Identical Particles

For two particles the wave-function is given by $\Psi(\bar{r}_1, \bar{r}_2, t)$. The time dependent Schrödinger equation becomes

$$i\hbar \frac{\partial \Psi(\bar{r}_1, \bar{r}_2, t)}{\partial t} = \hat{H} \Psi(\bar{r}_1, \bar{r}_2, t)$$

$$\hat{H} = \frac{\hat{P}_1^2}{2m_1} + \frac{\hat{P}_2^2}{2m_2} + V(\bar{r}_1, \bar{r}_2, t)$$

$$= -\frac{\hbar^2}{2}\left[\frac{\bar{\nabla}_1^2}{m_1} + \frac{\bar{\nabla}_2^2}{m_2}\right] + V(\bar{r}_1, \bar{r}_2, t)$$

$$\bar{\nabla}_i = \hat{i}\frac{\partial}{\partial x_i} + \hat{j}\frac{\partial}{\partial y_i} + \hat{k}\frac{\partial}{\partial z_i} \quad , \quad i = 1, 2 \text{ is the index denoting the particle number.}$$

Now $|\Psi(\bar{r}_1, \bar{r}_2, t)|^2 \, d^3\bar{r}_1 \, d^3\bar{r}_2 = $ probability

of finding first particle in a volume $d^3\bar{r}_1$ at $\bar{r}_1$ and the second one at $\bar{r}_2$ in a volume $d^3\bar{r}_2$.

Normalization is given by

$$\int |\Psi(\bar{r}_1, \bar{r}_2, t)|^2 \, d^3\bar{r}_1 \, d^3\bar{r}_2 = 1.$$

Also if $V(\bar{r}_1, \bar{r}_2, t) = V(\bar{r}_1, \bar{r}_2)$, i.e. V is independent of time then

we solve $\hat{H} \Psi_E(\bar{r}_1, \bar{r}_2) = E \Psi_E(\bar{r}_1, \bar{r}_2)$ for

E and $\Psi_E(\bar{r}_1, \bar{r}_2)$. Then

$$\Psi_E(\bar{r}_1, \bar{r}_2, t) = \Psi_E(\bar{r}_1, \bar{r}_2) \, e^{\frac{-iEt}{\hbar}} \, .$$

So far we have ignored spin. If we include spin then the wavefunction becomes

$$\Psi(1,2) = \Psi(\bar{r}_1, \bar{r}_2) \, \chi(\bar{s}_1, \bar{s}_2)$$

where $\bar{s}_1, \bar{s}_2$ are the spins of the two particles. Now we consider two identical particles such as electrons.

Postulate **VI** :—▷ Elementary identical particles come in two varieties namely bosons and fermions. Bosons have integer spins only. Fermions have $\frac{1}{2}$ integer spins only.

For bosons the total state $\Psi(1,2)$ of two particles is symmetric under exchange of the two indices 1 and 2.

$$\Rightarrow \quad \Psi_B(1,2) = \Psi_B(2,1)$$

For Fermions the state is antisymmetric under exchange

$$\Rightarrow \quad \Psi_F(1,2) = -\Psi_F(2,1) \, .$$

Consequences of Postulate VI :→

① Consider the exchange operator

$$\hat{P}_e \ni \quad \hat{P}_e \Psi(1,2) = \Psi(2,1)$$

$$\Rightarrow \quad \hat{P}_e^2 \Psi(1,2) = \hat{P}_e \Psi(2,1) = \Psi(1,2)$$

$$\Rightarrow \quad \hat{P}_e^2 = 1 \quad \Rightarrow \hat{P}_e = \pm 1$$

Now for indistinguishable or identical particles the mass $m_1 = m_2$ and

$$V(\bar{r}_1, \bar{r}_2) = V(\bar{r}_2, \bar{r}_1)$$

$$\Rightarrow \quad \hat{P}\hat{H} = \hat{H}\hat{P} \quad \Rightarrow [\hat{P}, \hat{H}] = 0$$

$$\Rightarrow \quad \Psi_E(1,2) = \pm \Psi_E(2,1).$$

The $+$ sign is for bosons
" $-$ " " " fermions.

$\Rightarrow$ We can choose solutions of $\hat{H}\Psi = E\Psi$ to be eigenfunctions of $\hat{P}_e$ with eigenvalues ± 1.

② Consider two functions $\Psi_a(x), \Psi_b(x) \ni$

$$\int_{-\infty}^{\infty} |\Psi_a|^2 dx = \int_{-\infty}^{\infty} |\Psi_b|^2 dx = 1 \quad \text{and}$$

$$\int_{-\infty}^{\infty} \Psi_a^* \Psi_b \, dx = \int_{-\infty}^{\infty} \Psi_b^* \Psi_a \, dx = 0,$$

Now construct a state

$$\Psi_d(x_1, x_2) = \Psi_a(x_1)\, \Psi_b(x_2)$$

Also construct $\Psi_\pm(x_1, x_2) = \frac{1}{\sqrt{2}}\Big[\Psi_a(x_1)\Psi_b(x_2) \pm$

$$\Psi_b(x_1)\Psi_a(x_2)\Big].$$

$+ \Longleftrightarrow$ bosonic state
$- \Longleftrightarrow$ fermionic state.

Now we calculate $\langle (x_1 - x_2)^2 \rangle_{d\atop\pm}$ in these 3

states.

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle.$$

Case (1) . for Ψ_d :

$$\langle (x_1 - x_2)^2 \rangle_d = \int_{-\infty}^{\infty} x_1^2 |\Psi_a|^2 dx_1 \int_{-\infty}^{\infty} |\Psi_b(x_2)|^2 dx_2 \Big\} \equiv \langle x^2 \rangle_a$$

$$+ \int_{-\infty}^{\infty} x_2^2 |\Psi_b(x_2)|^2 dx_2 \int_{-\infty}^{\infty} |\Psi_a|^2 dx_1 \qquad \Big\} \equiv \langle x^2 \rangle_b$$

$$- 2 \int_{-\infty}^{\infty} x_1 |\Psi_a(x_1)|^2 dx_1 \int_{-\infty}^{\infty} x_2 |\Psi_b(x_2)|^2 dx_2 \Big\} \equiv -2\langle x \rangle_a \langle x \rangle_b$$

$$\therefore \langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b.$$

Now $\langle (x_1 - x_2)^2 \rangle_+ = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2$

$$\Longrightarrow \langle (x_1 - x_2)^2 \rangle_\pm = \langle (x_1 - x_2)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2$$

FIGURE 5.1: Schematic picture of the covalent bond: (a) Symmetric configuration produces attractive force. (b) Antisymmetric configuration produces repulsive force.

Identical bosons (the upper signs) tend to be somewhat closer together, and identical fermions (the lower signs) somewhat farther apart, than distinguishable particles in the same two states. Notice that $\langle x \rangle_{ab}$ *vanishes* unless the two wave functions actually *overlap* [if $\psi_a(x)$ is zero wherever $\psi_b(x)$ is *non*zero, the integral in Equation 5.20 is zero]. So if ψ_a represents an electron in an atom in Chicago, and ψ_b represents an electron in an atom in Seattle, it's not going to make any difference whether you antisymmetrize the wave function or not. As a *practical* matter, therefore, it's okay to pretend that electrons with nonoverlapping wave functions are distinguishable. (Indeed, this is the only thing that allows physicists and chemists to proceed at *all*, for in *principle* every electron in the universe is linked to every other one, via the antisymmetrization of their wave functions, and if this really *mattered*, you wouldn't be able to talk about any *one* unless you were prepared to deal with them *all*!)

The *interesting* case is when there *is* some overlap of the wave functions. The system behaves as though there were a "force of attraction" between identical bosons, pulling them closer together, and a "force of repulsion" between identical fermions, pushing them apart (remember that we are for the moment ignoring spin). We call it an **exchange force**, although it's not really a force at all—no physical agency is pushing on the particles; rather, it is a purely *geometrical* consequence of the symmetrization requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart. Nevertheless, it has profound consequences. Consider, for example, the hydrogen molecule (H_2). Roughly speaking, the ground state consists of one electron in the atomic ground state (Equation 4.80) centered on nucleus 1, and one electron in the atomic ground state centered at nucleus 2. If electrons were *bosons*, the symmetrization requirement (or, if you like, the "exchange force") would tend to concentrate the electrons toward the middle, between the two protons (Figure 5.1(a)), and the resulting accumulation of negative charge would attract the protons inward, accounting for the **covalent bond**.[6] Unfortunately, electrons *aren't* bosons, they're fermions, and this means that the concentration of negative charge should actually be shifted to the wings (Figure 5.1(b)), tearing the molecule apart!

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[6]A covalent bond occurs when shared electrons congregate between the nuclei, pulling the atoms together. It need not involve *two* electrons—in Section 7.3 we'll encounter a covalent bond with just *one* electron.

$\Rightarrow \quad \langle (x_1 - x_2)^2 \rangle_{\pm} \quad \underset{>}{\leq} \langle (x_1 - x_2)^2 \rangle_d$

$\Rightarrow$ the symmetrization causes bosons to come closer and fermions to go farther apart as shown in Fig 5.1.

This is caused by exchange force which is not a real force but an effect of symmetrization.

For a system with many identical particles we get

$$\Psi_{\substack{B \\ F}}(1,2,\ldots i, i+1, \ldots, j, j+1, \ldots N) = \pm \Psi(1,2,\ldots j, i+1, \ldots, i, j+1, \ldots N)$$

$$\forall i, j \in 1, 2, \ldots N.$$

Atoms :→ Atomic ground states of the total state of all Z electrons are denoted by

$$^{2S+1}L_J$$

where $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$. Capital letters denote total spin S of all electrons and total orbital angular momentum state L of all Z electrons. Z = atomic number of the atom. Examples are shown in Table 5.1.

The values of S, L and J have to be consistent,

$$J \in \left[|L-S|, \; |L-S|+1, \ldots, \; L+S \right].$$

TABLE 5.1: Ground state electron configurations for the first four rows of the Periodic Table.

Z	Element	Configuration	
1	H	$(1s)$	$^2S_{1/2}$
2	He	$(1s)^2$	$^1S_0$
3	Li	$(He)(2s)$	$^2S_{1/2}$
4	Be	$(He)(2s)^2$	$^1S_0$
5	B	$(He)(2s)^2(2p)$	$^2P_{1/2}$
6	C	$(He)(2s)^2(2p)^2$	$^3P_0$
7	N	$(He)(2s)^2(2p)^3$	$^4S_{3/2}$
8	O	$(He)(2s)^2(2p)^4$	$^3P_2$
9	F	$(He)(2s)^2(2p)^5$	$^2P_{3/2}$
10	Ne	$(He)(2s)^2(2p)^6$	$^1S_0$
11	Na	$(Ne)(3s)$	$^2S_{1/2}$
12	Mg	$(Ne)(3s)^2$	$^1S_0$
13	Al	$(Ne)(3s)^2(3p)$	$^2P_{1/2}$
14	Si	$(Ne)(3s)^2(3p)^2$	$^3P_0$
15	P	$(Ne)(3s)^2(3p)^3$	$^4S_{3/2}$
16	S	$(Ne)(3s)^2(3p)^4$	$^3P_2$
17	Cl	$(Ne)(3s)^2(3p)^5$	$^2P_{3/2}$
18	Ar	$(Ne)(3s)^2(3p)^6$	$^1S_0$
19	K	$(Ar)(4s)$	$^2S_{1/2}$
20	Ca	$(Ar)(4s)^2$	$^1S_0$
21	Sc	$(Ar)(4s)^2(3d)$	$^2D_{3/2}$
22	Ti	$(Ar)(4s)^2(3d)^2$	$^3F_2$
23	V	$(Ar)(4s)^2(3d)^3$	$^4F_{3/2}$
24	Cr	$(Ar)(4s)(3d)^5$	$^7S_3$
25	Mn	$(Ar)(4s)^2(3d)^5$	$^6S_{5/2}$
26	Fe	$(Ar)(4s)^2(3d)^6$	$^5D_4$
27	Co	$(Ar)(4s)^2(3d)^7$	$^4F_{9/2}$
28	Ni	$(Ar)(4s)^2(3d)^8$	$^3F_4$
29	Cu	$(Ar)(4s)(3d)^{10}$	$^2S_{1/2}$
30	Zn	$(Ar)(4s)^2(3d)^{10}$	$^1S_0$
31	Ga	$(Ar)(4s)^2(3d)^{10}(4p)$	$^2P_{1/2}$
32	Ge	$(Ar)(4s)^2(3d)^{10}(4p)^2$	$^3P_0$
33	As	$(Ar)(4s)^2(3d)^{10}(4p)^3$	$^4S_{3/2}$
34	Se	$(Ar)(4s)^2(3d)^{10}(4p)^4$	$^3P_2$
35	Br	$(Ar)(4s)^2(3d)^{10}(4p)^5$	$^2P_{3/2}$
36	Kr	$(Ar)(4s)^2(3d)^{10}(4p)^6$	$^1S_0$