Notes for Lecture 6

Symmetry and conservation

We are now through with the full theory of the time independent perturbation. The degenerate perturbation has an intimate link to the *symmetry*, the topic that we will explore a bit. Students at this level are expected to be aware of symmetry issues and be competent in deriving economical solutions by making use of symmetry properties.

6.1 Symmetry—the art of physics

To clearly define what we mean by symmetry, we can start from its mundane meaning. If we say that something is symmetric, then it usually carries the connotation of beauty. Usually, "beauty" seems to require some repetition. I remember reading an article that said that a left-right symmetric face is more beautiful. Whether you agree with it or not, there is that notion of symmetry. One might argue that we look for repeating patterns and find them beautiful—we find flowers with a five-fold rotational symmetry, and fern leaves with "scale invariance." Artistic work often employ repeating patterns, also. Musical pieces are repetitive, as a rule, and some even have a forward-backward symmetry (crab canon). Viewed this way, we can summarize the word "symmetry" to mean that something is invariant under reflection, rotation, translation, or some other operation: it means **an invariance under a mathematical transformation**.

The notion of symmetry in physics is basically the same. Perhaps one distinction that one needs to keep in mind is that the object of beauty is the physical law when physicists speak of symmetry. When physicists make a statement that "the world/system is symmetric," it means that the law of physics is valid in any reference frame, at any point of space, at any point of time, and in any orientation. How do we know so? We know so because of reproducible experiments, which make science possible in the first place. Please read more extensive discussion about symmetry in `https://griffin.ucsc.edu/ph105-11/Lecture%2B?action=AttachFile&do=get&target=L09-Sym-Cons%2B.pdf`.

6.2 Symmetry in quantum mechanics

How do we describe symmetry in quantum mechanics?

Let us take an example of translation for a one dimensional system (x for position and p for momentum). In Section 2.1.4, we learned (Eq. 2.49) that a translation operator is given by $\hat{\mathcal{T}}(\Delta x) = \exp\left(-i\hat{p}\Delta x/\hbar\right)$. By this we meant that

$$\left\langle x \left| \hat{\mathcal{T}}(\Delta x) \right| \Psi \right\rangle = \langle x - \Delta x \,|\, \Psi \rangle = \Psi(x - \Delta x) \tag{6.1}$$

Since the first equality is true for any Ψ, we get this vector identity

$$\langle x | \hat{\mathcal{T}}(\Delta x) = \langle x - \Delta x | \tag{6.2}$$

$$\hat{\mathcal{T}}^\dagger(\Delta x) \, |x\rangle = |x - \Delta x\rangle \qquad \text{The Hermitian conjugte}$$

$$\hat{\mathcal{T}}(\Delta x) \, |x\rangle = |x + \Delta x\rangle \qquad \Delta x \to -\Delta x\text{: } \hat{\mathcal{T}}^\dagger(-\Delta x) = (\hat{\mathcal{T}}^\dagger)^{-1}(\Delta x) = (\hat{\mathcal{T}}^{-1})^{-1}(\Delta x) = \hat{\mathcal{T}}(\Delta x). \tag{6.3}$$

The last result is intuitively clear. By translation, we take a position eigenstate at x and move it to a position eigenstate $x + \Delta x$. This completely specifies the coordinate transformation that we call "translation," since it specifies completely how each state of a natural basis set (position eigenstates) transforms. Indeed, we could have used Eq. 6.3 to define what we mean by "translation," instead of Eq. 6.1.

Now, consider an operator $\hat{O}$, and let us ask the question: "how does $\hat{O}$ transform by $\hat{\mathcal{T}}(\Delta x)$?" This question, one of the most basic questions of Linear Algebra, is simple to answer. By definition, $\left|\hat{O}\Psi\right\rangle$ is a ket vector, and it must transform to $\hat{\mathcal{T}}(\Delta x)\left|\hat{O}\Psi\right\rangle$. Since, $|O\Psi\rangle \equiv \hat{O}\,|\Psi\rangle$ by definition, we see that

$$\begin{aligned}
\hat{O}\,|\Psi\rangle &\to \hat{\mathcal{T}}(\Delta x)\hat{O}\,|\Psi\rangle \\
&= \hat{\mathcal{T}}(\Delta x)\hat{O}\hat{\mathcal{T}}^{-1}(\Delta x)\hat{\mathcal{T}}(\Delta x)\,|\Psi\rangle \\
&= \hat{\mathcal{T}}(\Delta x)\hat{O}\hat{\mathcal{T}}^{-1}(\Delta x)\left|\hat{\mathcal{T}}(\Delta x)\Psi\right\rangle
\end{aligned}$$

So, we find that the operator transforms $\hat{O} \to \hat{\mathcal{T}}(\Delta x)\hat{O}\hat{\mathcal{T}}^{-1}$. This transformation property, involving the inverse of $\hat{\mathcal{T}}$, remains correct even if $\hat{\mathcal{T}}$ were not a unitary operator. However, $\hat{\mathcal{T}}$ *is* unitary, and so we get the following (more useful) result

$$\hat{O} \to \hat{\mathcal{T}}(\Delta x)\,\hat{O}\,\hat{\mathcal{T}}^\dagger(\Delta x) \tag{6.4}$$

We can generalize this result as

$$\hat{O} \to \hat{U}(u)\,\hat{O}\,\hat{U}^\dagger(u) \qquad \text{for } \textit{any} \text{ unitary operator } \hat{U}(u)\text{: } |\Psi\rangle \to \hat{U}(u)\,|\Psi\rangle \tag{6.5}$$

Note that from this result one can prove immediately that **the scalar quantity $\langle \alpha \,|\hat{O}|\, \beta \rangle$ is invariant under a unitary operator (cf. page 14 of LN 2)**. The proof is left for your exercise.

In the above equation, the symbol u is the amount of transformation, e.g. the translation amount Δx, or the rotation amount $\Delta\theta$. Note that

$$\hat{U}^\dagger(u) \;=\; \hat{U}^{-1}(u) \;=\; \hat{U}(-u) \tag{6.6}$$

For certain discrete transformation such as reflection, inversion, or particle exchange, the use of symbol u is totally unnecessary—in such a case, $\hat{U}$ is a Hermitian operator, whose inverse is itself.

Note that another way to get the above result is the following. Let us assume that the basis is a continuum set with each eigenvector labelled by x, while a mixed case or a discrete case can be dealt with as easily (the generalization to those cases is left for your exercise; cf. LN 1, page 8).

$$\hat{O} \;=\; \left[\int dx_1\, |x_1\rangle\langle x_1|\right]\hat{O}\left[\int dx_2\, |x_2\rangle\langle x_2|\right] \qquad [...] = 1 \text{ (resolution of identity)} \tag{6.7}$$

$$=\; \int dx_1 \int dx_2\, |x_1\rangle \langle x_1 \,|\hat{O}|\, x_2\rangle \langle x_2| \qquad \hat{O}\text{, by itself, is } \textit{not} \text{ a function of } x_1, x_2 \tag{6.8}$$

$$=\; \int dx_1 \int dx_2\, O(x_1,x_2)\; |x_1\rangle\langle x_2| \qquad O(x_1,x_2) \equiv \langle x_1\,|\hat{O}|\,x_2\rangle \tag{6.9}$$

Here, the fact that $\hat{O}$, by itself, cannot be a function of x_1, x_2 is used. As we covered in LN 2, an unrepresented state can be a function of t, at the most: the same is true for an unrepresented operator $\hat{O}$.

The last expression makes it clear that an operator $\hat{O}$ must transform like $|x_1\rangle\langle x_2|$, *if* we assume that $O(x_1, x_2)$ is a scalar under the transformation. So, if $|x\rangle \to \hat{U}\,|x\rangle$, then $\hat{O} \to \hat{U}\hat{O}\hat{U}^\dagger$.

Now, the reason why we have done this dry math so far in this section is because of the following non-dry essential physics.

If a system is invariant under a symmetry operator $\hat{U}(u)$, which we assume to be unitary, then it means that the Hamiltonian $\hat{H}$ of the system satisfies

$$\hat{U}(u)\,\hat{H}\,\hat{U}^\dagger(u) = \hat{H} \qquad (6.10)$$

In the case when the Hamiltonian has a counter part in classical mechanics, it is *not* necessary to use this QM definition to see if the Hamiltonian has a certain symmetry. If the classical form of Hamiltonian has a certain symmetry, the symmetry will be preserved in the quantum form. This is because the symmetry principle is a bigger principle than classical mechanics or quantum mechanics.

For instance, the free particle Hamiltonian $\hat{H} = \hat{p}^2/(2m)$ with $p \doteq -i\hbar\frac{\partial}{\partial x}$ is translationally invariant. The classical Hamiltonian is simply $H = p^2/(2m)$, with $p = mv$. In classical mechanics, the translational invariance can be established with the fact that $v = dx/dt = d(x - x_0)/dt$ for any constant x_0. In quantum mechanics, it is established with the fact that $p \doteq -i\hbar\frac{\partial}{\partial x} = -i\hbar\frac{\partial}{\partial(x-x_0)}$ for any constant x_0 (see below, for why we use $x - x_0$, instead of $x + x_0$). It is perfectly fine to use either argument to make the same conclusion regarding the symmetry.

The free particle Hamiltonian in three dimensions $\hat{H} = \hat{\vec{p}}^2/(2m)$ is rotationally invariant, in addition. Its classical mechanics counter part, $H = \vec{p}^2/(2m) = \vec{p}\cdot\vec{p}/(2m)$, is clearly rotationally invariant, since $\vec{p}$ is a vector and $\vec{p}\cdot\vec{p}$ is a scalar product, invariant under any rotation. In the QM case, $\vec{p}^2 \doteq -\hbar^2\nabla^2$, which is again a scalar product, implying that the free particle Hamiltonian is rotationally invariant.

These scalar products defined in the real space are invariant under reflection as well. That is, if $x \to -x$, then $p_x \to -p_x$ and p_x^2 remains invariant, and thus $\vec{p}\cdot\vec{p}$ is preserved under $x \to -x$, and similarly under other reflections. This is the so-called "**parity** symmetry."

It is of course possible to apply the criterion, Eq. 6.10, in a very strict QM manner to *any* QM problem. In simple cases, we can use the space representation of Eq. 6.10 to make our judgement. For instance, if $\hat{U} = \hat{\mathcal{T}}(x_0)$ then $\left\langle x \left| \hat{U}\,\hat{H}\,\hat{U}^\dagger \right| x' \right\rangle = \left\langle \hat{U}^\dagger x \left| \hat{H} \right| \hat{U}^\dagger x' \right\rangle = \left\langle \hat{\mathcal{T}}(-x_0)x \left| \hat{H} \right| \hat{\mathcal{T}}(-x_0)x' \right\rangle = \left\langle x - x_0 \left| \hat{H} \right| x' - x_0 \right\rangle$, which means that the real space representation of the translated Hamiltonian is obtained by simply making the substitution[1] $x \to x - x_0$. So, if $\hat{H} \doteq -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$, then when the system

[1] In this course, we will deal mostly with cases where $\hat{H}$ is diagonal in the real space representation, $\left\langle x \left| \hat{H} \right| x' \right\rangle = h(x)\delta(x - x')$. For the general case when $\hat{H}$ is not diagonal in the real space representation, we must, of course, make the substitution $x' \to x' - x_0$ as well.

is translated by x_0, the Hamiltonian transforms to $\hat{H} \doteq -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial(x-x_0)^2} + V(x-x_0) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x-x_0)$. So, it is plain to see that any non-zero potential $V(x)$ will break the translational symmetry along the x direction.

This usage of Eq. 6.10 is arguably inelegant, while it is fine to use, since a simple classical mechanical argument would have sufficed and since it requires the use of a representation. Arguably, the *elegant usage* of Eq. 6.10 involves the **commutator algebra**, which applies to any QM problem, including those ones without any classical analog, and for which no representation need be invoked. For instance, consider the free Hamiltonian $\hat{H} = \hat{p}^2/(2m)$. And, consider the operator for translation by x_0, $\hat{\mathcal{T}}(x_0) = \exp(-i\hat{p}x_0/\hbar)$. As we saw above, upon translation $\hat{H} \to \hat{\mathcal{T}}(x_0)\hat{H}\hat{\mathcal{T}}^\dagger(x_0)$. Since $\hat{\mathcal{T}}(x_0)$ is a function of $\hat{p}$ only[2], and since $\hat{p}$ commutes with itself or any function of itself, it follows that $\hat{\mathcal{T}}(x_0)$ commutes with the free particle Hamiltonian $\hat{H}$, and thus $\hat{H} \to \hat{\mathcal{T}}(x_0)\hat{H}\hat{\mathcal{T}}^\dagger(x_0) = \hat{H}\hat{\mathcal{T}}(x_0)\hat{\mathcal{T}}^\dagger(x_0) = \hat{H}$, proving the translational invariance. **Now, this is elegant!**

By the same token, $\hat{H} = \hat{\vec{p}}^2/(2m)$ is invariant under any rotation, since $\hat{\vec{p}}^2$ commutes with $\hat{L}_x$, $\hat{L}_y$ or $\hat{L}_z$, and a rotation operator is a function of these three angular momentum operators. Another example, $\hat{H} = \hat{\vec{p}}^2/(2m) + V(\hat{r})$, (central potential), also possess the full rotational symmetry, since[3] $\hat{r} \equiv \sqrt{\hat{\vec{r}}^2} = \sqrt{\hat{x}^2 + \hat{y}^2 + \hat{z}^2}$ commutes with all angular momentum operators, as well. As another example, if $\hat{H} = \hat{\vec{p}}^2/(2m) + V(\hat{z})$, then $\hat{H}$ commutes with $\hat{L}_z$, but not $\hat{L}_x$ or $\hat{L}_y$: in this case we have a cylindrically symmetric problem where the rotational symmetry is limited to the rotation around the z axis only. In this discussion of commutators, I have implicitly used the (well-known) commutation relations $\left[\hat{L}_j, \hat{p}_k\right] = i\hbar\sum_l \epsilon_{jkl}\hat{p}_l$ and $\left[\hat{L}_j, \hat{x}_k\right] = i\hbar\sum_l \epsilon_{jkl}\hat{x}_l$, where each of j, k, l can take the value of 1, 2, or 3 corresponding to x, y, or z, respectively (e.g., $\hat{x}_1 \equiv \hat{x}$, $\hat{x}_2 \equiv \hat{y}$, and $\hat{x}_3 \equiv \hat{z}$), and ϵ_{ijk} is the Levi-Civita symbol. **Exercise**: prove these commutation relations, starting from the canonical commutator $[\hat{x}_j, \hat{p}_k] = i\hbar\delta_{j,k}$ and the definition $\hat{\vec{L}} = \hat{\vec{x}} \times \hat{\vec{p}}$, and, then, prove subsequently that $\left[\hat{L}_j, \hat{\vec{p}}^2\right] = 0 = \left[\hat{L}_j, \hat{\vec{r}}^2\right]$.

Now, let us consider a case involving spin, for which no analog exists in classical mechanics. For the Larmor precession problem (Section 4.2.2), we can write

$$\hat{H} = \omega_L \hat{S}_z \tag{6.11}$$

where ω_L is the Larmor frequency. Recalling the fundamental commutation relation $\left[\hat{S}_j, \hat{S}_k\right] = i\hbar\sum_l \epsilon_{jkl}\hat{S}_l$, and recalling that the spin rotation operator is given by

[2] Of course, $\hat{\mathcal{T}}(\Delta x)$ is also a function of Δx, but that is just a number. Here, we are concerned only with operator algebra.

[3] Please keep in mind that, in this course, I (intend to) *never* use $\hat{x}$, $\hat{r}$, etc., to mean ordinary unit vectors in the Cartesian coordinate system of space. For those unit vectors, I use $\vec{e}_1, \vec{e}_r$ etc. In this course, anything with a hat (ˆ) is a quantum mechanical *operator* (cf. LN 1, page 5).

$\exp\left(-i\theta\hat{S}_\theta/\hbar\right)$ (Eq. 2.50 and the discussion below it), we see that this Hamiltonian has a cylindrical symmetry in the spin space—it is invariant under rotation of spin around the z axis, but not under any other rotation. Put simply, this Hamiltonian commutes with $\hat{S}_z$, but not with $\hat{S}_x, \hat{S}_y$, and so it is invariant under rotation of spin around the z axis, but not around the x or y axis.

What we covered in this section can be summarized as follows.

How to test the symmetry of a quantum system

Let us assume that a unitary operator $\hat{U}$ represents the symmetry that we like to test.

1. If there is a classical mechanics Hamiltonian (H_c) that corresponds to the quantum Hamiltonian in question, then study the symmetry of H_c, by all means. You get the same answer about the symmetry of the system, by doing so, and it is generally easier to do it the classical way.

2. Test $\hat{U}\hat{H}\hat{U}^\dagger \stackrel{?}{=} \hat{H}$ (Eq. 6.10) by asking $\hat{U}\hat{H} \stackrel{?}{=} \hat{H}\hat{U}$, i.e. $\left[\hat{H}, \hat{U}\right] \stackrel{?}{=} 0$. If the answer is yes, then the system has the symmetry. If $\hat{U}$ is translation, then the testing is equivalent to asking $\left[\hat{H}, \hat{p}\right] \stackrel{?}{=} 0$, where $\hat{p}$ is the momentum in the direction of the translation, thanks to Eq. 2.49. If $\hat{U}$ is rotation, then the testing is equivalent to asking $\left[\hat{H}, \hat{L}\right] \stackrel{?}{=} 0$, where $\hat{L}$ is the angular momentum in the direction of the rotation, thanks to Eq. 2.50 and the discussion below it.

6.3 Symmetry and conservation

Let us combine what we learned in the previous section with what we covered in Section 2.1.7, to summarize some commonly encountered important symmetries and resulting conservation principles. Recall from Section 2.1.7 that if an operator $\hat{O}$ is not explicitly dependent on time and if it commutes with $\hat{H}$, then it is a conserved quantity, i.e., $\frac{d}{dt}\left\langle\hat{O}\right\rangle = 0$ for any state $|\Psi\rangle$. This fact is used repeatedly in the discussion below.

6.3.1 Energy conservation

If $\hat{H}$ is not explicitly dependent on t, then it means that time is homogeneous. In this case, $\hat{H}$ is conserved. Time is homogeneous for any closed system.

6.3.2 Momentum conservation

If $\hat{H}$ is invariant under translation along a certain direction, then it means that space is homogeneous in that direction. To test this translational invariance, it suffices to test if $\hat{H}$ commutes with $\hat{p}$, the *total* momentum of the system along the direction. Thus, the translational invariance along a certain direction means the conservation of the total momentum along that direction. Space is homogeneous in all directions, for any closed system.

6.3.3 Angular momentum conservation

If $\hat{H}$ is invariant under rotation around a certain axis, then it means that the space is isotropic around that axis. Testing this rotational invariance is equivalent to testing if $\hat{H}$ commutes with $\hat{J}_\theta$, the *total* angular momentum of the system around the axis. Thus, the rotational invariance around a certain axis means the conservation of the total angular momentum around that axis. Space is fully isotropic, for any closed system.

The case of the angular momentum warrants some more words. What do we mean by "rotation" here? Generally, by rotation, we mean *two combined rotations*: the rotation in the ordinary space and the rotation in the spin space. Indeed, for a general closed system, we can say that the total angular momentum $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$, summed over all particles involved[4], is conserved due to the isotropy of space, but we *cannot* say whether $\hat{\vec{L}}$ or $\hat{\vec{S}}$ is conserved separately. To answer the latter question, we have to test whether the system is invariant under the ordinary rotation or the spin rotation, separately. The answer is not always yes, even for a closed system! This is due to the fact that the spin angular momentum and the orbital angular momentum are generally coupled by the so-called "spin-orbit interaction," a topic we will study shortly.

Lastly, note that the full isotropy means that all xyz components of the angular momentum are conserved. However, we must take notice that different angular

[4]So, in this sense, we are using the word "total" with full (double) meaning.

momentum components do not commute with each other. As we shall see in the next section, the choice of *compatible*, i.e. mutually commuting, conserved observables is often necessary. This is why we typically pick the magnitude of the angular momentum and the z component of the angular momentum as two conserved, and compatible, observables of choice, when the full isotropy is applicable.

Know your rotations!

Rotation in QM does *not just* mean ordinary rotation. It also includes rotation *in the spin space*, i.e. the rotation of the spin wave function. The total angular momentum $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ is conserved if the system is rotationally symmetric. If the system is rotationally symmetric *in the ordinary space*, then $\hat{\vec{L}}$ is conserved. If the system is rotationally symmetric *in the spin space*, then $\hat{\vec{S}}$ is conserved. Just because $\hat{\vec{J}}$ is conserved does not mean that $\hat{\vec{L}}$ or $\hat{\vec{S}}$ is conserved separately. For a general closed system, the isotropy of space guarantees the conservation of $\hat{\vec{J}}$, and *only* that in general.

6.3.4 Parity conservation

If $\hat{H}$ is invariant under reflection along a certain axis, then it means that the system has a mirror symmetry along that axis. If this is the case, then we say that the parity is conserved. This symmetry does *not* hold true for any closed system, as the weak interaction breaks this symmetry. In this course, though, we will only deal with electromagnetic interactions, and so, in this limited context, the parity is conserved for any closed system.

6.3.5 Others

Other symmetries that are encountered frequently in discussions of quantum mechanics include particle exchange symmetry, time reversal symmetry, and charge conjugation (i.e. particle-anti-particle) symmetry. Note that some of these symmetries (time reversal and charge conjugation) are described *not* by unitary operators, but by anti-unitary operators (footnotes 4,7 of LN 1), requiring a generalization of the concept of an operator, as we defined in page 5 of LN 1, since anti-unitary operators are anti-linear. We do not intend to be distracted by such a generalization here, since we will not be concerning ourselves much with these other symmetries in this course. However, let us do note in passing that charge conjugation and time reversal are not fundamental symmetries of a closed system, broken by the weak interaction: this is a situation similar to that for the parity symmetry. To our knowledge so far, however, the so-called CPT (charge conjugation, parity, and time-reversal, all together) symmetry holds for any physical laws.

Particle exchange symmetry is responsible for quantum particle statistics (fermions and bosons).

6.4 Symmetry and degeneracy

In this section, we will be considering the time independent Schrödinger equation $\hat{H}|E\rangle = E|E\rangle$ (Eq. 3.1), assuming that $\hat{H}$ is conserved. The following two principles are easy and extremely important.

Symmetry principle 1

Suppose $\hat{H}|E\rangle = E|E\rangle$ and $\hat{H}$ is invariant under a unitary transformation $\hat{U}$. Then, any transformed state $\hat{U}|E\rangle$ also have the same energy E.

Symmetry principle 2

If $\hat{H}$ and $\hat{O}$ commute, where $\hat{O}$ is diagonalizable (e.g., Hermitian or unitary), then $\hat{O}$ and $\hat{H}$ can be simultaneously diagonalized.

When these principles are referenced in this course, their consequences (those points described in the box in page 14) will also be lumped into these principles, automatically. Therefore, you are advised to revisit this page and refresh your memory *after* you have understood those properties that are derived from the above principles. *Also, note that these two principles can be extended to any pair of compatible diagonalizable operators* (cf., the next lecture note).

Principle 2 has been already mentioned in LN 2 (page 20), and is stated here again, in a more general form. Its proof is left for your exercise[5] (hint: you can apply

[5] Like any other exercise, feel free to discuss it on line, if you find a good solution, or simply have a question.

principle 1, in a general way!).

Let us prove principle 1. It is very easy to do so! Take $\hat{H}\hat{U}|E\rangle$. Since $\hat{H}$ commutes with $\hat{U}$, we get $\hat{H}\hat{U}|E\rangle = \hat{U}\hat{H}|E\rangle = \hat{U}E|E\rangle = E\hat{U}|E\rangle$, where in the second step $\hat{H}|E\rangle = E|E\rangle$ has been used. QED.

Example—rotational symmetry of a Hydrogen-like atom

What these principles have to do with degeneracy can be learned by first studying an example. To be specific, let us consider the rotational symmetry in a Hydrogen-like atom problem defined by

$$\hat{H} \doteq -\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r} \qquad \nabla \equiv \vec{e}_1\frac{\partial}{\partial x} + \vec{e}_2\frac{\partial}{\partial y} + \vec{e}_3\frac{\partial}{\partial z} \tag{6.12}$$

Here, we take Z to be a positive number that corresponds to the charge Ze of the nucleus. For the Hydrogen atom, $Z = 1$.

We will focus on $2p$ orbitals, initially, i.e. those states with $n = 2$ and $l = 1$. The eigenstate of the Hamiltonian will be written as $|n, l, m_z\rangle$ (where $m_z\hbar$ = eigenvalue of $\hat{L}_z$) in this section, ignoring the spin quantum number for now. We are concerned only with the ordinary rotation, in this section, as the above Hamiltonian is rotationally invariant in the ordinary space and is completely spin-independent.

The above problem has the following solutions in for $n = 2$ and $l = 1$.

$$|2,1,1\rangle \doteq R_{21}(r)\,Y_{11}(\theta,\phi) \tag{6.13}$$

$$|2,1,0\rangle \doteq R_{21}(r)\,Y_{10}(\theta,\phi) \tag{6.14}$$

$$|2,1,-1\rangle \doteq R_{21}(r)\,Y_{1,-1}(\theta,\phi) \tag{6.15}$$

$$R_{21}(r) = \left(\frac{Z}{2a_B}\right)^{3/2} \frac{Zr}{\sqrt{3}\,a_B} \exp\left(-\frac{Zr}{2a_B}\right) \tag{6.16}$$

$$Y_{1,\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\,\exp(\pm i\phi) \tag{6.17}$$

$$Y_{10}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{6.18}$$

$$a_B \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\hbar}{m_e c}\frac{1}{\alpha} = 0.5292\ \text{Å} \qquad \text{Bohr radius} \tag{6.19}$$

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.0} \qquad \text{Fine structre constant} \tag{6.20}$$

$$\frac{\hbar}{m_e c} = 386.2\ \text{fm} \qquad \text{(Reduced) } e \text{ Compton wavelength} \tag{6.21}$$

where the unit Å means 10^{-10} m (= 0.1 nm), and the unit fm means 10^{-5} Å. Also, note that the standard spherical coordinate system (r, θ, ϕ) is used for wave functions.

As we are focusing on $n = 2$ and $l = 1$ case, where the radial wave function is fixed, we can concentrate only on the angular wave function in the following discussion.

Let us ask a question. What happens if we rotate the states $|2,1,m_z\rangle$ with $m_z = 1, 0, -1$ around the z axis by ϕ_1? The answer is very simple. The rotation operator in this case is $\hat{\mathcal{R}}_z(\phi_1) = \exp\left(-i\phi_1 \hat{L}_z/\hbar\right)$, and since Y_{lm}'s are eigenstates of $\hat{L}_z$ ($\doteq -i\hbar\frac{\partial}{\partial\phi}$) with eigenvalues $m\hbar$, we simply get

$$\hat{\mathcal{R}}_z(\phi_1)\,|n,l,m_z\rangle \;=\; \exp\left(-im_z\phi_1\right)|n,l,m_z\rangle \tag{6.22}$$

Now, let us ask another question. What happens to $|n,l,m_z\rangle$ if they are rotated around the x axis by ϕ_1? The best thing to do is to express $|n,l,m_z\rangle$'s in terms of $|n,l,m_x\rangle$ with $\hbar m_x$ being the eigenvalue of $\hat{L}_x$. The angular momentum algebra (commutators, $\hat{J}_\pm|j,m\rangle = \sqrt{(j\mp m)(j\pm m+1)}\,|j,m\pm 1\rangle$, and $\hat{J}_\pm \equiv \hat{J}_x \pm i\hat{J}_y$) that you already learned in the first course of QM would be what you need in figuring the answer out, if the answer cannot be looked up in some convenient way. However, for the current problem, it is actually quite instructive to derive the answer in a more intuitive way, as follows.

Note that in terms of the Cartesian coordinates $Y_{10} = \sqrt{\frac{3}{4\pi}}\frac{z}{r}$, $Y_{1,\pm1} = \mp\sqrt{\frac{3}{4\pi}}\frac{1}{\sqrt{2}}\frac{x\pm iy}{r}$. This suggests using the following basis states

$$\begin{aligned}
|p_x\rangle \;&=\; -\frac{1}{\sqrt{2}}\Big(\,|l=1,m_z=1\rangle - |l=1,m_z=-1\rangle\,\Big) \doteq \sqrt{\frac{3}{4\pi}}\frac{x}{r} \\
|p_y\rangle \;&=\; \frac{i}{\sqrt{2}}\Big(\,|l=1,m_z=1\rangle + |l=1,m_z=-1\rangle\,\Big) \doteq \sqrt{\frac{3}{4\pi}}\frac{y}{r} \\
|p_z\rangle \;&=\; |l=1,m_z=0\rangle \doteq \sqrt{\frac{3}{4\pi}}\frac{z}{r}
\end{aligned} \tag{6.23}$$

It is left for your exercise to show that $\{|p_x\rangle, |p_y\rangle, |p_z\rangle\}$ form an orthonormal basis, replacing the orthonormal basis set formed by spherical harmonics for $l = 1$: $\{|l=1,m_z=1\rangle, |l=1,m_z=0\rangle, |l=1,m_z=-1\rangle\}$.

To go back to the original basis set, we can invert these equations to get

$$\begin{aligned}
|l=1,m_z=1\rangle \;&=\; -\frac{1}{\sqrt{2}}\Big(\,|p_x\rangle + i\,|p_y\rangle\,\Big) \\
|l=1,m_z=-1\rangle \;&=\; \frac{1}{\sqrt{2}}\Big(\,|p_x\rangle - i\,|p_y\rangle\,\Big) \\
|l=1,m_z=0\rangle \;&=\; |p_z\rangle
\end{aligned} \tag{6.24}$$

The advantage of using the new basis is that the above formula can be re-written quickly in terms of the spherical harmonics $|l=1,m_x\rangle$ or $|l=1,m_y\rangle$, with a mere cyclic permutation of subscripts x,y,z. For example, we get, from Eq. 6.23, by such a cyclic permutation of symbols $x,y,z \to y,z,x$:

$$\begin{aligned} |p_x\rangle &= |l=1,m_x=0\rangle \\ |p_y\rangle &= -\frac{1}{\sqrt{2}}\Big(|l=1,m_x=1\rangle - |l=1,m_x=-1\rangle\Big) \\ |p_z\rangle &= \frac{i}{\sqrt{2}}\Big(|l=1,m_x=1\rangle + |l=1,m_x=-1\rangle\Big) \end{aligned} \tag{6.25}$$

With Eqs. 6.25 and 6.24, we can express $|l=1,m_z\rangle$'s in terms of $|l=1,m_x\rangle$'s:

$$\begin{aligned} |l=1,m_z=1\rangle &= \frac{i}{2}|l=1,m_x=1\rangle - \frac{1}{\sqrt{2}}|l=1,m_x=0\rangle - \frac{i}{2}|l=1,m_x=-1\rangle \\ |l=1,m_z=0\rangle &= \frac{i}{\sqrt{2}}|l=1,m_x=1\rangle + \frac{i}{\sqrt{2}}|l=1,m_x=-1\rangle \\ |l=1,m_z=-1\rangle &= \frac{i}{2}|l=1,m_x=1\rangle + \frac{1}{\sqrt{2}}|l=1,m_x=0\rangle - \frac{i}{2}|l=1,m_x=-1\rangle \end{aligned} \tag{6.26}$$

From which the answer to the second question we asked above can be obtained with ease. If we apply the rotation operator $\hat{\mathcal{R}}_x(\phi_1) = \exp(-i\phi_1\hat{L}_x/\hbar)$ to these states, then we get (by noting that the eigenvalue of $\hat{L}_x$ is given by $m_x\hbar$)

$$\begin{aligned} \hat{\mathcal{R}}_x(\phi_1)|l=1,m_z=1\rangle &= \frac{ie^{-i\phi_1}}{2}|l=1,m_x=1\rangle - \frac{1}{\sqrt{2}}|l=1,m_x=0\rangle - \frac{ie^{i\phi_1}}{2}|l=1,m_x=-1\rangle \\ \hat{\mathcal{R}}_x(\phi_1)|l=1,m_z=0\rangle &= \frac{ie^{-i\phi_1}}{\sqrt{2}}|l=1,m_x=1\rangle + \frac{ie^{i\phi_1}}{\sqrt{2}}|l=1,m_x=-1\rangle \\ \hat{\mathcal{R}}_x(\phi_1)|l=1,m_z=-1\rangle &= \frac{ie^{-i\phi_1}}{2}|l=1,m_x=1\rangle + \frac{1}{\sqrt{2}}|l=1,m_x=0\rangle - \frac{ie^{i\phi_1}}{2}|l=1,m_x=-1\rangle \end{aligned}$$

With the details of the coefficients aside, there is a bigger lesson in all of this. Clearly these answers can be re-expressed in terms of m_z basis states, or p_x, p_y, p_z states. So far, we have found three equivalent orthonormal basis sets for $2p$ states. It is also clear that we can use m_y values to identify basis states. Thus, any of the four sets, $\{|l=1,m_z\rangle\}$, $\{|l=1,m_x\rangle\}$, $\{|l=1,m_y\rangle\}$, and $\{|p_x\rangle, |p_y\rangle, |p_z\rangle\}$, will serve as a perfectly valid basis set for $2p$ states. And, of course, these are merely four out of infinite number of choices one can make for the basis sets.

What is unchanging regardless of which basis set we choose is the fact that there are exactly three orthogonal states in the basis set. By the symmetry principle 1 above, all of these three states must be degenerate in energy. This is due to the full rotational symmetry of the problem. **What is important**

is the fact that it is impossible to reduce the basis set to a smaller basis set that is closed under all rotations. In this sense, any of our three state basis sets is *irreducible*[6]. For instance, if one takes $|p_x\rangle$ and $|p_y\rangle$ only, and consider rotating around the x axis by 90 degrees, then one would observe that $|p_y\rangle$ transforms into $|p_z\rangle$, which is orthogonal to both $|p_x\rangle$ and $|p_y\rangle$. In this sense, the three state basis set is irreducible. **The size of this irreducible basis set is the degeneracy that the system must have!**

As a matter of fact, the full symmetry (rotation + parity) of the system can be considered in place of the rotation symmetry. Please show it to yourself that any of the three state basis set is closed under rotation plus parity. **So any three state basis set that we identified above is irreducible under the full symmetry of the system.**

Perhaps the most intuitive basis set is $\{|p_x\rangle, |p_y\rangle, |p_z\rangle\}$. This basis set corresponds to the usual chemists' diagrams for p orbitals: each p orbital consists of two lobes with opposite signs, and is aligned along the x, y, or z axis. It may be intuitively clear why these three orbitals are closed under reflection and all possible rotations, and why it is not possible to reduce the basis set to a smaller set while preserving the closed property under all possible rotations and reflections.

In some cases, the actual degeneracy of the problem can be greater than the size of such an irreducible basis set. The Hydrogen problem is just such an example. Including the spin rotation symmetry, we expect that $2\times(2l+1)$ be the degeneracy expected from symmetry principle 1. However, the actual degeneracy is $\sum_{l=0}^{n-1} 2\times(2l+1)$. That is, in the current example, it turns out $2s$ ($l = 0$) state is degenerate with $2p$ states. And, $3s$, $3p$, $3d$ states are all degenerate for the Hamiltonian given by Eq. 6.12, as the energy eigenvalue depends only on n. This type of degeneracy, where the symmetry of the problem does not explain the degeneracy, is called an "accidental degeneracy." While this term is used frequently, there is often nothing "accidental" about an accidental degeneracy: many times, it turns out that there is a higher symmetry of the problem that we did not know! A simple example would be instructive. Consider a free boson with spin 0. In a free particle Hamiltonian, one may notice the translational symmetry and write the wave function as $|k\rangle \doteq A\exp(ikx)$. Upon translation, this state maps onto itself ($\hat{\mathcal{T}}(x_0)|k\rangle \doteq A\exp(ik(x-x_0)) = A_2\exp(ikx)$ with $A_2 = A\exp(-ikx_0)$), so the irreducible basis set of the translation symmetry is of size 1. This means that the degeneracy required by the translation symmetry is only 1. Then, one might notice that $\exp(ikx)$ and $\exp(-ikx)$ is degenerate, and one might

[6]In the language of the group theory, an important branch of mathematics, they form a basis for an *irreducible representation* of the full rotation group. Indeed, the group theory as applied to physics is precisely all about this type of thing—finding the irreducible representation of the full symmetry group of a given problem. However, this is formally a lengthy subject, and for that reason I will not use the group theory language anywhere during the course, except in this footnote.

call it an accidental degeneracy 2. Furthermore, one might notice that $\exp(i\vec{k}\cdot\vec{x})$ for $\vec{k}$ pointing in any direction with $|\vec{k}| = k$ is also degenerate. So, the degeneracy is infinite! This you can also call an accidental degeneracy. Of course, you would know that these additional degeneracies are due to the fact that parity and rotation are also valid symmetries of the problem. So, there is nothing accidental about accidental degeneracies in this case[7].

Symmetry and degeneracy

For a given Hamiltonian, identify as many symmetry operations as possible.

Symmetry principle 2 in action Then, identify a set of compatible operators, from symmetry operators or their generators (page 17 of LN 2). In general, there will be multiple such sets. Choose one. Find *the most general form* [a] of simultaneous eigenstates for all the operators in the set. Then, they are also energy eigenstates.

Symmetry principle 1 in action Take any one eigenstate that you obtained in step 1, and apply *all* known symmetry operations to it. Divide the resulting set into irreducible subsets that are each closed under all symmetry operations. The number of orthogonal states that are obtained in the process for each irreducible basis set gives the minimum degeneracy dictated, or protected, by the symmetry of the problem.

Extra degeneracy Any extra degeneracy that is additional to what you found in step 2, can be called an "accidental" degeneracy. Beware of some symmetry that you may not be unaware of, in such a case.

[a] Here is the explanation of this phrase. The issue arises when symmetry eigenstates are *degenerate* in symmetry eigenvalues. For instance, if parity is the only symmetry of the system, then we would know that an even or add function is an energy eigenfunction. Just what even or odd function is an energy eigenstate cannot be determined by symmetry argument alone. We clearly cannot claim that an *arbitrarily* shaped even or odd function is an energy eigenstate, while such a function is definitely a parity eigenstate. This is due to a massive degeneracy of parity eigenstates. As another example, let us consider the case when system has a full rotational symmetry in ordinary space. In this case, you would know for certain that spherical harmonics $Y_{lm}(\theta,\phi)$ are energy eigenfunctions, since lm values are non-degenerate.

[7] However, it cannot be said that accidental degeneracies can always be traced back to some symmetry.

6.5 Symmetry and perturbation

There are certain things that can be said with certainty about the relation between symmetry and perturbation, assuming certain typical situations arise.

If perturbation preserves symmetry...

Let us assume that the unperturbed Hamiltonian has a certain symmetry, and the perturbing Hamiltonian also has the same symmetry. Suppose this common symmetry implies a degeneracy from principle 1 above. **Such degeneracy can be completely ignored while working out the perturbation solution, in the sense that only one of the degenerate states can be considered for a perturbation solution. After the solution is obtained, you would know that that solution applies to all other degenerate states by principle 1.** However, an *accidental degeneracy* in the unperturbed solution would tend to be lifted by perturbation.

A simple example of this kind is the spin degeneracy of a problem whose Hamiltonian is spin independent. We simply do not have to worry about the spin aspect of such a problem due to the same spin symmetry of the problem before and after the perturbation. We shall encounter more non-trivial examples of this kind in the next lecture, where the accidental degeneracy is lifted. A simple example where an accidental degeneracy is lifted by perturbation is the example of the ammonia molecule (LN 5, "Maser chemical bonding, etc.").

If perturbation lowers symmetry...

Most often, the perturbation lowers the overall symmetry, reducing the degeneracy implied by symmetry. Indeed, this is the generic mechanism that is often responsible for the energy splitting of the "degenerate perturbation problem," as we have begun to see in the previous lecture. **Typically, "good zeroth order states" can be written down by observing the surviving symmetry, in such a case.**

The particle in 1D problem (Section 5.1) is an excellent example of this. In that example, the particle has the translation symmetry in θ and the parity symmetry in θ, when unperturbed. Let us first examine sets of compatible symmetry operators. The translation in θ and parity in θ do not commute. There may be many ways of seeing this. The simplest way to see this mathematically is to ask the question, does $\hat{L}_\theta \doteq -i\hbar\frac{\partial}{\partial\theta}$ and $\hat{P}_\theta \doteq P_\theta$, where $P_\theta w(\theta) \equiv w(-\theta)$ ($w(\theta)$ means "whatever expression that involves θ"), commute? It suffices to answer this question, since $\hat{L}_\theta$ is the generator for the translation in θ (Section 2.1.4). By taking an arbitrary function of θ, $f(\theta) \mathrel{\underset{\cdot}{=}} f(\hat{\theta})$:

$$
\begin{aligned}
\hat{L}_\theta \hat{P}_\theta f(\hat{\theta}) &\doteq -i\hbar\frac{\partial}{\partial\theta}P_\theta f(\theta) \;=\; -i\hbar\frac{\partial}{\partial\theta}f(-\theta) \\
\hat{P}_\theta \hat{L}_\theta f(\hat{\theta}) &\doteq -i\hbar P_\theta\frac{\partial}{\partial\theta}f(\theta) \;=\; -i\hbar\frac{\partial}{\partial(-\theta)}f(-\theta) \mathrel{\underset{\cdot}{=}} -\hat{L}_\theta\hat{P}_\theta f(\hat{\theta})
\end{aligned}
$$

So, we get, in fact, $\left[\hat{P}_\theta, \hat{L}_\theta\right] = 2\hat{P}_\theta\hat{L}_\theta$, which is clearly not zero. Therefore, for this problem, the set of compatible symmetry operators can be taken as either a set consisting of all translation operators, or a set consisting of one element $\hat{P}_\theta$. The first set of symmetry operators can be simultaneously diagonalized by functions of the form $\exp(im\theta)$. The second set of symmetry operators can be diagonalized only by even functions or odd functions of θ. Using prior knowledge of the plane wave being relevant to this problem, we can choose $\cos(m\theta)$ and $\sin(m\theta)$ as our parity eigenstates.

Let us now apply principle 1 of the previous section to figure out the minimum degeneracy of the problem. Starting with either set, we should get the same conclusion. For instance, if we start from $\exp(im\theta)$, then (1) by translating it we only get a phase constant out—so we don't get a new function, and (2) by applying $\hat{P}_\theta$ we get

$\exp(-im\theta)$. So, we must have a double degeneracy. Or, starting from $\cos(m\theta)$, we see that it is invariant under $\hat{P}_\theta$. However, when we translate it infinitesimally for instance, we get to differentiate the function and so we get $\sin(m\theta)$, which must have the same energy. So, we get degeneracy of 2, this way too, as we should.

If the perturbation term $V(\theta)$ (Eq. 5.4) is considered, then suddenly the translation symmetry is gone. And so, **good zeroth order states are** $\sin(m\theta)$ **and** $\cos(m\theta)$**, not plane waves,** as we found in the answers (Eqs. 5.7, 5.8 and discussions below them).