

## Physics 486 Discussion 13 – Spin

Now that we've added the electron's **spin** = intrinsic angular momentum to its orbital angular momentum (**OAM**), we are able to write down a complete description of an electron wavefunction. The ket  $|nlm_l m_s\rangle$  completely describes an electron in an eigenstate of the five commuting operators  $\hat{H}$ ,  $\hat{L}^2$ ,  $\hat{L}_z$ ,  $\hat{S}_z$ , &  $\hat{S}^2$ . We usually leave the quantum number  $s = 1/2$  out of the ket since its value is a fixed, intrinsic property of the electron (just as we leave out the fixed mass and charge of the electron.)

In QM, all of the results we obtained for angular momentum using the operator  $\hat{L} = \hat{r} \times \hat{p} = \vec{r} \times (-i\hbar\vec{\nabla})$  are directly copied over from OAM to spin. Commutators, eigenvalues, ladder operators, everything is simply copied from the orbital case to the spin case ... and it works. It may be argued that this is another QM axiom. Let's first summarize these results, with a focus on spin-1/2 particles. In the problems, you will work and derive the new items, which are the matrix representations of the spin operators. The operators for spin can only be represented in matrix notation since we have no coordinates like  $x,y,z$  or  $r,\theta,\phi$  with which to describe the intrinsic, internal angular momentum of an elementary particle. (We're not 100% sure what it is, honestly, it just behaves exactly like another form of angular momentum.) With no internal coordinates, there is no way to build any differential operators, so it's matrix-representation-only for the spin sector.

### Spin Summary

The eigenvalue equations for the complete electron eigenstates  $|nlm_l m_s\rangle$  are :

$$\begin{aligned} \hat{H} |nlm_l m_s\rangle &= E_n |nlm_l m_s\rangle \text{ where the energy function } E_n \text{ depends on the system (i.e. on } V(\vec{r})\text{),} \\ \hat{L}^2 |nlm_l m_s\rangle &= \hbar^2 l(l+1) |nlm_l m_s\rangle, & \hat{L}_z |nlm_l m_s\rangle &= \hbar m_l |nlm_l m_s\rangle, \\ \hat{S}^2 |nlm_l m_s\rangle &= \hbar^2 s(s+1) |nlm_l m_s\rangle, & \hat{S}_z |nlm_l m_s\rangle &= \hbar m_s |nlm_l m_s\rangle \end{aligned}$$

Any electron wavefunction can be written as a superposition of the eigenstates  $|nlm_l m_s\rangle$ , where the allowed values of the quantum numbers  $n, l, m_l, m_s$  are restricted in ways that may be system-dependent :

$$\begin{aligned} n &= 0, 1, 2, \dots & \text{for 3D-SHO;} & n &= 1, 2, 3, \dots & \text{for atomic e}^-; & \text{etc} \\ l &= n, n-2, n-4, \dots (0 \text{ or } 1) & \text{for 3D-SHO;} & l &= 0, 1, 2, \dots, n-1 & \text{for atomic e}^-; & \text{etc} \\ m_l &= -l, -l+1, \dots, +l \\ m_s &= -s, -s+1, \dots, +s & \text{which for a spin-1/2 particle is } & m_s &= -\frac{1}{2}, +\frac{1}{2} \end{aligned}$$

For a system with a central potential  $V(r)$ , the wavefunction for each eigenstate  $|nlm_l m_s\rangle$  separates neatly into radial  $R(r)$  and angular  $Y(\theta,\phi)$  parts ... and now an equally separate spin part  $\chi$  :

$$\text{wavefunction } \langle e_{r,\theta,\phi} |nlm_l m_s\rangle = R_{nl}(r) Y_l^{m_l}(\theta,\phi) \chi_{m_s}$$

The spin part  $\chi$  is called a **spinor**; it represents the electron's  $S_z$  value, i.e. the orientation of its spin. As we discussed in class, spin does not depend on any spatial coordinates  $(x,y,z)$  or  $(r,\theta,\phi)$ , so any operators that act on  $\chi$  cannot be differential operators like  $\hat{p}_x = -i\hbar\partial/\partial x$  or  $\hat{L} = \vec{r} \times (-i\hbar\vec{\nabla})$ . Instead, we represent the spinor and the operators that act on it in **matrix form**. First we pick an ordered basis for our matrix representation. For a spin 1/2 particle, there are only two states: **spin up** ( $m_s = +1/2$ ) and **spin down** ( $m_s = -1/2$ ) along our chosen quantization axis  $\hat{z}$ . Take spin-up to be the first basis state, and spin-down to be the second :

basis spinors are  $\text{spin}_{\text{up}} : \chi_+ \equiv \left| \frac{1}{2} + \frac{1}{2} \right\rangle_{s, m_s} \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$  &  $\text{spin}_{\text{down}} : \chi_- \equiv \left| \frac{1}{2} - \frac{1}{2} \right\rangle_{s, m_s} \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ ,

Now that we have our basis, we can write down the operators for  $S^2$  and  $S_z$  in matrix form, as well as the step-up and step-down operators  $S_+$  and  $S_-$  :

$$S^2 = \frac{3}{4} \hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

As you will see shortly, these are very easy to figure out! ☺ The operators for the components of the spin vector  $\vec{S} = (S_x, S_y, S_z)$  for a spin- $1/2$  particle are usually written as follows :

$$\boxed{S_{x,y,z} \equiv \frac{\hbar}{2} \sigma_{x,y,z}} \quad \text{with the **Pauli spin matrices** } \quad \boxed{\sigma_x, \sigma_y, \sigma_z = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}}$$

Finally, all the angular momentum algebra we derived for  $\vec{L}$  is copied straight over to  $\vec{S}$  :

- commutators:  $[\hat{S}^2, \hat{S}_{x,y,z}] = 0$ ,  $[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z$  & cyclic permutations
- ladder ops for  $\hat{S}_z$ :  $\hat{S}_{\pm} \equiv \hat{S}_x \pm i\hat{S}_y$ ,  $\hat{S}_{\pm} |s, m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} |s, m_s \pm 1\rangle$

### Problem 1 : A Spin Measurement

**Checkpoints** <sup>1</sup>

We have a spin- $1/2$  particle in this state :

$$\chi = A \begin{pmatrix} 3 \\ 4 \end{pmatrix} \equiv 3A \chi_+ + 4A \chi_-$$

- (a) Find the constant  $A$  required to normalize this spinor (i.e. to make it represent a total probability of 1).
- (b) If we measured  $S_z$ , what is the probability that we would find the spin in the  $-z$  direction?
- (c) If instead we measured  $S_x$ , what is the probability that we would find the spin in the  $+x$  direction ?
- (d) Wow! That's amazingly close to 1. Sanity-check your result by calculating the probability that we would instead find the spin in the  $-x$  direction. Does your result confirm what you found in part (b)? Why or why not?

### Problem 2 : Spin 1/2 Matrices

Let's build the operators  $\{S_x, S_y, S_z\}$  for a spin- $1/2$  particle ourselves so that they will never be mysterious.

- (a)  $S_z$  is easy to get because you know exactly what  $S_z$  does when it acts on our two basis spinors

<sup>1</sup> **Q1** (a) 1/5 (b) 16/25 (c) Hint: "Project Onto Eigenstates" ☺ .... bigger Hint: measuring a quantity  $Q$  in QM means (1) Find the **eigenstates**  $|e_q\rangle$  of the corresponding operator  $Q$  then ... what? ... (2) **project** the system's state  $|\psi\rangle$  onto each  $e$ -state  $|e_q\rangle$  in turn  $\rightarrow$  the  $| \text{magnitude} |^2$  of those projections is the probability of obtaining each eigenvalue  $q$  :  $\text{Prob}(q) = | \langle e_q | \psi \rangle |^2$  ... You are measuring  $S_x$  so you need the eigenvectors of  $S_x$ ; find the eigen-stuff of  $\sigma_x$  instead so you don't have to carry the spin-magnitude  $\hbar/2$  around ... for a 2x2 matrix, just *guess* the eigenvectors and/or eigenvalues; alternatively, you can go the full brute-force determinant route ... the eigenvalues of  $\sigma_x$  are obviously +1 and -1, as for all the Pauli spin matrices ... the eigenvectors of  $\sigma_x$  are (1 1) and (1 -1) ... except you have to normalize them, so you get a  $1/\sqrt{2}$  on each ... Answer: Prob of getting  $S_x$  positive is 49/50. (d) must be 1/50

$$\text{spin up} : \chi_+ \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \& \quad \text{spin down} : \chi_- \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

By construction these spinors are eigenfunctions of  $S_z$  so you know what you must get when  $S_z$  acts on each one. Using that knowledge, write down the matrix for the  $\hat{S}_z$  operator. (Need a reminder? → see Lec08B-3.)

(b) Now consider the step-up and step-down operators  $S_+$  and  $S_-$ . You know what they do to our basis states:

$$S_{\pm} |s m_s\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)} |s(m_s \pm 1)\rangle,$$

(You derived that big square-root factor on your homework for  $L_{\pm}$ .) Knowing the action of  $S_+$  and  $S_-$  on our basis states, go ahead and write down the matrices for  $S_+$  and  $S_-$ .

► NOTE: What do you get when you step-down the state with the *lowest* eigenvalue? The only answer that makes any sense is zero. You get zero when you step-down the bottom eigenstate ( $S_- \chi_- = 0$ ) or step-up the top eigenstate ( $S_+ \chi_+ = 0$ ). You can confirm that the boxed formula does indeed give you this necessary result.

(c) Finally, we will build the trickiest matrices, those for  $S_x$  and  $S_y$ , using the raising and lowering operators :

$$S_{\pm} = S_x \pm i S_y$$

Invert these relations to obtain  $S_x$  and  $S_y$  in terms of  $S_+$  and  $S_-$ . You already know what the  $S_+$  and  $S_-$  matrices are, so you can immediately get  $S_x$  and  $S_y$ ! Compare your results to the Pauli spin matrices given previously.

### Problem 3 : Spin 1 Matrices

*adapted from Gr 4.31*

Using the exact same strategy that you just used for spin- $\frac{1}{2}$ , construct the matrix representations of the operators  $S_z$  then  $S_x$  and  $S_y$  for the case of a **spin 1 particle**. Note that these spin matrices will be 3x3, not 2x2, since the spinor  $|s=1 m_s\rangle$  for a spin-1 particle has *three* possible states. Be sure to start with  $S_z$  to gain confidence ... then build the  $S_+$  and  $S_-$  matrices ... then  $S_x$  and  $S_y$ .

### Problem 4 : Spin 1/2 Practice!

*adapted from Gr 4.27, Checkpoints 2 & 3*

An electron is in the spin state  $\chi = A \begin{pmatrix} 3i \\ 4 \end{pmatrix}$ .

- Determine the normalization constant A.
- Find the expectation values of  $S_x$ ,  $S_y$ , and  $S_z$ .

<sup>2</sup> **Q3** First some **jargon busting!** → The word “**spinor**” just appeared without comment! What is that? It is simply a convenient word to refer to the spin portion of a particle’s wavefunction, whether in the form of a ket  $|s m_s\rangle$  or a column vector with  $2s+1$  entries. OK now the spin-1 matrices (or to be precise, the matrix representation of the spin-1 operators that were requested):

$$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \dots S_+ = \sqrt{2} \hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}, S_- = \sqrt{2} \hbar \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \dots S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, S_y = \frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

<sup>3</sup> **Q4** (a)  $A=1/5$  (b)  $\langle S_x \rangle = 0$ ,  $\langle S_y \rangle = -12\hbar/25$ ,  $\langle S_z \rangle = -7\hbar/50$  (c)  $\{ \sigma_{S_x}, \sigma_{S_y}, \sigma_{S_z} \} = \hbar \{ 1/2, 7/50, 12/25 \}$

(d1)  $\sigma_{S_x} \sigma_{S_y} = \hbar^2 7/100 \dots ? \geq ? \dots \hbar/2 | \langle S_z \rangle | = \hbar^2 7/100$  ✓ uncertainty limit saturated

(d2)  $\sigma_{S_y} \sigma_{S_z} = \hbar^2 84/1250 \dots ? \geq ? \dots \hbar/2 | \langle S_x \rangle | = 0$  ✓ uncertainty principle imposes no limits trivially fulfilled

(d3)  $\sigma_{S_z} \sigma_{S_x} = \hbar^2 6/25 \dots ? \geq ? \dots \hbar/2 | \langle S_y \rangle | = \hbar^2 6/25$  ✓ uncertainty limit saturated

(c) Find the “uncertainties” = standard deviations  $\sigma_{S_x}, \sigma_{S_y}, \sigma_{S_z}$ .

(d) Confirm that your results are consistent with all three uncertainty principles:

$$\sigma_{S_x} \sigma_{S_y} \geq \left| \frac{1}{2i} \langle [S_x, S_y] \rangle \right| = \frac{\hbar}{2} |\langle S_z \rangle| \quad \text{and its 2 cyclic permutations}$$

### Not-A-Problem : The Pauli Exclusion Principle

Chemistry is almost entirely explained by the way the electrons in atoms occupy the various states  $|n l m_l m_s\rangle$  (also called shells, or orbitals) that are available to them. So far we have only considered **hydrogenic** atoms, with **one electron**. What happens in the normal case when there are **many electrons** in a atom? We know there are many states  $|n l m_l m_s\rangle$  available for the electrons to occupy, but which states do they choose to occupy? Systems generally arrange themselves into the state of lowest potential energy, so the 17 electrons in a chlorine atom might all pile into the ground state  $n = 1, l = 0, m_l = 0, m_s = \pm 1/2$ . If they do, then the 18 electrons in an argon atom do as well ... but that is exceedingly unlikely because chlorine and argon behave in *totally different ways* as regards binding to other atoms. Chlorine loves to bind to atoms like sodium and potassium, making salts, while argon is a “noble gas” that doesn’t like to bind to *any* other atoms. Wolfgang Pauli figured out the solution in 1925 : two electrons can never occupy the same state. This was later broadened to the **generalized Pauli exclusion principle** :

Two identical particles with  $1/2$ -integer spin can never occupy the same state.

Particles with  $1/2$ -integer spin acquired the name **fermions**, with the electron being by far the most common example. Particles with integer spin are called **bosons** and they do *not* obey any exclusion principle, they can all pile into the same state, no problem.

The Pauli exclusion principle plus the spectrum of available electron states in an atom explains chemistry, more or less. The treatment of identical particles is coming up and it will bring us the 6<sup>th</sup> and final axiom of QM.