$

b) The solutions cannot be normalized. The k solution goes to infinity at positive infinity and the $-k$ solution goes to infinity at negative infinity.

c) The solutions can't be normalized, and so they can't be entire wave functions. This is consistent with our earlier finding—if indeed it isn't a later finding—that $E > V_{\min}$: thus there must be some region where $E > V$. But the solutions can be pieces of a wave function. In fact, just about any piece that doesn't include where they go infinite. The easy cases to identify are e^{kx} for some region extending to negative infinity and e^{-kx} for some region extending to positive infinity.

d) Assuming V constant is sort of likely assuming an average V. In which case our solutions are sort of average solutions. Thus in general we'd assume that wave function decay exponentially in regions where $V > E$.

e) Although quantum mechanically particles can be found in the classically forbidden region, for the ordinary potential we've been considering that probability is likely to be low. The solutions are roughly decaying exponentials in these regions. That means they must be decaying from some high probability region that is classically allowed. Thus it is likely that the most probable place for finding the particle is in the classically allowed regions. But there may be some weird class of systems in which the probability of finding the particle is higher in the classically forbidden region. I havn't given the matter any thought.

Redaction: Jeffery, 2001jan01

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002 qfull 01100 3 5 0 tough thinking: 1-d non-degeneracy

17. If there are no internal degrees of freedom (e.g., spin) and they are **NORMALIZABLE**, then one-particle, 1-dimensional energy eigenstates are non-degenerate. We (that is to say you) will prove this.

Actually, we know already that any 2nd order ordinary linear differential equation has only two linearly independent solutions (Ar-402) which means, in fact, that from the start we know there is a degeneracy of 2 at most. Degeneracy count is the number of independent solutions. If there is more than one independent solution, then infinitely many linear combinations of solutions have the same energy. But in an expansion of wave function, only a set linear independent solutions is needed and thus the number of such solutions is the physically relevant degeneracy. Of course, our proof means that one of the linearly independent solutions is not normalizable.

a) Assume you have two degenerate 1-dimensional energy eigenstates for Hamiltonian H: ψ_1 and ψ_2. Prove that $\psi_1\psi_2' - \psi_2\psi_1'$ equals a constant where the primes indicate derivative with respect to x the spatial variable. **HINT:** Write down the eigenproblem for both ψ_1 and ψ_2 and do some multiplying and subtraction and integration.

b) Prove that the constant in part (a) result must be zero. **HINT:** To be physically allowable eigenstates, the eigenstates must be normalizable.

c) Integrate the result of the part (b) answer and show that the two assumed solutions are not physically distinct. Show for all x that

$$\psi_2(x) = C\psi_1(x) \ ,$$

where C is a constant. This completes the proof of non-degeneracy since eigenstates that differ by a multiplicative constant are not physically (i.e., expansion) distinct. **HINT:** You have to show that there is no other way than having $\psi_2(x) = C\psi_1(x)$ to satisfy the condition found in the part (b) answer. Remember the eigenproblem is a linear, homogeneous differential equation.

SUGGESTED ANSWER:

a) Assume you have two degenerate 1-d energy eigenstates for Hamiltonian H: ψ_1 and ψ_2. Assume they are pure real to avoid complications of complexity. It can be proven that one can always construct a set of independent real eigenstates from a complex set (Gr-29). Then

$$H\psi_1 = E\psi_1 \qquad \text{and} \qquad H\psi_2 = E\psi_2 \ ,$$

and so

$$\psi_2 H\psi_1 = \psi_2 E\psi_1 \qquad \text{and} \qquad \psi_1 H\psi_2 = \psi_1 E\psi_2 \ .$$

If we subtract first from the second of these, we get

$$\psi_1 H\psi_2 - \psi_2 H\psi_1 = \psi_1 T\psi_2 - \psi_2 T\psi_1 = 0 \ ,$$

where T is the kinetic energy operator. Thus,

$$\psi_1\psi_2'' - \psi_2\psi_1'' = 0$$

which integrates to

$$\psi_1\psi_2' - \psi_2\psi_1' = \text{Constant}$$

which can be confirmed by differentiation.

b) To be normalizable, the energy eigenstates must be zero at infinity, and thus the constant form the part (a) result must be zero. Thus,

$$\psi_1\psi_2' - \psi_2\psi_1' = 0 \ .$$

The derivatives ought to be zero at infinity too. I can't see any case where it could be otherwise. Maybe there is pathological case. But if the wave function is continuous (as we usually demand) the derivatives can only be kinked. Thus, the derivatives really must be zero at infinity too.

Note that the free particle eigenstates (which are for zero potential) are not normalizable at infinity and are degenerate. There are two independent eigenstates for each energy:

$$\psi_+ = \frac{e^{ikx}}{\sqrt{2\pi}} \qquad \text{and} \qquad \psi_- = \frac{e^{-ikx}}{\sqrt{2\pi}} \ ,$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \ .$$

Actually, any unbound particle energy eigenstates out to be oscillatory at infinity where the potential is zero. Thus, at infinity, their energy eigenstates are also

$$\psi_+ = \frac{e^{ikx}}{\sqrt{2\pi}} \qquad \text{and} \qquad \psi_- = \frac{e^{-ikx}}{\sqrt{2\pi}} \ ,$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \ .$$

So these states have degeneneracy of 2 too.

c) Behold:

$$\begin{aligned}
\psi_1\psi_2' &= \psi_2\psi_1' \ , \\
\frac{\psi_2'}{\psi_2} &= \frac{\psi_1'}{\psi_1} \ , \\
\frac{d\psi_2}{\psi_2} &= \frac{d\psi_1}{\psi_1} \ , \\
\ln|\psi_2| &= \ln|\psi_1| + \text{Constant} \ ,
\end{aligned}$$

and finally

$$|\psi_2| = C|\psi_1| \ ,$$

where C is a positive constant and we have used

$$\frac{d\ln|x|}{dx} = \frac{1}{|x|}(\pm 1) = \frac{1}{x} \ ,$$

where the upper case is for $x > 0$ and the lower for $x < 0$. But sticking to real ψ_1 and ψ_2, we avoid any problems with integrating with repect to a complex variable.

Now the general solution of any 2nd order linear differential equation solution has the form

$$A_1\phi_1(x) + A_2\phi_2(x) \ ,$$

where A_1 and A_2 are constants and ϕ_1 and ϕ_2 are linearly independent solutions. Thus, if the value of the solution is specified at two points, the solution is specified everywhere.

Thus, if ψ_1 and ψ_2 have the same sign at two points, then aside from the constant C they are the same solutions everywhere. And if ψ_1 and ψ_2 have different signs at two points, then aside from the constant $-C$ they are the same solutions everywhere. Either way they are physically the same solution everywhere.

Are there any other possibilities? If ψ_1 and ψ_2 have the same sign at one point and are continuous as they must be to be physical solutions, then they have the same sign over a region. If ψ_1 and ψ_2 have different signs at one point and are continuous as they must be to be physical solutions, then they different signs over a region.

The upshot is that normalizable single-particle, 1-dimensional eigenstates (with no internal degrees of freedom) are non-degenerate. Any difference by a constant between two eigenstates does not make them phyiscally (i.e., expansion) distinct.

Could there be some pathological potential that gives a degenerate eigenstate? Doesn't seem likely, but in any case it would not likely turn up in nature.

Of course, if you have internal deqrees of freedom with no energy distinction in principle like spin, then degeneracy in 1-dimension is easily obtained. In nature, I believe some interaction always breaks spin or angular momentum degeneracy to some degree.

Redaction: Jeffery, 2001jan01

Appendix 2 Quantum Mechanics Equation Sheet

Note: This equation sheet is intended for students writing tests or reviewing material. Therefore it neither intended to be complete nor completely explicit. There are fewer symbols than variables, and so some symbols must be used for different things.

1 Constants not to High Accuracy

Constant Name	Symbol	Derived from CODATA 1998
Bohr radius	$a_{\text{Bohr}} = \dfrac{\lambda_{\text{Compton}}}{2\pi\alpha}$	$= 0.529\,\text{Å}$
Boltzmann's constant	k	$= 0.8617 \times 10^{-6}\,\text{eV K}^{-1}$
		$= 1.381 \times 10^{-16}\,\text{erg K}^{-1}$
Compton wavelength	$\lambda_{\text{Compton}} = \dfrac{h}{m_e c}$	$= 0.0246\,\text{Å}$
Electron rest energy	$m_e c^2$	$= 5.11 \times 10^5\,\text{eV}$
Elementary charge squared	e^2	$= 14.40\,\text{eV Å}$
Fine Structure constant	$\alpha = \dfrac{e^2}{\hbar c}$	$= 1/137.036$
Kinetic energy coefficient	$\dfrac{\hbar^2}{2m_e}$	$= 3.81\,\text{eV Å}^2$
	$\dfrac{\hbar^2}{m_e}$	$= 7.62\,\text{eV Å}^2$
Planck's constant	h	$= 4.15 \times 10^{-15}\,\text{eV}$
Planck's h-bar	$\hbar$	$= 6.58 \times 10^{-16}\,\text{eV}$
	hc	$= 12398.42\,\text{eV Å}$
	$\hbar c$	$= 1973.27\,\text{eV Å}$
Rydberg Energy	$E_{\text{Ryd}} = \dfrac{1}{2} m_e c^2 \alpha^2$	$= 13.606\,\text{eV}$

2 Some Useful Formulae

Leibniz's formula
$$\frac{d^n(fg)}{dx^n} = \sum_{k=0}^{n} \binom{n}{k} \frac{d^k f}{dx^k} \frac{d^{n-k} g}{dx^{n-k}}$$

Normalized Gaussian
$$P = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x - \langle x \rangle)^2}{2\sigma^2}\right]$$

3 Schrödinger's Equation

$$H\Psi(x,t) = \left[\frac{p^2}{2m} + V(x)\right]\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

$$H\psi(x) = \left[\frac{p^2}{2m} + V(x)\right]\psi(x) = E\psi(x)$$

$$H\Psi(\vec{r},t) = \left[\frac{p^2}{2m} + V(\vec{r})\right]\Psi(\vec{r},t) = i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} \qquad H|\Psi\rangle = i\hbar\frac{\partial}{\partial t}|\Psi\rangle$$

$$H\psi(\vec{r}) = \left[\frac{p^2}{2m} + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \qquad H|\psi\rangle = E|\psi\rangle$$

4 Some Operators

$$p = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad p^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$$

$$H = \frac{p^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

$$p = \frac{\hbar}{i}\nabla \qquad p^2 = -\hbar^2\nabla^2$$

$$H = \frac{p^2}{2m} + V(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

$$\nabla = \hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z} = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\theta}\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

---

5 Kronecker Delta and Levi-Civita Symbol

$$\delta_{ij} = \begin{cases} 1, & i = j; \\ 0, & \text{otherwise} \end{cases} \qquad \varepsilon_{ijk} = \begin{cases} 1, & ijk \text{ cyclic}; \\ -1, & ijk \text{ anticyclic}; \\ 0, & \text{if two indices the same.} \end{cases}$$

$$\varepsilon_{ijk}\varepsilon_{i\ell m} = \delta_{j\ell}\delta_{km} - \delta_{jm}\delta_{k\ell} \qquad \text{(Einstein summation on } i\text{)}$$

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6 Time Evolution Formulae

$$\text{General} \qquad \frac{d\langle A\rangle}{dt} = \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{1}{\hbar}\langle i[H(t), A]\rangle$$

$$\text{Ehrenfest's Theorem} \qquad \frac{d\langle \vec{r}\rangle}{dt} = \frac{1}{m}\langle \vec{p}\rangle \qquad \text{and} \qquad \frac{d\langle \vec{p}\rangle}{dt} = -\langle \nabla V(\vec{r})\rangle$$

$$|\Psi(t)\rangle = \sum_j c_j(0)e^{-iE_jt/\hbar}|\phi_j\rangle$$

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7 Simple Harmonic Oscillator (SHO) Formulae

$$V(x) = \frac{1}{2}m\omega^2x^2 \qquad \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2x^2\right)\psi = E\psi$$

$$\beta = \sqrt{\frac{m\omega}{\hbar}} \qquad \psi_n(x) = \frac{\beta^{1/2}}{\pi^{1/4}}\frac{1}{\sqrt{2^n n!}}H_n(\beta x)e^{-\beta^2x^2/2} \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$H_0(\beta x) = H_0(\xi) = 1 \qquad H_1(\beta x) = H_1(\xi) = 2\xi$$

$$H_2(\beta x) = H_2(\xi) = 4\xi^2 - 2 \qquad H_3(\beta x) = H_3(\xi) = 8\xi^3 - 12\xi$$

8 Position, Momentum, and Wavenumber Representations

$$p = \hbar k \qquad E_{\text{kinetic}} = E_T = \frac{\hbar^2 k^2}{2m}$$

$$|\Psi(p,t)|^2\, dp = |\Psi(k,t)|^2\, dk \qquad \Psi(p,t) = \frac{\Psi(k,t)}{\sqrt{\hbar}}$$

$$x_{\text{op}} = x \qquad p_{\text{op}} = \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad Q\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}, t\right) \qquad \text{position representation}$$

$$x_{\text{op}} = -\frac{\hbar}{i}\frac{\partial}{\partial p} \qquad p_{\text{op}} = p \qquad Q\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}, p, t\right) \qquad \text{momentum representation}$$

$$\delta(x) = \int_{-\infty}^{\infty} \frac{e^{ipx/\hbar}}{2\pi\hbar}\, dp \qquad \delta(x) = \int_{-\infty}^{\infty} \frac{e^{ikx}}{2\pi}\, dk$$

$$\Psi(x,t) = \int_{-\infty}^{\infty} \Psi(p,t)\frac{e^{ipx/\hbar}}{(2\pi\hbar)^{1/2}}\, dp \qquad \Psi(x,t) = \int_{-\infty}^{\infty} \Psi(k,t)\frac{e^{ikx}}{(2\pi)^{1/2}}\, dk$$

$$\Psi(p,t) = \int_{-\infty}^{\infty} \Psi(x,t)\frac{e^{-ipx/\hbar}}{(2\pi\hbar)^{1/2}}\, dx \qquad \Psi(k,t) = \int_{-\infty}^{\infty} \Psi(x,t)\frac{e^{-ikx}}{(2\pi)^{1/2}}\, dx$$

$$\Psi(\vec{r},t) = \int_{\text{all space}} \Psi(\vec{p},t)\frac{e^{i\vec{p}\cdot\vec{r}/\hbar}}{(2\pi\hbar)^{3/2}}\, d^3p \qquad \Psi(\vec{r},t) = \int_{\text{all space}} \Psi(\vec{k},t)\frac{e^{i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}}\, d^3k$$

$$\Psi(\vec{p},t) = \int_{\text{all space}} \Psi(\vec{r},t)\frac{e^{-i\vec{p}\cdot\vec{r}/\hbar}}{(2\pi\hbar)^{3/2}}\, d^3r \qquad \Psi(\vec{k},t) = \int_{\text{all space}} \Psi(\vec{r},t)\frac{e^{-i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}}\, d^3r$$

9 Commutator Formulae

$$[A, BC] = [A,B]C + B[A,C] \qquad \left[\sum_i a_i A_i, \sum_j b_j B_j\right] = \sum_{i,j} a_i b_j [A_i, b_j]$$

$$\text{if} \qquad [B,[A,B]] = 0 \qquad \text{then} \qquad [A, F(B)] = [A,B]F'(B)$$

$$[x,p] = i\hbar \qquad [x, f(p)] = i\hbar f'(p) \qquad [p, g(x)] = -i\hbar g'(x)$$

$$[a, a^\dagger] = 1 \qquad [N,a] = -a \qquad [N, a^\dagger] = a^\dagger$$

10 Uncertainty Relations and Inequalities

$$\sigma_x \sigma_p = \Delta x \Delta p \geq \frac{\hbar}{2} \qquad \sigma_Q \sigma_Q = \Delta Q \Delta R \geq \frac{1}{2} \left| \langle i[Q,R] \rangle \right|$$

$$\sigma_H \Delta t_{\text{scale time}} = \Delta E \Delta t_{\text{scale time}} \geq \frac{\hbar}{2}$$

11 Probability Amplitudes and Probabilities

$$\Psi(x,t) = \langle x | \Psi(t) \rangle \qquad P(dx) = |\Psi(x,t)|^2 \, dx \qquad c_i(t) = \langle \phi_i | \Psi(t) \rangle \qquad P(i) = |c_i(t)|^2$$

12 Spherical Harmonics

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \qquad Y_{1,0} = \left(\frac{3}{4\pi} \right)^{1/2} \cos(\theta) \qquad Y_{1,\pm 1} = \mp \left(\frac{3}{8\pi} \right)^{1/2} \sin(\theta) e^{\pm i \phi}$$

$$L^2 Y_{\ell m} = \ell(\ell+1) \hbar^2 Y_{\ell m} \qquad L_z Y_{\ell m} = m \hbar Y_{\ell m} \qquad |m| \leq \ell \qquad m = -\ell, -\ell+1, \ldots, \ell-1, \ell$$

0	1	2	3	4	5	6	...
s	p	d	f	g	h	i	...

13 Hydrogenic Atom

$$\psi_{n\ell m} = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \qquad \ell \leq n-1 \qquad \ell = 0, 1, 2, \ldots, n-1$$

$$a_z = \frac{a}{Z} \left(\frac{m_e}{m_{\text{reduced}}} \right) \qquad a_0 = \frac{\hbar}{m_e c \alpha} = \frac{\lambda_{\text{C}}}{2\pi\alpha} \qquad \alpha = \frac{e^2}{\hbar c}$$

$$R_{10} = 2 a_Z^{-3/2} e^{-r/a_Z} \qquad R_{20} = \frac{1}{\sqrt{2}} a_Z^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a_Z} \right) e^{-r/(2a_Z)}$$

$$R_{21} = \frac{1}{\sqrt{24}} a_Z^{-3/2} \frac{r}{a_Z} e^{-r/(2a_Z)}$$

$$R_{n\ell} = - \left\{ \left(\frac{2}{n a_Z} \right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho) \qquad \rho = \frac{2r}{n r_Z}$$

$$L_q(x) = e^x \left(\frac{d}{dx} \right)^q \left(e^{-x} x^q \right) \quad \text{Rodrigues's formula for the Laguerre polynomials}$$

$$L_q^j(x) = \left(\frac{d}{dx} \right)^j L_q(x) \qquad \text{Associated Laguerre polynomials}$$

$$\langle r \rangle_{n\ell m} = \frac{a_Z}{2} \left[3n^2 - \ell(\ell+1) \right]$$

$$\text{Nodes} = (n-1) - \ell \qquad \text{not counting zero or infinity}$$

$$E_n = -\frac{1}{2}m_e c^2 \alpha^2 \frac{Z^2}{n^2}\frac{m_{\text{reduced}}}{m_e} = -E_{\text{Ryd}}\frac{Z^2}{n^2}\frac{m_{\text{reduced}}}{m_e} = -13.606\frac{Z^2}{n^2}\frac{m_{\text{reduced}}}{m_e}\ \text{eV}$$

14 General Angular Momentum Formulae

$$[J_i, J_j] = i\hbar\varepsilon_{ijk}J_k \qquad \text{(Einstein summation on } k\text{)} \qquad [J^2, \vec{J}] = 0$$

$$J^2|jm\rangle = j(j+1)\hbar^2|jm\rangle \qquad J_z|jm\rangle = m\hbar|jm\rangle$$

$$J_\pm = J_x \pm iJ_y \qquad J_\pm|jm\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}|jm\pm 1\rangle$$

$$J_{\left\{\begin{smallmatrix}x\\y\end{smallmatrix}\right\}} = \begin{Bmatrix}\frac{1}{2}\\ \frac{1}{2i}\end{Bmatrix}(J_+ \pm J_-) \qquad J_\pm^\dagger J_\pm = J_\mp J_\pm = J^2 - J_z(J_z \pm \hbar)$$

$$[J_{fi}, J_{gj}] = \delta_{fg}i\hbar\varepsilon_{ijk}J_k \qquad \vec{J} = \vec{J_1} + \vec{J_2} \qquad J^2 = J_1^2 + J_2^2 + J_{1+}J_{2-} + J_{1-}J_{2+} + 2J_{1z}J_{2z}$$

$$J_\pm = J_{1\pm} + J_{2\pm} \qquad |j_1 j_2 jm\rangle = \sum_{m_1 m_2, m=m_1+m_2} |j_1 j_2 m_1 m_2\rangle\langle j_1 j_2 m_1 m_2|j_1 j_2 jm\rangle j_1 j_2 jm\rangle$$

$$|j_1 - j_2| \le j \le j_1 + j_2 \qquad \sum_{|j_1-j_2|}^{j_1+j_2}(2j+1) = (2j_1+1)(2j_2+1)$$

15 Spin 1/2 Formulae

$$S_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad S_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$|\pm\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle \pm |-\rangle) \qquad |\pm\rangle_y = \frac{1}{\sqrt{2}}(|+\rangle \pm i|-\rangle) \qquad |\pm\rangle_z = |\pm\rangle$$

$$|++\rangle = |1,+\rangle|2,+\rangle \qquad |+-\rangle = \frac{1}{\sqrt{2}}(|1,+\rangle|2,-\rangle \pm |1,-\rangle|2,+\rangle) \qquad |--\rangle = |1,-\rangle|2,-\rangle$$

$$\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad \sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$\sigma_i\sigma_j = \delta_{ij} + i\varepsilon_{ijk}\sigma_k \qquad [\sigma_i, \sigma_j] = 2i\varepsilon_{ijk}\sigma_k \qquad \{\sigma_i, \sigma_j\} = 2\delta_{ij}$$

$$(\vec{A}\cdot\vec{\sigma})(\vec{B}\cdot\vec{\sigma}) = \vec{A}\cdot\vec{B} + i(\vec{A}\times\vec{B})\cdot\vec{\sigma}$$

$$\frac{d(\vec{S}\cdot\hat{n})}{d\alpha} = -\frac{i}{\hbar}[\vec{S}\cdot\hat{\alpha}, \vec{S}\cdot\hat{n}] \qquad \vec{S}\cdot\hat{n} = e^{-i\vec{S}\cdot\vec{\alpha}}\vec{S}\cdot\hat{n}_0 e^{i\vec{S}\cdot\vec{\alpha}} \qquad |\hat{n}_\pm\rangle = e^{-i\vec{S}\cdot\vec{\alpha}}|\hat{z}_\pm\rangle$$

$$e^{ixA} = \mathbf{1}\cos(x) + iA\sin(x) \quad \text{if } A^2 = \mathbf{1} \qquad e^{-i\vec{\sigma}\cdot\vec{\alpha}/2} = \mathbf{1}\cos(x) - i\vec{\sigma}\cdot\hat{\alpha}\sin(x)$$

$$\sigma_i f(\sigma_j) = f(\sigma_j)\sigma_i\delta_{ij} + f(-\sigma_j)\sigma_i(1-\delta_{ij})$$

$$\mu_{\text{Bohr}} = \frac{e\hbar}{2m} = 0.927400915(23)\times 10^{-24}\,\text{J/T} = 5.7883817555(79)\times 10^{-5}\,\text{eV/T}$$

$$g = 2\left(1 + \frac{\alpha}{2\pi} + \ldots\right) = 2.0023193043622(15)$$

$$\vec{\mu}_{\text{orbital}} = -\mu_{\text{Bohr}}\frac{\vec{L}}{\hbar} \qquad \vec{\mu}_{\text{spin}} = -g\mu_{\text{Bohr}}\frac{\vec{S}}{\hbar} \qquad \vec{\mu}_{\text{total}} = \vec{\mu}_{\text{orbital}} + \vec{\mu}_{\text{spin}} = -\mu_{\text{Bohr}}\frac{(\vec{L}+g\vec{S})}{\hbar}$$

$$H_\mu = -\vec{\mu}\cdot\vec{B} \qquad H_\mu = \mu_{\text{Bohr}}B_z\frac{(L_z + gS_z)}{\hbar}$$

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16 Time-Independent Approximation Methods

$$H = H^{(0)} + \lambda H^{(1)} \qquad |\psi\rangle = N(\lambda)\sum_{k=0}^{\infty}\lambda^k|\psi_n^{(k)}\rangle$$

$$H^{(1)}|\psi_n^{(m-1)}\rangle(1-\delta_{m,0}) + H^{(0)}|\psi_n^{(m)}\rangle = \sum_{\ell=0}^{m}E^{(m-\ell)}|\psi_n^{(\ell)}\rangle \qquad |\psi_n^{(\ell>0)}\rangle = \sum_{m=0,\ m\neq n}^{\infty}a_{nm}|\psi_n^{(0)}\rangle$$

$$|\psi_n^{\text{1st}}\rangle = |\psi_n^{(0)}\rangle + \lambda\sum_{\text{all } k,\ k\neq n}\frac{\left\langle\psi_k^{(0)}|H^{(1)}|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_k^{(0)}}|\psi_k^{(0)}\rangle$$

$$E_n^{\text{1st}} = E_n^{(0)} + \lambda\left\langle\psi_n^{(0)}|H^{(1)}|\psi_n^{(0)}\right\rangle$$

$$E_n^{\text{2nd}} = E_n^{(0)} + \lambda\left\langle\psi_n^{(0)}|H^{(1)}|\psi_n^{(0)}\right\rangle + \lambda^2\sum_{\text{all } k,\ k\neq n}\frac{\left|\left\langle\psi_k^{(0)}|H^{(1)}|\psi_n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}}$$

$$E(\phi) = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} \qquad \delta E(\phi) = 0$$

$$H_{kj} = \langle\phi_k|H|\phi_j\rangle \qquad H\vec{c} = E\vec{c}$$

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17 Time-Dependent Perturbation Theory

$$\pi = \int_{-\infty}^{\infty}\frac{\sin^2(x)}{x^2}\,dx$$

$$\Gamma_{0\to n} = \frac{2\pi}{\hbar}|\langle n|H_{\text{perturbation}}|0\rangle|^2\delta(E_n - E_0)$$

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18 **Interaction of Radiation and Matter**

$$\vec{E}_{\text{op}} = -\frac{1}{c}\frac{\partial \vec{A}_{\text{op}}}{\partial t} \qquad \vec{B}_{\text{op}} = \nabla \times \vec{A}_{\text{op}}$$

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19 **Box Quantization**

$$kL = 2\pi n, \quad n = 0, \pm 1, \pm 2, \ldots \qquad k = \frac{2\pi n}{L} \qquad \Delta k_{\text{cell}} = \frac{2\pi}{L} \qquad \Delta k_{\text{cell}}^3 = \frac{(2\pi)^3}{V}$$

$$dN_{\text{states}} = g\frac{k^2\, dk\, d\Omega}{(2\pi)^3/V}$$

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20 **Identical Particles**

$$|a, b\rangle = \frac{1}{\sqrt{2}}\left(|1, a; 2, b\rangle \pm |1, b; 2, a\rangle\right)$$

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right)$$

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21 **Second Quantization**

$$[a_i, a_j^\dagger] = \delta_{ij} \qquad [a_i, a_j] = 0 \qquad [a_i^\dagger, a_j^\dagger] = 0 \qquad |N_1, \ldots, N_n\rangle = \frac{(a_n^\dagger)^{N_n}}{\sqrt{N_n!}} \ldots \frac{(a_1^\dagger)^{N_1}}{\sqrt{N_1!}}|0\rangle$$

$$\{a_i, a_j^\dagger\} = \delta_{ij} \qquad \{a_i, a_j\} = 0 \qquad \{a_i^\dagger, a_j^\dagger\} = 0 \qquad |N_1, \ldots, N_n\rangle = (a_n^\dagger)^{N_n} \ldots (a_1^\dagger)^{N_1}|0\rangle$$

$$\Psi_s(\vec{r})^\dagger = \sum_{\vec{p}} \frac{e^{-i\vec{p}\cdot\vec{r}}}{\sqrt{V}} a_{\vec{p}s}^\dagger \qquad \Psi_s(\vec{r}) = \sum_{\vec{p}} \frac{e^{i\vec{p}\cdot\vec{r}}}{\sqrt{V}} a_{\vec{p}s}$$

$$[\Psi_s(\vec{r}), \Psi_{s'}(\vec{r}')]_\mp = 0 \qquad [\Psi_s(\vec{r})^\dagger, \Psi_{s'}(\vec{r}')^\dagger]_\mp = 0 \qquad [\Psi_s(\vec{r}), \Psi_{s'}(\vec{r}')^\dagger]_\mp = \delta(\vec{r} - \vec{r}')\delta_{ss'}$$

$$|\vec{r}_1 s_1, \ldots, \vec{r}_n s_n\rangle = \frac{1}{\sqrt{n!}}\Psi_{s_n}(\vec{r}_n)^\dagger \ldots \Psi_{s_n}(\vec{r}_n)^\dagger|0\rangle$$

$$\Psi_s(\vec{r})^\dagger|\vec{r}_1 s_1, \ldots, \vec{r}_n s_n\rangle\sqrt{n+1}|\vec{r}_1 s_1, \ldots, \vec{r}_n s_n, \vec{r}s\rangle$$

$$|\Phi\rangle = \int d\vec{r}_1 \ldots d\vec{r}_n\, \Phi(\vec{r}_1, \ldots, \vec{r}_n)|\vec{r}_1 s_1, \ldots, \vec{r}_n s_n\rangle$$

$$1_n = \sum_{s_1 \ldots s_n} \int d\vec{r}_1 \ldots d\vec{r}_n\, |\vec{r}_1 s_1, \ldots, \vec{r}_n s_n\rangle\langle\vec{r}_1 s_1, \ldots, \vec{r}_n s_n| \qquad 1 = |0\rangle\langle 0| + \sum_{n=1}^{\infty} 1_n$$

$$N = \sum_{\vec{p}s} a^\dagger_{\vec{p}s} a_{\vec{p}s} \qquad T = \sum_{\vec{p}s} \frac{p^2}{2m} a^\dagger_{\vec{p}s} a_{\vec{p}s}$$

$$\rho_s(\vec{r}) = \Psi_s(\vec{r})^\dagger \Psi_s(\vec{r}) \qquad N = \sum_s \int d\vec{r}\, \rho_s(\vec{r}) \qquad T = \frac{1}{2m} \sum_s \int d\vec{r}\, \nabla\Psi_s(\vec{r})^\dagger \cdot \nabla\Psi_s(\vec{r})$$

$$\vec{j}_s(\vec{r}) = \frac{1}{2im}\left[\Psi_s(\vec{r})^\dagger \nabla\Psi_s(\vec{r}) - \Psi_s(\vec{r})\nabla\Psi_s(\vec{r})^\dagger\right]$$

$$G_s(\vec{r}-\vec{r}\,') = \frac{3n}{2}\frac{\sin(x) - x\cos(x)}{x^3} \qquad g_{ss'}(\vec{r}-\vec{r}\,') = 1 - \delta_{ss'}\frac{G_s(\vec{r}-\vec{r}\,')^2}{(n/2)^2}$$

$$v_{\text{2nd}} = \frac{1}{2}\sum_{ss'} \int d\vec{r} d\vec{r}\,'\, v(\vec{r}-\vec{r}\,')\Psi_s(\vec{r})^\dagger \Psi_{s'}(\vec{r}\,')^\dagger \Psi_{s'}(\vec{r}\,')\Psi_s(\vec{r})$$

$$v_{\text{2nd}} = \frac{1}{2V}\sum_{pp'qq'}\sum_{ss'} v_{\vec{p}-\vec{p}\,'}\delta_{\vec{p}+\vec{q},\vec{p}'+\vec{q}'} a^\dagger_{\vec{p}s} a^\dagger_{\vec{q}s'} a_{\vec{q}\,'s'} a_{\vec{p}\,'s} \qquad v_{\vec{p}-\vec{p}\,'} = \int d\vec{r}\, e^{-i(\vec{p}-\vec{p}\,')\cdot\vec{r}} v(\vec{r})$$

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22 Klein-Gordon Equation

$$E = \sqrt{p^2c^2 + m^2c^4} \qquad \frac{1}{c^2}\left(i\hbar\frac{\partial}{\partial t}\right)^2 \Psi(\vec{r},t) = \left[\left(\frac{\hbar}{i}\nabla\right)^2 + m^2c^2\right]\Psi(\vec{r},t)$$

$$\left[\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \left(\frac{mc}{\hbar}\right)^2\right]\Psi(\vec{r},t) = 0$$

$$\rho = \frac{i\hbar}{2mc^2}\left(\Psi^*\frac{\partial\Psi}{\partial t} - \Psi\frac{\partial\Psi^*}{\partial t}\right) \qquad \vec{j} = \frac{\hbar}{2im}\left(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*\right)$$

$$\frac{1}{c^2}\left(i\hbar\frac{\partial}{\partial t} - e\Phi\right)^2 \Psi(\vec{r},t) = \left[\left(\frac{\hbar}{i}\nabla - \frac{e}{c}\vec{A}\right)^2 + m^2c^2\right]\Psi(\vec{r},t)$$

$$\Psi_+(\vec{p},E) = e^{i(\vec{p}\cdot\vec{r}-Et)/\hbar} \qquad \Psi_-(\vec{p},E) = e^{-i(\vec{p}\cdot\vec{r}-Et)/\hbar}$$