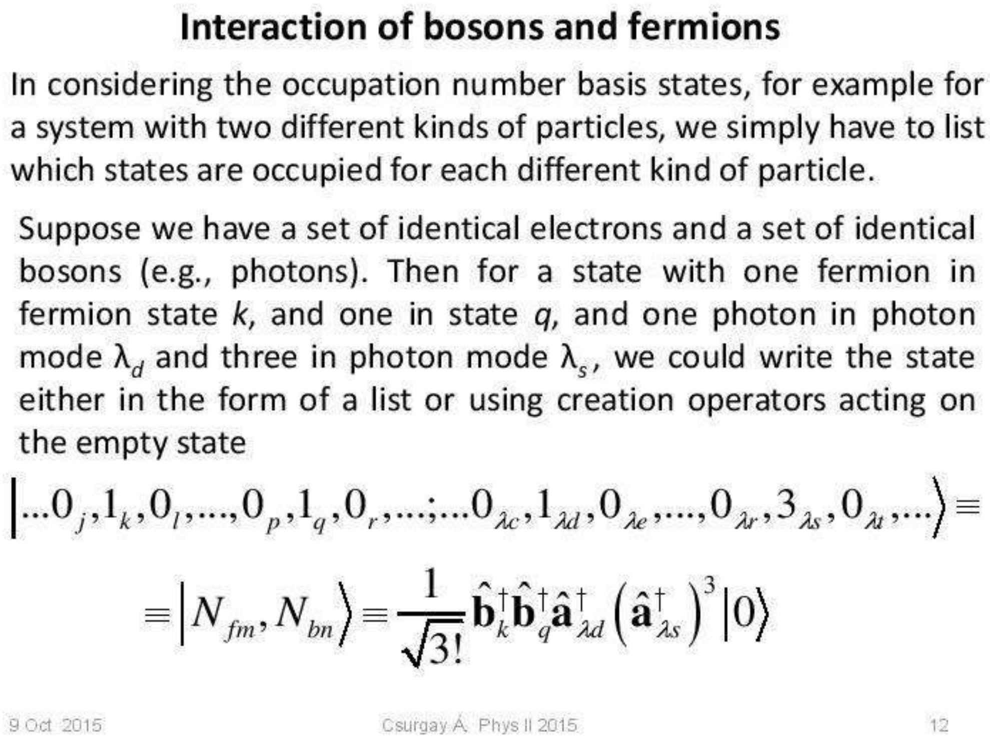
6. The Many-Body Problem in Quantum Mechanics

a. The identical two-body problem: bosons and fermions



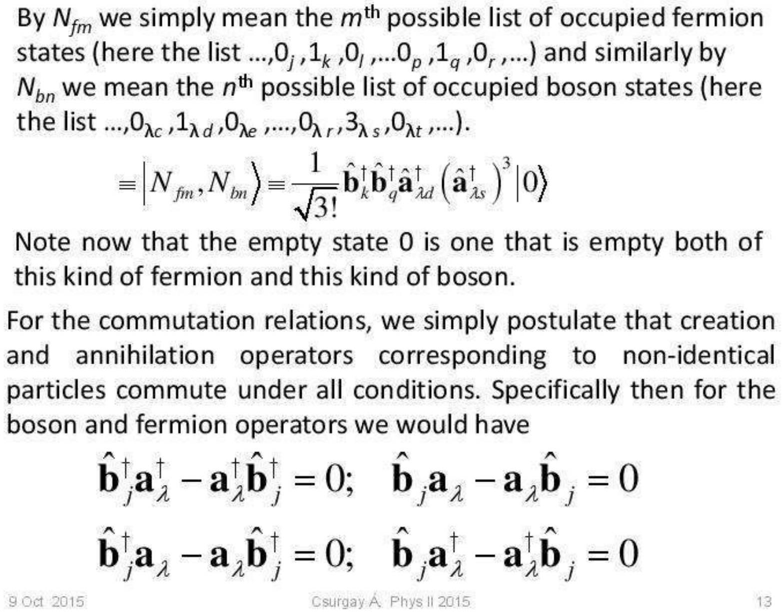
Interaction of bosons and fermions

In considering the occupation number basis states, for example for a system with two different kinds of particles, we simply have to list which states are occupied for each different kind of particle.

Suppose we have a set of identical electrons and a set of identical bosons (e.g., photons). Then for a state with one fermion in fermion state *k*, and one in state *q*, and one photon in photon mode λ_d and three in photon mode λ_s, we could write the state either in the form of a list or using creation operators acting on the empty state

$$\left|\ldots 0_j, 1_k, 0_l, \ldots, 0_p, 1_q, 0_r, \ldots; \ldots 0_{\lambda c}, 1_{\lambda d}, 0_{\lambda e}, \ldots, 0_{\lambda r}, 3_{\lambda s}, 0_{\lambda t}, \ldots\right\rangle \equiv$$

$$\equiv \left|N_{fm}, N_{bn}\right\rangle \equiv \frac{1}{\sqrt{3!}} \hat{\mathbf{b}}_k^\dagger \hat{\mathbf{b}}_q^\dagger \hat{\mathbf{a}}_{\lambda d}^\dagger \left(\hat{\mathbf{a}}_{\lambda s}^\dagger\right)^3 \left|0\right\rangle$$



By N_{fm} we simply mean the m^{th} possible list of occupied fermion states (here the list $\ldots, 0_j, 1_k, 0_l, \ldots 0_p, 1_q, 0_r, \ldots$) and similarly by N_{bn} we mean the n^{th} possible list of occupied boson states (here the list $\ldots, 0_{\lambda c}, 1_{\lambda d}, 0_{\lambda e}, \ldots, 0_{\lambda r}, 3_{\lambda s}, 0_{\lambda t}, \ldots$).

$$\equiv \left|N_{fm}, N_{bn}\right\rangle \equiv \frac{1}{\sqrt{3!}} \hat{\mathbf{b}}_k^\dagger \hat{\mathbf{b}}_q^\dagger \hat{\mathbf{a}}_{\lambda d}^\dagger \left(\hat{\mathbf{a}}_{\lambda s}^\dagger\right)^3 \left|0\right\rangle$$

Note now that the empty state 0 is one that is empty both of this kind of fermion and this kind of boson.

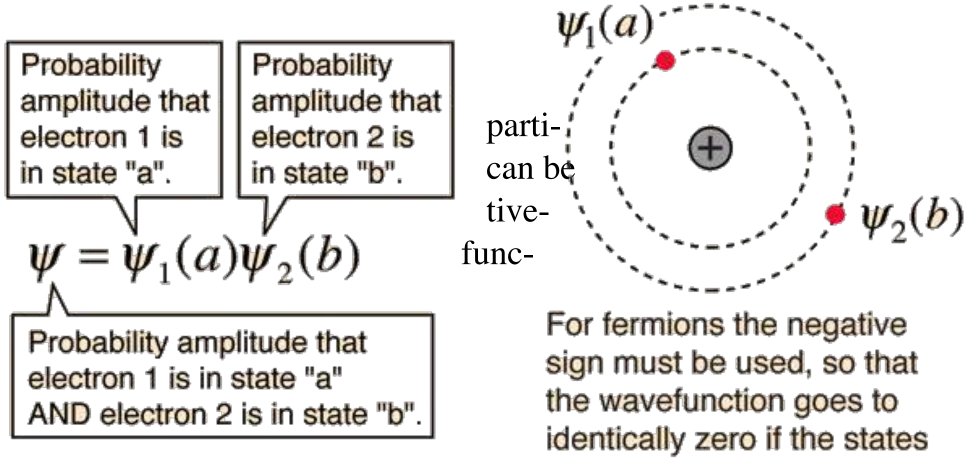
For the commutation relations, we simply postulate that creation and annihilation operators corresponding to non-identical particles commute under all conditions. Specifically then for the boson and fermion operators we would have

$$\hat{\mathbf{b}}_j^\dagger \mathbf{a}_\lambda^\dagger - \mathbf{a}_\lambda^\dagger \hat{\mathbf{b}}_j^\dagger = 0; \quad \hat{\mathbf{b}}_j \mathbf{a}_\lambda - \mathbf{a}_\lambda \hat{\mathbf{b}}_j = 0$$

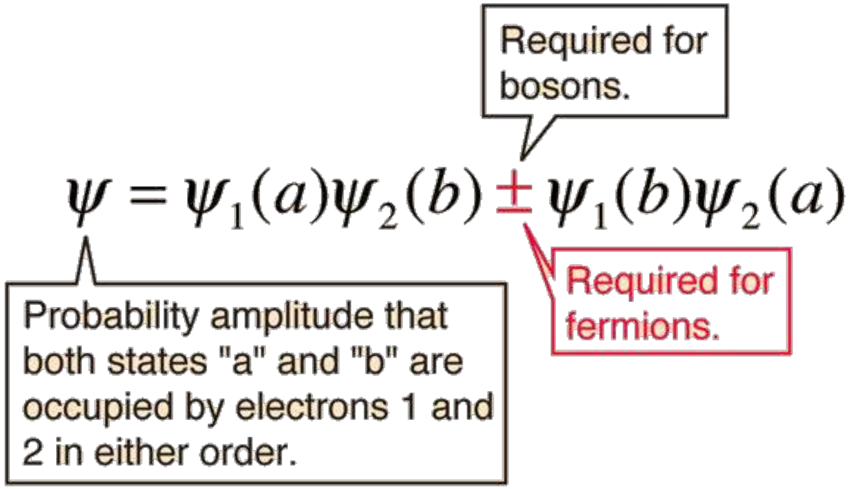
$$\hat{\mathbf{b}}_j^\dagger \mathbf{a}_\lambda - \mathbf{a}_\lambda \hat{\mathbf{b}}_j^\dagger = 0; \quad \hat{\mathbf{b}}_j \mathbf{a}_\lambda^\dagger - \mathbf{a}_\lambda^\dagger \hat{\mathbf{b}}_j = 0$$

b. The Pauli Principle. Slater determinant

No two electrons in an atom can have identical quantum numbers. This is an example of a general principle which applies not only to electrons but also to other particles of half-integer spin (fermions). It does not apply to particles of integer spin (bosons). The nature of the Pauli exclusion principle can be illustrated by supposing that electrons 1 and 2 are in states a and b respectively. The wavefunction for the two electron system would be but this wavefunction is unacceptable because the electrons are identical and indistinguishable. To account for this we must use a linear combination of the two possibilities since the determination of which electron is in which state is not possible to determine.

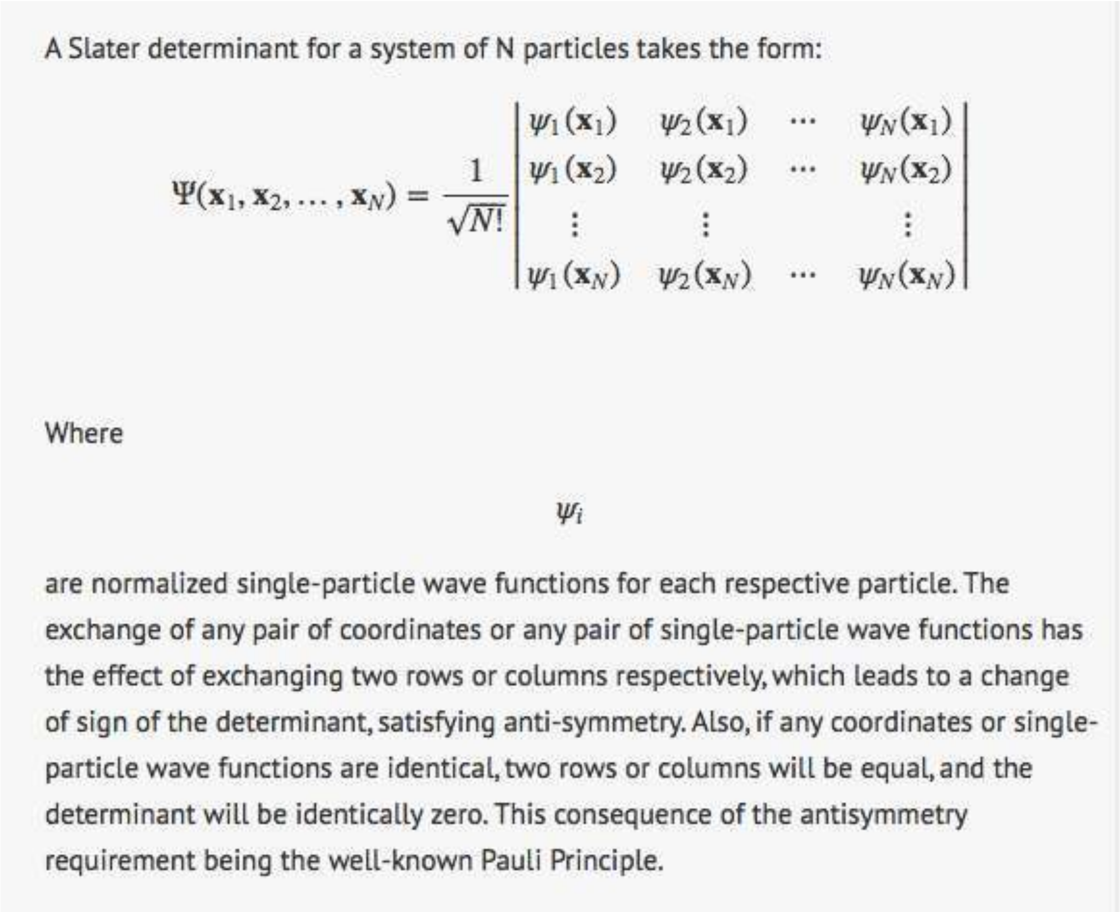


For fermions the negative sign must be used, so that the wavefunction goes to identically zero if the states a and b are identical.



The Pauli exclusion principle is part of one of our most basic observations of nature: particles of half-integer spin must have antisymmetric wavefunctions, and particles of integer spin must have symmetric wavefunctions. The minus sign in the above relationship forces the wavefunction to vanish identically if both states are "a" or "b", implying that it is impossible for both electrons to occupy the same state.

The wavefunction for the state in which both states "a" and "b" are occupied by the electrons can be written.



A Slater determinant for a system of N particles takes the form:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

Where

$$\psi_i$$

are normalized single-particle wave functions for each respective particle. The exchange of any pair of coordinates or any pair of single-particle wave functions has the effect of exchanging two rows or columns respectively, which leads to a change of sign of the determinant, satisfying anti-symmetry. Also, if any coordinates or single-particle wave functions are identical, two rows or columns will be equal, and the determinant will be identically zero. This consequence of the antisymmetry requirement being the well-known Pauli Principle.

c. The Periodic Table of Element

Ionization Energy (ionization potential)

Expelling an electron from an atom requires enough energy to overcome the magnetic pull of the positive charge of the nucleus. Therefore, ionization energy (I.E. or I) is the energy required to completely remove an electron from a gaseous atom or ion. The Ionization Energy is always positive.

The energy required to remove one valence electron is the first ionization energy, the second ionization energy is the energy required to remove a second valence electron, and so on.

Ionization energies increase relative to high effective charge. The highest ionization energies are the noble gases because they all have high effective charge due to their octet formation and require a high amount of energy to destroy that stable configuration. The highest amount of energy required occurs with the elements in the upper right hand corner. Additionally, elements in the left corner have a low ionization energy because losing an electron allows them to have the noble gas configuration. Therefore, it requires less energy to remove one of their valence electrons

Electron Affinity

Electron affinity (E.A.) is the energy change that occurs when an electron is added to a gaseous atom. Electron affinity can further be defined as the enthalpy change that results from the addition of an electron to a gaseous atom. It can be either positive or negative value. The greater the negative value, the more stable the anion is.

- (Exothermic) The electron affinity is positive

$$X_{(g)} + e^- \rightarrow X^- + \text{Energy}$$

- (Endothermic) The electron affinity is negative

$$X_{(g)} + e^- + \text{Energy} \rightarrow X^-$$

It is more difficult to come up with trends that describe the electron affinity. Generally, the elements on the right side of the periodic table will have large negative electron affinity. The electron affinities will become less negative as you go from the top to the bottom of the periodic table. However, Nitrogen, Oxygen, and Fluorine do not follow this trend. The noble gas electron configuration will be close to zero because they will not easily gain electrons.

Electronegativity

Electronegativity is the measurement of an atom to compete for electrons in a bond. The higher the electronegativity, the greater its ability to gain electrons in a bond. Electronegativity will be important when we later determine polar and nonpolar molecules. Electronegativity is related with ionization energy and electron affinity. Electrons with low ionization energies have low electronegativities because their nuclei do not exert a strong attractive force on electrons. Elements with high ionization energies have high electronegativities due to the strong pull exerted by the positive nucleus on the negative electrons. Therefore the electronegativity increases from bottom to top and from left to right.