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Degeneracies, however, can cause problems in PT:

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} | \psi_m^{(0)} \rangle$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

These denominators cause problems if states m & n are degenerate at zeroth order: $E_n^{(0)} - E_m^{(0)} \to 0$

Heck, even a small splitting could be trouble as our expansion is predicated on each term getting smaller for the series to converge!

<u>How can/should we deal with degeneracies?</u>

This is best done in the context of an example.

I am going to work a problem similar to 7.2 in your book, but will explore the content of <u>section</u> 7.2 along the way.

The problem is a perturbed 2-D QMHO, with a <u>single</u> particle in it.

$$H_0 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{k x^2}{2} + \frac{k y^2}{2}$$ Intentionally in k NOT ω for later!

Which clearly separates into x & y:

$$\psi^{(0)}_{n_x n_y}(x,y) = \psi^{(0)}_{n_x}(x)\,\psi^{(0)}_{n_y}(y)$$

→ 1-D QMHO wave functions.

With unperturbed energies $E^{(0)}_{n_x n_y} = (n_x + n_y + 1)\hbar\omega$ with $\omega = \sqrt{k/m}$

Note, the ground state $|n_x n_y\rangle = |00\rangle$ is <u>not</u> degenerate, but the first excited state <u>is</u>: $E^{(0)}_{10} = E^{(0)}_{01}$

<u>Our First Perturbation: $\lambda H' = \frac{\varepsilon}{2}(x^2 - y^2)$</u>

Do we "need" PT to solve this? Q

No! All we did was shift k_x & k_y: A

$$H = \left(\frac{p_x^2}{2m} + \frac{k}{2}x^2 + \frac{\varepsilon}{2}x^2\right) + \left(\frac{p_y^2}{2m} + \frac{k}{2}y^2 - \frac{\varepsilon}{2}y^2\right)$$

$$= \left[\frac{p_x^2}{2m} + \frac{1}{2}(k+\varepsilon)x^2\right] + \left[\frac{p_y^2}{2m} + \frac{1}{2}(k-\varepsilon)y^2\right]$$

Calling $k+\varepsilon = k_x$ & $k-\varepsilon = k_y$ we can simply write the energies down:

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$$E^{(0)}_{n_x n_y} = (n_x + 1/2)\hbar\omega_x + (n_y + 1/2)\hbar\omega_y$$

$$\Big|\ \omega_x = \sqrt{\frac{k+\varepsilon}{m}} \quad \& \quad \omega_y = \sqrt{\frac{k-\varepsilon}{m}}$$

Do we still have degeneracy, i.e. does $E_{10} = E_{01}$? Q
NO! A

This is key, perturbations will <u>often</u> break zeroth-order degeneracies!

- Degeneracies come from symmetries as we saw in our discussion of symmetries at the start of the semester.
- If the perturbation has a different symmetry than H_0, the degeneracy will be broken!

Let's Apply P.T. Anyway

As we saw the problem is the first-order corrections to ψ so let's look there (since $E_n^{(2)}$ has the same form, fixing $\psi^{(1)}$ will fix $E_n^{(2)}$).

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \, |\psi_m^{(0)}\rangle$$

The denominator is the problem.

However, if the numerator <u>also</u> is zero we <u>might</u> be okay: $0/0 \stackrel{?}{=} 0$!

Looking at the problem terms $|01\rangle$ & $|10\rangle$:

$$\langle n_x = 1\ n_y = 0 | H' | n_x = 0\ n_y = 1 \rangle =$$

$$= \int dx dy\ \psi_1^*(x) \psi_0^*(y) \frac{\varepsilon}{2}(x^2 - y^2) \psi_0(x) \psi_1(y)$$

$$= \frac{\varepsilon}{2} \left\{ \int dx dy\ \psi_1^*(x) \psi_0^*(y)\, x^2 \psi_0(x) \psi_1(y) - \int dx dy\ \psi_1^*(x) \psi_0^*(y)\, y^2 \psi_0(x) \psi_1(y) \right\}$$

$$= \frac{\varepsilon}{2} \left\{ \underline{\int dx\ \psi_1^*(x) x^2 \psi_0(x)}\ \underline{\int dy\ \psi_0^*(y) \psi_1(y)} - \underline{\int dy\ \psi_0^*(y) y^2 \psi_1(y)}\ \underline{\int dx\ \psi_1^*(x) \psi_0(x)} \right\}$$

These terms are zero by orthogonality

These terms are zero by symmetry:
(odd fcn) × (even fcn) × (even fcn) = (odd fcn)
which when integrated over $(-\infty, \infty)$ is zero.

∴ Our potentially problem terms not only have a zero denominator but also a zero numerator which saves us.

- In particular, our numerator is $0 \cdot 0 - 0 \cdot 0$ which is "stronger" than just 0 in the denominator.
- Here we <u>know</u> $0/0 = 0$ b/c we can solve it exactly!

Dealing with "True" Degeneracies

Objectives

By the end of today's class, you should be able to...

- Know that many contexts in which you would want to apply perturbation theory are degenerate.
- Articulate why degeneracies are so common in applications of perturbation theory.
- Describe the process by which we deal with degeneracies in perturbation theory: find linear combinations of the states which are degenerate under our unperturbed Hamiltonian but have a zero expectation value with our perturbing Hamiltonian. As a consequence, the numerators in our perturbative calculations, which have zero denominators, will also be zero.
- Know that such linear combinations are called "good states."
- Know that the good states, while degenerate under the unperturbed H_0, will generally not be degenerate when the perturbative corrections are applied at first order.
- Find the "good states" by brute force.

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Last time, we saw that the potential pitfalls with regards to zero denominators in the calculation of $\psi_n^{(1)}$ and $E_n^{(2)}$ can be potentially avoided if the numerators for such terms is also zero:

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} | \psi_m^{(0)} \rangle$$

As long as $\langle \psi_n^{(0)} | H' | \psi_m^{(0)} \rangle = 0$ when $(E_n^{(0)} - E_m^{(0)}) = 0$, we <u>might</u> be okay. (In this class $0/0 = 0$, though in reality you would have to check!).

Note, this does <u>NOT</u> necessarily imply $E_n^{(1)} = 0$!

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$$

this will be key: we can make states which avoid $1/0$, which simultaneously break the degeneracy.

In our prior example with $H' = \frac{\varepsilon}{2}(x^2 - y^2)$, the unperturbed $\psi_n^{(0)}$ already had this "good" numerator property (because it was exactly solvable).

Now let's look at a case where we seem to actually need TIPT and where $\psi_n^{(0)}$ will not automatically have good numerators:

$$\lambda H' = \varepsilon xy \text{ to our 2D-QMHO}$$

Once again, $|00\rangle$ is non-degenerate, but the two first-excited states are: $|n_x n_y\rangle = |10\rangle$ and $|01\rangle$.

These unperturbed states will be problematic when we calculate the first-order correction to ψ, $\psi_n^{(1)}$, or the second-order correction to energy $E_n^{(2)}$ as both calculations have the term:

$$\frac{\langle \psi_n^{(0)} | \lambda H' | \psi_m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

The problem → $E_n^{(0)} - E_m^{(0)}$

← Since these states are distinct (though degenerate) we will include $\langle 10 | H' | 01 \rangle$ in our sum.

In the last example, all these "difficult" numerators were zero when $(E_n^{(0)} - E_m^{(0)}) = 0$ saving (?) us from infinities in calculation while simultaneously breaking the degeneracy by having different values of $E_n^{(1)}$.

What about in this case? Are the "difficult numerators" still zero?

Let's check:

$$\varepsilon \langle 10 | xy | 01 \rangle$$

Recall, from our review at the start of the semester:

$$x = \sqrt{\frac{\hbar}{2m\omega}}\,(a_x + a_x^\dagger) \quad \& \quad y = \sqrt{\frac{\hbar}{2m\omega}}\,(a_y + a_y^\dagger)$$

$$\varepsilon \langle 10 | xy | 01 \rangle = \frac{\varepsilon\hbar}{2m\omega} \langle 10 | (a_x + a_x^\dagger)(a_y + a_y^\dagger) | 01 \rangle$$

$$= \frac{\varepsilon\hbar}{2m\omega} \langle 10 | a_x a_y + a_x a_y^\dagger + a_x^\dagger a_y + a_x^\dagger a_y^\dagger | 01 \rangle$$

All of these terms are zero, but

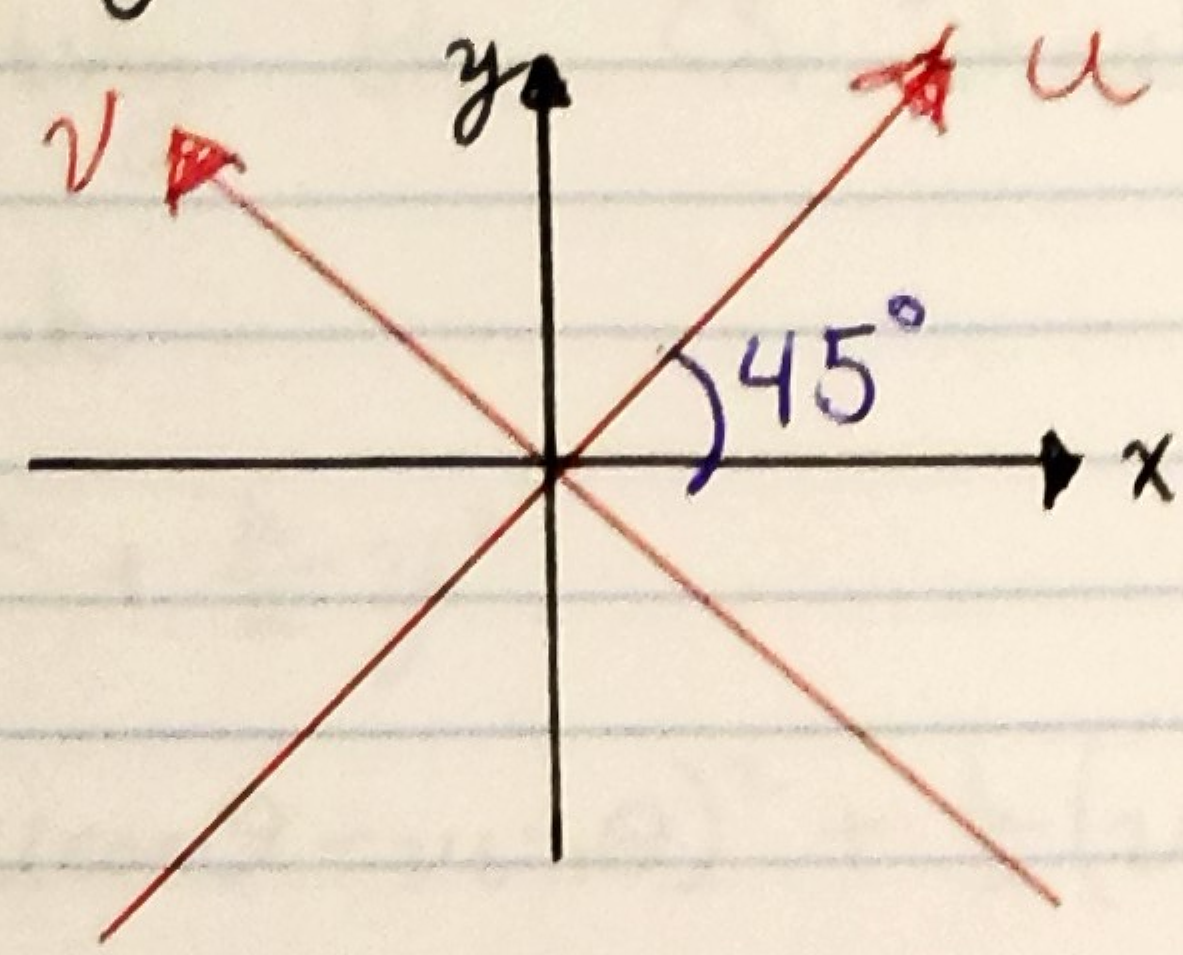
$$= \frac{\varepsilon\hbar}{2m\omega} \langle 10 | a_x^\dagger a_y | 01 \rangle$$

$$= \frac{\varepsilon\hbar}{2m\omega} \sqrt{1}\sqrt{1} \neq 0$$

So it seems we have a problem.

Do we though?

Let's look at what happens if we rotate our coordinate system $(x,y) \to (u,v)$ by $45°$:



Mathematically, this rotation is described by

$$\begin{pmatrix} u \\ v \end{pmatrix} = R(\theta)\begin{pmatrix} x \\ y \end{pmatrix} \to \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

Since $R(\theta) \in SO(2)$, $R^{-1}(\theta) = R^{T}(\theta) \Rightarrow$

$$\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix}$$

$\hookrightarrow \varepsilon xy = \varepsilon(u\cos\theta - v\sin\theta)(u\sin\theta + v\cos\theta)$

for $\theta = 45°$ $\cos\theta = \sin\theta = \frac{1}{\sqrt{2}}$:

$$\varepsilon xy = \left(\frac{u}{\sqrt{2}} - \frac{v}{\sqrt{2}}\right)\left(\frac{u}{\sqrt{2}} + \frac{v}{\sqrt{2}}\right) = \frac{\varepsilon}{2}(u^2 - v^2)$$

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What does this transformation do to H_0?

What should it do? Q

Nothing! H_0 is cylindrically symmetric so rotating the C.S. shouldn't do anything. A

Let's check

$$H_0 = \frac{k}{2}x^2 + \frac{k}{2}y^2$$

$$= \frac{k}{2}(u\cos\theta - v\sin\theta)^2 + \frac{k}{2}(u\cos\theta + v\sin\theta)^2$$

$$= \frac{k}{2}\Big[u^2\cos^2\theta + v^2\sin\theta - \cancel{2uv\cos\theta\sin\theta} + u^2\cos^2\theta + v^2\sin^2\theta + \cancel{2uv\cos\theta\sin\theta}\Big]$$

$$= \frac{k}{2}\left[u^2 + v^2\right] = \frac{k}{2}u^2 + \frac{k}{2}v^2 \leftarrow \text{Unchanged as expected}$$

[redacted] We're back to our first problem!

Apparently, we can get rid of our "problem numerators" by building linear combinations of the unperturbed eigenstates which are degenerate under H_0; with the right choice of such "good states," we can eliminate our "problem numerators" in $\Psi_n^{(1)}$ & $E_n^{(2)}$ while simultaneously breaking the degeneracy at $E_n^{(1)}$!

Using Symmetries to Find "Good States"

Objectives:
By the end of today's class, you should be able to...
- Explain why symmetries can be useful for finding the "good states" for degenerate P.T.
- Explain how to use such symmetries to find the aforementioned "good states"

Last time, we saw a brute-force approach to finding what Griffiths calls the good states: linear combinations of states, degenerate under H_0, ψ_+ and ψ_- in the doubly degenerate case, which:
1) Have "difficult numerators" $\langle \psi_+ | H' | \psi_- \rangle = 0$
2) Cause the degeneracy to split at first order: $E_+^{(1)} \neq E_-^{(1)}$ eventhough $E_+^{(0)} = E_-^{(0)}$

This approach is both
1) Mathematically cumbersome
2) Only effective for n-fold degeneracies for $n \leq 4$.

Is there a simpler way? Use Symmetries!

Theorem: Let A be some Hermitian operator such that $[H_0, A] = [H', A] = 0$. However, let ψ_+ and ψ_- have different eigenvalues under A:

$$A\psi_+ = a_+ \psi_+ \qquad A\psi_- = a_- \psi_-$$

$$a_+ \neq a_-$$

If you can find A, you've found the good states for degenerate P.T.!

The idea: use symmetries to find A!

E.g. Back to our 2-D QMHO with $H' = \varepsilon xy$

We already saw that the good states here can be found by rotating our CS by 45° $(x,y) \to (u,v)$!

$$x = \frac{1}{\sqrt{2}}(u-v) \qquad u = \frac{1}{\sqrt{2}}(x+y)$$
$$y = \frac{1}{\sqrt{2}}(u+v) \qquad v = \frac{1}{\sqrt{2}}(x-y)$$

$$H(x,y) = \underbrace{\left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{k}{2}x^2 + \frac{k}{2}y^2\right)}_{H_0} + \underbrace{\left(\varepsilon(xy)\right)}_{\lambda H'}$$

$$\Downarrow$$

$$H(u,v) = \left(\frac{p_u^2}{2m} + \frac{p_v^2}{2m} + \frac{k}{2}u^2 + \frac{k}{2}v^2\right) + \left(\frac{\varepsilon}{2}(u^2 - v^2)\right)$$

Where
$$\Psi_u = \Psi_+ = \frac{1}{\sqrt{2}}(|10\rangle + |01\rangle)$$
$$\Psi_v = \Psi_- = \frac{1}{\sqrt{2}}(|10\rangle - |01\rangle)$$

Both of these states have $E^{(0)} = \hbar\sqrt{\frac{k}{m}}$, but have different $E^{(0)} + E^{(1)}$ which are exactly solvable to be:

$$(E^{(0)} + E^{(1)})_+ = \hbar\sqrt{\frac{k+\varepsilon}{m}} \qquad (E^{(0)} + E^{(1)})_- = \hbar\sqrt{\frac{k-\varepsilon}{m}}$$

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What if we hadn't seen this coordinate transformation?

We could use the symmetry!

As per our theorem, we need a symmetry:
- Shared by H_0 & H'
- Where ψ_+ and ψ_- have different eigenvalues

First Try: Rotational Symmetries:

$H_0(x,y)$ has a continuous rotational symmetry

$H' = \varepsilon xy$, however, only has symmetry under discrete rotations that are multiples of π

Could this work? Let's check $R(\pi)$ on our degenerate states $|10\rangle$ and $|01\rangle$

$$R(\pi)|01\rangle = R(\pi)\,\psi_0(x)\,\psi_1(y)$$
$$\psi_0(-x)\,\psi_1(-y)$$

ψ_0 is an even function: $\psi_0(-x) = \psi_0(x)$
ψ_1, on the other hand, is odd: $\psi_1(-y) = -\psi_1(y)$

$$\therefore\ R(\pi)|01\rangle = [\psi_0(x)]\cdot[-\psi_1(y)]$$
$$= -|01\rangle$$

Similarly, $R(\pi)|10\rangle = -|10\rangle$

Since $|10\rangle$ and $|01\rangle$ have the same eigenvalue under $R(\pi)$, there are no linear combos w/ different e-values! CANNOT work!

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What about a different symmetry: $x \leftrightarrow y$?

$$S\Psi(x,y) \equiv \Psi(y,x)$$

Both H_0 & H' have this symmetry manifestly

Let's check our degenerate states:

$$S|10\rangle = S[\psi_1(x)\psi_0(y)]$$
$$= \psi_1(y)\psi_0(x) = |01\rangle$$

$\therefore$ $|10\rangle$ is not an eigenstate of S & neither is $|01\rangle$.

However, we can make combinations that are!
Moreover, if those linear combinations that are eigenstates of S have different eigenvalues, then our theorem says that those would be the *good states* for TIPT!

Can we make those? Sure!

$$\psi_+ = \tfrac{1}{\sqrt{2}}(|10\rangle + |01\rangle) \qquad \psi_- = \tfrac{1}{\sqrt{2}}(|10\rangle - |01\rangle)$$

$$S\psi_+ = \tfrac{1}{\sqrt{2}} S[|10\rangle + |01\rangle] \qquad S\psi_- = \tfrac{1}{\sqrt{2}} S[|10\rangle - |01\rangle]$$

$$= \tfrac{1}{\sqrt{2}}[|01\rangle + |10\rangle] \qquad = \tfrac{1}{\sqrt{2}}[|01\rangle - |10\rangle]$$

$$= +1\psi_+ \qquad = -1\psi_-$$

Different eigenvalues

Of course, these are the same states we found via coordinate transformation!

By finding a symmetry:

Key!
1) Shared by H_0 & H'
1.5) The degenerate states of H_0 need <u>NOT</u> <u>necessarily</u> be eigenstates of the symmetry :)
3) But where we <u>can</u> build linear combinations which <u>are</u> eigenstates of the symmetry with <u>different</u> eigenvalues

We have found the *good states* for TIPT

<u>Ex 2: A 3-D QMHO with a Radially-Symmetric H'</u>

$$H = \underbrace{\left(\frac{\vec{p}^2}{2m} + \frac{k}{2}\vec{r}^{\,2}\right)}_{H_0} + \underbrace{\left(\frac{\lambda}{2}\vec{r}^{\,4}\right)}_{\lambda H'}$$

Here, the first-excited-state is 3-fold degenerate:
$|n_x\, n_y\, n_z\rangle = \{|100\rangle, |010\rangle, |001\rangle\}$

Clearly, both H_0 & H' have a spherical symmetry ← Point #1

Clearly, the degenerate states are NOT eigenstates of L_z ← Point 1.5

However, we <u>can</u> build linear combinations which <u>are</u> eigenstates of L_z ← Point #2

<u>These</u> will be the good states for T.I.P.T.!

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The states, of course, are

$$\psi_{+1} = \frac{1}{\sqrt{2}}\left(|100\rangle + i|010\rangle\right) \qquad Y_{11} \propto (x+iy)$$

$$\psi_0 = |001\rangle \qquad Y_{10} \propto z$$

$$\psi_{-1} = \frac{1}{\sqrt{2}}\left(|100\rangle - i|010\rangle\right) \qquad Y_{1-1} \propto (x-iy)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \quad \Big| \quad a = \text{Bohr Radius} = \frac{4\pi\hbar^2\epsilon_0}{e^2 m} = \frac{\hbar c}{\alpha m c^2}$$

$$= \frac{1}{n^2}\,\frac{\alpha m c^2}{\hbar c}$$

$$\& \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l+\frac{1}{2})\, n^3 a^2} = \frac{1}{(l+\frac{1}{2})\, n^3}\left(\frac{\alpha m c^2}{\hbar c}\right)^2$$

Which, after putting it all together, we get

$$E_n^{(1)} = -\frac{1}{8}\,\frac{mc^2\alpha^4}{n^4}\left[\frac{4n}{l+1/2} - 3\right]$$

Note, it is $\propto \alpha^4$ as we expected!

$\blacksquare$

The 'Astute Reader' says, "Wait! You just used regular old TIPT even though $\psi_n^{(0)}$ are highly degenerate (l & m!)

Basically, we lucked out!

The unperturbed states $\psi_n^{(0)}$ are already "good"

1) Both H_0 & H' have spherical symmetry
2) The $\psi_n^{(0)}$ already have distinct eigenvalues under H' (i.e. $\psi_n^{(0)}$ are eigenfunctions of H'!)

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What symmetry does our perturbation lack that is present in H_0 then?

We know that some symmetry was broken because, as we discussed in the first week of class, degeneracies arise from symmetries.

What was broken is the Laplace-Runge-Lenz symmetry that is unique to H_0:

$$\vec{M} = \frac{\vec{p} \times \vec{L} - \vec{L} \times \vec{p}}{2m} - \frac{\alpha \hbar c}{r} \vec{r}$$

which is so contrived as we expect any perturbation would break it!

We still have the $(2l+1)$-fold m-degeneracy that we will talk about next time.

However, this is enough to explain another feature of the periodic table: that the 4s have lower energy than 3d! Slide