Lecture Notes for Phys. 362K

Sept. 2014

Starting with notes on perturbation theory

(Notes for first ~ 1 week of class, review topics from Phys. 373, not available)

Perturbation Theory - Nondegenerate states

Suppose we want to solve $\boxed{H|\psi_n\rangle = E_n|\psi_n\rangle}$

But it's too difficult.

Suppose also that we can write $\boxed{H = H_0 + H'}$

where we do know the solution to $\boxed{H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle}$

and H' is "small". We call H' the "perturbation"

Then, we can find an approximate solution to $H|\psi_n\rangle = E_n|\psi_n\rangle$ with a power series expansion (in powers of H'). This method is called "perturbation theory."

Let's introduce the dimensionless parameter λ, where $0 \le \lambda \le 1$.

Let $H(\lambda) = H_0 + \lambda H'$

$\lambda \to 0$: $H(\lambda) \to H_0$

$\lambda \to 1$: $H(\lambda) \to H_0 + H'$ — which is the problem we are trying to solve.

Let's try to solve $H(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle$

To do this, assume power series expansions as follows.

$$E(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$
$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots$$

Then $$H(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle$$

$$(H_0 + \lambda H')(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots)$$
$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \cdots)$$

This is an equation of the form $\sum_n a_n\lambda^n = \sum_n b_n\lambda^n$

The equation is satisfied if.f. $a_n = b_n$ for all n

$\Leftrightarrow$ equate coefficients of λ^n on each side

Coefficients of:

λ^0 : $H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$ ← by assumption we know solution to this equation already. This is called the "unperturbed" problem.

λ^1 : $H_0|\psi_n^{(1)}\rangle + H'|\psi_n^{(0)}\rangle$
$$= E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle$$

$$\Rightarrow (H_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (H' - E_n^{(1)})|\psi_n^{(0)}\rangle = 0$$

λ^2 : $(H_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + (H' - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^{(0)}\rangle = 0$

etc.

Let's take inner product of λ' equation with $\langle \psi_n^{(0)}|$:

$$\langle \psi_n^{(0)}| (H_0 - E_n^{(0)}) |\psi_n^{(1)}\rangle + \langle \psi_n^{(0)}| (H' - E_n^{(1)}) |\psi_n^{(0)}\rangle = 0$$

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

($\langle \psi_n^{(0)}| (H_0 - E_n^{(0)}) |\psi_n^{(1)}\rangle = 0$; $\langle \psi_n^{(0)} | \psi_n^{(0)}\rangle = 1$)

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

↪ To first order, the energy correction to the n^{th} eigenstate is the expectation value of the perturbation H' in the unperturbed state $|\psi_n^{(0)}\rangle$

i.e. $\boxed{E_n \cong E_n^{(0)} + E_n^{(1)}}$ 1st-order approximation for the energy.

Example Particle, mass m, in harmonic oscillator potential $V(x) = \frac{1}{2} m\omega^2 x^2$. It is perturbed by an added potential $H'(x) = \epsilon |x|$. Find the energy & the ground state to first order in H'!

Solution $H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 + \epsilon |x|$

Let $H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$ $\quad H' = \epsilon |x|$

Solution to $H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$ is known (just quantum harmonic oscillator)

$E_n^{(0)} = \left(n+\frac{1}{2}\right)\hbar\omega \qquad \psi_0^{(0)}(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}$

$E_0^{(1)} = \langle \psi_0^{(0)} | H' | \psi_0^{(0)} \rangle$ (ground state, $n=0$)

$$= \int_{-\infty}^{\infty} \psi_0^{(0)*}(x)\, \epsilon|x|\, \psi_0^{(0)}(x)\, dx = \int_{-\infty}^{\infty} |\psi_0^{(0)}(x)|^2 \epsilon|x|\, dx$$

$$= \epsilon \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar} |x|\, dx$$

$$= 2\epsilon \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_0^{\infty} e^{-m\omega x^2/\hbar} x\, dx \qquad \left[\int_{-\infty}^{\infty}[\,]\,dx = 2\int_0^{\infty}[\,]\,dx, \text{ since integrand is same for } +x \text{ and } -x\right]$$

$$= 2\epsilon \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{1}{2}\left(\frac{\hbar}{m\omega}\right) = \epsilon\left(\frac{\hbar}{\pi m\omega}\right)^{1/2}$$

$$\Rightarrow \boxed{E_0 \simeq E_0^{(0)} + E_0^{(1)} = \frac{1}{2}\hbar\omega + \epsilon\left(\frac{\hbar}{\pi m\omega}\right)^{1/2}}$$

Next take inner product of λ' equation with $\langle \psi_m^{(0)}|$: $(m \neq n)$

$$\langle \psi_m^{(0)} | (H_0 - E_n^{(0)}) |\psi_n^{(1)}\rangle + \langle \psi_m^{(0)} | (H' - E_n^{(1)}) |\psi_n^{(0)}\rangle = 0$$

$$\left(E_m^{(0)} - E_n^{(0)}\right)\langle \psi_m^{(0)} | \psi_n^{(1)}\rangle + \langle \psi_m^{(0)} | H' | \psi_n^{(0)}\rangle - E_n^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_n^{(0)}\rangle}_{0} = 0$$

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

We know that we can always write any vector, including $|\psi_n^{(1)}\rangle$ as a linear combination of the $|\psi_n^{(0)}\rangle$, $|\psi_n^{(1)}\rangle = \sum_m c_m |\psi_m^{(0)}\rangle$

Looking back at the λ^0, λ^1, λ^2, ... equations, we see that c_m, for $m=n$, is not determined. Therefore we can choose to set it to zero. This is the same thing as saying that with

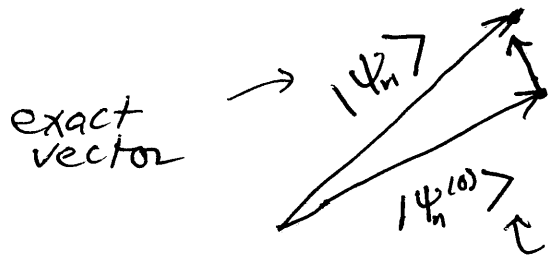
$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + \cdots$$

any "$|\psi_n^{(0)}\rangle$ component" of $|\psi_n^{(1)}\rangle$ is included in the zeroth-order term. Therefore with this assumption

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n} c_m |\psi_m^{(0)}\rangle \qquad \text{where } \sum_{m \neq n} \text{ means}$$

we include every value of m in the sum except $m=n$. (or we can say that $c_m = 0$, for $m=n$)

This means we can picture the vectors as follows:



$|\psi_n\rangle \approx |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle$ (but not exactly equal)

Recall that $1 = \sum_m |\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|$

$$|\psi_n^{(1)}\rangle = 1\cdot|\psi_n^{(1)}\rangle = \sum_m |\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle$$

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

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

$|\psi_n^{(1)}\rangle$ = 1st order correction to $|\psi_n^{(0)}\rangle$

$$\boxed{|\psi_n\rangle \cong |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle}$$

Next, take inner product of λ^2 equation with $\langle\psi_n^{(0)}|$:

$$\langle\psi_n^{(0)}|(H_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + \langle\psi_n^{(0)}|(H' - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 0$$

$\langle\psi_n^{(0)}|(H_0 - E_n^{(0)})$ acting on the left: $(E_n^{(0)} - E_n^{(0)}) = 0$; $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle = 1$

$$\langle\psi_n^{(0)}|(E_n^{(0)} - E_n^{(0)})|\psi_n^{(2)}\rangle + \langle\psi_n^{(0)}|H'|\psi_n^{(1)}\rangle - E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle - E_n^{(2)} = 0$$

0 $\qquad$ 0

$$E_n^{(2)} = \langle\psi_n^{(0)}|H'|\psi_n^{(1)}\rangle$$

substitute from above.

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

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

2nd order correction to the energy.

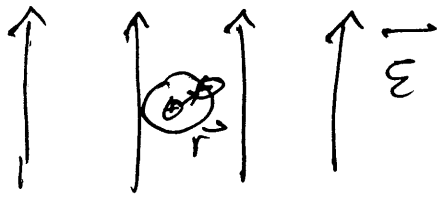
Improved approximation to energy:

$$E_n \cong E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

We could keep going to 3rd, 4th, 5th... order, and people do that for research calculations. But we will stop here for this class.

Stark effect, ground state of hydrogen

- Place H atom in electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$



H' = additional contribution to energy due to $\vec{\mathcal{E}}$

$$H' = -\int_0^{\vec{r}} \vec{F}_e \, d\vec{x} = -\int_0^{\vec{r}} (-e\vec{\mathcal{E}}) \cdot d\vec{x}$$

$$= \int_0^z e\mathcal{E} \, dz = e\mathcal{E}z$$

$$\Rightarrow \quad H = \underbrace{\frac{\vec{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r}}_{H_0} + \underbrace{e\mathcal{E}z}_{H'}$$

H_0 is just usual Hamiltonian of hydrogen atom.

$$\Rightarrow \quad H_0 |\psi_{100}^{(0)}\rangle = E_1^{(0)} |\psi_{100}^{(0)}\rangle$$

where $E_1^{(0)} = \frac{-e^2}{8\pi\epsilon_0 a_0} = -13.605\ eV$

(a_0: Bohr radius)

and $\psi_{100}^{(0)}(\vec{r}) = \langle \vec{r} | \psi_{100}^{(0)} \rangle = \sqrt{\frac{1}{\pi a_0^3}}\, e^{-r/a_0}$

Want to solve $H|\psi_{100}\rangle = E_1 |\psi_{100}\rangle$

[Turns out to be possible, but difficult]

$\Rightarrow$ Use perturbation theory.

$$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)} + \cdots$$

$$E_1^{(1)} = \langle \psi_{100}^{(0)} | H' | \psi_{100}^{(0)} \rangle$$

$$= \int |\psi_{100}^{(0)}(\vec{r})|^2 e\mathcal{E}z\, d^3r$$

$$= e\mathcal{E} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{\pi a_0^3} e^{-2r/a_0} \underbrace{r\cos\theta}_{z} \cdot \underbrace{r^2 \sin\theta\, dr\, d\theta\, d\phi}_{d^3r}$$

$$= e\mathcal{E} \int_0^{\pi} \cos\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\infty} \frac{1}{\pi a_0^3} e^{-2r/a_0} r^3\, dr$$

But $\int_0^{\pi} \cos\theta \sin\theta \, d\theta = \frac{\sin^2\theta}{2}\Big]_0^{\pi} = 0 - 0 = 0$

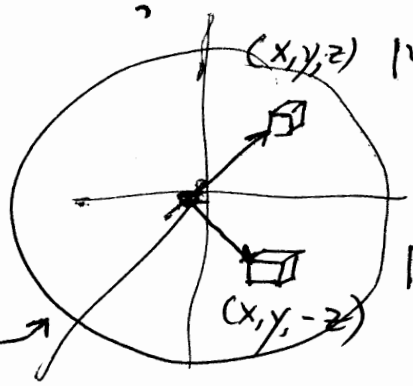
So $\boxed{E_1^{(1)} = 0}$ there is no shift to first order in ε

Also: can see this is zero by symmetry

$\int |\psi|^2 z \, d^3r$

= sum of $|\psi|^2 z$ over all volume elements.

Can sum volume elements over pairs like this →



Contribution to integral for each pair is zero, since contributions are opposite ($|\psi|^2$ = same, z = opposite). Hence integral is zero.

$\boxed{\int |\psi|^2 z \, d^3r = 0}$

$$|\psi_{100}\rangle = |\psi_{100}^{(0)}\rangle + |\psi_{100}^{(1)}\rangle + \cdots$$

$$|\psi_{100}^{(1)}\rangle = \sum_{(n\ell m)\neq 100} \frac{\langle \psi_{n\ell m}^{(0)} | H' | \psi_{100}^{(0)} \rangle}{E_1^{(0)} - E_n^{(0)}} |\psi_{n\ell m}^{(0)}\rangle$$

⇒ need $\langle \psi_{n\ell m}^{(0)} | z | \psi_{100}^{(0)} \rangle$ since $H' = e\mathcal{E}z$ ↑

General case $\langle \psi_{n\ell m}^{(0)} | z | \psi_{n'\ell'm'}^{(0)} \rangle$

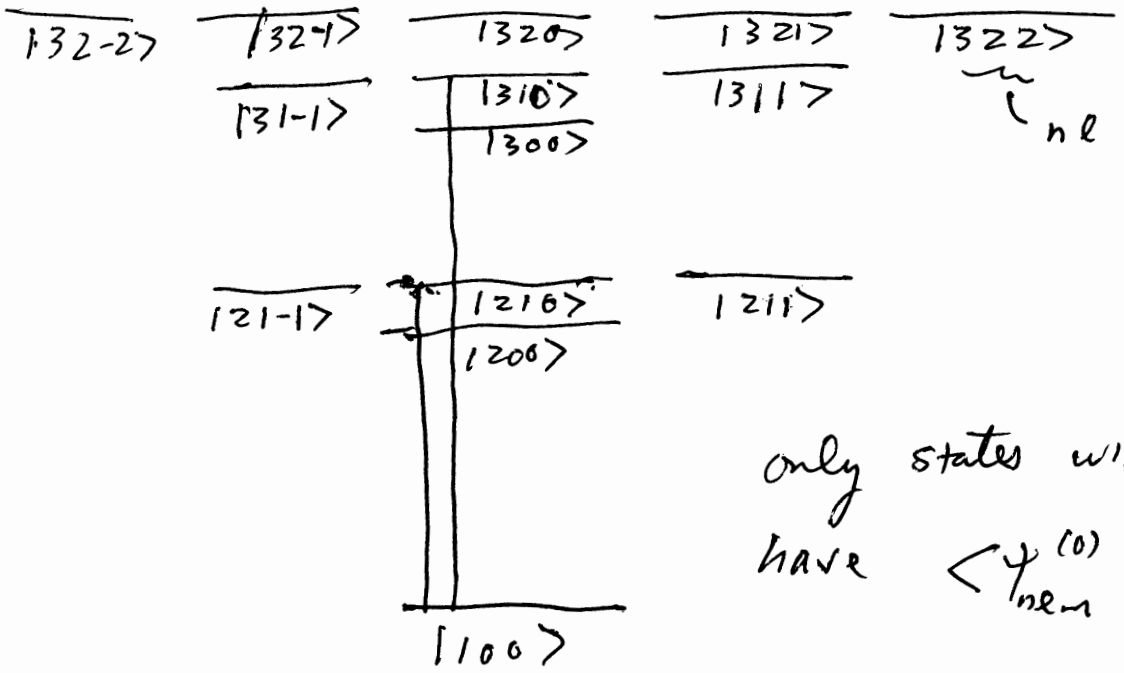
Can show (HW problem)

$$\langle \psi^{(0)}_{n\ell m} | z | \psi^{(0)}_{n'\ell'm'} \rangle = 0$$

unless [(m=m') AND [$\ell = \ell' + 1$ OR $\ell = \ell' - 1$]]

This is called a "selection rule".

Hydrogen states: show non-zero $\langle \psi^{(0)}_{n\ell m} | z | \psi^{(0)}_{100} \rangle$ with connecting line. Only those states contribute to $|\psi^{(1)}_{100}\rangle$



only states with $\ell = 1$, $m = 0$ have $\langle \psi^{(0)}_{n\ell m} | z | \psi^{(0)}_{100} \rangle \neq 0$

Hence

$$|\psi^{(1)}_{100}\rangle = \sum_{n=2}^{\infty} \frac{\langle \psi^{(0)}_{n10} | H' | \psi^{(0)}_{100} \rangle}{E_1^{(0)} - E_n^{(0)}} |\psi^{(0)}_{n10}\rangle$$

$$\langle \psi^{(0)}_{n10} | z | \psi^{(0)}_{100} \rangle = \int_0^\infty R_{n1}(r)\, R_{10}(r)\, r^3 dr \cdot$$

$$\times \int_0^{2\pi} d\phi \int_0^{\pi} Y_{10}(\theta,\phi)\; Y_{00}(\theta,\phi)\, \cos\theta \sin\theta\, d\theta$$

$$= \int_0^\infty R_{n1}(r) R_{10}(r) r^3 dr \int_0^{2\pi} d\phi \int_0^{\pi} \sqrt{\frac{3}{4\pi}} \cos\theta \sqrt{\frac{1}{4\pi}}\; \cos\theta \sin\theta\, d\theta$$

$$= \int_0^\infty R_{n1}(r) R_{10}(r) r^3 dr \;\; 2\pi \frac{\sqrt{3}}{4\pi} \left(-\frac{\cos^3\theta}{3} \right)_0^{\pi}$$

$$= \frac{1}{\sqrt{3}} \int_0^\infty R_{n1}(r) R_{10}(r)\, r^3 dr$$

for $n = 2$

$$\langle \psi^{(0)}_{210} | z | \psi^{(0)}_{100} \rangle = \frac{1}{\sqrt{3}} \int_0^\infty \left(\frac{1}{\sqrt{24}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \right) \left(\frac{2}{a_0^{3/2}} e^{-r/a_0} \right) r^3 dr$$

$$= \frac{1}{\sqrt{3}} \frac{2}{\sqrt{24}} a_0 \int_0^\infty x^4 e^{-\frac{3}{2}x} dx \qquad \left(x \equiv \frac{r}{a_0} \right)$$

Mathematica

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NIntegrate[x^4 Exp[-3x/2], {x, 0, Infinity}]
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Output 3.16049

$$\Rightarrow \langle \psi^{(0)}_{210} | z | \psi^{(0)}_{100} \rangle = \frac{1}{\sqrt{2}} \frac{2}{\sqrt{24}} a_0 \times 3.16049 = 0.7449\, a_0$$

Similarly: $n=3$: $\langle \psi^{(0)}_{310} | z | \psi^{(0)}_{100} \rangle = 0.2983\, a_0$

$n=4$: $\langle \psi^{(0)}_{410} | z | \psi^{(0)}_{100} \rangle = 0.1759\, a_0$

etc.

So, $(E_n^{(0)} = E_1^{(0)}/n^2)$

$$|\psi_{100}^{(1)}\rangle = \sum_{n=2}^{\infty} \frac{e\mathcal{E}}{E_1^{(0)}} \frac{\langle \psi_{n10}^{(0)} | z | \psi_{100}^{(0)} \rangle}{1 - \frac{1}{n^2}} |\psi_{n10}^{(0)}\rangle$$

$$= \sum_{n=2}^{\infty} C_n^{(1)} |\psi_{n10}^{(0)}\rangle$$

$$C_2^{(1)} = \frac{e\mathcal{E}(0.7449)a_0}{E_1^{(0)}\left(1-\frac{1}{4}\right)} = 0.9932 \frac{e\mathcal{E}a_0}{E_1^{(0)}}$$

$$C_3^{(1)} = \frac{e\mathcal{E}(0.2983\, a_0)}{E_1^{(0)}\left(1-\frac{1}{9}\right)} = 0.3356 \frac{e\mathcal{E}a_0}{E_1^{(0)}}$$

$$\vdots$$

$$|\psi_{100}\rangle \cong |\psi_{100}^{(0)}\rangle + |\psi_{100}^{(1)}\rangle$$

$$= |\psi_{100}^{(0)}\rangle + \left[0.9932 \frac{e\mathcal{E}a_0}{E_1^{(0)}} |\psi_{210}^{(0)}\rangle + 0.3356 \frac{e\mathcal{E}a_0}{E_1^{(0)}} |\psi_{310}^{(0)}\rangle + 0.1809 \frac{e\mathcal{E}a_0}{E_1^{(0)}} |\psi_{410}^{(0)}\rangle + \cdots\right]$$

Largest practical $\mathcal{E}$ in lab: $\mathcal{E} = 10^7 \frac{V}{m}$

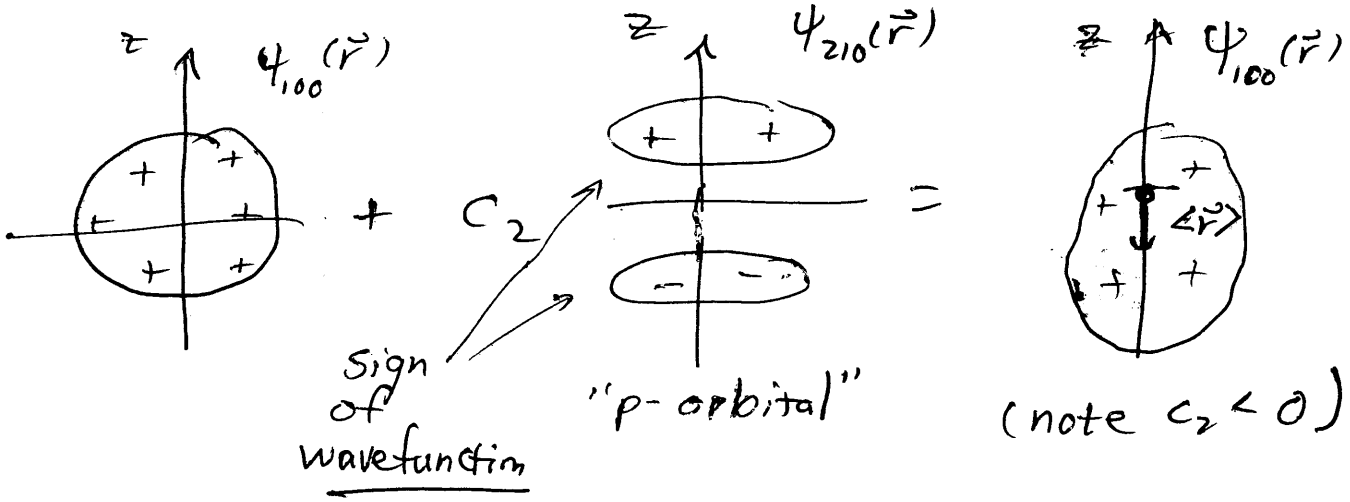
For $\mathcal{E} = 10^7 \frac{V}{m}$, $\frac{e\mathcal{E}a_0}{E_1^{(0)}} = \frac{(1.602\times10^{-19})(10^7)(0.5292\times10^{-10})}{-13.605 \times 1.602\times10^{-19}}$

$$\frac{e\mathcal{E}a_0}{E_1^{(0)}} = \underline{-3.890\times10^{-5}}$$

$$\Rightarrow \quad C_2 = \underline{-3.86\times10^{-5}}$$

Crude approximation

$$|\psi_{100}\rangle \cong |\psi_{100}^{(0)}\rangle + c_2 |\psi_{210}^{(0)}\rangle$$



Application of $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$ $\Rightarrow$ electron shifts down

$\Rightarrow$ atom polarizes (develops nonzero electric dipole moment)

induced dipole moment $\langle \vec{d} \rangle = -e\langle \vec{r} \rangle = \int -e\vec{r}\,|\psi|^2 d^3r$

Definition $\langle \vec{d} \rangle = \alpha \vec{\mathcal{E}}$ α = polarizability

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Energy shift $E_1^{(2)} = \dfrac{e^2\mathcal{E}^2}{E_1^{(0)}} \displaystyle\sum_{n=2}^{\infty} \frac{|\langle \psi_{n10}^{(0)} | z | \psi_{100}^{(0)} \rangle|^2}{1 - \frac{1}{n^2}}$

$$\frac{e^2\mathcal{E}^2}{E_1^{(0)}} = \frac{e^2\mathcal{E}^2 8\pi\epsilon_0 a_0}{-e^2} = -2 \cdot 4\pi\epsilon_0 a_0 \mathcal{E}^2$$

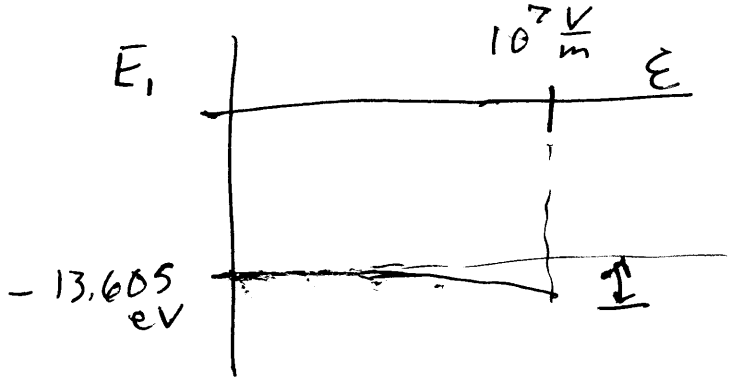
$$E_1^{(2)} = -2\cdot 4\pi\epsilon_0 a_0 \mathcal{E}^2 \sum_{n=2}^{\infty} \frac{|\langle \psi_{n10}^{(0)} | z | \psi_{100}^{(0)} \rangle|^2}{1 - \frac{1}{n^2}}$$

$$= -4\pi\epsilon_0 a_0 \mathcal{E}^2 \left[\frac{2\,(0{,}7449\, a_0)^2}{1 - \frac{1}{4}} + \frac{2(0{,}2983 a_0)^2}{1 - \frac{1}{9}} + \cdots \right]$$

$$E_1^{(2)} \cong -(1.478 + 0{,}2000 + \cdots)\, 4\pi\epsilon_0 a_0^3 \mathcal{E}^2$$

Exact result for sum is $\frac{9}{4} = 2.250$

$$\Rightarrow E_1 \cong E_1^{(0)} - 2.250\,(4\pi\epsilon_0 a_0^3 \mathcal{E}^2)$$



ground state shifts down $\propto \mathcal{E}^2$

Q. Why isn't $\Delta E_1 = -\vec{d}\cdot\vec{\mathcal{E}} \propto \mathcal{E}$?

A. This formula only applies if $\vec{d}$ is constant as $\vec{\mathcal{E}}$ is turned on. Here, $\vec{d} \propto \vec{\mathcal{E}}$, so

$$E_1^{(2)} = -\int_0^{\mathcal{E}} d\,(d\mathcal{E}) = -\int_0^{\mathcal{E}} (\alpha\mathcal{E})\, d\mathcal{E} = -\frac{1}{2}\alpha\mathcal{E}^2$$

Degenerate Perturbation Theory

A. Perturbation of degenerate levels

Consider the expression we derived for the first-order correction to the eigenstate $\left|\psi_{\alpha_k}^{(0)}\right\rangle$ of $H^{(0)}$, due to a perturbation H':

$$\left|\psi_{\alpha_k}^{(1)}\right\rangle = \sum_{\alpha_j \neq \alpha_k} \frac{\left\langle \psi_{\alpha_j}^{(0)} \middle| H' \middle| \psi_{\alpha_k}^{(0)} \right\rangle}{E_{\alpha_k}^{(0)} - E_{\alpha_j}^{(0)}} \left|\psi_{\alpha_j}^{(0)}\right\rangle \tag{2.1}$$

where α_k denotes a set of quantum numbers sufficient to specify a specific solution to the unperturbed problem

$$H^{(0)}\left|\psi_{\alpha_k}^{(0)}\right\rangle = E_{\alpha_k}^{(0)}\left|\psi_{\alpha_k}^{(0)}\right\rangle \tag{2.2}$$

Suppose now that two or more levels are degenerate, *i.e.* $E_{\alpha_j}^{(0)} = E_{\alpha_k}^{(0)}$ for some j and k. Such level degeneracy is very common. For example, the $n = 2$ levels of the unperturbed hydrogen atom are degenerate:

$$E_{200}^{(0)} = E_{210}^{(0)} = E_{211}^{(0)} = E_{21-1}^{(0)} \tag{2.3}$$

where the subscripts give the values of $n\ell m$.

It's cle. from eq. (2.1) that we'll run into trouble if two levels have the same energy. In order to deal with this situation, we will first adopt a new labeling method, as illustrated in Fig. 2.1. We will label the unperturbed level energies $E_n^{(0)}$ with an index $n = 1, 2, 3,\ldots$, in order of increasing energy. And if the nth unperturbed level energy is g_n-fold degenerate, we will choose a second index $i = 1, 2, \ldots g_n$ to label a specific unperturbed state vector $\left|\psi_{ni}^{(0)}\right\rangle$ belonging to that level.

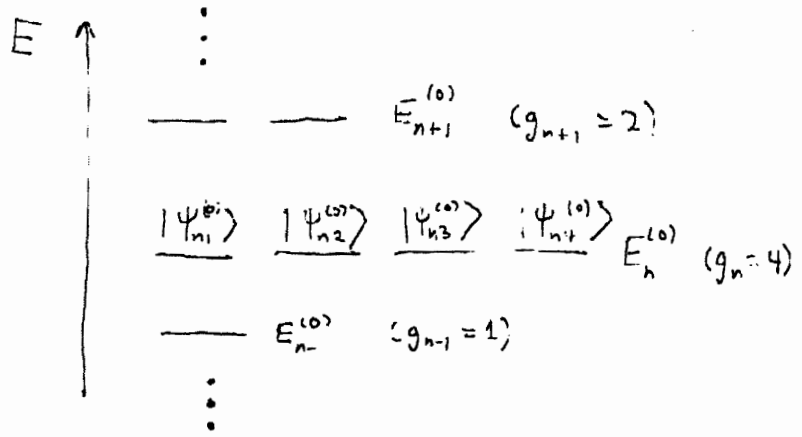


Fig. 2.1. Unperturbed energy level spectrum with degeneracy.

For example, for the hydrogen atom n would be identical to the principal quantum number. And for the $n = 2$ level, we would have a degeneracy $g_n = 4$. One way to label the unperturbed state vectors belonging to the $n = 2$ energy level would be

$$\begin{aligned}
\left|\psi_{21}^{(0)}\right\rangle &= \left|\psi_{200}^{(0)}\right\rangle \\
\left|\psi_{22}^{(0)}\right\rangle &= \left|\psi_{210}^{(0)}\right\rangle \\
\left|\psi_{23}^{(0)}\right\rangle &= \left|\psi_{211}^{(0)}\right\rangle \\
\left|\psi_{24}^{(0)}\right\rangle &= \left|\psi_{21-1}^{(0)}\right\rangle
\end{aligned} \tag{2.4}$$

$|\psi_{ni}^{(0)}\rangle$ $|\psi_{n\ell m}^{(0)}\rangle$

There are other ways we could have assigned the specific $\left|\psi_{\alpha_j}^{(0)}\right\rangle$ vectors to the $\left|\psi_{ni}^{(0)}\right\rangle$ vectors. The specific choice is not important; we just need to make a choice and stick with it throughout the calculation.

Now, suppose that the perturbation is $\lambda H'$, and that we can adjust the parameter λ continuously from 0 to 1. The non-zero perturbation may lead to a breaking of the degeneracy, similar to that illustrated in Fig. 2.2. The breaking of the degeneracy may be total, so that g_n distinct energy levels emerge from the level with unperturbed energy $E_n^{(0)}$. Or, the breaking of the degeneracy may be partial, so that some number of distinct energies $f_n < g_n$ emerge, with one or more of the perturbed levels having a remaining degeneracy. This case is illustrated for the nth level in Fig. 2, where only $f_n = 3$ distinct energies emerge from the nth unperturbed level, with one of those levels remaining doubly degenerate

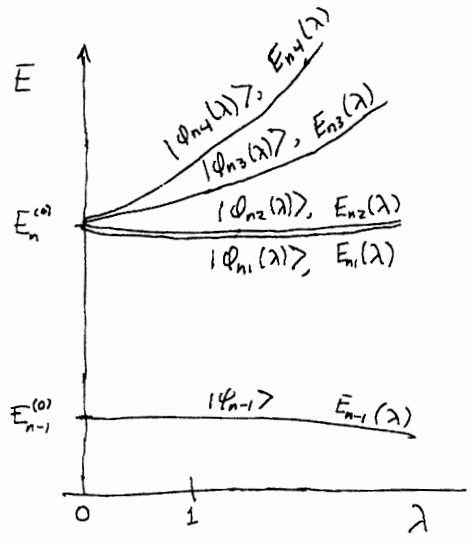


Fig. 2.2. Lifting of a degeneracy by a perturbation $\lambda H'$. In this example, we have a non-degenerate unperturbed level with energy $E_{n-1}^{(0)}$, and a unperturbed level with degeneracy $g_n = 4$ with energy $E_n^{(0)}$. The degeneracy of the *n*th level is partly but not totally lifted by the perturbation. In the limit as $\lambda \to 0$, the energies of $g_n = 4$ different levels must have a limiting value $E_n^{(0)}$. We label these levels with the indexes *n* and $i = 1,..., g_n$, with the exact eigenvector denoted as $|\varphi_{ni}\rangle$. The zeroth-order eigenvector is defined as $|\varphi_{ni}^{(0)}\rangle = \lim_{\lambda\to 0} |\varphi_{ni}(\lambda)\rangle$.

$(E_{n1} = E_{n2})$. Another possibility is that the degeneracy is not broken by the perturbation, so that the energies of all g_n states have the same dependence on λ.

Now, to calculate the state vector and energy for a non-degenerate unperturbed state, such as the state $|\psi_{n-1}\rangle$ illustrated in Fig. 2.2, we can use the methods of non-degenerate perturbation theory that we've already covered. This is true even if some or all of the other unperturbed levels are degenerate. However, if we want to find the energies and state vectors of the states with a degenerate unperturbed energy, we run into trouble if we try to apply non-degenerate perturbation theory. That's because the coefficient in eq. (2.1) $\dfrac{\left|\langle \psi_{\alpha_j}^{(0)} | H' | \psi_{\alpha_k}^{(0)} \rangle\right|}{\left|E_{\alpha_k}^{(0)} - E_{\alpha_j}^{(0)}\right|} \to \infty$. (A possible exception is the case in which the numerator is also goes to zero.)

In order to proceed, we'll introduce another notation. Consider those g_n states that, in the limit $\lambda \to 0$, have energy $E_n^{(0)}$. We will denote the eigenvector for these states as $|\varphi_{ni}\rangle$, where $i = 1,..., g_n$; *i.e.*

$$H(\lambda)|\varphi_{ni}(\lambda)\rangle = \left(H^{(0)} + \lambda H'\right)|\varphi_{ni}(\lambda)\rangle = E_{ni}(\lambda)|\varphi_{ni}(\lambda)\rangle \tag{2.5}$$

In addition, we'll define the zero-order state vector for these levels to be

$$\left|\varphi_{ni}^{(0)}\right\rangle = \lim_{\lambda\to 0}\left|\varphi_{ni}(\lambda)\right\rangle \tag{2.6}$$

Now, you may wonder why we are adopting a new notation for these levels and not just using the notation $\left|\psi_{ni}^{(0)}\right\rangle$. The reason is that $\left|\psi_{ni}^{(0)}\right\rangle$ is the solution to the problem $H^{(0)}\left|\psi_{ni}^{(0)}\right\rangle = E_n^{(0)}\left|\psi_{ni}^{(0)}\right\rangle$ alone; we did not take into account H' when we solved this equation. Since the level is g_n-fold degenerate, that means that the set of functions $\left\{\left|\psi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$ spans a g_n-dimensional degenerate subspace of the eigenstates of $H^{(0)}$. It follows that any linear combination of these g_n states is also an eigenstate of $H^{(0)}$ with energy $E_n^{(0)}$:

$$\text{If } \left|\varphi\right\rangle = \sum_{j=1}^{g_n} c_j \left|\psi_{nj}^{(0)}\right\rangle, \tag{2.7}$$

$$\text{then } H^{(0)}\left|\varphi\right\rangle = E_n^{(0)}\left|\varphi\right\rangle. \tag{2.8}$$

If we wanted to we could use superpositions of the form (2.7) to make a new set of four orthornormal state vectors that span the same space as the set $\left\{\left|\psi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$. Since the basis set is adjustable in this way, there is no guarantee that the basis set $\left\{\left|\psi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$ that we found in our first solution of $H^{(0)}\left|\psi_{ni}^{(0)}\right\rangle = E_n^{(0)}\left|\psi_{ni}^{(0)}\right\rangle$ will match the set of states $\left\{\left|\varphi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$. But, we do know that the states $\left\{\left|\varphi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$ must be expressible in terms of linear superpositions of the form (2.7). To put this another way, the sets $\left\{\left|\psi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$ and $\left\{\left|\varphi_{ni}^{(0)}\right\rangle; i=1,...,g_n\right\}$ just constitute two different basis sets for the degenerate subspace of eigenvectors of $H^{(0)}$ with energy $E_n^{(0)}$.

You can also see this from eq. (2.1). That equation tells you that for H' small, the perturbation will strongly mix states together that belong to the same energy, but cause almost no mixing of states belonging to different energies. So in the limit as $H' \to 0$, the perturbed states close in energy to $E_n^{(0)}$ must just be linear combinations of the zero order wavefunctions. So we can take these wavefunctions to be of the form

$$\left|\varphi_{ni}^{(0)}\right\rangle = \sum_{j=1}^{g_n} c_{ij}\left|\psi_{nj}^{(0)}\right\rangle \tag{2.9}$$

Since the eigenvectors of a Hamiltonian can always be chosen to be orthogonal and normalized, we'll assume that

$$\left\langle\varphi_{nj}^{(0)}\middle|\varphi_{ni}^{(0)}\right\rangle = \delta_{ji} \tag{2.10}$$

We can determine the value for c_{ij} by taking the inner product of eq. (2.9) with the bra $\langle \psi_{nk}^{(0)} |$:

$$\langle \psi_{nk}^{(0)} | \varphi_{ni}^{(0)} \rangle = \sum_{j=1}^{g_n} c_{ij} \langle \psi_{nk}^{(0)} | \psi_{nj}^{(0)} \rangle = \sum_{j=1}^{g_n} c_{ij} \delta_{kj} = c_{ik} \tag{2.11}$$

Changing dummy indices $k \rightarrow j$, we find

$$c_{ij} = \langle \psi_{nj}^{(0)} | \varphi_{ni}^{(0)} \rangle \tag{2.12}$$

Now, let's revisit the "λ^1 equation" that we derived earlier. Since $\{|\varphi_{ni}^{(0)}\rangle\}$ and $\{|\psi_{ni}^{(0)}\rangle\}$ are just alternative basis sets, the "λ^1 equation" also can be applied to $|\varphi_{ni}^{(0)}\rangle$

$$\left(H^{(0)} - E_n^{(0)}\right)|\varphi_{ni}^{(1)}\rangle + \left(H' - E_{ni}^{(1)}\right)|\varphi_{ni}^{(0)}\rangle = 0 \tag{2.13}$$

The eigenvectors that satisfy this equation are the correct solutions for the set $\{|\varphi_{ni}^{(0)}\rangle\}$.

Let's take the inner product of this equation with the bra $\langle \psi_{nj}^{(0)} |$. Doing so, we find that

$$\langle \psi_{nj}^{(0)} | \left(H^{(0)} - E_n^{(0)}\right)|\varphi_{ni}^{(1)}\rangle + \langle \psi_{nj}^{(0)} | \left(H' - E_{ni}^{(1)}\right)|\varphi_{ni}^{(0)}\rangle = 0, \text{ or}$$

$$\langle \psi_{nj}^{(0)} | \left(E_n^{(0)} - E_n^{(0)}\right)|\varphi_{ni}^{(1)}\rangle + \langle \psi_{nj}^{(0)} | H' | \varphi_{ni}^{(0)} \rangle - E_{ni}^{(1)} \langle \psi_{nj}^{(0)} | \varphi_{ni}^{(0)} \rangle = 0, \text{ which gives}$$

$$E_{ni}^{(1)} \langle \psi_{nj}^{(0)} | \varphi_{ni}^{(0)} \rangle = \langle \psi_{nj}^{(0)} | H' | \varphi_{ni}^{(0)} \rangle \tag{2.14}$$

Next, we'll use the closure identity

$$1 = \sum_m \sum_k |\psi_{mk}^{(0)}\rangle \langle \psi_{mk}^{(0)}| \tag{2.15}$$

to rewrite eq. (2.14) as

$$\begin{aligned} E_{ni}^{(1)} \langle \psi_{nj}^{(0)} | \varphi_{ni}^{(0)} \rangle &= \sum_m \sum_k \langle \psi_{nj}^{(0)} | H' | \psi_{mk}^{(0)} \rangle \langle \psi_{mk}^{(0)} | \varphi_{ni}^{(0)} \rangle \\ &= \sum_m \sum_k \langle \psi_{nj}^{(0)} | H' | \psi_{nk}^{(0)} \rangle \langle \psi_{nk}^{(0)} | \varphi_{ni}^{(0)} \rangle \delta_{mn} = \sum_k \langle \psi_{nj}^{(0)} | H' | \psi_{nk}^{(0)} \rangle \langle \psi_{nk}^{(0)} | \varphi_{ni}^{(0)} \rangle \end{aligned} \tag{2.16}$$

since any state vector belonging to the *n*th energy level is orthogonal to any state vector belonging to the *m*th energy level, with $m \neq n$. This equation can be rewritten as

$$\sum_k H'_{jk} c_{ik} - E_{ni}^{(1)} c_{ij} = 0 \tag{2.17}$$

where $H'_{jk} = \langle \psi_{nj}^{(0)} | H' | \psi_{nk}^{(0)} \rangle$ (2.18)

is the matrix element of the perturbation H' between the jth and kth unperturbed eigenvectors in the degenerate subspace. Note that we haven't included the subscript "n" with every symbol (for instance on H'), but it should be kept in mind that all equations apply only to the nth degenerate subspace. There will be a different set of equations for a different degenerate subspace. For a fixed value of i, the expression (2.17) is a set of g_n equations corresponding to $j = 1, 2, \ldots g_n$. We can write these equations in matrix form as

$$\begin{bmatrix} H'_{11} & H'_{12} & \cdots & H'_{1g_n} \\ H'_{21} & H'_{22} & \cdots & H'_{2g_n} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{g_n 1} & H'_{g_n 2} & \cdots & H'_{g_n g_n} \end{bmatrix} \begin{bmatrix} c_{i1} \\ c_{i2} \\ \vdots \\ c_{ig_n} \end{bmatrix} = E_{ni}^{(1)} \begin{bmatrix} c_{i1} \\ c_{i2} \\ \vdots \\ c_{ig_n} \end{bmatrix} \tag{2.19}$$

or more simply as

$$H' \left| \varphi_{ni}^{(0)} \right\rangle = E_{ni}^{(1)} \left| \varphi_{ni}^{(0)} \right\rangle, \tag{2.20}$$

since the matrix of $\left| \varphi_{ni}^{(0)} \right\rangle = c_{i1} \left| \psi_{n1}^{(0)} \right\rangle + c_{i2} \left| \psi_{n2}^{(0)} \right\rangle + \cdots + c_{ig_n} \left| \psi_{ng_n}^{(0)} \right\rangle$ in the basis $\left\{ \left| \psi_{n1}^{(0)} \right\rangle \right\}$ is $\begin{bmatrix} c_{i1} \\ c_{i2} \\ \vdots \\ c_{ig_n} \end{bmatrix}$.

Equation (2.17) (or (2.19) or (2.20)) is just an *eigenvalue equation* for the energies $E_{ni}^{(1)}$ and eigenvectors $\left| \varphi_{ni}^{(0)} \right\rangle$. Since H' has dimension $g_n \times g_n$, there will be g_n eigenvalues, which we'll label with index $i = 1, \ldots, g_n$. According to eqs. ((2.17)-(2.20)) these eigenvalues are just the first order perturbations to the energies. The corresponding eigenvectors are just the eigenvectors $\left| \varphi_{ni}^{(0)} \right\rangle$ of $H^{(0)} + H'$, correct to zeroth order.

To summarize, this is the key prescription of degenerate perturbation theory:

> *To calculate the eigenvalues (to first order) and the eigenstates (to zeroth order) of the Hamiltonian corresponding to a degenerate unperturbed state $E_n^{(0)}$, diagonalize the matrix $H'_{jk} = \left\langle \psi_{nj}^{(0)} \right| H' \left| \psi_{nk}^{(0)} \right\rangle$ of the perturbation in the degenerate subspace of eigenstates $\left\{ \left| \psi_{nk}^{(0)} \right\rangle \right\}$ of $H^{(0)}$. The eigenvalues of H' give the first order corrections to the energy, and the corresponding eigenvectors of H' are the correct zeroth-order eigenvectors of $H = H^{(0)} + H'$.*

The solution for the state vectors (to zeroth order) and their energies (to first order), for the levels in the *n*th near degenerate subspace are:

state vectors	energies
$\left\|\varphi_{n1}^{(0)}\right\rangle$	$E_n^{(0)} + E_{n1}^{(1)}$
$\left\|\varphi_{n2}^{(0)}\right\rangle$	$E_n^{(0)} + E_{n2}^{(1)}$
$\vdots$	$\vdots$
$\left\|\varphi_{ng_n}^{(0)}\right\rangle$	$E_n^{(0)} + E_{ng_n}^{(1)}$

B. Example: Stark effect in the $n = 2$ state of hydrogen

We again consider the hydrogen atom placed in an electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$, with Hamiltonian

$$H = -\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} + e\mathcal{E}z = H^{(0)} + H' \tag{2.21}$$

where again $H^{(0)} = -\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r}$ is the unperturbed Hamiltonian of the hydrogen atom, and $H' = e\mathcal{E}z$ is the energy of the electron in the applied electric field. (We are now going to drop the different notation for the position operator Z and the position eigenvalue *z*, as is common practice. The meaning of the symbol *z* – operator or eigenvalue – will be determined by context.) The unperturbed eigenstates are $\left|\psi_{n\ell m}^{(0)}\right\rangle$, and their energies are $E_n^{(0)} = -\frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{n^2}\right)$.

This time, our goal is to calculate the state vectors and energy shifts for the levels belonging to $E_2^{(0)}$. This energy level has a degeneracy $g_2 = 4$. We need to identify which unperturbed eigenstate we will choose for the *i*th one; $i = 1,...,4$. We will make the arbitrary choice

$$\begin{aligned}
\left|\psi_{21}^{(0)}\right\rangle &= \left|\psi_{200}^{(0)}\right\rangle \\
\left|\psi_{22}^{(0)}\right\rangle &= \left|\psi_{210}^{(0)}\right\rangle \\
\left|\psi_{23}^{(0)}\right\rangle &= \left|\psi_{211}^{(0)}\right\rangle \\
\left|\psi_{24}^{(0)}\right\rangle &= \left|\psi_{21-1}^{(0)}\right\rangle
\end{aligned} \tag{2.22}$$

Next, we need to construct the matrix $H'_{ij} = \left\langle\psi_{2i}^{(0)}\right|H'\left|\psi_{2j}^{(0)}\right\rangle$. These matrix elements are of the form

$$\left\langle\psi_{2i}^{(0)}\right|H'\left|\psi_{2j}^{(0)}\right\rangle = e\mathcal{E}\left\langle\psi_{2\ell_i m_i}^{(0)}\right|z\left|\psi_{2\ell_j m_j}^{(0)}\right\rangle \tag{2.23}$$

We'll need the matrix elements of z to solve this problem. Let's start by reviewing a few of the properties of spherical harmonics. First, they form a complete, orthonormal set of functions on the surface of a sphere of radius 1, *i.e.* an arbitrary function $f(\theta,\phi)$, with $0<\theta<\pi$, and $0<\phi<2\pi$, can always be written as

$$f(\theta,\phi)=\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}c_{\ell m}Y_{\ell m}(\theta,\phi) \tag{2.24}$$

and the $Y_{\ell m}$ obey the relation

$$\langle \ell' m' | \ell m\rangle = \int_{4\pi} Y^*_{\ell' m'}(\theta,\phi)Y_{\ell m}(\theta,\phi)d\Omega = \int_0^{2\pi}\int_0^{\pi} Y^*_{\ell' m'}(\theta,\phi)Y_{\ell m}(\theta,\phi)\sin(\theta)d\theta d\phi = \delta_{\ell\ell'}\delta_{mm'} \tag{2.25}$$

The functional form of the spherical harmonic is given by

$$Y_{\ell m}(\theta,\phi)=\langle\theta,\phi|\ell m\rangle=\varepsilon\left[\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}\right]^{1/2}P_\ell^{|m|}(\cos(\theta))e^{im\phi} \tag{2.26}$$

where $P_\ell^m(x)$ is the associated Legendre function, and

$$\varepsilon=\begin{cases}(-1)^m, & \text{if } m>0\\ 1, & \text{if } m\le 0\end{cases} \tag{2.27}$$

The associated Legendre functions obey the following recursion relations:

$$(2\ell+1)\cos(\theta)P_\ell^m(\cos(\theta))=(\ell+1-m)P_{\ell+1}^m(\cos(\theta))+(\ell+m)P_{\ell-1}^m(\cos(\theta)) \tag{2.28}$$

$$(2\ell+1)\sin(\theta)P_\ell^{m-1}(\cos(\theta))=P_{\ell+1}^m(\cos(\theta))-P_{\ell-1}^m(\cos(\theta)) \tag{2.29}$$

The associated Legendre functions also obey an orthogonality relation

$$\int_{-1}^{1}P_\ell^{|m|}(x)P_{\ell'}^{|m|}(x)dx=\frac{2}{2\ell+1}\frac{(\ell+|m|)!}{(\ell-|m|)!}\delta_{\ell\ell'} \tag{2.30}$$

The matrix element of z between two arbitrary bound states of the hydrogen atom is

$$\left\langle\psi^{(0)}_{n_i\ell_i m_i}\middle|z\middle|\psi^{(0)}_{n_j\ell_j m_j}\right\rangle=\int\psi^{(0)^*}_{n_i\ell_i m_i}(\vec{r})z\psi^{(0)}_{n_j\ell_j m_j}(\vec{r})d^3r \tag{2.31}$$

I will leave it as a homework problem to show that

$$\left\langle\psi^{(0)}_{n_i\ell_i m_i}\middle|z\middle|\psi^{(0)}_{n_j\ell_j m_j}\right\rangle=0 \text{ if } m_i\neq m_j \text{ or if } (\ell_i\neq\ell_j+1 \text{ or } \ell_j-1) \tag{2.32}$$

Eq. (2.32) will save a lot of work for problems involving matrix elements of z for the hydrogen atom, because it means most of the matrix elements will be zero, and you can use that equation to quickly determine which ones are zero.

The selection rule (2.32) does not depend on whether $n_i = n_j$, so it is still valid for our case with $n_i = n_j = 2$. This means, for instance, that $H'_{13} = e\mathcal{E}\left\langle \psi^{(0)}_{21} \middle| z \middle| \psi^{(0)}_{23} \right\rangle = e\mathcal{E}\left\langle \psi^{(0)}_{200} \middle| z \middle| \psi^{(0)}_{211} \right\rangle = 0$, since $(m_1 = 0) \neq (m_3 = 1)$. Similarly $H'_{23} = e\mathcal{E}\left\langle \psi^{(0)}_{22} \middle| z \middle| \psi^{(0)}_{23} \right\rangle = e\mathcal{E}\left\langle \psi^{(0)}_{210} \middle| z \middle| \psi^{(0)}_{211} \right\rangle = 0$, since $\ell_2 \neq \ell_3 + 1$ or $\ell_3 - 1$ $(\ell_2 = \ell_3 = 1)$ (and also $m_2 \neq m_3$). Working our way through the 16 elements of the H' matrix, we find that all but two are non-zero, as follows:

$$H' = \begin{bmatrix} 0 & H'_{12} & 0 & 0 \\ H'_{21} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \tag{2.33}$$

It is at this point that the identification of the basis vectors given in eqs. (2.22) matters. Equation (2.23) gives the matrix of H' in the *ordered basis* $\left\{ \left|\psi^{(0)}_{21}\right\rangle, \left|\psi^{(0)}_{22}\right\rangle, \left|\psi^{(0)}_{23}\right\rangle, \left|\psi^{(0)}_{24}\right\rangle \right\}$. If we had chosen some identification for those vectors other than eqs. (2.22), the non-zero matrix elements in eq. (2.33) would have appeared in different places in the matrix. But we could still solve the problem with that ordering. We just need to adopt a particular order for the basis vectors and stick with it.

One of the non-zero matrix elements is

$$\begin{aligned} H'_{12} &= e\mathcal{E}\left\langle \psi^{(0)}_{21} \middle| z \middle| \psi^{(0)}_{22} \right\rangle = e\mathcal{E}\left\langle \psi^{(0)}_{200} \middle| z \middle| \psi^{(0)}_{210} \right\rangle \\ &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \Big(R_{20}(r)Y^*_{00}(\theta,\varphi)\Big)\Big(r\cos(\theta)\Big)\Big(R_{21}(r)Y_{10}(\theta,\varphi)\Big)\Big(r^2\sin(\theta)\,dr\,d\theta\,d\varphi\Big) \\ &= -3e\mathcal{E}a_0 \end{aligned} \tag{2.34}$$

where a_0 is the Bohr radius, and I have skipped over the work of carrying out the integral. Since H' is Hermitian, it follows that $H'_{21} = H'^{*}_{12} = 3e\mathcal{E}a_0$. So we finally have

$$H' = \begin{bmatrix} \begin{bmatrix} 0 & -3e\mathcal{E}a_0 \\ -3e\mathcal{E}a_0 & 0 \end{bmatrix} & \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} \\ \begin{matrix} 0 & 0 \\ 0 & 0 \end{matrix} & \begin{bmatrix} [0] & 0 \\ 0 & [0] \end{bmatrix} \end{bmatrix} \tag{2.35}$$

The prescription is to diagonalize this matrix. As indicated by the brackets inside the H' matrix, H' is in block diagonal form, with one 2x2, one 1x1, and another 1x1 matrix along the diagonal, and with all zeros outside the diagonal matrices. To diagonalize a block diagonal matrix, all you have to do is to diagonalize each block separately. So, we start with the 2x2 block:

$$\begin{bmatrix} 0 & -3e\mathcal{E}a_0 \\ -3e\mathcal{E}a_0 & 0 \end{bmatrix}\begin{bmatrix} c_{i1} \\ c_{i2} \end{bmatrix} = E_{2i}^{(1)}\begin{bmatrix} c_{i1} \\ c_{i2} \end{bmatrix} \tag{2.36}$$

This has a solution if the characteristic equation is satisfied:

$$\det\begin{bmatrix} -E_{2i}^{(1)} & -3e\mathcal{E}a_0 \\ -3e\mathcal{E}a_0 & -E_{2i}^{(1)} \end{bmatrix} = 0 \tag{2.37}$$

or $\left(E_{2i}^{(1)}\right)^2 = \left(3e\mathcal{E}a_0\right)^2$. This has two solutions, which we label as $i=1$ and $i=2$:

$$E_{21}^{(1)} = -3e\mathcal{E}a_0 \tag{2.38}$$

$$E_{22}^{(1)} = +3e\mathcal{E}a_0 \tag{2.39}$$

The corresponding eigenvectors are derived from eq. (2.36), and we easily find that $c_{11} = c_{12}$, and $c_{21} = -c_{22}$. If we normalize the eigenvectors, then we'll have to take $|c_{11}| = |c_{12}| = |c_{21}| = |c_{22}| = \frac{1}{\sqrt{2}}$. Other than that, we are free to choose the phase of the vectors however we like; we'll just use $c_{11} = \frac{1}{\sqrt{2}}$ and $c_{21} = \frac{1}{\sqrt{2}}$. It follows that the normalized eigenvectors are

$$\left|\varphi_{21}^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_{200}^{(0)}\right\rangle + \left|\psi_{210}^{(0)}\right\rangle\right) \tag{2.40}$$

$$\left|\varphi_{22}^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_{200}^{(0)}\right\rangle - \left|\psi_{210}^{(0)}\right\rangle\right) \tag{2.41}$$

The next, 1x1 block diagonal equation reads:

$$0\, c_{i3} = E_{2i}^{(1)} c_{i3} \tag{2.42}$$

and has solution $E_{2i}^{(1)} = 0$ and $c_{i3} = 1$. We'll choose to label this as the $i=3$ solution, so that

$$E_{23}^{(1)} = 0 \tag{2.43}$$

$$\left|\varphi_{23}^{(0)}\right\rangle = \left|\psi_{23}^{(0)}\right\rangle = \left|\psi_{211}^{(0)}\right\rangle \tag{2.44}$$

By the same argument applied to the last 1x1 block,

$$E_{24}^{(1)} = 0 \tag{2.45}$$

$$\left|\varphi_{24}^{(0)}\right\rangle = \left|\psi_{24}^{(0)}\right\rangle = \left|\psi_{21-1}^{(0)}\right\rangle \tag{2.46}$$

We can combine these results to give the energies, correct to first order, and the wavefunctions, correct to zeroth order, for the $n = 2$ levels of hydrogen in an electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$:

$$\left|\varphi_{21}^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_{200}^{(0)}\right\rangle + \left|\psi_{210}^{(0)}\right\rangle\right) \qquad E_{21} \approx E_2^{(0)} - 3e\mathcal{E}a_0 \tag{2.47) (a}$$

$$\left|\varphi_{22}^{(0)}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi_{200}^{(0)}\right\rangle - \left|\psi_{210}^{(0)}\right\rangle\right) \qquad E_{22} \approx E_2^{(0)} + 3e\mathcal{E}a_0 \tag{2.50)(b}$$

$$\left|\varphi_{23}^{(0)}\right\rangle = \left|\psi_{211}^{(0)}\right\rangle \qquad E_{23} \approx E_2^{(0)} \tag{2.50)(c}$$

$$\left|\varphi_{24}^{(0)}\right\rangle = \left|\psi_{21-1}^{(0)}\right\rangle \qquad E_{24} \approx E_2^{(0)} \tag{2.50)(d}$$

with $E_2^{(0)} = -\frac{e^2}{8\pi\varepsilon_0 a}\left(\frac{1}{4}\right)$. I've illustrated these levels and energies in Fig. 2. Notice that *the degeneracy is partially lifted by the perturbation.* Two levels (i = 1 and 2) become non-degenerate with non-zero field strength, whereas another two levels (i = 3 and 4) are unshifted and remain degenerate even at non-zero field strength.

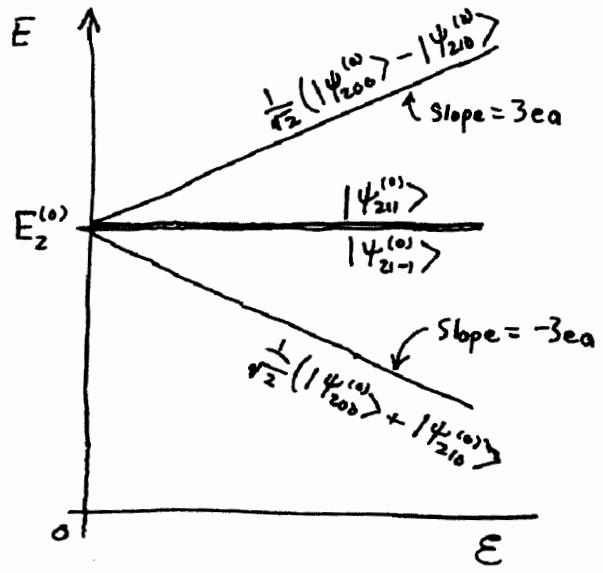


Fig. 2.3. Energies of the $n = 2$ levels of hydrogen vs. electric field strength.