Quantum Mechanics NAME:

Homework 5: Multiple-Particle Systems, Identical Particles, and The Symmetrization Principle

1. A central force is one which always points radially inward or outward from a fixed point which is the center of the central force. The magnitude of central force depends only on:

   a) the angle of the particle.
   b) the vector $\vec{r}$ from the center to the particle.
   c) the radial distance r from the center to the particle.
   d) the magnetic quantum number of the particle.
   e) the uncertainty principle.

2. Say you have a differential equation of two independent variables x and y and you want to look for solutions that can be factorized thusly $f(x,y) = g(x)h(y)$. Say then it is possible to reorder equation into the form

   $$\mathrm{LHS}(x) = \mathrm{RHS}(y) ,$$

   where LHS stands for left-hand side and RHS for right-hand side. Well LHS is explicitly independent of y and implicitly independent of x:

   $$\frac{\partial \mathrm{LHS}}{\partial y} = 0 \qquad \text{and} \qquad \frac{\partial \mathrm{LHS}}{\partial x} = \frac{\partial \mathrm{RHS}}{\partial x} = 0 .$$

   Thus, LHS is equal to a constant C and necessarily RHS is equal to the same constant C which is called the constant of separation (e.g., Arf-383). The solutions for $g(x)$ and $h(y)$ can be found separately and are related to each other through C. The solutions for $f(x,y)$ that cannot be factorized are not obtained, of course, by the described procedured. However, if one obtains complete sets of $g(x)$ and $h(y)$ solutions for the x-y region of interest, then any solution $f(x,y)$ can be constructed at least to within some approximation (Arf-443). Thus, the generalization of the described procedure is very general and powerful. It is called:

   a) separation of the left- and right-hand sides. b) partitioning.
   c) separation of the variables. d) solution factorization. e) the King Lear method.

3. "Let's play *Jeopardy*! For \$100, the answer is: By writing the two-body Schrödinger equation in relative/center-of-mass coordinates."

   How do you ____________, Alex?

   a) reduce a **ONE-BODY** problem to a **TWO-BODY** problem
   b) reduce a **TWO-BODY** problem to a **ONE-BODY** problem
   c) solve a one-dimensional infinite square well problem
   d) solve for the simple harmonic oscillator eigenvalues
   e) reduce a **TWO-BODY** problem to a **TWO-BODY** problem

4. The formula for the reduced mass m for two-body system (with bodies labeled 1 and 2) is:

   a) $m = m_1 m_2$. b) $m = \dfrac{1}{m_1 m_2}$. c) $m = \dfrac{m_1 + m_2}{m_1 m_2}$. d) $m = \dfrac{m_1 m_2}{m_1 + m_2}$. e) $m = \dfrac{1}{m_1}$.

5. The eigensolutions of the angular part of the Hamiltonian for the central force problem are the:

   a) linear harmonics. b) spherical harmonics. c) square harmonics.
   d) Pythagorean harmonics. e) Galilean harmonics.

6. Just about the only spherical harmonic that people remember—and they really should remember it too—is Y_{00} =:

   a) $e^{im\phi}$. b) r^2. c) $\dfrac{1}{\sqrt{4\pi}}$. d) θ^2. e) $2a^{-3/2}e^{-r/a}$.

7. Conventionally, the spherical harmonic eigenstates for angular momentum quantum numbers

   $$\ell = 0, 1, 2, 3, 4, ...$$

are designated by:

a) a, b, c, d, e, etc.
b) s, p, d, f, and then alphabetically following f: i.e., g, h, etc.
c) x, y, z, xx, yy, zz, xxx, etc.
d) A, C, B, D, E, etc.
e) $@%&*!!

8. The 2-body time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E_{\text{total}}\psi \ .$$

If the V depends only on $\vec{r} = \vec{r}_2 - r_1$ (the relative vector), then the problem can be separated into two problems: a relative problem 1-body equivalent problem and a center-of-mass 1-body equivalent problem. The center of mass vector is

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M} \ ,$$

where $M = m_1 + m_2$.

a) Determine the expressions for $\vec{r}_1$ and $\vec{r}_2$ in terms of $\vec{R}$ and $\vec{r}$.

b) Determine the expressions for ∇_1^2 and ∇_2^2 in terms of ∇_{cm}^2 (the center-of-mass Laplacian operator) and ∇^2 (the relative Laplacian operator). Then re-express the kinetic operator

$$-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2$$

in terms of ∇_{cm}^2 and ∇^2. **HINTS:** The x, y, and z direction components of vectors can all be treated separately and identically since x components of $\vec{R}$ and $\vec{r}$) (i.e., X and x) depend only on x_1 and x_2, etc. You can introduce a reduced mass to make the transformed kinetic energy operator simpler.

c) Now separate the 2-body Schrödinger equation assuming $V = V(\vec{r}) + V_{\text{cm}}(\vec{R})$. What are the solutions of the center-of-mass problem if $V_{\text{cm}}(\vec{R}) = 0$? How would you interpret the solutions of the relative problem? **HINT:** I'm only looking for a short answer to the interpretation question.

9. In the central force problem, the separated azimuthal part of the Schrödinger equation is:

$$\frac{d^2\Phi}{d\phi^2} = \kappa^2\Phi \ ,$$

where κ^2 is the constant of separation for the azimuthal part. The constant has been parameterized in terms of κ^2 because clairvoyance tells this is the good way.

a) Since the differential equation is second order, there should should be two independent solutions for each value of κ^2: i.e., the eigenvalue problem has degeneracy of 2 for the eigenvalue. Solve for the general solution Φ for each κ^2: i.e., the solution that is a linear combination of the two independent solutions with undetermined coefficients. Note that writing the separation constant as κ^2 is so far just a parameterization and nothing yet demands that κ^2 be greater than zero: it could be zero or less than zero. **HINT:** Use an exponential trial function. But do not forget the special case of $\kappa^2 = 0$.

b) Quantum mechanics that wave functions and their derivatives be continuous, except that discontinuities in derivatives are allowed when a potential goes to infinity which is just unreachable ideal limit. For our system, we are not allowing any infinite potentials. Our solutions and all order of derivatives are, in fact, continuous.

The space for azimuthal part is, in fact, finite, but unbounded. The coordinate $\phi = 0$ runs from 0 to 2π, but when you move 2π you are back where you started. So in a sense there are no boundary conditions. But quantum mechanics also demands that wave functions be single-valued.

Since we have no interpretation for multi-valuedness, we micropostulate that it doesn't happen. The single-valuedness condition replaces the boundary conditions for the azimuthal part. Impose the single-valuedness condition on the general solution obtained in the part (a) answer and its derivative, and so that this leads to κ (not κ^2 note) must be an integer times the imaginary unit i. Remember to consider the special case where $\kappa^2 = 0$?

c) Writing im for κ where m is any integer, write down a general formula solution of the azimuthal part for a single m value. The solutions for m and $-|m|$ are the degenerate solutions for κ^2. By convention, no normalization constant is applied to the azimuthal part solutionsd: i.e., the coefficient of the special function that is the solution is left as just 1. The normalization is applied to the entire angular solutions which are the spherical harmonics. **HINT:** This is easy.

d) The orbital angular momentum z-component observable

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \ .$$

To be Hermitian this operator, the only allowed solutions must satisfy certain boundary conditions which for the interval $[0, 2\pi]$. The single-valuedness condition tells us these boundary conditions must be periodic boundary conditions. What are the eigen states for this observable that satisfy the periodic boundary conditions? Are the eigenvalues pure real as they should be? What is the relationship between these eigen states and thos of the azimuthal angle part we found in the part (c) answer?

e) Normalize the allowed eigensolutions of L_z Note these solutions are, in fact, conventionally left unnormalized: i.e., the coefficient of the special function that is the solution is left as just 1. Normalization is conventionally imposed on the total orbital angular momentum solutions, spherical harmonics.

10. "Let's play *Jeopardy*! For \$100, the answer is: It is the quantum mechanics **POSTULATE** that the state for identical fundamental particles must be symmetrized: i.e., must be symmetric or antisymmetric under the exchange of any two particles in the state expression. Bosons have symmetric state and fermions antisymmetric states. A second part of the postulate is that integer spin particles are bosons and half-integer spin particles are fermions. The postulate evolved in the 1920s from the work of Pauli, Fierz, Weisskopf, Heisenberg, Dirac, and others: there seems to be no one discoverer. An immediate corollary of the postulate is that composite particles with identical constituent elementary particles obey the postulates too even though the composite particles are not identical in their states because of excitations and perturbations. The composite particles are identical in their properties (though not their state), and so are called identical too. A composite particle is boson if it contains an even number of fermions and a fermion if it contains an odd number of fermions.

    Actually one needs to define exchange. A general definition is too much for here. For simplicity, we will only consider two particles whose state is given in the spatial representation: i.e., by a wave function. The formalism (justifed by it working) is to give each particle its own spatial coordinate and spin coordinate. Particle 1 has coordinate set $\vec{r}_1 m_1$ and particle 2 has coordinate set $\vec{r}_2 m_2$. The state of the system is the wave function

$$\psi(\vec{r}_1 m_1, \vec{r}_2 m_2) \ .$$

    In general, the function will have a different dependence on the two coordinate sets. If we exchange we get the new state

$$\psi_{\text{new}}(\vec{r}_1 m_1, \vec{r}_2 m_2) = \psi(\vec{r}_2 m_2, \vec{r}_1 m_1) \ .$$

    In quatnum mechancis jargon, the coordinate set exchange is called exchanging the particles. The new state is clearly in general a different mathematical state of the formal coordinate sets. The new state will be the same mathematically as the old state only if it is symmetric: i.e., only if

$$\psi(\vec{r}_2 m_2, \vec{r}_1 m_1) = \psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$$

    for all values of the coordinate sets.

    If the particles are physically distinct, we create in general a different state by particle exchange. This is because the new state will evolve differently in time in general because the distinct particles are affected by different potentials in general. Note that the two particles do have to have the same spin for the exchange to be mathematically and physically consistent. The only way the new state could be the same physical state as the original state is if

$$\psi(\vec{r}_2m_2,\vec{r}_1m_1) = e^{i\phi}\psi(\vec{r}_1m_1,\vec{r}_2m_2) \ ,$$

where ϕ is a constant phase factor. A constant phase factor does not change the physical state though, of course, it changes the mathematical state.

If the two particles are identical, then particle exchange creates clearly does not create a different physical state even though it creates a different mathematical state. But this causes a paradox which is called the exchange paradox. A linear combination state

$$\psi_{\text{com}}(\vec{r}_1m_1,\vec{r}_2m_2) = c_i\psi(\vec{r}_1m_1,\vec{r}_2m_2) + c_j\psi(\vec{r}_2m_2,\vec{r}_1m_1)$$

is mathematically and, a priori, physically distince from $\psi(\vec{r}_1m_1,\vec{r}_2m_2)$. The coefficients c_i and c_j are only constrained, a priori, by the requirement that $\psi_{\text{com}}(\vec{r}_1m_1,\vec{r}_2m_2)$ be normalized. In quantum mechanics, $\psi_{\text{com}}(\vec{r}_1m_1,\vec{r}_2m_2)$ describes the system in a superposition of states $\psi(\vec{r}_1m_1,\vec{r}_2m_2)$ and $\psi(\vec{r}_2m_2,\vec{r}_1m_1)$. But how can an infinite continuum of distinct states be created by the superposition of a state with itself. The paradox has no derivable solution. It is resolved by the postulate we are describing.

To see the resolution, say that state $\psi(\vec{r}_1m_1,\vec{r}_2m_2)$ has the general exchange property that

$$\psi(\vec{r}_2,\vec{r}_1) = e^{i\phi}\psi(\vec{r}_1,\vec{r}_2) \ .$$

Now the linear combination state

$$\psi_{\text{com}}(\vec{r}_1m_1,\vec{r}_2m_2) = c_i\psi(\vec{r}_1m_1,\vec{r}_2m_2)+c_j\psi(\vec{r}_2m_2,\vec{r}_1m_1) = c_i\psi(\vec{r}_1m_1,\vec{r}_2m_2)+c_je^{i\phi}\psi(\vec{r}_1m_1,\vec{r}_2m_2) = (c_i+c_je^{i\phi})\psi(\vec{r}_1m_1,\vec{r}_2$$

which is physically the same state as before: mathematically it differs by a constant phase factor. The general exchange property resolves the exchange paradox. But what sets the phase factor $e^{i\phi}$. Arguments we will not go into here suggest that only $e^{i\phi} = \pm 1$ are reasonable phase factor values. Observation tells us that $e^{i\phi} = 1$ holds for integer spin particles and $e^{i\phi} = -1$ holds for half-integer spin particles. This observation becomes part of the postulate we are describing. Actually, the spin-statistics theorem proves the spin rule, but that theorem itself depends on hypotheses which may not be true (CT-1387). Also actually quasiparticles called anyons that exist in two-dimensional systems have the general exchange property rather than just the $e^{i\phi} = \pm 1$ possibilities.

What is ____________, Alex?

a) Born's hypothesis b) Schrödinger's dilemma c) Dirac's paradox
d) Wigner's last stand e) the symmetrization principle or postulate

11. The permutation operator P for functions of two variables has the seemingly arbitrary, but well defined, property that

$$Pf(x_1,x_2) = f(x_2,x_1) \ ,$$

where $f(x_1,x_2)$ is a general complex function of two real number variables or, one could say, coordinates. Note that an operator is formally a mathematical entity that changes a function into another function or, in a more general context, changes a generalized vector into another generalized vector. Thus $Pf(x_1,x_2)$ is **NOT** $f(x_1,x_2)$ evaluated with exchanged argument values, but a new function of coordinates x_1 and x_2 that has values equal to $f(x_2,x_1)$. Of course, if one views x_1 and x_2 as just particular values and not coordinates, then one can view $Pf(x_1,x_2)$ just as $f(x_1,x_2)$ evaluated with exchanged argument values—but that's not the way we view things in this question.

a) Say x_1 and x_2 are orthogonal coordinates with the x_2 counterclockwise from the x_1. Describe $Pf(x_1,x_2)$ in comparison to $f(x_1,x_2)$. **HINT:** It might be helpful to consider specific points in the x_1-x_2 plane (a,b) and (b,a) which are obviously mirror reflection positions relative to each other about the $x_1 = x_2$ line.

b) Prove that P is a linear operator: i.e., that

$$P[f(x_1,x_2) + g(x_1,x_2)] = Pf(x_1,x_2) + Pg(x_1,x_2)] \ .$$

HINT: Define

$$h(x_1, x_2) = f(x_1, x_2) + g(x_1, x_2) \ .$$

c) What is

$$P\left[\frac{\partial f(x_1, x_2)}{\partial x_1}\right]$$

equal to. **HINT:** You might consider a specific example first, e.g., one with

$$f(x_1, x_2) = x_1^3 x_2 \ .$$

But for a general proof, recall the definition of the derivative

$$\frac{df(x)}{dx} = \lim_{h\to 0}\frac{f(x+h) - f(x)}{h} \ .$$

d) Show that the permutation operation and the complex conjugation operation commute: i.e., show that

$$[Pf(x_1, x_2)]^* = P\left[f(x_1, x_2)^*\right] \ .$$

HINT: Decompose $f(x_1, x_2)$ into real and imaginary parts.

e) Show from the definition of the Hermitian conjugate,

$$\langle\phi|Q|\psi\rangle = \langle\psi|Q^\dagger|\phi\rangle^*$$

(where Q is any operator), that P is a Hermitian operator: i.e., that $P = P^\dagger$. **HINT:** Recall that for two spatial dimensions

$$\langle\phi|Q|\psi\rangle = \int_1\int_2 \phi(x_1, x_2)^* Q\psi(x_1, x_2)\, dx_1\, dx_2 \ .$$

f) Solve for **ALL** the eigenvalues of P.

g) Show that any function $f(x_1, x_2)$ can be expanded in eigenfunctions of P, and thus the eigenfunctions of P form a complete set for the space of functions of two coordinates including wave function spaces of two coordinates. Show explicitly that the eigenfunctions of different eigenvalues are orthogonal. Since P is Hermitian and has a complete set of eigenfunctions for any wave function space of two arguments, it is formally a quantum mechanical observable.

h) Given that $A(x_1, x_2)$ is an operator, show that

$$PA(x_1, x_2)f(x_1, x_2) = A(x_2, x_1)Pf(x_1, x_2) \ ,$$

where $A(x_2, x_1)$ could be a function operator, a differentiating operator or both. Recall that operators act on everything to the right—except, of course, when they don't: but that situation is usually (but not always) made explicit with brackets. Do P and A commute in general? When do they commute?

i) Show that P and the Hamiltonian for identical particles,

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_1, x_2) \ ,$$

commute. Show that if $\psi(x_1, x_2)$ is an eigenstate of the Hamiltonian, then $P\psi(x_1, x_2)$ is an eigenstate. If $\psi(x_1, x_2)$ is non-degenerate in energy, is $P\psi(x_1, x_2)$ a physically distinct state? Show that there are only two possibilities for what $P\psi(x_1, x_2)$ is?

j) Given that P and H commute, show that P is a constant of the motion as far as Schrödinger equation evolution goes.

12. Consider the general normalized wave function for two particles

$$\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$$

where $\vec{r}$ is the spatial coordinate, m is the spin coordinate, and the labels 1 and 2 are formally assigned to particles 1 and 2.

a) First, let's assume that the two particles are physically distinct. This means that under some circumstances, but not all in general, they we behave differently. Say we now act on the state with the permutation operator $P_{2,1}$ and obtain

$$P_{2,1}\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) = \Psi(\vec{r}_2 m_2, \vec{r}_1 m_1) = \pm\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) ,$$

where we recall that the two-particle permutation operator is Hermitian and only has eigenvalues ± 1. Have we created a new physical state? Explain. Say we now act on the state with the permutation operator $P_{2,1}$

$$P_{2,1}\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) = \Psi(\vec{r}_2 m_2, \vec{r}_1 m_1) \neq \pm\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) .$$

Have we created a new physical state? Explain.

b) Now let's say that the two particles are identical and

$$P_{2,1}\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) = \Psi(\vec{r}_2 m_2, \vec{r}_1 m_1) \neq \pm\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) ,$$

where we recall that the two-particle permutation operator is Hermitian and only has eigenvalues ± 1. Have we created a physically distinct state? Explain. (For the moment, we are not assuming the symmetrization principle.)

c) Carrying over the assumptions of part (b), consider the mixed state

$$\Psi_{\text{mixed}} = c_i\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2) + c_j\Psi(\vec{r}_2 m_2, \vec{r}_1 m_1) ,$$

where the only constraint on coefficients c_i and c_j is the the normalization constraint coefficients c_i and c_j

$$|c_i|^1 + |c_j|^2 + \text{Re}[c_i c_j \langle\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)|\Psi(\vec{r}_2 m_2, \vec{r}_1 m_1)\rangle] = 1 .$$

Note we are not assuming $\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$ and $P_{21}\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$ are orthogonal.

Argue that Ψ_{mixed} is physically distinct from $\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$ and $P_{21}\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$?

Actually, there is a continuum infinity of possible Ψ_{mixed} which is only constrained by the normalization constraint. This infinity of states that can be constructed from $\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$ and $P_{21}\Psi(\vec{r}_1 m_1, \vec{r}_2 m_2)$ is called the exchange degeneracy (CT-1375).

Given the widely, but not universally, accepted quantum mechanical interpretation, that a linear combination of states constitutes a particle or a set of particles in a superposition of those states argue that the exchange degeneracy creates a paradox.

d) The paradox of part (c) is eliminated by invoking the symmetrization principle that states that the only physically allowed state for a set of identical particles is one that is symmetrized: i.e., is one that is symmetric (i.e., an eigenstate of the permutation operator with eigenvalue 1) or antisymmetric (i.e., an eigenstate of the permutation operator with eigenvalue -1) under the exchange of any pair of particles. Note identical particles of one type can have only one kind of symmetrized wave functions: i.e., they must either have only symmetric ones in all cases (in which case they are called bosons) or only antisymmetric ones in all cases (in which case they are called fermions). A separate postulate or if one prefers an extra part of the symmetrization principle is that integer-spin particles are bosons and half-integer-spin particles are fermions. Explain how the symmetrization principle eliminated the paradox.

e) The Hamiltonian for a set of identical particles is necessarily symmetric. What does this imply for the symmetrization state of the state as time passes?

f) Say that you had a set of non-identical particles that in a certain system had a symmetric Hamiltonian. Say the particles were put into a symmetrized state. Would the state stay symmetrized as time passes?

- g) The symmetrization principle can be taken as stated for fundamental particles only. But it applies as an immediate corollary to identical composite particles where whether particle is boson or fermion depends on whether it contains an even or odd number of fermions. Prove the corollary.
- h) The Pauli exclusion principle is actually a corollary of the symmetrization principle. One version is that the probability amplitude and therefore probability of density for two identical fundamental fermions at the spatial coordinate and spin coordinate is zero. Prove this.

13. Say $|ai\rangle$ and $|bi\rangle$ are **ORTHONORMAL** single-particle states, where i is a particle label. The label can be thought of as labeling the coordinates to be integrated or summed over in an inner product: see below. The symbolic combination of such states for two particles, one in a and one in b is

$$|12\rangle = |a1\rangle|b2\rangle \ ,$$

where 1 and 2 are particle labels. This combination is actually a tensor product, but let's not worry about that now. The inner product of such a combined state is written

$$\langle 12|12\rangle = \langle a1|a1\rangle\langle b2|b2\rangle \ .$$

If one expanded the inner product in the position and spinor representation assuming the wave function and spinor parts can be separated (which in general is not the case),

$$\langle 12|12\rangle = \left[\int \psi_a(x_1)^*\psi_a(x_1)\,dx_1\,(\,c_{a+}^* \quad c_{a-}^*\,)_1 \begin{pmatrix} c_{a+} \\ c_{a-} \end{pmatrix}_1\right] \\ \times \left[\int \psi_b(x_2)^*\psi_b(x_2)\,dx_2\,(\,c_{b+}^* \quad c_{b-}^*\,)_2 \begin{pmatrix} c_{b+} \\ c_{b-} \end{pmatrix}_2\right] \ .$$

A lot of conventions go into the last expression: don't worry too much about them.

- a) Let particles 1 and 2 be distinct particles. What are the two simplest and most obvious normalized 2-particle states that can be constructed from states a and b? What happens if $a = b$ (i.e., the two single-particle states are only one state actually)?
- b) Say particles 1 and 2 are identical bosons or identical fermions. What is the only normalized physical 2-particle state that can be constructed in either case allowing for the possibility that $a = b$ (i.e., the two single-particle states are only one state actually)? What happens if $a = b$ for fermions?

14. Say that we have obtained four distinct orthonormal single-particle eigenstates for identical spin 1/2 particles:

$$\psi_a(\vec r\,)\chi_+ \ , \qquad \psi_a(\vec r\,)\chi_- \ , \qquad \psi_b(\vec r\,)\chi_+ \ , \qquad \psi_b(\vec r\,)\chi_- \ ,$$

where the spinors are

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \ .$$

To label a state for a particular particle i, we can write for example

$$\psi_a(\vec r_i)\chi_{+,i} \ .$$

- a) How many distinct two-particle product states can be constructed for identical particles 1 and 2 that are consistent with the Pauli exclusion principle? There is no distinction between which factor state you give to which particle: i.e.,

$$\psi_a(\vec r_1)\chi_{+,1}\psi_a(\vec r_2)\chi_{-,1} \qquad \text{and} \qquad \psi_a(\vec r_2)\chi_{+,2}\psi_a(\vec r_1)\chi_{-,2}$$

are the same product state for identical particles. Write down the product states. Are the product states orthornormal? If the particles were distinct, how many distinct two-particle product states could be constructed? How many distinct linearly-independent symmetrized states can be constructed from the two-particle product states? **HINT:** The first part is a problem of choosing k objects from n objects with no replacement and no distinction on ordering of choices.

b) Are the linearly-independent symmetrized states created from orthonormal product states of single particles always orthonormal? Prove your answer. **HINT:** The proof takes a bit of thinking.

c) Using the Slater determinant formalism construct from the part (a) product states all the symmetrized states in which the only one kind of single-particle spatial state occurs. Remember to normalize the symmetrized states. What kind of states are these in spin description?

d) Using the Slater determinant formalism construct from the part (a) product states all the symmetrized states in which two distinct single-particle spatial states occur. Remember to normalize the symmetrized states. What kind of states are these in spin description?

e) Two of the states constructed in the part (d) answer are neither triplet nor singlet states. But you can construct by linear combination a triplet state and singlet state from these two. Do so. Then you have full triplet-singlet set of symmetrized states comprising the two unused states from the part (d) answer and the two newly constructed states.

f) Discuss when you would expect the four symmetrizied states of the part (d) answer to be stationary states and when the you would expect the triplet-singlet set of symmetrized states to the stationary states.

15. The set of individual eigen states for a 1-dimensional, infinite square well confined to $[0, a]$ can be written $|n\rangle$ where $n = 1, 2, 3, \ldots$ The energies of the states are given by

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

(e.g., Gr-26). For convenience $E_{\text{red}}(n) = n^2$ can be called the reduced energy of state n.

a) Say we have two non-interacting particles a and b in the well. Write write down the Hamiltonian for this case. The particles have the same mass m, but are not necessarily identical.

b) The reduced energy of a 2-particle state that satisfy the Schrödinger equation of part (a) can be written

$$E_{\text{red}}(n_1, n_2) = n_1^2 + n_2^2 \ .$$

Write a small computer code to exhaustively calculate the possible reduced energy levels up to and including $E_{\text{red}} = 50$ and the n_1 and n_2 combinations that yield these energies. The code should also calculate the degeneracy of each energy for the cases of non-identical particles, bosons, and fermions. I'll left you off easily, accidental degeneracies can be idendified by eye. (Note: An accidental degeneracy is when a distinct pair of n values (i.e., a pair not counting order) gives the same reduced energy.)

c) Write down the normalized vector expressions for all the 2-particle states up to the 4th allowed energy level for the cases of non-identical particles, identical bosons, and identical fermions. Just to get you started the non-identical particle ground state is

$$|a1, b1\rangle = |a1\rangle|b1\rangle \qquad \text{with} \qquad E_{\text{red}} = 2 \ .$$

16. Say we have orthonormal single-particle states $|a\rangle$ and $|b\rangle$. If we have distinct particles 1 and 2 in, respectively, $|a\rangle$ and $|b\rangle$, the net state is

$$|a1, b2\rangle = |a1\rangle|b2\rangle \ .$$

Of course, each of particles 1 and 2 could be in linear combinations of the two states if the states physically allowed the distinct particles to be in either one. In that case the linear combined state would be a four term state. But we have no interest in pursuing that digression at the moment.

Now two identical particles in states $|a\rangle$ and $|b\rangle$ have no choice, but to be in a symmetrized state by the symmetry postulate:

$$|1, 2\rangle = \frac{1}{\sqrt{2(1 + \delta_{ab})}}\left(|a1, b2\rangle \pm |a2, b1\rangle\right) \ ,$$

where the upper case is for identical bosons and the lower case for identical fermions. If the two states are actually the same state $|a\rangle$, then the state for bosons reduces to

$$|1,2\rangle = |a1,a2\rangle$$

and for fermions the state reduces to the null state $|0\rangle$ which is not a physical state, and thus the Pauli exclusion principle is incorporated in the state expression.

Note products of kets are actually tensor products (CT-154). In taking scalar products, the bras with index i (e.g., 1 or 2 above) act on the kets of index i. For example, for the state $|1a,2b\rangle = |a1\rangle|a2\rangle$ the norm squared is

$$\langle a1,b2|a1,b2\rangle = \langle a1|a1\rangle\langle a2|a2\rangle \ .$$

The fact that identical particles must be in symmetrized states means that their wave functions will be more or less clumped depending on whether they are bosons or fermions than if they could be fitted into simple product states like distinct particles. We are not bothering with the complication of spin for this problem. We will assume that all the particles are in the same spin state: e.g., they are all in the spin up state.

The clumping/declumping effect is called the **EXCHANGE FORCE**. Obviously, it is not really a force, but rather a result of the symmetrization principle requirements on physical states for identical particles. Still for some practical purposes one can certainly consider it as force. In this problem, we investigate the effect of the **EXCHANGE FORCE**.

a) Expand $\langle\Delta x^2\rangle = \langle(x_1-x_2)^2\rangle$ into three terms that can be evaluated individually.

b) For the given two-particle state for **DISTINCT PARTICLES** $|a1,b2\rangle = |a1\rangle|b2\rangle$, formally show that

$$\langle\Delta x^2\rangle = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b \ ,$$

where the particle labels can be dropped from the single-particle state expectation values, but these values must be identified by the single-particle state that they are for: i.e., for states $|a\rangle$ and $|b\rangle$. What happens in the case that $|a\rangle = |b\rangle$? **HINT:** Remember that variance is defined by

$$\sigma^2 = \langle x^2\rangle - \langle x\rangle^2 \ .$$

c) There is an identity that is needed for part (d) and is useful in many other contexts. Say $|\alpha\rangle$ and $|\beta\rangle$ are general states (e.g., they could be one-particle or two-particle states). Say that

$$|\Psi\rangle = c_\alpha|\alpha\rangle + c_\beta|\beta\rangle$$

and we have general observable Q. We have the identity

$$\langle\Psi|\Psi\rangle = |c_\alpha|^2\langle\alpha|\alpha\rangle + |c_\beta|^2\langle\beta|\beta\rangle + 2\mathrm{Re}(c_\alpha^* c_\beta\langle\alpha|Q|\beta\rangle) \ .$$

Prove the identity.

d) For the given two-particle state for **IDENTICAL PARTICLES**

$$|1,2\rangle = \frac{1}{\sqrt{2(1+\delta_{ab})}}\left(|a1,b2\rangle \pm |a2,b1\rangle\right) \ ,$$

determine $\langle\Delta x^2\rangle$ for identical bosons and fermions. What happens in the case that $|a\rangle = |b\rangle$? **HINT:** Recall that

$$\langle a|b\rangle = \delta_{ab} \ ,$$

since the states are orthonormal.

17. Imagine two non-interacting particles in an infinite square in the range $[0,a]$. Recall the eigen-functions for this case are

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

for $n = 1,2,3,\ldots$. Recall also the results of the Gr-182 and Gr-29:2.5 questions.

a) Say the particles are distinguishable and are in states n and m. What is $\langle \Delta x^2 \rangle = \langle (x_1 - x_2)^2 \rangle$ for this case? What is it if $n = m$?

b) Say the particles are identical bosons/fermions and are in the only allowed combination of states n and m. What is $\langle \Delta x^2 \rangle = \langle (x_1 - x_2)^2 \rangle$ for this case? What is it if $n = m$?

18. There are two particles subject to separate simple harmonic oscillator (SHO) potentials. They are also coupled by a SHO interaction. The full Hamiltonian is:

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{1}{2}m_1\omega^2 x_1^2 + \frac{1}{2}m_2\omega^2 x_2^2 + \frac{1}{2}k(x_1 - x_2)^2 \ ,$$

where $k > 0$ which in this context means the interaction is attractive. The problem is 1-dimensional: it is in the x dimension only.

a) Write down the formulae for the center-of-mass (CM) and relative (REL) coordinate and their inverses (i.e., CM coordinate X and relative x expressed in terms of x_1 and x_2).

b) Transform the Hamiltonian to the center-of-mass-relative (CM-REL) coordinates (showing all the steps).

c) Now show that the time-independent Schrödinger equation for the Hamiltonian separates into CM and REL time-independent Schrödinger equations. Define

$$\tilde{\omega} = \sqrt{\omega^2 + \frac{k}{\mu}} = \omega\sqrt{1 + \frac{k}{\mu\omega^2}}$$

in order to simplify the REL equation. Does the overall time-independent Schrödinger equation have an exact solution?

d) Write down the general expression for the eigen-energies of the total stationary states in terms of the SHO quantum numbers $n_{\rm CM}$ and $n_{\rm REL}$ for the respective CM and REL parts.

e) Next write the expression for the eigen-energies in the case that $k = 0$. Define a new quantum number n that alone gives the eigen-energy and the degeneracy of the eigen-energy. What is the degeneracy of an eigen-energy of quantum number n?

f) Now assume that $k > 0$, but that $k/(\mu\omega^2) << 1$. Write down a first order correct expression for the energy in terms of n and $n_{\rm REL}$. Give a schematic energy-level diagram.

g) Now assume that $k/(\mu\omega^2) >> 1$. Give a schematic energy-level diagram in this case.

h) Now assume that the two particles are identical spin-0 bosons. Note that identical means they now have the same mass. Given the symmetry requirement for boson states, which solutions (specified by the $n_{\rm CM}$ and $n_{\rm REL}$ quantum numbers) are not physically allowed?

i) Now assume that the two particles are identical spin-1/2 fermions. Note again that identical means they now have the same mass. But also note they arn't electrons. Their interactions are determined by the given Hamiltonian only. Because the particles are spin-1/2 fermions, the stationary state wave functions for system must be multiplied by appropriate eigen-spinors to specify the full stationary state. Given the antisymmetry requirement for fermion states, what restrictions are put on the wave function and spinor quantum numbers of an eigenstate?

19. Say that you solve a Schrödinger equation for N identical particles to get the normalized wave function $\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N)$. How would you symmetrize the wave function for bosons? Then how would you symmetrize for fermions all in the spin-up state so that you don't have spinors to complicate the question? How would you normalize the wave function?

20. Say you put two electrons into the $n = 2$ principle quantum number shell of a neutral helium atom and immediately one electron is ejected and the other decays to the ground of the He$^+$ ion. What approximately is the kinetic energy of the ejected electron. **NOTE:** Without a detailed specification of the doubly-excited helium atom we cannot know exactly what the energies of the excited electrons are. There are two simple approximate choices for their energies: 1) assume that the energy levels of the singly-excited helium atom apply (see, e.g., Gr-189); 2) assume that the $Z = 2$ hydrogenic energy

levels apply. The first choice is probably most in error because it assumes too much electron-electron interaction: the electrons may further apart in the actual doubly-excited state; but, in fact, where they are depends on exactly what doubly excited state they are in. The 2nd choice is certainly wrong by assuming zero electron-electron interaction.

21. Describe qualitatively how the helium atom energy level diagram would plausibly change under the following conditions.

    a) Say the electrons were spin zero bosons.

    b) Say the electrons were spin 1/2 bosons—a contradiction in postulates, but for the sake of argument have it so.

    c) Say the electrons were spin 1/2 fermions, but were quantum mechanically distinguishable particles. **HINT:** In this case the answer is going to be pretty much indefinite.

22. In statistical mechanics, the symmetrization requirement on identical bosons enters in the way that probabilities are assigned to the global states they can form. We will investigate how symmetrization manifests itself in this case.

    a) Say you had g single-particle states and n distinct particles. How many distinct global states can you form? What is the probability of each global state assuming that each has equal probability?

    b) Now a trickier case. Say you had g single-particle states and n identical particles. The probability p_i that a particle goes into single-particle state i is **INDEPENDENT** of what the other particles do: note $\sum_{i=1}^{g} p_i = 1$, of course. You can construct all possible global states by inserting one particle at a time into the system—can you imagine a global state that cannot be so constructed? Say you do insert the n particles one at a time to the system. The probability of an n-particle global state formed by the insertion sequence $ijk\ldots\ell$ is $p_i p_j p_k \ldots p_\ell$ which has n factors, of course. But because the particles are identical, each (distinct) global state can be constructed in general by multiple insertion sequences. How many distinct insertion sequences for n particles correspond to a single global state with occupation number set $\{n_i\}$? If all the p_i are equal, what is the probability of a global state with occupation number set $\{n_i\}$ formed by random insertion of particles?

       The sum of the probabilities for all insertion sequences is 1. Why must this be so on general grounds? Now prove more explicitly that the sum of all inserttion sequence probabilities is 1. **HINT:** Consider

       $$1 = \left(\sum_{i=1}^{g} p_i \right)^n$$

       and a proof by induction.

    c) Now in the part (b) answer, we didn't find out how many distinct global states there were. To find this out you need a different counting procedure. Let's consider finding all possible global states given the following conditions. Imagine that all n particles were distinct and that the order in which you choose the single-particle states to slot them into also matters. To start with you must select a state: you can't put a particle in a non-state. Then proceed selecting a particle for the current state or a new state until you are out of particles and states. Now did the order of the states matter or the order of the choice of particles?

    d) Now for classical, non-interacting particles randomly slotted into single-particle states, the probability of each global state is as determined in part (b). Quantum mechanical non-interacting bosons do not act like classical particles. Because of the symmetrization principle—in a way the instructor has never found out—each distinct global state has equal probability. What is this probability for n bosons in g single-particle states? Say that we have all n bosons in one single-particle state. What is the classical probability of this global state? Which is larger the classical probability or the boson probability? What does the last result suggest about the random distributions of bosons relative to classical random distributions?

    e) Consider two identical coins—say quarters. How many distinct global physical states can be made given that the single-coin states are head and tail? Now toss them up together in a completely randomizing way 36 times. Count the number of distinct global states of each kind that you get? Do the probabilities of each distinct global state appear to be classically random or boson random?

23. An atom is a stable bound system of electrons and:

    a) a single nucleus. b) two nuclei. c) three nuclei. d) a single quark. e) two quarks.

24. "Let's play *Jeopardy*! For $100, the answer is: A favored approximation in the simpler solutions for the electronic structure of atoms in quantum mechanics."

    What is the ____________, Alex?

    a) central potential approximation b) non-central potential approximation
    c) grand central approximation d) atom-approximated-as-molecule method
    e) electrons-as-bosons approximation

25. Write down the ground state electronic configurations of the atoms from hydrogen to calcium.

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

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

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

---

6 Time Evolution Formulae

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

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

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

---

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

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \qquad Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2}\cos(\theta) \qquad Y_{1,\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin(\theta)e^{\pm i\phi}$$

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

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

---

13 Hydrogenic Atom

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

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

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

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

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

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

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

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

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

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

---

14 General Angular Momentum Formulae

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

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

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

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

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

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

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

---

15 Spin 1/2 Formulae

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

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

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

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

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

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

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

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

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

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

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

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

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

16 Time-Independent Approximation Methods

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

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

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

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

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

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

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

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

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

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

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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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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22 Klein-Gordon Equation

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

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

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

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

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