Quantum Physics I

Identical Particles and Multielectron Atoms

Sources:

Townsend Ch 7

French and Taylor Ch 13; Eisberg and Resnick 9

Motivation and background

- Wavefunctions of multiple particles must account for the fact that identical particles are indistinguishable.
- Pauli Exclusion Principle: No two electrons in the same system can be in the same state.
- These effects lead to profound changes in the physical world.
- How does particle symmetry requirement affect properties of atoms?

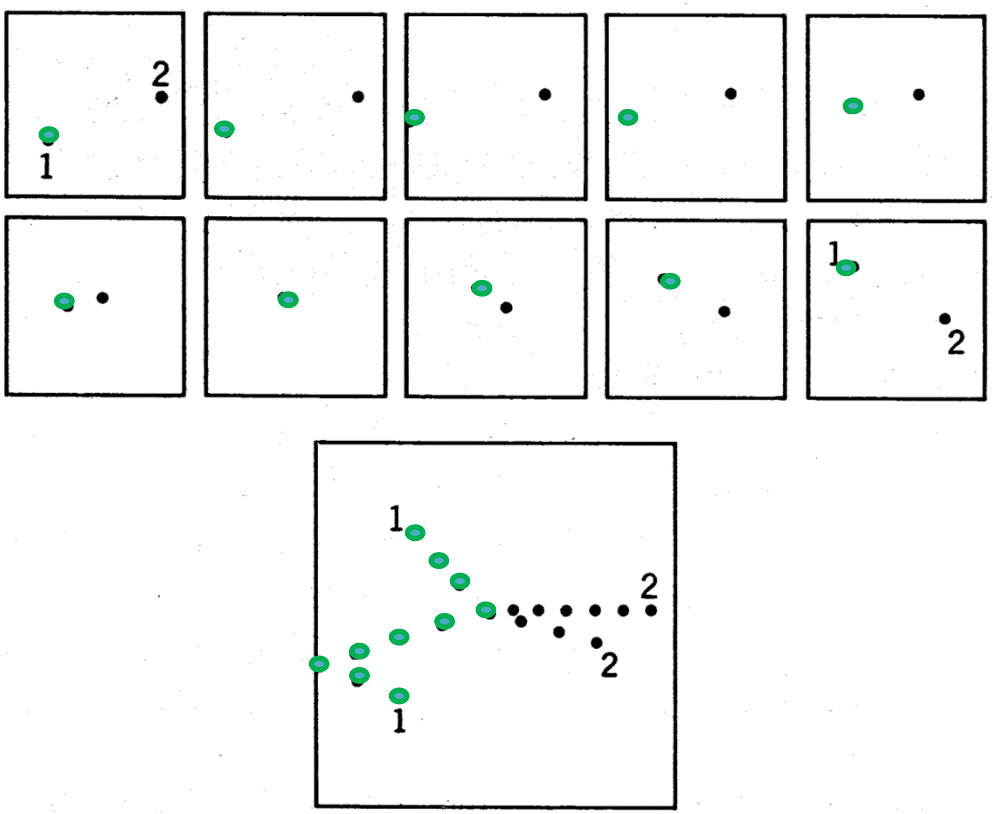
AND

- It is not possible to calculate the properties of multiparticle systems in closed form, but we can understand trends and overall behavior using symmetry and approximation arguments.
- Computational approaches such as Hartree-Fock and Density Functional Theory can produce useful quantitative results.

The Plan

- Wavefunction and energies for two noninteracting particles in a system.
- Two noninteracting identical particles.
- The helium atom – interacting identical particles.
- Approaches to solving multielectron atoms.
- Systematics of multielectron atoms – the periodic table.
  - Ionization energies;
  - X-ray emission lines;
  - Chemistry

When two non-identical particles collide you can tell which is which before and after the collision – a "movie"



We can write a wavefunction that describes both of the particles as a product of individual wavefunctions.

$$\Psi_{12} = \Psi_1(x_1)\Psi_2(x_2)$$

Two non-interacting non-identical particles

Two nonidentical particles: m_1, m_2 in positions x_1, x_2 respectively experiencing potentials $V_1(x_1), V_2(x_2)$. (Although environment is the same, the potentials may be different. e.g. − different charges)

$$\frac{p_1^2}{2m_1} + V_1(x_1) + \frac{p_2^2}{2m_2} + V_2(x_2) = E$$

$$-\frac{\hbar^2}{2m_1}\frac{\partial^2\Psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2\Psi}{\partial x_2^2} + V_1(x_1)\Psi + V_2(x_2)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Since the variables are independent, we guess a product solution:
$\Psi = \psi_A(x_1)\psi_B(x_2)f(t)$ and substituting:

$$\frac{1}{\psi_A}\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2\psi_A}{\partial x_1^2} + V_1(x_1)\psi_A\right] + \frac{1}{\psi_B}\left[-\frac{\hbar^2}{2m_2}\frac{\partial^2\psi_B}{\partial x_2^2} + V_2(x_2)\psi_B\right] = -i\hbar\frac{\partial f}{\partial t}$$

which can only be true if both sides equal a constant: $We\ choose\ E$
Separating variables again:

$$\frac{1}{\psi_A}\left[-\frac{\hbar^2}{2m_1}\frac{\partial^2\psi_A}{\partial x_1^2} + V_1(x_1)\psi_A\right] = -\frac{1}{\psi_B}\left[-\frac{\hbar^2}{2m_2}\frac{\partial^2\psi_B}{\partial x_2^2} + V_2(x_2)\psi_B\right] + E = E_A$$

$$-E_B + E = E_A \quad \Rightarrow \quad (E_A + E_B)f = i\hbar\frac{\partial f}{\partial t} \;\; so \;\; f(t) = e^{-i(E_A+E_B)t/\hbar}$$

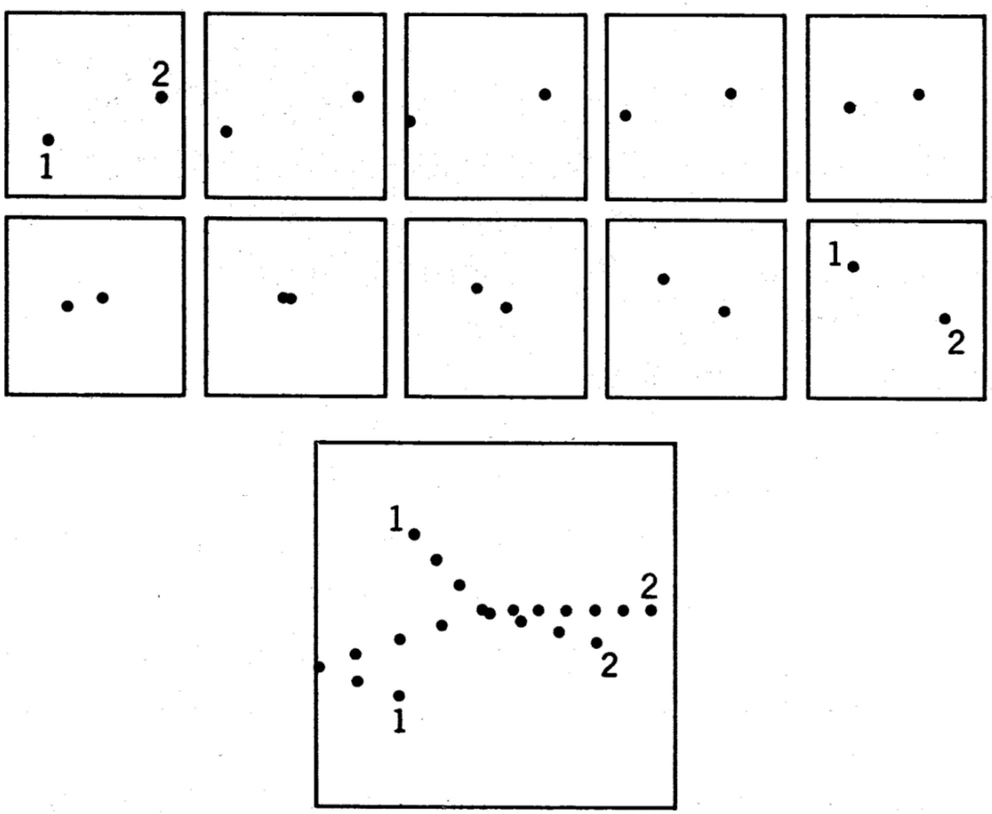
Two noninteracting non-identical particles (2)

$$\Psi = \psi_A(x_1)\psi_B(x_2)e^{-i(E_A+E_B)t/\hbar}$$

The solution is the product of two independent space functions, but whose time dependence is given by the total energy of the two particles.

The probability dP of finding particle 1 in a region dx_1 and particle 2 in region dx_2 is
dP=$|\Psi|^2 dx_1 dx_2 = |\psi_A|^2 dx_1 |\psi_B|^2 dx_2$ (as expected for independent particles)

BUT
When two identical particles collide you can't tell which is which after the collision



The probability density should be identical under exchange of the two particles:

$\psi_A(x_1)\psi_B(x_2)$

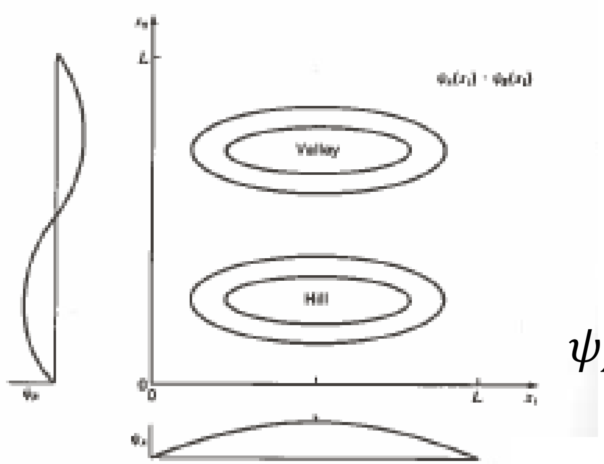
same as
$\psi_A(x_2)\psi_B(x_1)$

Figure and logic is from French and Taylor

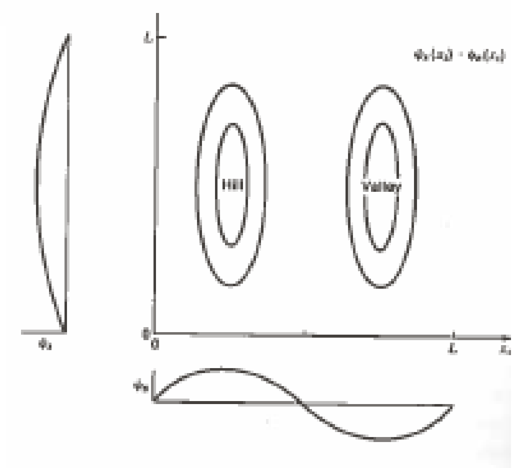
But simple product wavefunctions differ when particles are exchanged

Example of two particles in the first and second states of a box:

$$\psi_A = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right);\ \psi_B = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$$

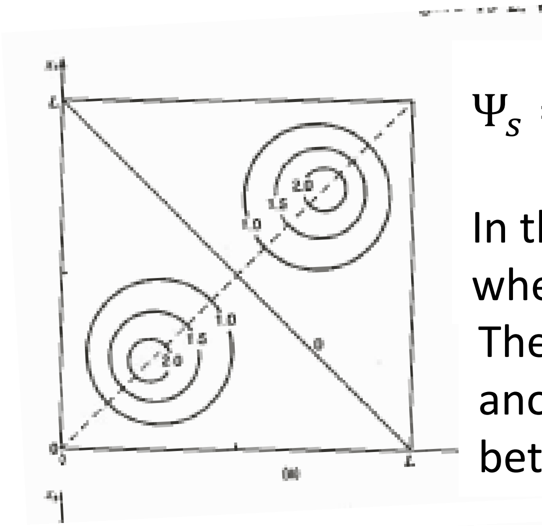


$$\psi_A(x_1)\psi_B(x_2) = \frac{2}{L}\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right)$$



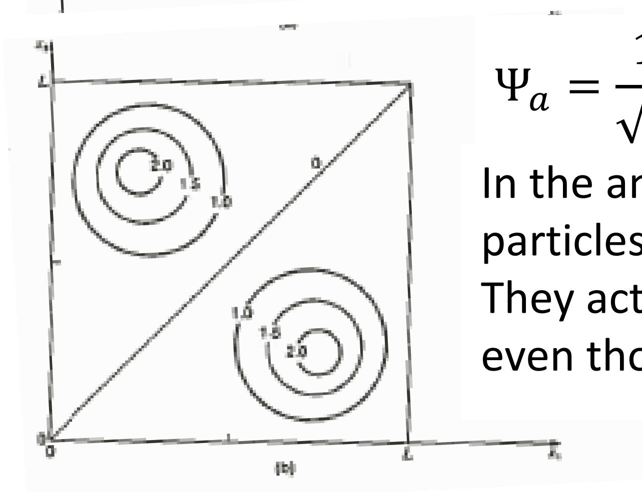
$$\psi_A(x_2)\psi_B(x_1) = \frac{2}{L}\sin\left(\frac{\pi x_2}{L}\right)\sin\left(\frac{2\pi x_1}{L}\right)$$

Constructing a probability density that does not change under particle exchange



$$\Psi_s = \frac{1}{\sqrt{2}}(\psi_A(x_1)\psi_B(x_2) + \psi_A(x_2)\psi_B(x_1))$$

In the symmetric state, $P(x_1,x_2)$ is a maximum when the particles are close together. They act as though they are attracted to one another even though there is no force between them.



$$\Psi_a = \frac{1}{\sqrt{2}}(\psi_A(x_1)\psi_B(x_2) - \psi_A(x_2)\psi_B(x_1))$$

In the antisymmetric state, P is a maximum when the particles are far apart and is zero along the x_1=x_2 line. They act as though they are repelling one another, even though there is no force between them.

Three Identical Particles

- Symmetric

$$\Psi_s(1,2,3) = \frac{1}{\sqrt{6}}\left[\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3) + \psi_\beta(1)\psi_\gamma(2)\psi_\alpha(3) + \psi_\gamma(1)\psi_\alpha(2)\psi_\beta(3) + \psi_\gamma(1)\psi_\beta(2)\psi_\alpha(3) + \psi_\beta(1)\psi_\alpha(2)\psi_\gamma(3) + \psi_\alpha(1)\psi_\gamma(2)\psi_\beta(3)\right]$$

- Antisymmetric

$$\Psi_A(1,2,3) = \frac{1}{\sqrt{6}}\left[\psi_\alpha(1)\psi_\beta(2)\psi_\gamma(3) + \psi_\beta(1)\psi_\gamma(2)\psi_\alpha(3) + \psi_\gamma(1)\psi_\alpha(2)\psi_\beta(3) - \psi_\gamma(1)\psi_\beta(2)\psi_\alpha(3) - \psi_\beta(1)\psi_\alpha(2)\psi_\gamma(3) - \psi_\alpha(1)\psi_\gamma(2)\psi_\beta(3)\right]$$

3 Identical Particles: Antisymmetric Case
The Slater Determinant

$$\Psi_A(1,2,3)$$
$$= \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_\alpha(1) & \psi_\alpha(2) & \psi_\alpha(3) \\ \psi_\beta(1) & \psi_\beta(2) & \psi_\beta(3) \\ \psi_\alpha(1) & \psi_\alpha(2) & \psi_\alpha(3) \end{vmatrix}$$

To make the symmetric case, just switch all (-) signs to (+).

Which choice, Symmetric or Antisymmetric, does nature take?

- The answer is: Sometimes one, sometimes the other, depending on the type of particle involved, but ...
- to address this question properly we need to consider the complete wavefunction, which includes properties like intrinsic spin, isospin, strangeness, charm, beauty ...
- We'll just worry about spin for now.

Spin states for two particles

In a magnetic field, we know that spin ½ particles can be in a spin up (↑) or spin down (↓) state. Possible combinations are,

$\uparrow(1)\uparrow(2) \quad \uparrow(1)\downarrow(2) \quad \downarrow(1)\uparrow(2) \quad \downarrow(1)\downarrow(2)$

The first and last are symmetric wrt exchange.

Second and third can be combined to make

Symmetric: $\frac{1}{\sqrt{2}}(\uparrow(1)\downarrow(2)+\uparrow(2)\downarrow(1))$

Antisymmetric: $\frac{1}{\sqrt{2}}(\uparrow(1)\downarrow(2)-\uparrow(2)\downarrow(1))$

I'll call the spin up state α and down β.

Symmetric (Triplet)

$\alpha(1)\alpha(2)$ (up,up S_z=+1)

$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)+\alpha(2)\beta(1))$ (S_z=0)

$\beta(1)\beta(2)$ (down,down) (S_z=−1)

Antisymmetric (Singlet)

$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2)-\alpha(2)\beta(1))$ (S_z=0)

Total Wavefunction symmetry

- The total wavefunction for two identical particles is the product of one of the possible spatial wavefunction combinations and one of the possible spin wavefunctions.

$$\Psi = \psi(x_1, x_2)\chi(s_1, s_2)$$

- It is the overall symmetry of the total wavefunction that is important for exchange symmetry and the Pauli Exclusion Principle.

Fermions and Bosons

- Particles with half-integer intrinsic spin are called fermions and are antisymmetric with respect to exchange of identical particles*.
  - electron, muon, proton, neutron, He^3 atom
- Particles with integer spin are called bosons and are symmetric with respect to exchange of identical particles.
  - photon, pi meson, alpha particle, He_4 atom

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The Connection Between Spin and Statistics[1]

W. PAULI
Physikalisches Institut, Eidg. Technischen Hochschule, Zürich, Switzerland and Institute for Advanced Study, Princeton, New Jersey

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In the following paper we conclude for the relativistically invariant wave equation for free particles: From postulate (I), according to which the energy must be positive, the necessity of *Fermi-Dirac* statistics for particles with arbitrary half-integral spin; from postulate (II), according to which observables on different space-time points with a space-like distance are commutable, the necessity of *Einstein-Bose* statistics for particles with arbitrary integral spin. It has been found useful to divide the quantities which are irreducible against Lorentz transformations into four symmetry classes which have a commutable multiplication like $+1$, -1, $+\epsilon$, $-\epsilon$ with $\epsilon^2=1$.

§1. UNITS AND NOTATIONS

SINCE the requirements of the relativity theory and the quantum theory are fundamental for every theory, it is natural to use as units the vacuum velocity of light c, and Planck's constant divided by 2π which we shall simply denote by $\hbar$. This convention means that all quantities are brought to the dimension of the power of a length by multiplication with powers of $\hbar$ and c. The reciprocal length corresponding to the rest mass m is denoted by $\kappa = mc/\hbar$.

As time coordinate we use accordingly the length of the light path. In specific cases, however, we do not wish to give up the use of the imaginary time coordinate. Accordingly, a tensor index denoted by small Latin letters i, refers to the imaginary time coordinate and runs from 1 to 4. A special convention for denoting the complex conjugate seems desirable. Whereas for quantities with the index 0 an asterisk signifies the complex-conjugate in the ordinary sense (e.g., for the current vector S_i the quantity S_0^* is the complex conjugate of the charge density S_0), in general $U^*_{ik\ldots}$ signifies: the complex-conjugate of $U_{ik\ldots}$ multiplied with $(-1)^n$, where n is the number of occurrences of the digit 4 among the $i, k, \cdots$ (e.g. $S_4 = iS_0$, $S_4^* = iS_0^*$).

Dirac's spinors u_ρ with $\rho = 1, \cdots, 4$ have always a Greek index running from 1 to 4, and u_ρ^* means the complex-conjugate of u_ρ in the ordinary sense.

Wave functions, insofar as they are ordinary vectors or tensors, are denoted in general with capital letters, U_i, $U_{ik}\ldots$. The symmetry character of these tensors must in general be added explicitly. As classical fields the electromagnetic and the gravitational fields, as well as fields with rest mass zero, take a special place, and are therefore denoted with the usual letters φ_i, $f_{ik} = -f_{ki}$, and $g_{ik} = g_{ki}$, respectively.

The energy-momentum tensor T_{ik} is so defined, that the energy-density W and the momentum density G_k are given in natural units by $W = -T_{44}$ and $G_k = -iT_{k4}$ with $k = 1, 2, 3$.

§2. IRREDUCIBLE TENSORS. DEFINITION OF SPINS

We shall use only a few general properties of those quantities which transform according to irreducible representations of the Lorentz group.[2] The proper Lorentz group is that continuous linear group the transformations of which leave the form

$$\sum_{k=1}^{4} x_k^2 = \mathbf{x}^2 - x_0^2$$

invariant and in addition to that satisfy the condition that they have the determinant $+1$

[1] This paper is part of a report which was prepared by the author for the Solvay Congress 1939 and in which slight improvements have since been made. In view of the unfavorable times, the Congress did not take place, and the publication of the reports has been postponed for an indefinite length of time. The relation between the present discussion of the connection between spin and statistics, and the somewhat less general one of Belinfante, based on the concept of charge invariance, has been cleared up by W. Pauli and F. J. Belinfante, Physica **7**, 177 (1940).

[2] See B. L. v. d. Waerden, *Die gruppentheoretische Methode in der Quantentheorie* (Berlin, 1932).

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*The proof is sophisticated – see W. Pauli, Phys Rev, **58**, 716 (1940).

Pauli Exclusion is a consequence of the antisymmetry requirement

Class activity: Show that the wavefunction amplitude for two electrons in the same antisymmetric spatial state is zero. Don’t forget about spin.

(This question is on the worksheet.)

Consequences of Exchange Symmetry

- Pauli exclusion principle leads to building up of electrons in multi-electron atoms.
- Corrections to the energies of multi-particle states.

- The Simplest Testable Example:
  The Helium Atom

You proved (a few slides ago) in the activity in class that two particles with antisymmetric exchange symmetry cannot be in the same state.
We can therefore put only two electrons in the ground state of He. (They must have different spin)