Quantum Mechanics **NAME:**

Homework 2b: 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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003 qmult 00050 1 1 1 easy memory: infinite square well

1. In quantum mechanics, the infinite square well can be regarded as the prototype of:

   a) all bound systems. b) all unbound systems. c) both bound and unbound systems.
   d) neither bound nor unbound systems. e) Prometheus unbound.

   SUGGESTED ANSWER: (a)

   Wrong answers:

   e) Prometheus was chained to a rock with vultures perpetually munching his innards for giving fire to mortals. Herakles freed him at last, reconciling revolution and order (i.e., Prometheus and Zeus).

   Redaction: Jeffery, 2001jan01

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003 qmult 00100 2 4 2 moderate deducto-memory: infinite square well BCs

2. In the infinite square well problem, the wave function and its first spatial derivative are:

   a) both continuous at the boundaries.
   b) continuous and discontinuous at the boundaries, respectively.
   c) both discontinuous at the boundaries.
   d) discontinuous and continuous at the boundaries, respectively.
   e) both infinite at the boundaries.

   SUGGESTED ANSWER: (b)

   Wrong Answers:

   e) Can this ever be arranged for any system?

   Redaction: Jeffery, 2001jan01

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003 qmult 00300 1 1 3 easy memory: boundary conditions

3. Meeting the boundary conditions of bound quantum mechanical systems imposes:

   a) Heisenberg's uncertainty principle. b) Schrödinger's equation. c) quantization.
   d) a vector potential. e) a time-dependent potential.

   SUGGESTED ANSWER: (c)

   Wrong answers:

   e) Nah.

   Redaction: Jeffery, 2001jan01

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003 qmult 00400 1 1 5 easy memory: continuum of unbound states

4. At energies higher than the bound stationary states there:

   a) are between one and several tens of unbound states. b) are only two unbound states.
   c) is a single unbound state. d) are no states. e) is a continuum of unbound states.

   SUGGESTED ANSWER: (e)

   Wrong answers:

   d) This is only true for infinitely deep potential wells and such systems are only idealizations. No infinitely deep wells exist: you can always get out of a well.

   Redaction: Jeffery, 2001jan01

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003 qmult 00500 1 4 2 easy deducto-memory: tunneling

5. "Let's play *Jeopardy*! For $100, the answer is: This effect occurs because wave functions can extend (in an exponentially decreasing way albeit) into the classically forbidden region: i.e., the region where a classical particle would have negative kinetic energy."

   What is ____________, Alex?

a) stimulated radiative emission b) quantum mechanical tunneling c) quantization
d) symmetrization e) normalization

SUGGESTED ANSWER: (b)

Wrong answers:

d) Symmetrization is another fundamental property of quantum systems—but beyond our scope.

Redaction: Jeffery, 2001jan01

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003 qmult 00600 2 1 2 moderate memory: benzene ring model

6. A simple model of the outer electronic structure of a benzene molecule is a 1-dimensional infinite square well with:

a) vanishing boundary conditions. b) periodic boundary conditions.
c) aperiodic boundary conditions. d) no boundary conditions.
e) incorrect boundary conditions.

SUGGESTED ANSWER: (b)

Wrong Answers:

e) One can use incorrect boundary conditions as a simplification in cases where the boundary conditions have no significant effect. But in this case the system is small and correct boundary conditions are important.

Redaction: Jeffery, 2001jan01

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003 qfull 00100 2 3 0 moderate math: infinite square well in 1-d

7. You are given the time-independent Schrödinger equation

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

and the infinite square well potential

$$V(x) = \begin{cases} 0\,, & x \in [0,a]; \\ \infty & \text{otherwise.} \end{cases}$$

a) What must the wave function be outside of the well (i.e., outside of the region $[0,a]$) in order to satisfy the Schrödinger equation? Why?

b) What boundary conditions must the wave function satisfy? Why must it satisfy these boundary conditions?

c) Reduce Schrödinger's equation inside the well to an equation of the same form as the **CLASSICAL** simple harmonic oscillator differential equation with all the constants combined into a factor of $-k^2$, where k is newly defined constant. What is k's definition?

d) Solve for the general solution for a **SINGLE** k value, but don't impose boundary conditions or normalization yet. A solution by inspection is adequate. Why can't we allow solutions with $E \leq 0$? Think carefully: it's not because k is imaginary when $E < 0$.

e) Use the boundary conditions to eliminate most of the solutions with $E > 0$ and to impose quantization on the allowed set of distinct solutions (i.e., on the allowed k values). Give the general wave function with the boundary conditions imposed and give the quantization rule for k in terms of a dimensionless quantum number n. Note that the multiplication of a wave function by an arbitrary global phase factor $e^{i\phi}$ (where ϕ is arbitrary) does not create a physically distinct wave function (i.e., does not create a new wave function as recognized by nature.) (Note the orthogonality relation used in expanding general functions in eigenfunctions also does not distinguish eigenfunctions that differ by global phase factors either: i.e., it gives the expansion coefficients only for distinct eigenfunctions. So the idea of distinct eigenfunctions arises in pure mathematics as well as in physics.)

f) Normalize the solutions.

g) Determine the general formula for the eigenenergies in terms of the quantum number n.

SUGGESTED ANSWER:

a) Outside the well any wave function is zero in order to satisfy the Schrödinger equation. This is because if the potential goes to infinity over a finite region, the only reasonable way to satisfy the Schrödinger equation is with a zero wave function in that region.

b) For a finite potential, the wave function and its 1st derivative must be continuous: the 1st derivative is allowed to have kinks. If the potential becomes infinite at a point, then the first derivative is allowed to have finite discontinuity there and the wave function is allowed to have kink there. In our case, all the well walls require by themselves is that the wave function be continuous there and thus be zero there. It is known (but exactly how is seldom gone into) that in this case no condition is imposed on the continuity of the 1st derivative of the wave function and no condition is needed. I append a note discussing the continuity of the wave function and its 1st derivative below: it's prolix.

c) Inside the well one has

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

Defining

$$k = \frac{\sqrt{2mE}}{\hbar} \ ,$$

we obain

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

This last equation has the same form as the classical simple harmonic oscillator differential equation.

d) By inspection and lots of experience, the general solution for $E > 0$ is

$$\psi(x) = A\sin(kx) + B\cos(kx) \ ,$$

where A and B are constants. This solution, of course, only applies inside the well. Outside of the well $\psi = 0$ everywhere.

We cannot allow $E \leq 0$ as we show in the following. If we did allow $E \leq 0$, we would have the differential equation

$$\frac{\partial^2\psi}{\partial x^2} = \kappa^2\psi \ ,$$

where

$$\kappa = \frac{\sqrt{2m|E|}}{\hbar} \ .$$

Note by our definition, k would be imaginary in this case, but that has no consequence since the eigenvalues in our Hermitian operator equation for $E \leq 0$ are still real.

For $E < 0$, the general solution is

$$\psi = Ae^{\kappa x} + Be^{-\kappa x} \ ,$$

where A and B are constants. Neither of the terms of this solution are ever zero (unless $A = B = 0$) and since one term is strictly increasing and the other strictly decreasing, only one zero can be created by linear combination. The linear combination that gives the one zero at any x satisfies the ratio

$$\frac{A}{B} = -e^{-2\kappa x} \ .$$

Because there is only one zero at most, the $E < 0$ solution cannot satisfy the boundary conditions and must be ruled out. For $E = 0$, the general solution is

$$\psi = Ax + B \ ,$$

where A and B are constants. This solution can only be zero at one point (unless $A = B = 0$), and thus cannot satisfy the boundary conditions and must be ruled out. If $A = B = 0$ for

$E \leq 0$, the boundary conditions are satisfied, but the solutions cannot be normalized, and so must be ruled out. So all cases of $E \leq 0$ give physically invalid solutions.

Note there is a general proof that $E > V_{\text{min}}$, except that $E = V_{\text{min}}$ is allowed for a constant wave function solution to a system with periodic boundary conditions: see the solution to the problem suggested by Griffiths's problem Gr-24:2.2. For the infinite square well, the boundary conditions are not periodic and $V_{\text{min}} = 0$. Thus we find that solutions must have $E > 0$ by the general proof.

e) To satisfy the boundary conditions (ψ continuous, but no continuity constraint on $\partial\psi/\partial x$ because of the infinite potential), we must have $\psi(0) = \psi(ka) = 0$. Thus, $B = 0$ (i.e., no cosine solutions are allowed) and

$$k = \frac{n\pi}{a} ,$$

where n must be an integer. The fact that n must be an integer gives the quantization of allowed states: the boundary conditions have imposed this quantization, in fact. The number n is the dimensionless quantum number.

The $n = 0$ case gives a zero eigenfunction which cannot be normalized and the negative n values because of the oddness of the sine function do not give physically distinct solutions from their positive counterparts (i.e, the $-n$ values). Recall wave functions that differ by a global phase factor (i.e., $e^{i\phi}$ where ϕ is any real number) are not physically distinct: nature does not recognize them as different states. Because of the global phase factor freedom, there are actually infinitely many mathematical states for each physically distinct state. But physically distinct functions are mathematically distinct too as we stated in the question. The physically distinct functions collectively are a complete set for the Hilbert space of functions to which they belong. Any expansion in that complete set contains only the physically distinct functions—which are thus mathematically distinct too in an expansion sense.

Finally, we find that n runs over all positive integers only: $n = 1, 2, 3, \ldots$. The allowed solutions are

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right) .$$

A few other remarks can be made. We can see that k is, in fact, a wavenumber since the solution is periodic for every $\Delta x = 2\pi/k$. The wavelength λ is, in fact, that Δx:

$$\lambda = \frac{2\pi}{k} = \frac{2a}{n} .$$

Consequently, we find

$$n\frac{\lambda}{2} = a$$

which implies that the nth wave function will have n antinodes and $n + 1$ nodes. Two of the nodes are at the boundaries, of course.

f) For normalization, we require

$$\begin{aligned}
1 &= A^2 \int_0^a \sin^2(kx)\,dx = A^2 \frac{1}{k} \int_0^{ka} \sin^2(y)\,dy \\
&= A^2 \frac{1}{2k} \int_0^{ka} [1 - \cos(2y)]\,dy = A^2 \frac{1}{2k} \left[y - \frac{\sin(2y)}{2} \right] \Bigg|_0^{ka=n\pi} \\
&= A^2 \frac{1}{2k}(ka) = A^2 \frac{a}{2} ,
\end{aligned}$$

and thus

$$A = \sqrt{\frac{2}{a}} ,$$

where we have chosen A to be pure real. Thus the normalized general solution is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) .$$

g) The energy of the nth eigenstate is given by

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 n^2 \ ,$$

where n runs over all positive integers only: $n = 1, 2, 3, \ldots$. Thus the energies are quantized with n being the quantum number. The quantization is imposed by the boundary conditions and the requirement of normalizability. All bound energy-eigen states are, in fact, quantized. But we won't prove that here.

NOTE: Herein we consider the continuity properties of the wave function and its 1st derivative at some length. We will first only consider stationary states. We'll briefly consider non-stationary states afterward.

We recall that the wave function must be normalizable: i.e.,

$$\int_{-\infty}^{\infty} |\psi|^2 \, dx$$

must be non-infinite. This implies that the wave function (both real and imaginary parts) cannot be infinite over any finite range (i.e., over any region bigger than a point). If it were infinite over any finite range, then it would not be normalizable.

What about the wave function going to infinity at a point. Normalization doesn't rule that out completely. There are functions with infinities that integrate to a finite value: e.g., the derivative of $\pm\sqrt{\pm x}$ (with upper case for $x > 0$ and lower case for $x < 0$) has such infinity at $x = 0$). But let's rule those pathological cases that are unlikely to turn up physically or even in useful limiting cases. There is an exception, of course. We allow Dirac delta wave functions, but only as position eigenstates that a particle cannot actually be in.

Now what of infinite potentials and infinite eigenenergies? They probably do not exist in any real sense. But infinite potentials are useful limiting cases of very large real potentials, and so we will consider them below. There seems no reason to consider states with infinite eigenenergies even as limiting cases.

Now for the continuity conditions for non-infinite potentials. First note that the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi'' + V\psi = E\psi$$

can be rewritten as

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

We allow V to have discontinuities, but no infinities. Maybe some real potentials do have discontinuities in some sense, but in any case potentials with discontinuities are useful limiting cases of potentials with very steep regions. At first we cannot rule out discontinuities in ψ. From the rewritten Schrödinger equation, we see that ψ'' can have no infinities though it can have discontinuities at least from those we allow in the potential. This means that ψ' has no discontinuities since they would generate infinities in ψ''. So ψ' is continuous. But ψ' is allowed to have kinks.

Here we define kink to be a place where the function is continuous, but the derivative is not. So kinks in the ψ' mean discontinuities in ψ''. There must be genuine math term for "kink", but I can't locate it nohow. It's not "cusp" anyway.

Now any kinks in ψ would cause discontinuities in ψ'. So ψ can have no kinks.

I think there is no non-pathological way that ψ can have a kinkless discontinuity without leading to infinity in ψ''. So ψ has to be continuous. And I think there is no non-pathological way that ψ' can have continuous infinity without leading to an infinity in ψ''. So I think ψ' can have no infinities.

The upshot is that without pathological cases, ψ and ψ' should be continuous and non-infinite everywhere where the potential is non-infinite. And ψ'' can have discontinuities, but no infinities.

If one encounters pathological cases, one probably must deal with them on a case by case basis.

As aforementioned, as idealized limit we do invoke infinite potentials both over finite regions (as in the infinite square well case) and at points. What the continuity conditions in these cases?

First what happens to ψ if V goes to infinity over a finite range? Consider the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi'' + V\psi = E\psi \ .$$

Say V becomes infinite over the finite range. The only way for Schrödinger equation to be satisfied with ψ and ψ'' not allowed to be infinite over the finite range and E staying non-infinite is to make ψ (and therefore ψ'') zero over the range. Note that it would require a very pathological ψ to non-infinite over the range, but have ψ'' infinite over the range. In fact, we don't need to consider such pathological ψ's for any reason I think.

So we take it that if V is infinite over a finite range, ψ is zero in that range.

Inside a finite range of infinite V, ψ and ψ' must be zero and therefore are continouts. Outside of the range V is finite and we have our earlier result that ψ and ψ' are continuous. What about at the position where V goes from being finite to infinite? Let's call the position the potential wall. To analyze the continuity conditions are the potential wall let's say the wall is at $x = 0$ (without loss of generality) and start by saying that the potential for $x < 0$ is a finite V_- and the potential for $x > 0$ is a finite V. There is a discontinuity in potential at the potential wall and we will let V_- go to infinity and become our infinite potential. On both sides of the wall, there are small regions where the potential can be approximated as constant.

Let's find the general solution for time-independent Schrödinger equation for a small enough region that V can be approximated as constant in it. We can rewrite the time-independent Schrödinger equation to the form

$$\psi'' = \kappa^2\psi \ ,$$

where we define

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

Note that if $E > V$, then

$$\kappa = ik \ ,$$

where

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

Over the sufficiently small region where V can be approximated as a constant, the general solution of Schrödinger equation is

$$\psi = Ae^{\kappa x} + Be^{-\kappa x} \ ,$$

where A and B are set by the full solution for the system (including the boundary conditions) and the normalization condition. If $E = V$ exactly (which must be a so rare as to be negligible case usually),

$$\psi = A + Bx \ .$$

Now as long as V_- is finite, the wave function is non-zero for $x < 0$. From the above solution, *mutatis mutandis*, the solution for the small region just below $x = 0$ is

$$\psi_- = Ce^{\kappa_- x} + De^{-\kappa_- x} \ ,$$

where

$$\kappa_- = \sqrt{\frac{2m}{\hbar^2}(V_- - E)} \ .$$

For the small region just above $x = 0$, we have

$$\psi_+ = Ae^{\kappa x} + Be^{-\kappa x} \ .$$

We are assuming $E \neq V_-$ and $E \neq V$. The former is always OK since we will let V_- go to infinity. The latter is certainly almost always OK, but we will consider the case of $E = V$ exactly below.

Now as long as V_- is finite our original continuity conditions apply and we demand the potential wall conditions

$$C + D = A + B \qquad \text{and} \qquad \kappa_-(C - D) = \kappa(A + B) \ .$$

Note these potential wall conditions just give us two relations between the coefficients A, B, C, and D. We would have to incorporate information from the whole system (including boundary conditions) and impose normalization to determine the coefficients.

Now we let V_- go to infinity. By our earlier considerations, $\psi(x<0)$ must go to zero. This implies that C goes to zero. Our potential wall conditions are now

$$D = A + B \qquad \text{and} \qquad \lim_{V_-\to\infty} \kappa_-(-D) = \kappa(A+B) \ .$$

Now A, B and κ must be non-infinite and κ_- goes to infinity as V_- go to infinity. Therefore D actually has to go to zero as V_- go to infinity, but in such a way that $\kappa_-(-D)$ is finite and equal to $\psi'_+(0)$. So our potential wall conditions become

$$0 = A + B \qquad \text{and} \qquad \psi'_+(0) = \kappa(A-B) \ .$$

So we find that $B = -A$ and thus that

$$\psi_+ = A(e^{\kappa x} - e^{-\kappa x}) \ , \qquad \psi_+(0) = 0 \ , \qquad \psi'_+(0) = 2\kappa A \ .$$

So the wave function must be continuous as the boundary, but in general the 1st derivative is not.

Note for $V_- = \infty$, we only have a relationship relating A and B. To determine them we would have to incorporate information from the whole system (including boundary conditions) and impose normalization. The determination would also give us $\psi'_+(0)$, of course. It is certainly possible that $\psi'_+(0)$ could turn out to be zero making the 1st derivative zero at $x = 0$, but nothing demands it. In fact, we know from the infinite square well case that $\psi'_+(0)$ does not turn out to be zero in that case at the points where the potential becomes infinite. Actually, it seems that cases where $\psi'_+(0)$ is zero are probably pretty rare. The system would have to be rather fine-tuned to get $\psi'_+(0) = 0$.

There is a kind of conservation of information we note. For V_- non-infinite, we have two relations for wave function and its derivative at the potential wall, but no exact determination of either value. For V_- infinite, we have only one relationship for derivative at the potential wall, but know exactly what the wave function is at the boudnary: it is zero.

Now what of that pesky case of $E = V$ exactly. Well here

$$\psi_+ = A + Bx \ .$$

The potential wall conditions before sending V_- to infinity are

$$C + D = A \qquad \text{and} \qquad \kappa_-(C-D) = B \ .$$

When we send V_- to infinity, C and D go to zero again, D in such a way that $\kappa_-(-D)$ is finite and equal to $\psi'_+(0)$. So we get that $A = 0$, and thus

$$\psi_+ = Bx \ , \qquad \psi_+(0) = 0 \ , \qquad \psi'_+(0) = B \ .$$

So the wave function is continuous at the wall boundary and is zero there and the 1st derivative is not continuous and its value must be determined from the whole solution. The situation is essentially the same as for $E \neq V$ which is not surprising since the $E = V$ case is the limit for the $E < V$ and $E > V$ cases which are both the same as seen by the joint treatment above.

Now for the case that V is infinite at a point.

Well maybe in the 2020s, I'll get to that case. enough is enough right now.

Redaction: Jeffery, 2001jan01

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003 qfull 00400 2 3 0 moderate math: moments of infinite square well

Extra keywords: (Gr-29:2.4)

8. Calculate $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, $\langle p^2\rangle$, σ_x, and σ_p for the 1-dimensional infinite square well with range $[0,a]$. Recall the general solution is

$$\psi = \sqrt{\frac{2}{a}}\sin(kx) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \ ,$$

where $n = 1, 2, 3, \ldots$. Also check that the Heisenberg uncertainty principle is satisfied.

SUGGESTED ANSWER: Well

$$\begin{aligned}
\langle x^\ell \rangle &= \frac{2}{a} \int_0^a x^\ell \sin^2(kx)\, dx \\
&= \frac{a^\ell}{(n\pi)^{\ell+1}} \int_0^{n\pi} \theta^\ell \left[1 - \cos(2\theta)\right] d\theta \\
&= \frac{a^\ell}{(n\pi)^{\ell+1}} \left[\frac{(n\pi)^{\ell+1}}{\ell+1} - \int_0^{n\pi} \theta^\ell \cos(2\theta)\, d\theta \right] \\
&= a^\ell \left[\frac{1}{\ell+1} - \left(\frac{1}{2n\pi} \right)^{\ell+1} \int_0^{2n\pi} y^\ell \cos(y)\, dy \right] .
\end{aligned}$$

So much for generality. Now

$$\begin{aligned}
\langle x \rangle &= \frac{a}{2} - a \left(\frac{1}{2n\pi} \right)^{\ell+1} \left[\cos(y) + y \sin(y)\right] \Big|_0^{2n\pi} \\
&= \frac{a}{2}
\end{aligned}$$

and

$$\begin{aligned}
\langle x^2 \rangle &= \frac{a^2}{3} - \frac{a^2}{(2n\pi)^3} \left[y^2 \sin(y) + 2y \cos(y) - 2\sin(y) \right] \Big|_0^{2n\pi} \\
&= \frac{a^2}{3} - \frac{2a^2}{(2n\pi)^2} \\
&= a^2 \left[\frac{1}{3} - \frac{1}{2(n\pi)^2} \right] .
\end{aligned}$$

Thus

$$\sigma_x = \frac{a}{2} \sqrt{\frac{1}{3} - \frac{2}{(n\pi)^2}}$$

which for $n >> 1$ implies

$$\sigma_x \approx \frac{a}{3.5} .$$

For the momentum side of the coin,

$$\begin{aligned}
\langle p^\ell \rangle &= \frac{2}{a} \left(\frac{\hbar}{i} \right)^\ell \int_0^a \sin(kx) \left(\frac{\partial}{\partial x} \right)^\ell \sin(kx)\, dx \\
&= \frac{2}{a} \left(\frac{\hbar k}{i} \right)^\ell \frac{1}{k} \int_0^{n\pi} \sin(y) \left(\frac{\partial}{\partial y} \right)^\ell \sin(y)\, dy \\
&= \left[\frac{1 + (-1)^\ell}{2} \right] (-1)^{\ell/2} \left(\frac{1}{i} \right)^\ell \frac{2}{a} \left(\hbar k \right)^\ell \frac{1}{k} \int_0^{n\pi} \sin^2(y)\, dy \\
&= \left[\frac{1 + (-1)^\ell}{2} \right] \frac{2}{n\pi} \left(\frac{\hbar n\pi}{a} \right)^\ell \frac{n\pi}{2} \\
&= \left[\frac{1 + (-1)^\ell}{2} \right] \left(\frac{\hbar \pi}{a} \right)^\ell n^\ell .
\end{aligned}$$

Thus

$$\langle p \rangle = 0 , \qquad \langle p^2 \rangle = \left(\frac{\hbar\pi}{a} \right)^2 n^2 , \qquad \text{and} \qquad \sigma_p = \frac{\hbar\pi}{a} n .$$

In this case we find

$$\sigma_x \sigma_p = \frac{\hbar n\pi}{2} \sqrt{\frac{1}{3} - \frac{2}{(n\pi)^2}} = \frac{\hbar}{2} \sqrt{\frac{(n\pi)^2}{3} - 2} > \frac{\hbar}{2} ,$$

and so the position and momentum standard deviations do satisfy the Heisenberg uncertainty principle. In fact in this case the principle is always an inequality.

Redaction: Jeffery, 2001jan01

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003 qfull 00500 3 5 0 tough thinking: mixed states of infinite square well

Extra keywords: (Gr-29:2.6)

9. A particle is in a mixed state in a 1-dimensional infinite square well where the well spans $[0, a]$ and the solutions are in the standard form of Gr-26. At time zero the state is

$$\Psi(x, 0) = A\left[\psi_1(x) + \psi_2(x)\right] \ ,$$

where $\psi_1(x)$ and $\psi_2(x)$ are the time-independent 1st and 2nd stationary states of the infinite square well.

a) Determine the normalization constant A. Remember the stationary states are orthonormal. Also is the normalization a constant with time? Prove this from the general time evolution equation

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

b) Now write down $\Psi(x, t)$. Give the argument for why it is the solution. As a simplfication in the solution use

$$\omega_1 = \frac{E_1}{\hbar} = \frac{\hbar}{2m}\left(\frac{\pi}{a}\right)^2 \ ,$$

where E_1 is the ground state energy of the infinite square well.

c) Write out $|\Psi(x, t)|^2$ and simplify it so that it is clear that it is pure real. Make use Euler's formula: $e^{ix} = \cos x + i \sin x$. What's different about our mixed state from a stationary state?

d) Determine $\langle x\rangle$ for the mixed state. Note that the solution is oscillatory. What is the angular frequency $w_{\rm q}$ and amplitude of the oscillation. Why would you be wrong if your amplitude was greater than $a/2$.

e) Determine $\langle p\rangle$ for the mixed state. As Peter Lorre (playing Dr. Einstein—Herman Einstein, Heidelberg 1919) said in *Arsenic and Old Lace* "the quick way, Chonny."

f) Determine $\langle H\rangle$ for the mixed state. How does it compare to E_1 and E_2?

g) Say a classical particle had kinetic energy equal to the energy $\langle H\rangle$ found in the part (f) answer. The particle is bounces back and forth between the walls of the infinite square well. What would its angular frequency be in terms of $\omega_{\rm q}$ and the angular frequency found in the part (d) answer.

SUGGESTED ANSWER:

a) From orthonormality it follows at once that

$$1 = |A|^2(1 + 1) = 2|A|^2 \ ,$$

and thus that

$$|A| = \frac{1}{\sqrt{2}} \ .$$

Since the global or overall phase of a wave function is physically irrelevant, we can choose A to be real: thus

$$A = \frac{1}{\sqrt{2}} \ .$$

The normalization is a constant in time since probability is conserved in quantum mechanics. But since we have to prove this *de novo*, we just note that the norm operator is 1. Then from the general time evolution equation we find that

$$\frac{d\langle 1\rangle}{dt} = \left\langle \frac{\partial 1}{\partial t} \right\rangle + \frac{1}{\hbar}\langle i[H, 1]\rangle = 0$$

since 1 has no explicit time dependence and 1 commutes with H. Thus normalization or total probability is conserved.

b) Well the solution must be

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left[\psi_1(x)e^{-i\omega_1 t} + \psi_2(x)e^{-i(4\omega_1)t}\right] .$$

Why is this the right solution? Well it satisfies the initial condition at $t = 0$, the individual time-dependent stationary states satisfy the Schrödinger equation as we know, and the Schrödinger equation is linear so a linear combination of solutions satisfies Schrödinger equation. Thus the given solution satisfies the initial conditions and the Schrödinger equation: it must be the unique physical solution.

c) Behold:

$$\begin{aligned}
|\Psi(x,t)|^2 &= \frac{1}{2}\left[\psi_1^*\psi_1 + \psi_2^*\psi_2 + \psi_1^*\psi_2 e^{-i(3\omega_1)t} + \psi_1\psi_2^* e^{i(3\omega_1)t}\right] \\
&= \frac{1}{2}\left\{\psi_1\psi_1 + \psi_2\psi_2 + 2\psi_1\psi_2 \mathrm{Re}[e^{i(3\omega_1)t}]\right\} \\
&= \frac{1}{2}\left[\psi_1\psi_1 + \psi_2\psi_2 + 2\psi_1\psi_2\cos(3\omega_1 t)\right] ,
\end{aligned}$$

where we have made use of the fact that the infinite square well stationary states that we use are pure pure and the Euler's formula. The mixed state gives rise to a time varying probability density. Stationary states don't do that.

d) Behold:

$$\begin{aligned}
\langle x\rangle &= \int_0^a \Psi^* x\Psi\, dx \\
&= \frac{a}{2} + \frac{2}{a}\cos(3\omega_1 t)\int_0^a x\sin\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}x\right)\, dx \\
&= \frac{a}{2} + \frac{2a}{\pi^2}\cos(3\omega_1 t)\int_0^\pi y\sin(y)\sin(2y)\, dy \\
&= \frac{a}{2} + \frac{4a}{\pi^2}\cos(3\omega_1 t)\int_0^\pi y\sin^2(y)\cos(y)\, dy \\
&= \frac{a}{2} + \frac{4a}{3\pi^2}\cos(3\omega_1 t)\left[y\sin^3(y)|_0^\pi - \int_0^\pi \sin^3(y)\, dy\right] \\
&= \frac{a}{2} + \frac{4a}{3\pi^2}\cos(3\omega_1 t)\left[0 - \left(2 - \frac{2}{3}\right)\right] \\
&= \frac{a}{2} - \frac{16a}{9\pi^2}\cos(3\omega_1 t) \\
&= \frac{a}{2}\left[1 - \frac{32}{9\pi^2}\cos(3\omega_1 t)\right] ,
\end{aligned}$$

where we have used that the fact $\langle x\rangle_{\mathrm{stat}} = a/2$ as should have been proven earlier, transformations, trig identities, and table integrals as needed. We not that $\langle x\rangle$ oscillates about the $a/2$ (the midpoint of the infinite square well) with an angular frequency $\omega_{\mathrm{q}} = 3\omega_1$ and an amplitude

$$\frac{16a}{9\pi^2} \approx \frac{a}{5} .$$

The amplitude is certainly consistent with no part of the wave function extending beyond the boundaries of the infinite square well. The amplitude can't greater than $a/2$ since there is no non-zero part of the wave function beyond the boundaries which are both $a/2$ from the midpoint.

e) From earlier efforts we should know that

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

i.e., the first formula of Ehrenfest's theorem (e.g., CT-242). Thus in the present case

$$\langle p\rangle = \frac{16a\omega_1 m}{3\pi^2}\sin(3\omega_1 t) = \frac{8\hbar}{3a}\sin(3\omega_1 t)\ ,$$

where we note that $\hbar/a$ has units of momentum.

f) In general

$$\langle H\rangle = \int_{-\infty}^{\infty}\Psi^* H\Psi\,dx = \sum_k^{\infty}|c_k|^2 E_i\ ,$$

where we have assumed that Ψ has been expanded into orthonormal stationary states with expansion coefficients c_k and eigen-energies E_i. In the present case

$$\langle H\rangle = \frac{1}{2}E_1 + \frac{1}{2}E_2 = \frac{5}{2}E_1 = \frac{5}{2}\hbar\omega_1 = \frac{5}{2}\frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2\ .$$

We see that the mean energy of the system is $5/2$ times larger than E_1 the ground state energy and $5/8$ times the size of the first excited state energy $E_2 = 4E_1$. Thus the mean energy is a weighted average of E_1 and E_2. If you made ideal measurements of the system energy you would get only energies E_1 and E_2 each with a 50 % probability: i.e., $|c_1|^2 = |c_2|^2 = 1/2$.

g) The classical angular frequency would be

$$\omega_{\rm cl} = \frac{2\pi}{2a/v_{\rm cl}} = \frac{\pi}{a}v_{\rm cl}\ ,$$

where $v_{\rm cl}$ is the classical velocity. Thus

$$\omega_{\rm cl} = \frac{\pi}{a}v_{\rm cl} = \frac{\pi}{a}\sqrt{\frac{2\langle H\rangle}{m}} = \sqrt{\left(\frac{\pi}{a}\right)^2\frac{\hbar}{2m}\frac{4\langle H\rangle}{\hbar}} = \omega_1\sqrt{10} = 3\omega_1\frac{\sqrt{10}}{3} = \omega_{\rm q}\frac{\sqrt{10}}{3} \approx \omega_{\rm q} = 3\omega_1\ .$$

Thus the classical angular frequency is $\sqrt{10}$ times ω_1 and $\sqrt{10}/3 \approx 1$ times the angular frequency $\omega_{\rm q}$ of $\langle x\rangle$.

It is somewhat coincidental that the classical angular frequency is approximately the angular frequency of $\langle x\rangle$. No macroscopic object can actually be put into a single stationary state or a small number mixture of stationary states, except for Bose-Einstein condensates and related systems which are all low temperature systems. The energy of most macroscopic systems is so variable on the scale of the energy differences between stationary states that they may be vast mixed states with a constant fluctuation of the mixing. On the other hand, macroscopic classical states may be in some kind of perpetual "wave function collapse" situation when describe quantum mechanically. Either way the quantum mechanical description of macroscopic classical states is not exactly specifiable yet. Still the simple mixed state we've investigated here sloshes the probability distribution around: that's more like a classical state than a stationary state.

Redaction: Jeffery, 2001jan01

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004 qmult 00100 2 4 1 moderate deducto-memory: SHO eigen-energies

10. "Let's play *Jeopardy*! For \$100, the answer is: $\hbar\omega$.

a) What is the energy difference between adjacent simple harmonic ocsillator energy levels, Alex?
b) What is the energy difference between adjacent infinite square well energy levels, Alex?
c) What is the energy difference between most adjacent infinite square well energy levels, Alex?
d) What is the energy difference between the first two simple harmonic ocsillator energy levels **ONLY,** Alex?
e) What is the bar where physicists hang out in Las Vegas, Alex?

SUGGESTED ANSWER: (a)

Wrong answers:

e) One only wishes.

Redaction: Jeffery, 2001jan01

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004 qfull 00100 2 3 0 moderate math: SHO ground state analyzed

Extra keywords: (Gr-19:1.14)

11. The simple harmonic oscillator (SHO) ground state is

$$\Psi_0(x,t) = Ae^{-\beta^2 x^2/2 - iE_0 t/\hbar} ,$$

where

$$E_0 = \frac{\hbar\omega}{2} \qquad \text{and} \qquad \beta = \sqrt{\frac{m\omega}{\hbar}} .$$

a) Verify that the wave function satisfies the full Schrödinger equation for the SHO. Recall that the SHO potential is $V(x) = (1/2)m\omega^2 x^2$.

b) Determine the normalization constant A.

c) Calculate the expectation values of x, x^2, p, and p^2.

d) Calculate σ_x and σ_p, and show that they satisfy the Heisenberg uncertainty principle.

SUGGESTED ANSWER:

a) The full Schrödinger equation is

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

For our function the right-hand side is

$$H\Psi_0 = \left[-\frac{\hbar^2}{2m}\left(-\beta^2 + \beta^4 x^2\right) + \frac{1}{2}m\omega^2 x^2\right]\Psi_0 = \frac{1}{2}\hbar\omega\Psi_0 = E_0\Psi_0$$

and the left is

$$i\hbar\frac{\partial\Psi_0}{\partial t} = \frac{1}{2}\hbar\omega\Psi_0 = E_0\Psi_0 .$$

The two expressions are equal, and so our function is indeed a solution of the full Schrödinger equation.

b) The normalization constant follows from

$$1 = A^2\int_{-\infty}^{\infty} e^{-\beta^2 x^2}\,dx = A^2\frac{\sqrt{\pi}}{\beta} ,$$

where we have chosen A to be real. Thus

$$A = \frac{\sqrt{\beta}}{\pi^{1/4}} = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} .$$

c) The expectation values are

$$\langle x\rangle = 0$$

by symmetry (i.e., an odd function integrated over an even interval),

$$\langle x^2\rangle = \frac{\beta}{\sqrt{\pi}}\int_{-\infty}^{\infty} x^2 e^{-\beta^2 x^2}\,dx = \frac{\beta}{\sqrt{\pi}}\frac{\sqrt{\pi}}{2}\frac{1}{\beta^3} = \frac{1}{2\beta^2} = \frac{1}{2}\frac{\hbar}{m\omega}$$

using a Gaussian integral formula,

$$\langle p\rangle = 0$$

by symmetry (i.e., an odd function integrated over an even interval), and

$$\begin{aligned}
\langle p^2\rangle &= \int_{-\infty}^{\infty} \Psi_0^* p^2 \Psi_0\, dx \\
&= \frac{\hbar}{i}\Psi_0^* p\Psi_0\big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} p\Psi_0^* p\Psi_0\, dx \\
&= 0 + \hbar^2 \int_{-\infty}^{\infty} \left|\frac{\partial\Psi_0}{\partial x}\right|^2 dx \\
&= \hbar^2 A^2 \int_{-\infty}^{\infty} \beta^4 x^2 e^{-\beta^2 x^2}\, dx \\
&= \hbar^2 \frac{\beta}{\sqrt{\pi}}\beta \int_{-\infty}^{\infty} y^2 e^{-y^2}\, dy \\
&= \frac{1}{2}\hbar^2\beta^2 \\
&= \frac{1}{2}\hbar\omega m \ ,
\end{aligned}$$

where we have used integration by parts and transformation of variables as needed.

d) In this case

$$\sqrt{\langle x^2\rangle\langle p^2\rangle} = \sigma_x\sigma_p = \frac{\hbar}{2} \geq \frac{\hbar}{2} \ ,$$

and thus the Heisenberg uncertainty principle is satisfied. In fact, the equality holds which is only true for Gaussian wave functions (see Gr-111–112). The common examples of Gaussian wave functions are the SHO ground state and Gaussian free particle wave packet.

Redaction: Jeffery, 2001jan01

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004 qfull 00300 2 5 0 moderate thinking: mixed SHO stationary states

Extra keywords: (Gr-43:2.17)

12. A particle in a simple harmonic oscillator (SHO) potential has initial wave function

$$\Psi(x,0) = A\left[\psi_0 + \psi_1\right] \ ,$$

where A is the normalization constant and the ψ_i are the standard form 0th and 1st SHO eigenstates. Recall the potential is

$$V(x) = \frac{1}{2}m\omega^2 x^2 \ .$$

Note ω is just an angular frequency parameter of the potential and not **NECESSARILY** the frequency of anything in particular. In the classical oscillator case ω is the frequency of oscillation, of course.

a) Determine A assuming it is pure real as we are always free to do.

b) Write down $\Psi(x,t)$. There is no need to express the ψ_i explicitly. Why must this $\Psi(x,t)$ be the solution?

c) Determine $|\Psi(x,t)|^2$ in simplified form. There should be a sinusoidal function of time in your simplified form.

d) Determine $\langle x\rangle$. Note that $\langle x\rangle$ oscillates in time. What is its angular frequency and amplitude.

e) Determine $\langle p\rangle$ the quick way using the 1st formula of Ehrenfest's theorem. Check that the 2nd formula of Ehrenfest's theorem holds.

SUGGESTED ANSWER:

a) By inspection relying on orthonormality

$$A = \frac{1}{\sqrt{2}} \ .$$

b) By inspection

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\left[\psi_0 e^{-iE_0t/\hbar} + \psi_1 e^{-iE_1t/\hbar}\right] \ .$$

This expression satisfies the initial conditions and the Schrödinger equation and thus is the solution.

c) Behold:

$$\begin{aligned}
|\Psi(x,t)|^2 &= \frac{1}{2}\left[|\psi_0|^2 + |\psi_1|^2 + \psi_0^*\psi_1 e^{-i(E_1-E_0)t/\hbar} + \psi_0\psi_1^* e^{i(E_1-E_0)t/\hbar}\right] \\
&= \frac{1}{2}\left[\psi_0^2 + \psi_1^2 + 2\psi_0\psi_1\cos(\omega t)\right] \ ,
\end{aligned}$$

where we have used the fact that the standard eigen-solutions of the SHO are pure real and where ω is the angular frequency parameter from the definition of the SHO potential $(1/2)m\omega^2x^2$.

d) Behold:

$$\begin{aligned}
\langle x\rangle &= \int_{-\infty}^{\infty}\Psi^* x\Psi\,dx = \int_{-\infty}^{\infty} x|\Psi(x,t)|^2\,dx \\
&= \cos(\omega t)\frac{\beta^2}{\sqrt{\pi}}\sqrt{2}\int_{-\infty}^{\infty} x^2 e^{-\beta^2x^2}\,dx \\
&= \frac{1}{\sqrt{2}\beta}\cos(\omega t) \\
&= \sqrt{\frac{\hbar}{2m\omega}}\cos(\omega t) \ ,
\end{aligned}$$

where we have used the definitions and expressions on Gr-37 and Gr-41. Note that only the cross term contributes to $\langle x\rangle$: the other two terms both contribute zeros since they give odd functions in the integration for the expectation value. The angular frequency of oscillation is ω: this is exactly SHO potential angular frequency parameter. The amplitude is $[1/(\sqrt{2}\beta)] = \sqrt{\hbar/2m\omega}$.

e) Behold:

$$\langle p\rangle = m\frac{d\langle x\rangle}{dt} = -m\omega\sqrt{\frac{\hbar}{2m\omega}}\sin(\omega t) = -\sqrt{\frac{\hbar\omega m}{2}}\sin(\omega t) \ ,$$

where we have used the first Ehrenfest formula (e.g., CT-242). Now

$$\begin{aligned}
\frac{d\langle p\rangle}{dt} &= -\omega\sqrt{\frac{\hbar\omega m}{2}}\cos(\omega t) = -m\omega^2\langle x\rangle = -\langle m\omega^2 x\rangle \\
&= -\left\langle\frac{\partial(\frac{1}{2}m\omega^2x^2)}{\partial x}\right\rangle \\
&= -\left\langle\frac{\partial V_{\rm SHO}}{\partial x}\right\rangle
\end{aligned}$$

which confirms the 2nd Ehrenfest formula (e.g., CT-242)

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

We note the interesting fact that

$$m\frac{d^2\langle x\rangle}{dt^2} = \frac{d\langle p\rangle}{dt} = -\frac{\partial(\frac{1}{2}m\omega^2\langle x\rangle^2)}{\partial\langle x\rangle} \ ,$$

and so in a sense $\langle x\rangle$ obeys Newton's 2nd law. This is a curious result that also holds for constant potentials and potentials linear in x. I can't see that it has any great significance.

Redaction: Jeffery, 2001jan01

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004 qfull 01000 3 5 0 tough thinking: infinite square well/SHO hybrid
Extra keywords: (Mo-424:9.4)

13. Say you have the potential

$$V(x) = \begin{cases} \infty \ , & x < 0; \\ \dfrac{1}{2}m\omega^2 x^2 & x \geq 0. \end{cases}$$

a) By reflecting on the nature of the potential **AND** on the boundary conditions, identify the set of Schrödinger equation eigenfunctions satisfy this potential. Justify your answer. **HINTS:** Don't try solving the Schrödinger equation directly, just use an already known set of eigenfunctions to identify the new set. This shouldn't take long.

b) What is the expression for the eigen-energies of your eigenfunctions?

c) What factor must multiply the already-known (and already normalized) eigenfunctions you used to construct the new set you found in part (a) in order to normalize the new eigenfunctions? **HINT:** Use the evenness or oddness (i.e., definite parity) of the already-known set.

d) Show that your new eigenfunctions are orthogonal. **HINT:** Use orthogonality and the definite parity of the already-known set.

e) Show that your eigenfunctions form a complete set given that the already-known set was complete. **HINTS:** Remember completeness only requires that you can expand any suitably well-behaved function (which means I think it has to be piecewise continuous (Ar-435) and square-integrable (CT-99) satisfying the same boundary conditions as the set used in the expansion. You don't have to be able to expand any function. Also, use the completeness of the already-known set.

SUGGESTED ANSWER:

a) On the positive side the potential is just the simple harmonic oscillator (SHO) potential. Thus all SHO stationary states satisfy the Schrödinger equation there. On the negative side the eigenfunctions must be strictly zero to satisfy the Schrödinger equation. To match the boundary condition at $x = 0$ (i.e., the wave function must be zero there), it's clear that only the odd SHO stationary states are allowed solutions on the positive side. Recall the SHO stationary states are either even or odd: their parity is the same as that of the SHO quantum number n. Thus

$$\Psi_n(x) = \begin{cases} 0 \ , & x < 0; \\ \sqrt{2}\Psi_{n,\,\mathrm{SHO}}(x) & x \geq 0, \end{cases}$$

where n runs over all odd positive integers and the $\sqrt{2}$ is needed for normalization as we show explicitly in part (c).

b) The eigen-energies of the new set are given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \ ,$$

where again n runs over all positive odd integers.

c) Normalization can be found and orthogonality proven for the new set simultaneously and compactly. Behold:

$$\begin{aligned} \delta_{mn} &= \int_{-\infty}^{\infty} \Psi_{m,\,\mathrm{SHO}}(x)^* \Psi_{n,\,\mathrm{SHO}}(x)\,dx \\ &= 2\int_0^{\infty} \Psi_{m,\,\mathrm{SHO}}(x)^* \Psi_{n,\,\mathrm{SHO}}(x)\,dx \\ &= \int_0^{\infty} \Psi_m(x)^* \Psi_n(x)\,dx \ , \end{aligned}$$

where the first equality follows from the properties of SHO eigenfunctions, the second, from evenness of the integrand, and the third, from choosing the extra normalizing factor for our new set to be $\sqrt{2}$. With the extra normalizing factor it is clear our new set is orthonormal.

d) We answered part (d) in part (c).

e) Consider any function $f(x)$ defined on the interval $[0,\infty]$ that satisfies our boundary condition (i.e., $f(0) = 0$) and is square-integrable (implying $f(\infty) = 0$ among other things. We can extend this function to the interval $[-\infty, 0]$ by defining $f(-x) = -f(x)$ for $x \geq 0$ (i.e., $-x \leq 0$). The extended $f(x)$ is an odd function. The expansion of extended $f(x)$ in SHO eigenfunctions includes only odd SHO eigenfunctions since integrand for even expansion coefficients is odd and causes the even coefficients to be all zero. This expansion considered only for the interval $[0,\infty]$ is

$$
\begin{aligned}
f(x) &= \sum_{n,\ \mathrm{odd}} C_{n,\ \mathrm{SHO}} \Psi_{n,\ \mathrm{SHO}}(x) \\
&= \sum_{n,\ \mathrm{odd}} \frac{C_{n,\ \mathrm{SHO}}}{\sqrt{2}} \Psi_n(x) \\
&= \sum_{n,\ \mathrm{odd}} C_n \Psi_n(x) \ ,
\end{aligned}
$$

where we have defined $C_n = C_{n,\ \mathrm{SHO}}/\sqrt{2}$. It follows that the new set is complete since any function $f(x)$ satisfying the requirments of completeness can be expanded in terms of the new set.

That the C_n can be evaluated just as usual for a complete set should be clear in principle since the new set is orthonormal and normalized on the interval $[0,\infty]$. But to be explicit:

$$
\begin{aligned}
C_n &= \int_0^\infty \Psi_n(x)^* f(x)\, dx \\
&= \sqrt{2} \int_0^\infty \Psi_{n,\ \mathrm{SHO}}(x)^* f(x)\, dx \\
&= \frac{1}{\sqrt{2}} \int_{-\infty}^\infty \Psi_{n,\ \mathrm{SHO}}(x)^* f(x)\, dx \\
&= \frac{C_{n,\ \mathrm{SHO}}}{\sqrt{2}} \ ,
\end{aligned}
$$

where we have again used the extended $f(x)$ function.

Redaction: Jeffery, 2001jan01

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004 qfull 01100 3 5 0 tough thinking: Hermite polynomials 1

14. The generating function method is a powerful method for obtaining the eigenfunctions of Sturm-Liouville Hermitian operators and some of their general properties. One can possibly obtain with only moderately arduous labor some special values, the norm value, a general series formula for the eigenfunctions, and recurrence relations for iteratively constructing the complete set of eigenfunctions. The only problem is who the devil thought up the generating function?

In the case of Hermite polynomials, the generating function—which may or may not have been thought up by French mathematician Charles Hermite (1822–1901)—is

$$
g(x,t) = e^{-t^2+2tx} = \sum_{n=0}^{\infty} H_n \frac{t^n}{n!}
$$

(Ar-609ff; WA-644). The H_n are the Hermite polynomials: they are functions of x and n is their order.

Actually, the **HERMITE EQUATION** needs a weight function e^{-x^2} to be put in Sturm-Liouville self-adjoint form (Ar-426, WA-486). Alternatively, the Hermite polynomials times $e^{-x^2/2}$ satisfy a Sturm-Liouville Hermitian operator equation which happens to be the time-independent Schrödinger equation for the 1-dimensional quantum mechanical simple harmonic oscillator (Ar-612, WA-638). The

1-dimensional quantum mechanical simple harmonic oscillator is one of those few quantum mechanical systems with an analytic solution.

NOTE: The parts of this question are independent: i.e., you should be able to do any of the parts without having done the other parts.

a) Find the 1st recurrence relation
$$H_{n+1} = 2xH_n - 2nH_{n-1}$$
by differentiating both the generating function and its and series expansion with respect to t. This recurrence relation provides a means of finding any order of Hermite polynomial. **HINT:** You will need to re-index summations and make use of the uniqueness theorem of power series.

b) Find the 2nd recurrence relation
$$H'_n = 2nH_{n-1}$$
by differentiating both the generating function and its and series expansion with respect to x. **HINT:** You will need to re-index summations and make use of the uniqueness theorem of power series.

c) Use the 1st recurrence relation to work out and tabulate the polynomials up to 3rd order: i.e., find H_0, H_1, H_2, and H_3. You can find the first two polynomials (i.e., the 0th and 1st order polynomials) needed to start the recurrence process by a simple Taylor's series expansion of generating function.

d) Use the 1st recurrence relation to prove that the order of a Hermite polynomial agrees with its polynomial degree (which is the degree of its highest degree term) and that even order Hermite polynomials are even functions and the odd order ones are odd functions. The last result means that the Hermite polynomials have definite parity (i.e., are either even or odd functions). **HINT:** Use proof by induction and refer to collectively to the results to be proven as "the results to be proven". If you didn't get H_0 and H_1 explicitly in part (c), you can assume H_0 has degree 0 and H_1 has degree 1.

SUGGESTED ANSWER:

a) Well
$$\frac{\partial g}{\partial t} = (-2t + 2x)e^{-t^2+2tx} = (-2t + 2x)g(x,t)$$
and
$$\frac{\partial g}{\partial t} = \sum_{n=1}^{\infty} H_n \frac{t^{n-1}}{(n-1)!}$$
imply
$$\sum_{n=1}^{\infty} H_n \frac{t^{n-1}}{(n-1)!} = -2\sum_{n=0}^{\infty} H_n \frac{t^{n+1}}{n!} + 2x\sum_{n=0}^{\infty} H_n \frac{t^n}{n!} \ .$$
Re-indexing gives
$$\sum_{n=0}^{\infty} H_{n+1} \frac{t^n}{n!} = -2\sum_{n=1}^{\infty} H_{n-1} \frac{t^n}{(n-1)!} + 2x\sum_{n=0}^{\infty} H_n \frac{t^n}{n!}$$
or
$$\sum_{n=0}^{\infty} H_{n+1} \frac{t^n}{n!} = -2\sum_{n=0}^{\infty} H_{n-1} \frac{t^n}{(n-1)!} + 2x\sum_{n=0}^{\infty} H_n \frac{t^n}{n!}$$
provided we define $H_{-1} = 0$. We are free to make this definition since there is no constraint on what H_{-1} is from the generating function or anything else.

The uniqueness of power series implies
$$H_{n+1}\frac{1}{n!} = -2H_{n-1}\frac{1}{(n-1)!} + 2xH_n\frac{1}{n!}$$
or
$$H_{n+1} = 2xH_n - 2nH_{n-1} \ .$$
This last expression is the 1st recurrence relation.

Note that $n = 0$ is a special case since in this case the H_{n-1} term in the preantepenultimate equation is absent. We get a consistent treatment by defining $H_{-1} = 0$ as we have done. In the $n = 0$ case,

$$H_1 = 2xH_0 \ .$$

b) Now

$$\frac{\partial g}{\partial x} = 2te^{-t^2+2tx} = 2tg(x,t)$$

and

$$\frac{\partial g}{\partial x} = \sum_{n=0}^{\infty} H'_n \frac{t^n}{n!}$$

imply

$$\sum_{n=0}^{\infty} H'_n \frac{t^n}{n!} = 2\sum_{n=0}^{\infty} H_n \frac{t^{n+1}}{n!} = 2\sum_{n=1}^{\infty} H_{n-1} \frac{t^n}{(n-1)!}$$

from which, making use of the uniqueness of power series, one finds for $n \geq 1$

$$H'_n = 2nH_{n-1}$$

and for $n = 0$

$$H'_n = 0 \ .$$

In fact, the penultimate equation is valid for $n \geq 0$ as long as we take $0 \times H_{-1} = 0$. As noted in the part (a) answer, there is no constraint on H_{-1} and it can be anything we want. We want it to be 0. So demanding $0 \times H_{-1} = 0$ is consistent.

So the 2nd recurrence relation $n \geq 0$ is

$$H'_n = 2nH_{n-1} \ .$$

c) The generating function Taylor's series expanded in t is

$$g(x,t) = e^{-t^2+2tx} = 1 + (-t^2 + 2xt) + O(t^2) \approx 1 + 2xt \ ,$$

where $O(t^2)$ stands for terms of order 2 and higher and the last expression is good to 1st order in t. From the uniqueness of power series, the 0th and 1st order Hermite polynomials are, respectively, 1 and $2x$.

So the 2nd and 3rd order Hermite polynomials are, respectively,

$$H_2 = 2x(2x) - 2 \times 1 \times 1 = 4x^2 - 2$$

and

$$H_3 = 2x(4x^2 - 2) - 2 \times 2 \times 2x = 8x^3 - 12x \ .$$

Using an instructor's privilege, I just looked up the Hermite polynomials required and a few more and put them in the table below.

Table: Hermite Polynomials

Order	Polynomial
0	$H_0 = 1$
1	$H_1 = 2x$
2	$H_2 = 4x^2 - 2$
3	$H_3 = 8x^3 - 12x$
4	$H_4 = 16x^4 - 48x^2 + 12$
5	$H_5 = 32x^5 - 160x^3 + 120x$
6	$H_6 = 64x^6 - 480x^4 + 720x^2 - 120$

d) Given the 1st recurrence relation and H_0 and H_1, the results to be proven are proven by inspection—if one is non-paranoid—but if the universe is out to get you, you have to do the proof by induction.

i) By inspection of the part (c) answer, we know that H_0 and H_1 have, respectively, degree 0 and 1 which are also their respective order numbers. Also by inspection of the part (c) answer, we know that H_0 is even and its order is even and and H_1 is odd and its order is odd. Thus, H_0 and H_1 conform to the results to be proven.

ii) We assume all polynomials up to nth order conform to the results to be proven. The nth order could be the 1st order for example.

iii) From (ii) are know that H_{n-1} and H_n conform to the results to be proven. The H_{n-1} polynomial has degree $n-1$ (thus order and degree agree) and is even/odd if $n-1$ is even/odd. The H_n polynomial has degree n (thus order and degree agree) and is even/odd if n is even/odd. From these assumptions and the 1st recurrence relation

$$H_{n+1} = 2xH_n - 2nH_{n-1} ,$$

it follows that H_{n+1} is a degree $n+1$ polynomial (thus order and degree agree) and if $n+1$ is even/odd, H_{n+1} is even/odd.

One can be explicit. Say n is an even number, then $n-1$ and $n+1$ are odd numbers. In this case, H_n is an even function, $2xH_n$ is an odd function, and H_{n-1} is an odd function. Thus, H_{n+1} is an odd function too and its order and degree are equal. Say n is an aodd number, then $n-1$ and $n+1$ are even numbers. In this case, H_n is an odd function, $2xH_n$ is an even function, and H_{n-1} is an even function. Thus, H_{n+1} is an even function too and its order and degree are equal.

The proof is complete.

Redaction: Jeffery, 2001jan01

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005 qmult 00100 1 1 2 easy deducto-memory: definition free particle

15. A free particle is:

a) bound. b) unbound. c) both bound and unbound.
d) neither bound nor unbound. e) neither here nor there.

SUGGESTED ANSWER: (b)

Wrong Answers:

a) Just seems wrong terminologically speaking.
c) Not possible if the sets are exclusive.
d) Not possible if the union of the sets includes all cases.
e) Nonsense answer.

Redaction: Jeffery, 2001jan01

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005 qmult 00200 1 4 5 easy deducto-mem: free particle system

16. The free particle system is one with where the potential is:

a) the simple harmonic oscillator potential (SHO). b) a quasi-SHO potential.
c) an infinite square well potential. d) a finite square well potential.
e) zero (or a constant) everywhere.

SUGGESTED ANSWER: (e)

If the energy is greater than the potential at infinity, then a particle is unbound. In this case, the particle can travel to infinity. But the term free particle is reserved for the case of zero or constant potential. Free particles are necessarily unbound particles.

Wrong Answers:

c) There cannot be a free particle at all in system that consists only of an infinite well of any sort.

Redaction: Jeffery, 2001jan01

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005 qmult 00300 1 4 4 easy deducto-mem: free particle eigenfunction

17. The general expression for the free particle energy eigenfunction in 1-dimension is:

    a) e^{ikx}, where $k = \pm E$. b) e^{kx}, where $k = \pm E$. c) e^{kx}, where $k = \pm\sqrt{2mE/\hbar^2}$.
    d) e^{ikx}, where $k = \pm\sqrt{2mE/\hbar^2}$. e) e^{kx^2}, where $k = \pm\sqrt{2mE/\hbar^2}$.

    SUGGESTED ANSWER: (d)

    Wrong Answers:
    a) The wavenumber-energy relation is wrong.

    Redaction: Jeffery, 2001jan01

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005 qmult 00400 1 4 1 easy deducto-mem: free particle normalization 1

18. The free particle energy eigenfunctions are not physical states that a particle can actually be in because they:

    a) can't be normalized (i.e., they arn't square-integrable).
    b) can be normalized (i.e., they are square-integrable).
    c) are growing exponentials.
    d) don't exist.
    e) do exist.

    SUGGESTED ANSWER: (a)

    Wrong Answers:
    b) Exactly wrong.
    d) This would certainly preclude their representing physical states.
    e) They do exist as mathematical entities, but this doesn't in itself preclude their representing physical states.

    Redaction: Jeffery, 2001jan01

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005 qfull 00100 2 5 0 easy thinking: momentum representation
Extra keywords: (Gr-49:2.21)

19. The initial wave function of a free particle is

$$\Psi(x,0) = \begin{cases} A\ , & x \in [-a,a]; \\ 0\ , & \text{otherwise,} \end{cases}$$

where a and A are positive real numbers. The particle is in a completely zero potential environment since it is a free particle.

a) Determine A from normalization.

b) Determine $\psi(k) = \Psi(k,0)$ the time-zero wavenumber representation of the particle state. It is the Fourier transform of $\Psi(x,0)$. What is $\Psi(k,t)$? Sketch $\psi(k)$. Locate the global maximum and the zeros of $\psi(k)$. Give the expression for the zeros (i.e., for the location of the zeros).

c) Determine the wavenumber space probability density $|\Psi(k,t)|^2$ and show then that $\Psi(k,t)$ is normalized in wavenumber space. (You can use a table integral.) Sketch $|\Psi(k,t)|^2$ and locate the global maximum and the zeros. Give the expression for the zeros.

d) Crudely estimate and then calculate exactly σ_x, σ_k, and σ_p for time zero. Are the results consistent with the Heisenberg uncertainty principle?

SUGGESTED ANSWER:

a) The normalization integral is

$$1 = A^2 \int_{-a}^{a} dx = 2aA\ ,$$

and so

$$A = \frac{1}{\sqrt{2a}} \ .$$

b) We find

$$\begin{aligned}
\psi(k) &= \int_{-\infty}^{\infty} \Psi(x,0)\frac{e^{-ikx}}{\sqrt{2\pi}}\,dx \\
&= \int_{-a}^{a} \Psi(x,0)\frac{[\cos(kx) - i\sin(kx)]}{\sqrt{2\pi}}\,dx \\
&= \int_{-a}^{a} \Psi(x,0)\frac{\cos(kx)}{\sqrt{2\pi}}\,dx \\
&= \frac{2}{\sqrt{2\pi}}\int_{0}^{a} A\cos(kx)\,dx \\
&= \frac{1}{\sqrt{\pi a}}\frac{\sin(ka)}{k} \\
&= \sqrt{\frac{a}{\pi}}\frac{\sin(ka)}{ka} = \sqrt{\frac{a}{\pi}}\frac{\sin(z)}{z} \ ,
\end{aligned}$$

where we dropped the $\sin(kx)$ term after using Euler's formula since it makes no contribution because it gives an odd integrand and where we let $z = ka$ for niceness. The function with the z parameter can be called the reduced function.

Well the wave packet wave function is

$$\Psi(x,t) = \int_{-\infty}^{\infty} \psi(k)\frac{e^{ikx-\omega t}}{\sqrt{2\pi}}\,dk$$

since the intial condition of $\Psi(x,0)$ is satisfied and since the equation satisfies the Schrödinger equation because it is a linear combination of solutions. Recall

$$\omega = \frac{\hbar k^2}{2m} \ ,$$

and so is k dependent. Thus, we identify

$$\Psi(k,t) = \psi(k)e^{-i\omega t} \ .$$

The sketch you will have to imagine. The $\psi(k)$ function is an even function of k with global maximum of height $\sqrt{a/\pi}$ at the origin. Near the origin, one finds that the reduced function divided by the cofficient is

$$\frac{\sin(z)}{z} \approx 1 - \frac{z^2}{6}$$

by a 2nd order Taylor's series expansion. Except near the origin, the function is a sinusoid enveloped by $1/|z|$ factor. The zeros occur at $z = n\pi$ or $k = n\pi/a$ for all integer n, except $n = 0$.

Though it goes beyond the question, one can solve for the extrema of $\psi(k)$. The solution for the extrema follows setting

$$y = \frac{\sin(z)}{z}$$

and then setting

$$\frac{dy}{dz} = \frac{z\cos(z) - \sin(z)}{z^2} = 0 \ .$$

For small, z the derivative becomes

$$\frac{dy}{dz} \approx \frac{z(1 - z^2/2) - (z - z^3/6)}{z^2} = -\frac{z}{3} \ ,$$

Thus $z = 0$ is an extremum: obviously a maximum since

$$\lim_{z\to 0} \frac{\sin(z)}{z} = 1 \ .$$

The other extrema follow from the transcendental equation

$$z = \tan(z) \ :$$

accidentally so does the extremum at 0, but it had to be verified that that extremum existed by finding the small z form of the derivative.

The extrema occur for $|z| > \pi$ as we know from the shape of the tangent function. One only needs to find the $z > 0$ extrema since these times -1 give the $z < 0$ extrema since the y function is even. The extrema in k are obtained from $k = z/a$.

c) Well

$$|\Psi(k,t)|^2 = |\psi(k)|^2 = \frac{a}{\pi}\frac{\sin^2(ka)}{(ka)^2} = \frac{a}{\pi}\frac{\sin^2(z)}{(z)^2} \ ,$$

where we note that the time dependence has canceled out. Now

$$\int_{-\infty}^{\infty} |\Psi(k)|^2\,dk = \frac{a}{\pi}\int_{-\infty}^{\infty} \frac{\sin^2(ka)}{(ka)^2}\,dk = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\sin^2(z)}{z^2}\,dz = 1 \ ,$$

where we have used a table integral (e.g., MAT).

The sketch you will have to imagine. Except near the origin, the reduced function is a squared sinusoid enveloped by the $1/z^2$ factor. The zeros occur at $z = n\pi$ or $k = n\pi/a$ for all integer n, except $n = 0$. Because of the envelope factor $1/z^2 = 1/(kx)^2$, the probability of measuring a particular k is high only for $|k| \lesssim \pi/a$.

d) Given the shapes of $\Psi(x,0)$ and $\psi(k)$, we might estimate

$$\sigma_x \sim a \ , \qquad \sigma_k \sim \frac{\pi}{a} \ , \qquad \text{and} \qquad \sigma_p \sim \frac{\hbar\pi}{a} \ .$$

Are these results any good?

Well

$$\sigma_x^2 = \langle x^2\rangle = \int_{-\infty}^{\infty} \Psi(x,0)^* x^2 \Psi(x,0)\,dx = \int_{-a}^{a} \frac{x^2}{2a}\,dx = \frac{a^2}{3} \ ,$$

and so

$$\sigma_x = \frac{a}{\sqrt{3}} \approx \frac{a}{2} \ .$$

So our estimate was factor of 2 good. Now

$$\sigma_k^2 = \langle k^2\rangle = \frac{1}{\pi a}\int_{-\infty}^{\infty} \sin^2(ka)\,dk = \infty \ .$$

Well our estimate for σ_k is clearly very wrong. The standard deviation is infinite (or undefined) for $\Psi(k)$. Well there is nothing wrong with that: $\Psi(k)$ is still physically allowed since it is normalizable. Now $\sigma_p = \hbar\sigma_k$, and so σ_p is infinite too. Clearly

$$\sigma_x\sigma_p = \infty \geq \frac{\hbar}{2} \ ,$$

and so the uncertainty principle is satisfied.

But what was our original estimate of σ_k? Well it isn't σ_k even approximately, but it is still a characteristic width $\Delta k = \pi/a$ of $\Psi(k)$. We find, in fact, that

$$\sigma_x\Delta k = \frac{\pi}{\sqrt{3}} \approx \sqrt{3} \qquad \text{and} \qquad \sigma_x\Delta p = \sigma_x\hbar\Delta k \approx \hbar\sqrt{3} > \frac{\hbar}{2} \ .$$

Thus in this special case we find that even a characteristic width of the wavenumber representation wave function which is much smaller than σ_p is still large enough that $\sigma_x\Delta p > \hbar/2$.

The uncertainty principle is proven (e.g., Gr-108). The minimum-uncertainty wave packet is a Gaussian which gives $\sigma_x\sigma_p = \hbar/2$ (e.g., Gr-111).

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	$= 0.8617 \times 10^{-6}\,\text{eV}\,\text{K}^{-1}$ $= 1.381 \times 10^{-16}\,\text{erg}\,\text{K}^{-1}$
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	$= 14.40\,\text{eV}\,\text{Å}$
Fine Structure constant	$\alpha = \dfrac{e^2}{\hbar c}$	$= 1/137.036$
Kinetic energy coefficient	$\dfrac{\hbar^2}{2m_e}$	$= 3.81\,\text{eV}\,\text{Å}^2$
	$\dfrac{\hbar^2}{m_e}$	$= 7.62\,\text{eV}\,\text{Å}^2$
Planck's constant	h	$= 4.15 \times 10^{-15}\,\text{eV}$
Planck's h-bar	$\hbar$	$= 6.58 \times 10^{-16}\,\text{eV}$
	hc	$= 12398.42\,\text{eV}\,\text{Å}$
	$\hbar c$	$= 1973.27\,\text{eV}\,\text{Å}$
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

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

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

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

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7 Simple Harmonic Oscillator (SHO) Formulae

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

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

$$H_0(\beta x) = H_0(\xi) = 1 \qquad H_1(\beta x) = H_1(\xi) = 2\xi$$
$$H_2(\beta x) = H_2(\xi) = 4\xi^2 - 2 \qquad H_3(\beta x) = H_3(\xi) = 8\xi^3 - 12\xi$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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14 General Angular Momentum Formulae

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

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

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

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

$$[J_{fi}, J_{gj}] = \delta_{fg} i\hbar\varepsilon_{ijk}J_k \qquad \vec{J} = \vec{J}_1 + \vec{J}_2 \qquad J^2 = J_1^2 + J_2^2 + J_{1+}J_{2-} + J_{1-}J_{2+} + 2J_{1z}J_{2z}$$

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

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

---

15 Spin 1/2 Formulae

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

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

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

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

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

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

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

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

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

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

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

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

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

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16 Time-Independent Approximation Methods

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

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

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

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

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

17 Time-Dependent Perturbation Theory

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

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

18 Interaction of Radiation and Matter

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

19 Box Quantization

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

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

20 Identical Particles

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

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

21 Second Quantization

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

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

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

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

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

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

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

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

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

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

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

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

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

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

22 **Klein-Gordon Equation**

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

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

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

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

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