Physics 143a – Workshop 11

Hydrogenic Atoms and Two-Particle States

Week Summary

- **Hydrogenic Atoms, Energy Eigenfunctions, and Eigenvalues:** The radial Schrödinger equation and energy eigenvalues of hydrogenic atoms are, respectively,

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u_{n,\ell} + \left[-\frac{Ze^2}{r} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]u_{n,\ell} = E_n u_{n,\ell}, \qquad E_n = -\frac{\mu}{2\hbar^2}(Ze^2)^2\frac{1}{n^2} = Z^2\frac{E_1}{n^2} \tag{1}$$

where Ze is the charge of the nucleus, $\mu = m_{\text{nucleus}}m_e/(m_e + m_{\text{nucleus}})$ is the reduced mass of the system, and $E_1 = -13.6$ eV is the binding energy of the ground state of hydrogen. The ground state wave function of hydrogenic atoms is given by

$$\psi_{100}(r,\theta,\phi) = R_{10}(r)Y_{0,0}(\theta,\phi) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}, \tag{2}$$

where $a_0 = \hbar^2/\mu e^2$ is the Bohr radius.

- **Two-Particle States:** Employing tensor product notation, a two-particle state $|\alpha_1\alpha_2\rangle$ is written more precisely as

$$|\alpha_1\alpha_2\rangle \equiv |\alpha_1 \otimes \alpha_2\rangle \quad \text{or} \quad |\alpha_1\alpha_2\rangle \equiv |\alpha_1\rangle \otimes |\alpha_2\rangle, \tag{3}$$

where $|\alpha_1\rangle$ is the state of the first particle and $|\alpha_2\rangle$ is the state of the second particle. The tensor product in Eq.(3) denotes the fact that $|\alpha_1\rangle$ and $|\alpha_2\rangle$ "live" in two different Hilbert spaces in a similar way to how points on x and y axes "live" on different real lines.

- **Triplet and Singlet States:** A state consisting of two spin $\frac{1}{2}$ particles has four basis states:

$$|\uparrow\uparrow\rangle, \quad |\uparrow\downarrow\rangle, \quad |\downarrow\uparrow\rangle, \quad \text{and} \quad |\downarrow\downarrow\rangle, \tag{4}$$

where in each ket, the first arrow signifies the spin-z direction of the first particle and the second arrow signifies the spin-z direction of the second particle. It is possible to write an arbitrary two spin $\frac{1}{2}$ particle state as a linear combination of the states in Eq.(4), but we could also use a basis defined by the possible total spins of this two-particle system. Such a basis would require the spin 1 **triplet** and spin 0 **singlet** states:

$$\text{triplet state}: \begin{cases} |1,1\rangle = |\uparrow\uparrow\rangle \\ |1,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right), \\ |1,-1\rangle = |\downarrow\downarrow\rangle \end{cases} \quad \text{singlet state:} \quad |0,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \tag{5}$$

where $|s,m\rangle$ stands for the state with total spin s and net spin in the z direction of m. We can interpret the triplet and single states as a different basis for the two spin $\frac{1}{2}$ particle system where total spin and net-spin in the z direction are the defining quantum numbers rather than the z direction spins of each particle.

1 Problems

1. **Spin and position states**
The electron in the hydrogen atom occupies the following combined spin and position state:

$$\sqrt{\frac{1}{3}}R_{32}(r)Y_{20}(\theta,\phi)|+,\mathbf{z}\rangle + \sqrt{\frac{2}{3}}R_{21}(r)Y_{11}(\theta,\phi)|-,\mathbf{z}\rangle \tag{6}$$

   (a) If you measured the orbital angular momentum squared ($\mathbf{L}^2$), what values might you get, and what is the probability of each?
   (b) Same for the z component of orbital angular momentum (L_z)
   (c) Same for the spin angular momentum squared ($\mathbf{S}^2$)
   (d) What is the average energy of this system? (Write the result in terms of E_1)

2. **Practice with Tensor Product Notation**
Operators acting on a two-particle state act separately on each space of particles. Therefore, the total spin-z operator $\hat{S}_z$ acting on an arbitrary two-particle state can be written as

$$\hat{S}_z \equiv \hat{S}_{1z} \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{S}_{2z}, \tag{7}$$

which implies that the operator $\hat{S}_z$ is equivalent to adding the operator which acts on the first particle with $\hat{S}_{1z}$ and leaves the second particle state unchanged (i.e., multiplies it by the identity matrix) to the operator which leaves the first particle unchanged and acts on the second particle with $\hat{S}_{2z}$. For example, acting on the state $|\uparrow\uparrow\rangle$ with $\hat{S}_z$, we find

$$\begin{aligned}\hat{S}_z|\uparrow\uparrow\rangle &\equiv \left(\hat{S}_{1z} \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{S}_{2z}\right)|\uparrow\rangle \otimes |\uparrow\rangle \\ &= \hat{S}_{1z}|\uparrow\rangle \otimes |\uparrow\rangle + |\uparrow\rangle \otimes \hat{S}_{2z}|\uparrow\rangle \\ &= \tfrac{\hbar}{2}|\uparrow\rangle \otimes |\uparrow\rangle + \tfrac{\hbar}{2}|\uparrow\rangle \otimes |\uparrow\rangle \\ &= \hbar|\uparrow\rangle \otimes |\uparrow\rangle \equiv \hbar|\uparrow\uparrow\rangle. \end{aligned} \tag{8}$$

   (a) Using Eq.(8) as a model, derive how $\hat{S}_z$ (total spin-z operator) acts on all of the triplet and singlet states.
   (b) Determine how the operators $\hat{S}_{1x} \otimes \hat{S}_{2x}$, $\hat{S}_{1y} \otimes \hat{S}_{2y}$, and $\hat{S}_{1z} \otimes \hat{S}_{2z}$ act on all the particle states in Eq.(4). (*Hint:* You should get 12 answers. It might help if your final answer is a table)
   (c) For the two particle state, we define the total-spin squared operator as

$$\begin{aligned}\hat{\mathbf{S}}^2 &\equiv \left(\hat{\mathbf{S}}_1 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{\mathbf{S}}_2\right)^2 \\ &= \hat{\mathbf{S}}_1^2 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{\mathbf{S}}_2^2 + 2\left(\hat{S}_{1x} \otimes \hat{S}_{2x} + \hat{S}_{1y} \otimes \hat{S}_{2y} + \hat{S}_{1z} \otimes \hat{S}_{2z}\right). \end{aligned} \tag{9}$$

   Given that $\mathbf{S}_1^2 = \hbar^2\frac{1}{2}(\frac{1}{2}+1)\mathbb{I}_1 = \frac{3\hbar^2}{4}\mathbb{I}_1$ and $\mathbf{S}_2^2 = \frac{3\hbar^2}{4}\mathbb{I}_2$, compute

$$\hat{\mathbf{S}}^2|1,1\rangle, \quad \text{and} \quad \hat{\mathbf{S}}^2|1,-1\rangle. \tag{10}$$

   (d) **Optional:** Compute $\hat{\mathbf{S}}^2|1,0\rangle$ and $\hat{\mathbf{S}}^2|0,0\rangle$.

2 Solution

1. (a) For the wave function

$$\psi(r,\theta,\phi) = \sqrt{\frac{1}{3}}R_{32}(r)Y_{20}(\theta,\phi)|+,\mathbf{z}\rangle + \sqrt{\frac{2}{3}}R_{21}(r)Y_{11}(\theta,\phi)|-,\mathbf{z}\rangle, \tag{11}$$

the possible values of ℓ are 2 and 1. In ket notation, the state can be represented as

$$|\psi\rangle = \sqrt{\frac{1}{3}}|3,2,0\rangle|+,\mathbf{z}\rangle + \sqrt{\frac{2}{3}}|2,1,1\rangle|-,\mathbf{z}\rangle. \tag{12}$$

Thus given the coefficients of the states and the eigenvalue equation $\hat{\mathbf{L}}^2|\ell,m\rangle = \hbar^2\ell(\ell+1)|\ell,m\rangle$ we find

$$\text{Prob }(\mathbf{L}^2 = 2\hbar^2) = \frac{2}{3}, \tag{13}$$

$$\text{Prob }(\mathbf{L}^2 = 6\hbar^2) = \frac{1}{3}. \tag{14}$$

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(b) Similarly to part (a) we find

$$\text{Prob }(L_z = \hbar) = \frac{2}{3}, \tag{15}$$

$$\text{Prob }(L_z = 0) = \frac{1}{3}. \tag{16}$$

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(c) Since we are dealing with a spin $\frac{1}{2}$ particle, the only unique eigenvalue of the $\hat{\mathbf{S}}^2$ operator is $\hbar^2\frac{1}{2}(1+\frac{1}{2}) = \frac{3\hbar^2}{4}$. Thus we have

$$\text{Prob }(\mathbf{S}^2 = 3\hbar^2/4) = 1. \tag{17}$$

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(d) The values of n in Eq.(12) are $n = 3$ and $n = 2$. Given that the energy eigenvalues of the electron in the hydrogen atom are $E_n = E_1/n^2$, we find the average energy of the state Eq.(12) is

$$\langle E\rangle = \frac{1}{3}\times\frac{E_1}{9} + \frac{2}{3}\times\frac{E_1}{4} = \frac{11E_1}{54}. \tag{18}$$

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2. (a) To compute how the spin operator $\hat{S}_z = \hat{S}_{1z}\otimes\mathbb{I}_2 + \mathbb{I}_1\otimes\hat{S}_{2z}$ acts on the states in Eq.(5), we express the triplet and singlet states in terms of their two-particle spin states. We thus find

$$\begin{aligned}
\hat{S}_z|1,1\rangle &= \left(\hat{S}_{1z}\otimes\mathbb{I}_2 + \mathbb{I}_1\otimes\hat{S}_{2z}\right)|\uparrow\rangle\otimes|\uparrow\rangle \\
&= \hat{S}_{1z}|\uparrow\rangle\otimes|\uparrow\rangle + |\uparrow\rangle\otimes\hat{S}_{2z}|\uparrow\rangle \\
&= \tfrac{\hbar}{2}|\uparrow\rangle\otimes|\uparrow\rangle + \tfrac{\hbar}{2}|\uparrow\rangle\otimes|\uparrow\rangle \\
&= \hbar|\uparrow\rangle\otimes|\uparrow\rangle = \hbar|1,1\rangle
\end{aligned}$$

$$
\begin{aligned}
\hat{S}_z|1,0\rangle &= \left(\hat{S}_{1z}\otimes\mathbb{I}_2+\mathbb{I}_1\otimes\hat{S}_{2z}\right)\left(\frac{1}{\sqrt{2}}|\uparrow\rangle\otimes|\downarrow\rangle-\frac{1}{\sqrt{2}}|\downarrow\rangle\otimes|\uparrow\rangle\right)\\
&= \frac{\hbar}{2\sqrt{2}}\Big(|\uparrow\rangle\otimes|\downarrow\rangle-|\downarrow\rangle\otimes|\uparrow\rangle-|\uparrow\rangle\otimes|\downarrow\rangle+|\downarrow\rangle\otimes|\uparrow\rangle\Big)=0\\
\hat{S}_z|1,-1\rangle &= \left(\hat{S}_{1z}\otimes\mathbb{I}_2+\mathbb{I}_1\otimes\hat{S}_{2z}\right)|\downarrow\rangle\otimes|\downarrow\rangle\\
&= \hat{S}_{1z}|\downarrow\rangle\otimes|\downarrow\rangle+|\downarrow\rangle\otimes\hat{S}_{2z}|\downarrow\rangle\\
&= \tfrac{\hbar}{2}|\downarrow\rangle\otimes|\downarrow\rangle+\tfrac{\hbar}{2}|\downarrow\rangle\otimes|\downarrow\rangle\\
&= \hbar|\downarrow\rangle\otimes|\downarrow\rangle=\hbar|1,-1\rangle\\
\hat{S}_z|0,0\rangle &= \left(\hat{S}_{1z}\otimes\mathbb{I}_2+\mathbb{I}_1\otimes\hat{S}_{2z}\right)\left(\frac{1}{\sqrt{2}}|\uparrow\rangle\otimes|\downarrow\rangle+\frac{1}{\sqrt{2}}|\downarrow\rangle\otimes|\uparrow\rangle\right)\\
&= \frac{\hbar}{2\sqrt{2}}\Big(|\uparrow\rangle\otimes|\downarrow\rangle+|\downarrow\rangle\otimes|\uparrow\rangle-|\uparrow\rangle\otimes|\downarrow\rangle-|\downarrow\rangle\otimes|\uparrow\rangle\Big)=0. \qquad (19)
\end{aligned}
$$

Given the interpretation of the triplet and singlet states as $|s,m\rangle$ states where s is the total spin quantum number and m is the quantum number for net spin in the z direction, these results are consistent with our expectations and the formula

$$\hat{S}_z|s,m\rangle=\hbar\, m|s,m\rangle. \qquad (20)$$

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(b) As an example, we compute how $\hat{S}_{1x}\otimes\hat{S}_{2x}$ acts on $|\uparrow\uparrow\rangle$. We find

$$
\begin{aligned}
\hat{S}_{1x}\hat{S}_{2x}|\uparrow\uparrow\rangle &= \left(\hat{S}_{1x}\otimes\hat{S}_{2x}\right)|\uparrow\rangle\otimes|\uparrow\rangle\\
&= \hat{S}_{1x}|\uparrow\rangle\otimes\hat{S}_{2x}|\uparrow\rangle\\
&= \frac{\hbar}{2}|\downarrow\rangle\otimes\frac{\hbar}{2}|\downarrow\rangle=\frac{\hbar^2}{4}|\downarrow\downarrow\rangle, \qquad (21)
\end{aligned}
$$

Repeating this calculation for all combinations of $\hat{S}_{1x}\otimes\hat{S}_{2x}$, $\hat{S}_{1y}\otimes\hat{S}_{2y}$, and $\hat{S}_{1z}\otimes\hat{S}_{2z}$ and the states in Eq.(4), we obtain the following table:

	$\hat{S}_{1x}\hat{S}_{2x}$	$\hat{S}_{1y}\hat{S}_{2y}$	$\hat{S}_{1z}\hat{S}_{2z}$
$\vert\uparrow\uparrow\rangle$	$\frac{\hbar^2}{4}\vert\downarrow\downarrow\rangle$	$-\frac{\hbar^2}{4}\vert\downarrow\downarrow\rangle$	$\frac{\hbar^2}{4}\vert\uparrow\uparrow\rangle$
$\vert\uparrow\downarrow\rangle$	$\frac{\hbar^2}{4}\vert\downarrow\uparrow\rangle$	$\frac{\hbar^2}{4}\vert\downarrow\uparrow\rangle$	$-\frac{\hbar^2}{4}\vert\uparrow\downarrow\rangle$
$\vert\downarrow\uparrow\rangle$	$\frac{\hbar^2}{4}\vert\uparrow\downarrow\rangle$	$\frac{\hbar^2}{4}\vert\uparrow\downarrow\rangle$	$-\frac{\hbar^2}{4}\vert\downarrow\uparrow\rangle$
$\vert\downarrow\downarrow\rangle$	$\frac{\hbar^2}{4}\vert\uparrow\uparrow\rangle$	$-\frac{\hbar^2}{4}\vert\uparrow\uparrow\rangle$	$\frac{\hbar^2}{4}\vert\downarrow\downarrow\rangle$

Table 1

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(c) Applying $\hat{\mathbf{S}}^2$ to the state $|1,1\rangle$, and using the result from (b), we find

$$\hat{\mathbf{S}}^2|1,1\rangle=\left[\hat{\mathbf{S}}_1^2\otimes\mathbb{I}_2+\mathbb{I}_1\otimes\hat{\mathbf{S}}_2^2+2\left(\hat{S}_{1x}\otimes\hat{S}_{2x}+\hat{S}_{1y}\otimes\hat{S}_{2y}+\hat{S}_{1z}\otimes\hat{S}_{2z}\right)\right]|\uparrow\rangle\otimes|\uparrow\rangle$$

$$
\begin{aligned}
&= \frac{3\hbar^2}{2}|\uparrow\uparrow\rangle + \frac{\hbar^2}{2}\left(|\downarrow\downarrow\rangle - |\downarrow\downarrow\rangle + |\uparrow\uparrow\rangle\right) \\
&= \frac{3\hbar^2}{2}|\uparrow\uparrow\rangle + \frac{\hbar^2}{2}|\uparrow\uparrow\rangle = 2\hbar^2|1,1\rangle.
\end{aligned} \tag{22}
$$

And, similarly, applying $\hat{\mathbf{S}}^2$ to the state $|1,-1\rangle$ gives us

$$
\begin{aligned}
\hat{\mathbf{S}}^2|1,-1\rangle &= \left[\hat{\mathbf{S}}_1^2 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{\mathbf{S}}_2^2 + 2\left(\hat{S}_{1x} \otimes \hat{S}_{2x} + \hat{S}_{1y} \otimes \hat{S}_{2y} + \hat{S}_{1z} \otimes \hat{S}_{2z}\right)\right] |\downarrow\rangle \otimes |\downarrow\rangle \\
&= \frac{3\hbar^2}{2}|\downarrow\downarrow\rangle + \frac{\hbar^2}{2}\left(|\uparrow\uparrow\rangle - |\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle\right) \\
&= \frac{3\hbar^2}{2}|\downarrow\downarrow\rangle + \frac{\hbar^2}{2}|\downarrow\downarrow\rangle = 2\hbar^2|1,-1\rangle.
\end{aligned} \tag{23}
$$

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(d) Applying $\hat{\mathbf{S}}^2$ to the state $|1,0\rangle$, we have

$$
\begin{aligned}
\hat{\mathbf{S}}^2|1,0\rangle &= \left[\hat{\mathbf{S}}_1^2 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{\mathbf{S}}_2^2 + 2\left(\hat{S}_{1x} \otimes \hat{S}_{2x} + \hat{S}_{1y} \otimes \hat{S}_{2y} + \hat{S}_{1z} \otimes \hat{S}_{2z}\right)\right] \\
&\quad \left(\frac{1}{\sqrt{2}}|\uparrow\rangle \otimes |\downarrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\rangle \otimes |\uparrow\rangle\right) \\
&= \frac{3\hbar^2}{2}\left(\frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle\right) + \frac{\hbar^2}{2\sqrt{2}}\Big(|\downarrow\uparrow\rangle + |\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle + |\uparrow\downarrow\rangle + |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big) \\
&= \frac{3\hbar^2}{2}\left(\frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle + \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle\right) + \frac{\hbar^2}{2}\left(\frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle + \frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle\right) = 2\hbar^2|1,0\rangle.
\end{aligned} \tag{24}
$$

And, similarly, applying $\hat{\mathbf{S}}^2$ to the state $|0,0\rangle$ gives us

$$
\begin{aligned}
\hat{\mathbf{S}}^2|0,0\rangle &= \left[\hat{\mathbf{S}}_1^2 \otimes \mathbb{I}_2 + \mathbb{I}_1 \otimes \hat{\mathbf{S}}_2^2 + 2\left(\hat{S}_{1x} \otimes \hat{S}_{2x} + \hat{S}_{1y} \otimes \hat{S}_{2y} + \hat{S}_{1z} \otimes \hat{S}_{2z}\right)\right] \\
&\quad \left(\frac{1}{\sqrt{2}}|\uparrow\rangle \otimes |\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\rangle \otimes |\uparrow\rangle\right) \\
&= \frac{3\hbar^2}{2}\left(\frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle\right) + \frac{\hbar^2}{2\sqrt{2}}\Big(|\downarrow\uparrow\rangle + |\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\Big) \\
&= \frac{3\hbar^2}{2}\left(\frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle\right) + \frac{3\hbar^2}{2}\left(\frac{1}{\sqrt{2}}|\downarrow\uparrow\rangle - \frac{1}{\sqrt{2}}|\uparrow\downarrow\rangle\right) = 0.
\end{aligned} \tag{25}
$$

The results of (c) and (d) are consistent with the interpretation of the state $|s,m\rangle$ as representing a particle of spin $s=1$ or $s=0$. In particular all of the results are special cases of the eigenvalue-eigenket relation

$$
\hat{\mathbf{S}}^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle. \tag{26}
$$

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References