Notes for Quantum Mechanics

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Lecture 29
Identical Particles

How do we tell something is something, and not something else? One typically answers - by its characteristics. How do we describe a state in QM? - The answer is - by its wave function - which is in turn described by its quantum numbers. So for our electron it has quantum numbers n, l, m_l,s, m_s or equivalently n, l,s, j, m_j giving us a state in the position representation as $R_{\mathrm{nl}}(r)\, Y_l^m(\theta, \phi)|\pm\rangle$

I once had a friend - Anne- in college. She always told me about her twin sister Beth, but I had never met her. She went to grad school in NYC where I also went. Her sister also came to NYC to go to grad school. When I arrived in NY I ran into Beth (they were living into the same living complex as me). I could have been dead certain it was Anne - but she didn't recognize me. To me they looked EXACTLY the same. As one person put it - when Beth and Anne were together- it was like looking at them in stereo. Now the two twins were really different people, and eventually we all learned the subtle differences between them - their features of ever so slightly different. Their personalities were very different.

Suppose, however, that you have a pair of electrons in front of you. You close your eyes for a moment, and then open them. How could you be certain that they had not switched places? The answer is you couldn't. In fact nature demands that you cannot - as we will see.

Now lets see if we can write down a ket for a two electrons. Lets let k' and k" stand for sets of quantum numbers. Then a first guess as to the ket might be

$|k'\rangle_1 |k''\rangle_2$ where electron-1 has quantum numbers k' and electron-2 has quantum numbers k". Now lets make a measurement of some quantity. If we measure k' then we might think we got the quantum numbers for electron-1. But you cannot tell if the ket was really $|k''\rangle_1 |k'\rangle_2$ and you had measured electron-2 since you cant tell them apart. In fact any linear combination of the form $c_\alpha\, |k'\rangle_1\, |k''\rangle_2 + c_\beta |k''\rangle_1\, |k'\rangle_2$ could give us a measurement k'. This is called the exchange degeneracy of identical particles. You might argue that there might be some other characteristics of the two electrons which might allow us to tell them apart *but* if there were - they would not be identical particles.

We have a problem here since the specification of the eigenvalues k' and k" does not completely determine the state (and hence we have a degeneracy) Now nature actually avoids this problem in a rather interesting way.

Now lets define a permutation operator $\hat{P}_{12}\, |k'\rangle_1 |k''\rangle_2 \;= |k'\rangle_2 |k''\rangle_1 \;= |k''\rangle_1 |k'\rangle_2$ i.e. it just switches the labels of electrons 1 and 2. (Note - two kets multiplied together which represent different particles - or degrees of freedom commute)

Now clearly $\hat{P}_{12}=\hat{P}_{21}$ and $\hat{P}_{12}{}^2=1$

Now when we the spin operator for a particle - we will have to give it a label e.g. $\hat{S}_1$ etc. So for some operator $\hat{A}$ we will get

$\hat{A}_1\, |a'\rangle_1 |a''\rangle_2 = a'\, |a'\rangle_1 |a''\rangle_2$ and $\hat{A}_2\, |a'\rangle_1 |a''\rangle_2 = a''\, |a'\rangle_1 |a''\rangle_2$

Now lets apply $\hat{P}_{12}$ to the left eqn

$\hat{P}_{12}\, \hat{A}_1\, \hat{P}_{12}{}^{-1}\, \hat{P}_{12}\, |a'\rangle_1 |a''\rangle_2 = a'\, \hat{P}_{12}\, |a'\rangle_1 |a''\rangle_2$

$\hat{P}_{12}\, \hat{A}_1\, \hat{P}_{12}{}^{-1} |a''\rangle_2 |a'\rangle_1 = a' |a''\rangle_2 |a'\rangle_1 = \hat{A}_2\; |a''\rangle_2 |a'\rangle_1$

$\hat{P}_{12}\, \hat{A}_1\, \hat{P}_{12}{}^{-1} |a''\rangle_1 |a'\rangle_2 = a' |a''\rangle_1 |a'\rangle_2 = \hat{A}_2\; |a''\rangle_1 |a'\rangle_2$

Hence we have that $\hat{P}_{12}\, \hat{A}_1\, \hat{P}_{12}{}^{-1} = \hat{A}_2$

Now lets let $\hat{A}$ be a Hamiltonian for two particles. Clearly it has to be the same whichever way we label the particles. For instance for our two electrons orbiting a nucleus it might be

$\hat{H} = \frac{\hat{\boldsymbol{p}}_1{}^2}{2m} + \frac{\hat{\boldsymbol{p}}_2{}^2}{2m} + V(\boldsymbol{r}_1) + V(\boldsymbol{r}_2) + V_{\text{pair}}\,(\,|\,\boldsymbol{r_1} - \boldsymbol{r_2}\,|)$ Where V_{pair} is the coulomb interaction between the two electrons.

Now remember when we transform an operator $\hat{H}$ with a transformation operator $\hat{A}$ then $\hat{H} \longrightarrow \hat{A}\, \hat{H}\, \hat{A}^{-1}$

So since the hamiltonian doesn't care which way we label the particles we must have

$\hat{P}_{12}\, \hat{H}\, \hat{P}_{12}{}^{-1} = \hat{H}$ or $[\hat{H}, \hat{P}_{12}]=0$

Which means that the eigenkets of $\hat{H}$ must be eigenkets of $\hat{P}_{12}$ as well. The eigenvalues must be ±1 because $\hat{P}_{12}{}^2=1$

OK. SO let take our ket $c_\alpha\, |k'\rangle_1\, |k''\rangle_2 + c_\beta |k''\rangle_1\, |k'\rangle_2$ and make sure it is an eigenket of $\hat{P}_{12}$

The following two combinations work

$|k'\, k''\rangle_+ = \frac{1}{\sqrt{2}}\; |k'\rangle_1\, |k''\rangle_2 + \frac{1}{\sqrt{2}} |k''\rangle_1\, |k'\rangle_2$ and $|k'\, k''\rangle_- = \frac{1}{\sqrt{2}}\; |k'\rangle_1\, |k''\rangle_2 - \frac{1}{\sqrt{2}} |k''\rangle_1\, |k'\rangle_2$

The first called the symmetric state has a +1 eigenvalue, and the second called the anti-symmetric state has a -1 eigenvalue.

It is convenient to define two operators - a symmetrizer and anti-symmetrizer as follows

$\hat{\mathcal{S}}_{12} \equiv \frac{1}{2}(1+\hat{P}_{12})$ and $\hat{\mathcal{A}}_{12} = \frac{1}{2}\left(1 - \hat{P}_{12}\right)$ These things will nicely take any linear combination

$c_\alpha\, |k'\rangle_1\, |k''\rangle_2 + c_\beta |k''\rangle_1\, |k'\rangle_2$ and make the symmetric and anti-symmetric states for us.

$$\left\{ \begin{matrix} \hat{\mathcal{S}}_{12} \\ \hat{\mathcal{A}}_{12} \end{matrix} \right\} [\; c_\alpha\, |k'\rangle_1\, |k''\rangle_2 + c_\beta |k''\rangle_1\, |k'\rangle_2\;] = \frac{1}{2} \left\{ \begin{matrix} 1+\hat{P}_{12} \\ 1-\hat{P}_{12} \end{matrix} \right\} [\; c_\alpha\, |k'\rangle_1\, |k''\rangle_2 + c_\beta |k''\rangle_1\, |k'\rangle_2\;] =$$

$$\frac{1}{2} [\; c_\alpha\, |k'\rangle_1\, |k''\rangle_2 + c_\beta |k''\rangle_1\, |k'\rangle_2 \pm c_\alpha\, |k''\rangle_1\, |k'\rangle_2 \pm c_\beta |k'\rangle_1\, |k''\rangle_2] = \frac{c_\alpha \pm c_\beta}{2} [\; |k'\rangle_1\, |k''\rangle_2 \pm |k''\rangle_1\, |k'\rangle_2\;]$$

These symmetrization considerations also can be applied to 3 or more particles- in which case you would have 3 operators $\hat{P}_{12}$, $\hat{P}_{23}$, and $\hat{P}_{13}$. A symmetric or antisymmetric, or a partially symmetric+partially anti-symmetric state must be an eigenket of all of these. For the case of three particles, $|k'\rangle_1\,|k''\rangle_2\,|k'''\rangle_3$ there should be 3!=6 possible combinations. Now if we insist that these be *totally* symmetric or *totally* anti-symmetric; it turns out there is only one of each. There are 4 others of mixed symmetry.

Bosons, Fermions and the Pauli exclusion principle.

Now we come to one of the most curious things in physics. Lets ask the question - does nature prefer symmetric states, anti-symmetric states, or something else. It turns out that nature has divided particles in one of two types -

Bosons - which are in a totally symmetric state - and which are of integer spin - and which obey Bose-Einstein statistics

Fermions - which are in a totally anti-symmetric state, which are of half-integer spin - and which obey Fermi-Dirac statistics

There is another class - for "classical particles" which do not have any requirements on symmetry - we say these obey Maxwell-Boltzmann statistics. There are really no such things, but we often think of particles as M-B particles for the sake of convenience.

There is nothing which is partially symmetric+partially anti-symmetric. I can be proven (in the context of quantum field theory) that spin a half particles must be fermions, and integer spin particles must be bosons.

This means that for some permutation operator $\hat{P}_{ij}$ we have

$\hat{P}_{ij}|\text{N identical bosons}\rangle = +\,|\text{N identical bosons}\rangle$

$\hat{P}_{ij}|\text{N identical fermions}\rangle = -\,|\text{N identical fermions}\rangle$

Now lets take two identical fermions one of which is in the state k', the other in state k". We will then see what happens when k'=k" i.e. when the are in the *same* state - in other words, when their quantum numbers are identical.

For fermions, which are in an anti-symmetric state there is only one possibility

$\frac{1}{\sqrt{2}}[\,|k'\rangle_1\,|k''\rangle_2 - |k''\rangle_1\,|k'\rangle_2\,]$

For bosons, we can have $|k'\rangle_1\,|k'\rangle_2$ $\quad|k''\rangle_1\,|k''\rangle_2$ $\quad$ or $\quad\frac{1}{\sqrt{2}}[\,|k'\rangle_1\,|k''\rangle_2 + |k''\rangle_1\,|k'\rangle_2\,]$

As an aside - in the case of M-B statistics we have $|k'\rangle_1\,|k''\rangle_2$; $|k''\rangle_1\,|k'\rangle_2$; $|k'\rangle_1\,|k'\rangle_2$; $|k''\rangle_1\,|k''\rangle_2$

Now lets see what happens if k'=k". In the Bose-Einstein case we are OK.

In the case of fermions however, we get

$\frac{1}{\sqrt{2}}[\,|k'\rangle_1\,|k'\rangle_2 - |k'\rangle_1\,|k'\rangle_2\,] = 0$!!! i.e. two fermions CANNOT be in the same state. This is the famous Pauli-Exclusion principle.

Now suppose we had a two particles and two possible sets of quantum numbers k' and k"

If they are F-D , they cannot be in the same state. One must be in k' and the other in k"

If they are M-B then 2 out of 4 cases would have the two in the same state.

If they are B-E then 2 out of 3 cases are in the same state. So in that sense Bosons are the most gregarious. They like to be together in the same state. This is the basis of the famous Bose-Einstein Condensate where a whole group of atoms (bosons-like atoms) go into the same state.

This is also now the basis of atomic orbitals and the periodic table. Each electron - since it is spin $\frac{1}{2}$ must occupy its own state, that is they the numbers n, l, m_l, s, m_s must be different. Now $s = \frac{1}{2}$ and m_s = either $+\frac{1}{2}$ or $\frac{-1}{2}$

This means that any combination of n, l, m_l must have only two electrons. One which is $m_s = \frac{+1}{2}$ and the other with $m_s = \frac{-1}{2}$. Each of these levels is like a bookshelf which can only hold 2 books (electrons). As more and more electrons are added, they must go into different shells.