G25.2666: Quantum Chemistry and Dynamics

Notes for Lecture 5

I. EXPERIMENTAL EVIDENCE FOR ELECTRON SPIN

Up to now, we have considered quantum particles to have three degrees of freedom, x, y, and z. This, then, leads to three quantum numbers that characterize the states. For example, in a central potential, the three quantum numbers are n, l and m, the radial, total angular momentum, and z-component of angular momentum numbers, respectively.

However, there is substantial experimental evidence to suggest that there are additional degrees of freedom still missing from this simple picture that need to be accounted for. Some of this evidence will be reviewed below.

A. Fine structure of spectral lines

Recall that the energy levels of a hydrogen atom are given by

$$E_n = -\frac{13.6\ \text{eV}}{n^2} \qquad n = 1, 2, ..., \infty$$

This will give rise to a series of spectral lines at a set of allowed transition frequencies when the electron in the atom is excited.

$$\omega_{n_i \to n_f} = \frac{E_{n_i} - E_{n_f}}{\hbar}$$

Here, n_i and n_f represent the initial energy level to which the electron is excited and n_f represents the final level to which it decays. In the decay process, electromagnetic radiation is emitted which can be detected in a spectrometer.

If one examines, the Lyman spectrum, for example, which corresponds to $n_f = 1$ and produces spectral lines in the ultraviolet part of the electromagnetic spectrum, one finds that the individual lines are actually several lines of nearly identical frequency. For example, the $2p \longrightarrow 1s$ transition is actually a doublet, with the two components being separated by $\sim 10^{-4}$ eV which is also on the order of a few tens of wavenumbers, which is about 10^5 times smaller than the splitting predicted from the formula, i.e., 10.2 eV. Clearly, the simple theory based on the above formulae is not sufficient to explain the multiplicity of lines actually observed.

B. Anomalous Zeeman effect

When an atom is placed in a magnetic field, each of its fine structure lines further splits into a series of equidistant lines with a spacing proportional to the magnetic field strength.

Theoretically, this is explained by recognizing that the electron has an orbital magnetic moment

$$\mathbf{M} = \frac{\mu_{\text{B}}}{\hbar}\mathbf{L}$$

where $\mathbf{L}$ is the angular momentum operator, μ_B is the Bohr magneton

$$\mu_{\text{B}} = \frac{e\hbar}{m_{\text{e}}}$$

The orbital magnetic moment gives rise to an interaction with a magnetic field proportional to $\mathbf{M}\cdot\mathbf{B}$, where $\mathbf{B}$ is the magnetic field vector.

This interaction gives rise to the so called *normal Zeeman effect.* The normal Zeeman effect would predict a number of lines equal to $(2l + 1)$, the number of L_z eigenvalues. Note that, since l must be an integer, this number is always *odd.*

However, there is an *anomalous Zeeman effect* which shows up particularly for atoms with odd atomic number Z (hydrogen, for example). In such cases, it is found that the number of Zeeman sub-levels is actually **even** rather than **odd**. This cannot be explained within the normal Zeeman theory. However, it suggests the possible existence of an angular momentum like quantity that can take on half-integer values.

C. Evidence for half-integer "angular momentum"

If a beam of neutral, paramagnetic atoms, such as silver atoms, is shot through a magnetic field, the beam can be split into two beams by the field as shown below:

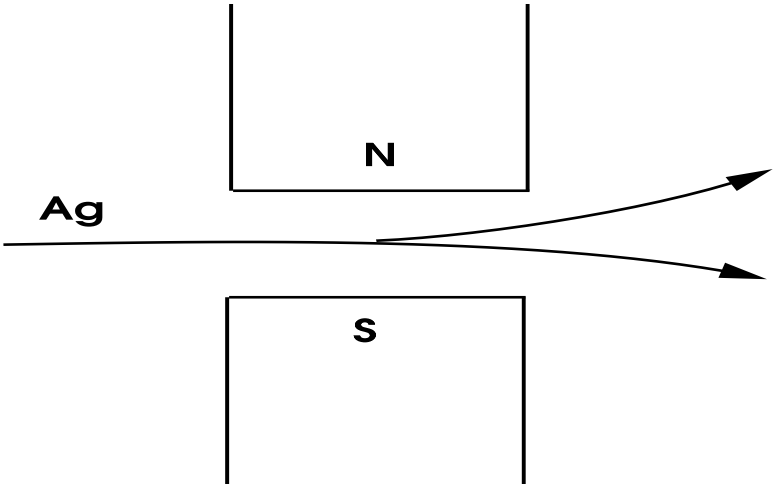

FIG. 1.

This is known as a *Stern-Gerlach* experiment. The fact that the magnetic field can split the beam into two suggests that there must be some intrinsic property that couples to the magnetic field like an angular momentum but that can take on half-integer values. This cannot be an orbital angular momentum, since l can only take on integral values.

D. The Uhlenbeck and Goudsmit proposal

In 1925, Uhlenbeck and Goudsmit postulated the existence of a new intrinsic property of particles that behaved like an angular momentum as a means of explaining these results. This intrinsic property was later termed *spin* by Pauli, however, the image of a spinning sphere is not likely an accurate one. This new property needs to be viewed as an intrinsic property like mass and charge that is particular to a given type of particle. Note that, unlike mass and charge, there is no classical analog to spin!

As we will see, it was Dirac who later showed that spin arises very naturally in a correct relativistic formulation of the quantum theory. This formulation is embodied in the relativistic generalization of the Schrödinger equation called the *Dirac equation*.

According to the Uhlenbeck and Goudsmit proposal, the spin of a particle should behave like an angular momentum and, therefore, should have an associated magnetic moment

$$\mathbf{M}_s = \frac{g\mu_{\rm B}}{\hbar}\mathbf{S}$$

where $\mathbf{S}$ is the *spin operator*. g is a constant introduced to produce the best fit with experiment. The interaction with a magnetic field is proportional to $\mathbf{M}_s \cdot \mathbf{B}$, which is the basis of the NMR technique. It is found that good fits to experimental data are obtained when $g = 2$, which means that the *spin gyromagnetic ratio*, defined to be $g\mu_{\rm B}/\hbar$ is twice as large as the *orbital gyromagnetic ratio* $\mu_{\rm B}/\hbar$.

II. AMENDING THE POSTULATES OF QUANTUM MECHANICS TO INCLUDE SPIN

It was Pauli who formalized the incorporation of spin into the non-relativistic framework of quantum mechanics. In order to do this, he needed to supplement the fundamental postulates of quantum mechanics with a few new ones. These are discussed below:

1. To the position **R** and momentum **P** operators describing a particle, we now add the variable **S**, which is a vector of operators

   $$\mathbf{S} = (S_x, S_y, S_z)$$

   These operators satisfy the commutation rules of an angular momentum, namely

   $$\begin{aligned} [S_x, S_y] &= i\hbar S_z \\ [S_y, S_z] &= i\hbar S_x \\ [S_z, S_x] &= i\hbar S_y \end{aligned}$$

   This is an example of a *Lie algebra.* More generally, a Lie algebra is defined by the condition that a set of n operators $X_1, ..., X_n$ obey commutation relations of the form

   $$[X_i, X_j] = \sum_i C_{ijk} X_k$$

   In the above, the operators X_i constitute the *generators* of a *Lie group* and the constants C_{ijk} are called the *structure constants* of the group.

   In the case of the spin operators, the commutation relations can be written compactly in terms of a vector cross product as

   $$\mathbf{S} \times \mathbf{S} = i\hbar \mathbf{S}$$

   which can also be written as

   $$[S_i, S_j] = i\hbar \sum_k \epsilon_k S_k$$

   Here, ϵ_{ijk} is called the *Levi-Civita* tensor and is defined by

   $$\begin{aligned} \epsilon_{ijk} &= 1 && \text{if } ijk \text{ is a cyclic permutation of 123} \\ &= -1 && \text{if } ijk \text{ is a cyclic permutation of 321} \\ &= 0 && \text{otherwise} \end{aligned}$$

   The ϵ_{ijk} are the structure constants of the spin Lie algebra.

2. Like an angular momentum, there will be a Hilbert space $\mathcal{H}_s$ associated with spin which supports the spin eigenstates. Like an angular momentum, a set of basis vectors for this Hilbert space can be constructed out of simultaneous eigenvectors of the operators $S^2 = |\mathbf{S}|^2$ and S_z. The associated eigenvalues s and m_s satisfy the eigenvalue equations

   $$\begin{aligned} S^2 |s\ m_s\rangle &= s(s+1)\hbar^2 |s\ m_s\rangle \\ S_z |s\ m_s\rangle &= m_s \hbar |s\ m_s\rangle \end{aligned}$$

   Here, $|s\ m_s\rangle$ are the simultaneous eigenstates which satisfy

   $$\langle s\ m_s | s\ m_{s'}\rangle = \delta_{m_s m_s'}$$

   Here, also,

   $$S^2 = S_x^2 + S_y^2 + S_z^2$$

   satisfies

   $$\left[S^2, S_z\right] = \left[S^2, S_y\right] = \left[S^2, S_z\right] = 0$$

   and is an example of what is called a *Casimir* operator. Generally, a Casimir operator is any operator which commutes with all members of the group. In the case, the members are just S_x, S_y and S_z.

3. The spin Hilbert space $\mathcal{H}_s$ must be joined to the Hilbert space $\mathcal{H}_r$ associated with the classical variables $\mathbf{R}$ and $\mathbf{P}$. This is done by forming a direct product or tensor product space:

$$\mathcal{H} = \mathcal{H}_r \bigotimes \mathcal{H}_s$$

so that the spin variables commute with the $\mathbf{R}$ and $\mathbf{P}$:

$$[S_i, R_j] = [S_i, P_j] = 0$$

Now it can be seen that complete sets of commuting observables (CSCOs) which are used to describe a particle, e.g.,

$$\{X, Y, Z, S^2, S_z\} \qquad \{P_x, P_y, P_z, S^2, S_z\}$$

or, for spherically symmetric potentials:

$$\{H, L^2, L_z, S^2, S_z\}$$

where H is the Hamiltonian. Thus, now *five* observables are needed to describe a particle. This means that there will be *five* associated quantum numbers. For a spherically symmetric potential independent of spin, these would then be n, l, m, s, m_s.

4. The spin of a particle can take on half-integer values. In particular, the electron is a spin-$\frac{1}{2}$ particle ($s = 1/2$) with two m_s values $-1/2$ and $1/2$ so that, for an electron, the Hilbert space is two-dimensional.

III. EXPLICIT DESCRIPTION OF SPIN-1/2

The Hilbert space of a spin-1/2 particle is two-dimensional. Moreover, m_s, the S_z eigenvalue, can take on two values $-1/2$ and $1/2$. Therefore, S_z should be represented by a 2×2 matrix. If we choose to work in a basis in which S_z is diagonal, then as a matrix, it will be given by

$$S_z = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix}$$

The two eigenvectors are

$$\left| m_s = \frac{1}{2} \right\rangle \equiv \left| \frac{1}{2} \right\rangle . = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$\left| m_s = -\frac{1}{2} \right\rangle \equiv \left| -\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

These clearly satisfy

$$\left\langle \frac{1}{2} \middle| \frac{1}{2} \right\rangle = \left\langle -\frac{1}{2} \middle| -\frac{1}{2} \right\rangle = 1$$
$$\left\langle \frac{1}{2} \middle| -\frac{1}{2} \right\rangle = \left\langle -\frac{1}{2} \middle| \frac{1}{2} \right\rangle = 0$$

Thus, they form an orthonormal set of vectors and span the Hilbert space $\mathcal{H}_s$. The other spin operators are

$$S_x = \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} \qquad S_y = \begin{pmatrix} 0 & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & 0 \end{pmatrix}$$

It is straightforward to show that these satisfy the commutation relations $\mathbf{S} \times \mathbf{S} = i\hbar\mathbf{S}$ and both have eigenvalues $\pm\hbar/2$.

Let us use these to calculate the Casimir operator S^2:

$$\begin{aligned}
S^2 &= S_x^2 + S_y^2 + S_z^2 \\
&= \frac{\hbar^2}{4}\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right] \\
&= \frac{\hbar^2}{4}\left[\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \\
&= \begin{pmatrix} \frac{3}{4}\hbar^2 & 0 \\ 0 & \frac{3}{4}\hbar^2 \end{pmatrix}
\end{aligned}$$

Note, however, that

$$s(s+1)\hbar^2 = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 = \frac{3}{4}\hbar^2$$

Also, $\left|\frac{1}{2}\right\rangle$ and $\left|-\frac{1}{2}\right\rangle$ are eigenvectors of S^2, both with eigenvalues $3\hbar^2/4$. Finally, since

$$S^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

it is clear that S^2 commutes with S_x, S_y and S_z as expected for a Casimir operator.
Thus, the spin states are most generally denoted as

$$\begin{aligned}
|s\ m_s\rangle = \left|\frac{1}{2}\ \ \frac{1}{2}\right\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\
= \left|\frac{1}{2}\ \ -\frac{1}{2}\right\rangle &= \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\end{aligned}$$

It is also possible to change from one spin state to another by means of the *raising* and *lowering* operators, which are defined by

$$\begin{aligned}
\hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} &= S_x + iS_y = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\
\hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} &= S_x - iS_y = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}
\end{aligned}$$

which satisfy the following commutation rules:

$$\begin{aligned}
[S_+, S_-] &= 2S_z \\
[S_+, S_z] &= -\frac{\hbar}{2}S_- \\
[S_-, S_z] &= \frac{\hbar}{2}S_+
\end{aligned}$$

and additionally:

$$\begin{aligned}
S^2 &= \frac{1}{2}\left(S_+S_- + S_-S_+\right) + S_z^2 \\
&= \frac{1}{2}\left[S_+, S_-\right]_+ + S_z^2
\end{aligned}$$

where $[A,B]_+$ denotes the *anticommutator* between A and B defined to be $AB + BA$.

The action of the raising (S_+) and lowering (S_-) operators on the states can be worked out straightforwardly:

$$
\begin{aligned}
S_+\left|\frac{1}{2}\ \frac{1}{2}\right\rangle &= \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = 0\\
S_+\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle &= \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} = \hbar\begin{pmatrix}1\\ 0\end{pmatrix} = \hbar\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\\
S_-\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle &= \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} = 0\\
S_-\left|\frac{1}{2}\ \frac{1}{2}\right\rangle &= \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \hbar\begin{pmatrix}0\\ 1\end{pmatrix} = \hbar\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle
\end{aligned}
$$

Generally, for spin-1/2,

$$
\begin{aligned}
S_+|s\ m_s\rangle &= \hbar|s\ m_s+1\rangle\\
S_-|s\ m_s\rangle &= \hbar|s\ m_s-1\rangle
\end{aligned}
$$

It is customary to define the spin operators in terms of the so called *Pauli matrices*

$$
\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad \sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}
$$

such that

$$
\mathbf{S} = \frac{\hbar}{2}\sigma
$$

The Pauli matrices satisfy the following properties

$$
\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}^2 = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}^2 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}^2 = \mathrm{I}
$$

1.

2. Anticommutation:

$$
[\sigma_i, \sigma_j]_+ = 0 \qquad \text{for } i \neq j
$$

3. Commutation:

$$
\sigma \times \sigma = 2i\sigma
$$

4. Cyclic multiplication:

$$
\sigma_x\sigma_y = i\sigma_z \qquad \sigma_y\sigma_z = i\sigma_x \qquad \sigma_z\sigma_x = i\sigma_y
$$

5. Tracelessness:

$$
\mathrm{Tr}(\sigma_i) = 0
$$

6. Determinant:

$$\det(\sigma_i) = -1$$

7. The Pauli matrices plus the identity matrix form a kind of “basis” in the space of all possible 2×2 matrices. Thus, any 2×2 matrix, A can be expressed as a linear combination of σ and I:

$$\mathrm{A} = \alpha_0 \mathrm{I} + \sum_{j=x,y,z} \alpha_j \sigma_j$$

   where α_0, α_x, α_y and α_z can, in general, be complex numbers.

8. Finally, for two arbitrary vectors **a** and **b**, the following identity can be proven:

$$(\sigma \cdot \mathbf{a})\,(\sigma \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\sigma \cdot (\mathbf{a} \times \mathbf{b})$$