17.2 Some examples

(i) Charged particle bound by spring (harmonic oscillator), subjected to an external electric field E:

$V = -qEx$, $\hat{H} = \hat{H}^0 + \hat{H}' = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 - qE\hat{x}$

Let us assume E is weak enough so that we can use perturbation theory.

First order energy shift:

$$E_n' = \langle n^0|\hat{H}'|n^0\rangle = -qE\langle n^0|\hat{x}|n\rangle = 0$$

since all harmonic oscillator eigenstates have $\langle\hat{x}\rangle = 0$.

However, the states will be affected by the electric field: For the harmonic oscillator, the probabilities to find the particle at x and $-x$ are equal, but as we turn on the electric field, the particle will be pulled by it to one side:

$$|n\rangle = |n^0\rangle + |n'\rangle$$

$$|n'\rangle = \sum_m{}' \frac{\langle m^0|-qE\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}+\hat{a}^+)|n^0\rangle}{E_n^0 - E_m^0}|m^0\rangle$$

$$= -qE\sqrt{\frac{\hbar}{2m\omega}}\sum_m{}'\left[\delta_{m,n-1}|(n-1)^0\rangle\cdot\frac{\sqrt{n}}{\hbar\omega} + \delta_{m,n+1}\frac{\sqrt{n+1}}{-\hbar\omega}|(n+1)^0\rangle\right]$$

$$= \frac{qE}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\,|(n+1)^0\rangle - \sqrt{n}\,|(n-1)^0\rangle\right)$$

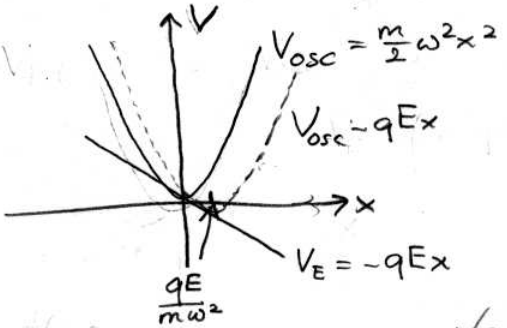
To first order, the interaction mixes only neighboring states. The mixing is inversely proportional to the energy difference two, i.e. it gets weaker when the oscillator potential gets narrower, i.e. the spring gets stronger.

The first-order change of the states gives rise to an energy shift at second order:

$$E_n^2 = \sum_m{}' \frac{|\langle m^\circ | H' | n^\circ \rangle|^2}{E_n^\circ - E_m^\circ} = q^2E^2 \frac{\hbar}{2m\omega}\left[\frac{n+1}{-\hbar\omega} + \frac{n}{\hbar\omega}\right]$$

$$= -\frac{q^2E^2}{2m\omega^2}$$

All energy eigenvalues get shifted down!



- In this case we can test how well perturbation theory works because for the perturbed Hamiltonian the eigenvalue problem can be solved exactly:

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{m}{2}\omega^2\hat{X}^2 - qE\hat{X} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\left(\hat{X} - \frac{qE}{m\omega^2}\right)^2 - \frac{q^2E^2}{2m\omega^2}$$

This is a harmonic oscillator with the same frequency centered at $X_0 = \frac{qE}{m\omega^2}$ and shifted down by a constant $-\frac{q^2E^2}{2m\omega^2}$

The frequency remains unchanged.

We can immediately see that

$$\boxed{E_n = E_n^0 - \frac{q^2E^2}{2m\omega^2}} \quad \text{(exact)}$$

This is second order in E, so there should indeed be no first-order shift in perturbation theory. The coefficient of the term $\sim E^2$ agrees with second-order pert. theory, so all higher-order corrections in pert. theory either vanish exactly order by order or miraculously add up to zero. One can show that here the first is the case (i.e. all higher-order terms vanish individually), but examples of the other kind are also known (see scattering off a Coulomb potential.).

The state vectors can also be easily obtained exactly from the solutions of $\hat{H}^0$: since the oscillator minimum is simply shifted in x by $\frac{qE}{m\omega^2}$, and a downward shift of the potential by a constant doesn't affect the wavefunctions, we can write

$$|n\rangle = \hat{T}\left(\frac{qE}{m\omega^2}\right)|n^0\rangle$$

where $\hat{T}(a)$ is the translation operator for a translation by a in x direction,

$$\hat{T}\left(\frac{qE}{m\omega^2}\right) = e^{-\frac{i}{\hbar}\frac{qE}{m\omega^2}\hat{p}}$$

We can expand this in a Taylor series and use

$$\hat{P} = \sqrt{\frac{\hbar m\omega}{2}}\,\frac{\hat{a}-\hat{a}^+}{i}$$

$$|n\rangle \approx |n^0\rangle - \frac{qE}{m\omega^2\hbar}\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}-\hat{a}^+)|n^0\rangle$$

$$= |n^0\rangle + \frac{qE}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\,|(n+1)^0\rangle - \sqrt{n}\,|(n-1)^0\rangle\right)$$

which just the result we obtained in 1st order perturbation theory. Higher orders in the Taylor expansion of $\hat{T}$ generate higher orders in the perturbative expansion in powers of qE, i.e. higher orders in perturbation theory. Such terms come with higher powers of $\hat{P}$, $\hat{P}^m \sim (\hat{a}-\hat{a}^+)^m$, which generate terms $|(n\pm m)^0\rangle$, $|(n\pm(m-2))^0\rangle$, ... etc. Still, it is not immediately obvious and requires an explicit calculation to show that (for $m>1$) none of them contributes to the energy shift of the eigenstates.

(ii) Selection rules

Selection rules tell us that certain matrix elements must be zero, without need to calculate them. They vastly simplify many perturbative calculations.

If the perturbation $\hat{H}'$ commutes with some observable $\hat{\Omega}$, $[\hat{\Omega}, \hat{H}'] = 0$, then

$$\langle \alpha_2 \omega_2 | \hat{H}' | \alpha_1 \omega_1 \rangle = 0 \quad \text{for} \quad \omega_2 \neq \omega_1$$

(here α_i denotes any other quantum numbers used to classify the states (usually eigenstates of H^0)).

Proof $$0 = \langle \alpha_2 \omega_2 | \hat{\Omega} \hat{H}' - H' \hat{\Omega} | \alpha_1 \omega_1 \rangle$$

$$= (\omega_2 - \omega_1) \langle \alpha_2 \omega_2 | \hat{H}' | \alpha_1 \omega_1 \rangle$$

Examples: (i) $\hat{H}' = \lambda \hat{Z}$, this is invariant under rotations around the z-axis, $[\hat{L}_z, \hat{H}'] = 0$

Thus $\langle \alpha_2 m_2 | \hat{H}' | \alpha_1 m_1 \rangle = 0$ for $m_2 \neq m_1$ between eigenstates of $\hat{L}_z$. So if $\hat{H}^0$ is azimuthally symmetric, such that we can classify its eigenstates by magnetic quantum numbers (i.e. find a basis of simultaneous eigenstates with $\hat{L}_z$), a perturbation $\hat{H}' = \lambda \hat{Z}$ is diagonal in m in that basis.

(ii) Similarly, if $\hat{H}'$ has good parity (say $\hat{H}' = \lambda \hat{Z}^2$) then its matrix elements between states of opposite parity vanish.

We can say "if $\hat{H}'$ carries no $\hat{\Omega}$" then it is diagonal in the $\hat{\Omega}$-basis. ($[H', \hat{\Omega}] = 0$)

We can generalize this selection rule to cases where

$\hat{H}'$ "carries a definite non-zero amount of $\hat{\Omega}$".

Consider as an example again $\hat{H}' = \lambda \hat{z}$

and remember that we can write

$$z = r\cos\vartheta = \sqrt{\frac{4\pi}{3}}\, r\, Y_{10}(\vartheta,\varphi)$$

We see that $\hat{z}$ carries 1 unit of orbital angular momentum, but no l_z. Therefore

$$\langle \alpha_2 j_2 m_2 | \hat{z} | \alpha j_1 m_1 \rangle = 0 \text{ for } m_2 \neq m_1,\ j_2 \neq j_1+1, j_1, \text{or } j_1-1$$

Similarly, x and y are $\sim Y_{1,\pm 1}$ and thus

$$\langle \alpha_2 j_2 m_2 | \hat{X} \text{ or } \hat{Y} | \alpha_1 j_1 m_1 \rangle = 0 \text{ for } \begin{matrix} m_2 \neq m_1 \pm 1 \\ j_2 \neq j_1+1, j_1, \text{or } j_1-1 \end{matrix}$$

Along the same lines, if we have an operator of definite negative parity, such as $\hat{X}$, $\hat{Y}$, or $\hat{Z}$,

$$\hat{\Pi}^+ \hat{X} \hat{\Pi} = -\hat{X},$$

then if $\hat{X}$ acts on a state with definite parity, it will change the parity of the state; hence matrix elements of $\hat{X}$ between parity eigenstates vanish unless they have opposite parity.

More generally, if $\hat{\Pi}^+ \hat{\Omega} \hat{\Pi} = -\hat{\Omega}$, then

then the matrix elements of $\hat{\Sigma}$ between parity eigenstates vanish unless they have opposite parity.

So let us again look at the matrix elements of $\hat{Z}$, but now between orbital angular momentum states (for spin-independent problems)

$\langle \alpha_2 l_2 m_2 | \hat{Z} | \alpha_1 l_1 m_1 \rangle = 0$ unless $l_2 = l_1 \pm 1$ and $m_2 = m_1$

The case $l_2 = l_1$ is excluded by parity.

$\langle \alpha_2 l_2 m_2 | \hat{X} \text{ or } \hat{Y} | \alpha_1 l_1 m_1 \rangle = 0$ unless $l_2 = l \pm 1$, and $m_2 = m_1 \pm 1$

→ "dipole selection rule"

Example hydrogen in an external electric field

$\vec{E} = \mathcal{E}\vec{e}_z$. ("Stark effect")

Classically, $\vec{E} = -\vec{\nabla}\phi$ and $\mathcal{H}' = -e\phi(\vec{r}_e) + e\phi(\vec{r}_p)$ (electron, proton)

$= e(\phi(\vec{r}_p) - \phi(\vec{r}_e))$

$= e(\vec{r}_e - \vec{r}_p)\cdot\vec{E} = e\vec{r}\cdot\vec{E}$

where $\vec{r}$ = electron position in a c.o.s. where the proton sits at the origin. If we assume $\frac{m_e}{M_p} = 0$, then $\vec{r}$ is the electron position in the CM frame.

Defining the electric dipole moment $\vec{p}_e = -e\vec{r}$ w.r.t.

the CM, then $\mathcal{H}' = -\vec{p}_e \cdot \vec{E}$ (electric dipole interaction).

So, if $\vec{E} = \mathcal{E}\vec{e}_z$, we have

$$\boxed{\hat{H}' = e\hat{Z}\mathcal{E}}$$

Let us calculate the first-order energy shift of the hydrogen ground state:

$$E'_{100} = \langle 100 | e\mathcal{E}\hat{Z} | 100 \rangle = 0$$

It is zero because of the dipole selection rule, and because of parity. Physically this result comes about because the electron, in its spherical ground state, probes regions $\phi(-\vec{r}) = -\phi(\vec{r})$ equally. (We saw the same result in the 1-d case (oscillator + electric field) before.)

At second order, we get

$$E^2_{100} = \sum_{nlm}{}' e^2\mathcal{E}^2 \frac{|\langle nlm|\hat{Z}|100\rangle|^2}{E^0_{100} - E^0_{nlm}} \qquad (*)$$

where $E^0_{100} - E^0_{nlm} = -Ry\left(1 - \frac{1}{n^2}\right) = Ry\,\frac{1-n^2}{n^2}$

$\Rightarrow$

We can use dipole selection rules to conclude $l=1$ and $m=0$ and reduce (*) to

$$E_{100}^2 = -\sum_{n=2}^{\infty} \frac{e^2\mathcal{E}^2}{Ry} \frac{n^2}{n^2-1} |\langle n10|\hat{Z}|100\rangle|^2 < 0$$

But there are other ways to proceed that turn out to be useful, not only here, but generally.

(1) Since $\frac{n^2}{n^2-1}$ grows with n, approaching 1 for $n\to\infty$, we have the inequality

$$|E_{100}^2| \leq \frac{e^2\mathcal{E}^2}{|E_1^0 - E_2^0|} \sum_{nlm}{}' |\langle nlm|Z|100\rangle|^2$$

$$= \frac{e^2\mathcal{E}^2}{Ry}\frac{4}{3} \sum_{nlm}{}' \langle 100|Z|nlm\rangle\langle nlm|Z|100\rangle$$

$$= \frac{e^2\mathcal{E}^2}{Ry}\frac{4}{3}\left(\sum_{nlm} \langle 100|Z|nlm\rangle\langle nlm|Z|100\rangle - \langle 100|Z|100\rangle^2 \right)$$

$$= \frac{e^2\mathcal{E}^2}{Ry}\frac{4}{3}\left(\underbrace{\langle 100|Z^2|100\rangle}_{a_0^2} - \underbrace{\langle 100|Z|100\rangle^2}_{0} \right)$$

$$= \frac{4}{3}\frac{e^2\mathcal{E}^2}{e^2/2a_0} a_0^2 = \frac{8}{3} a_0^3 \mathcal{E}^2 \quad \Rightarrow \quad \boxed{|E_{100}^2| \leq \frac{8}{3} a_0^3 \mathcal{E}^2}$$

This trick uses completeness together with the fact that the eigenenergies are monotonically increasing with n.

A lower limit can be obtained by using the fact that all terms in (*) have the same sign, by keeping only the first term in the sum:

$$|E_{100}^2| \geq \frac{4}{3}\frac{e^2\mathcal{E}^2}{e^2/2a_0}\underbrace{|\langle 210|\hat{z}|100\rangle|^2}_{\frac{2^{15}}{3^{10}}a_0^2 \approx 0.55 a_0^2} \cong 0.55 * \frac{8}{3}a_0^3\mathcal{E}^2$$

So $$\boxed{-\frac{8}{3}\mathcal{E}^2 a_0^3 \leq E_{100}^2 \leq -(0.55)\cdot\frac{8}{3}\mathcal{E}^2 a_0^3}$$

(2) Let us return to the general problem of evaluating

$$E_n^2 = \sum_m{}' \frac{\langle n^0|\hat{H}'|m^0\rangle\langle m^0|\hat{H}'|n^0\rangle}{E_n^0 - E_m^0}$$

If it weren't for the energy denominator, we could use completeness to do the sum. There is a trick to get rid of the energy denominator: all we need is to find an operator $\hat{\Omega}$ such that it generates the perturbation $\hat{H}'$ from $\hat{H}^0$ according to

$$\hat{H}' = [\hat{\Omega}, \hat{H}^0]$$

If we can achieve that, then

$$E_n^2 = \sum_m{}' \frac{\langle n^0|\hat{H}'|m^0\rangle\langle m^0|\hat{\Omega}\hat{H}^0 - \hat{H}^0\hat{\Omega}|n^0\rangle}{E_n^0 - E_m^0}$$

$$= \sum_m{}' \langle n^0|\hat{H}'|m^0\rangle\langle m^0|\hat{\Omega}|n^0\rangle = \langle n^0|\hat{H}'\hat{\Omega}|n^0\rangle - \langle n^0|\hat{H}'|n^0\rangle\langle n^0|\hat{\Omega}|n^0\rangle$$

So now we need to work out just 3 expectation values in the unperturbed state.

The problem is that in general it is very hard to find such an $\hat{\Omega}$. However, for this trick to work we don't need to solve $\hat{H}' = [\hat{\Omega}, \hat{H}^0]$ in general, but it is enough, for each state n, to find an $\hat{\Omega}_n$ such that

$$\hat{H}'|n^0\rangle = [\hat{\Omega}_n, \hat{H}^0]|n^0\rangle \quad \text{for this } n \text{ only.}$$

In our case, to get E^2_{100}, we need to find $\hat{\Omega}_0$ such that

$$\hat{H}'|100\rangle = [\hat{\Omega}_0, \hat{H}^0]|100\rangle$$

Let's write this in the coordinate basis:

$$\langle \vec{r}|e\mathcal{E}\hat{z}|100\rangle = e\mathcal{E} r\cos\vartheta\, \psi_{100}(r,\vartheta,\varphi) =$$

$$= \left(\Omega_0\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{a^2}{r}\right) - \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)\Omega_0\right)\psi_{100}(r,\vartheta,\varphi)$$

where here Ω_0 denotes the matrix element of $\hat{\Omega}$ in the coordinate basis. Assuming that $\hat{\Omega}_0$ depends only on $\hat{\vec{r}}$ and not on $\hat{\vec{p}}$ (such that it commutes with e^2/r), we need to find Ω_0 with

$$\nabla^2(\Omega_0\psi_{100}) - \Omega_0(\nabla^2\psi_{100}) = \frac{2me\mathcal{E}}{\hbar^2} r\cos\vartheta\, \psi_{100}$$

Use $\nabla^2(fg) = g\nabla^2 f + 2\vec{\nabla}f\cdot\vec{\nabla}g + f\nabla^2 g$ with $f = \Omega_0$, $g = \psi_{100}$:

$\Rightarrow$ we need

$$\nabla^2\Omega_0 + 2\vec{\nabla}\Omega_0 \cdot \frac{\vec{\nabla}\psi_{100}}{\psi_{100}} = \frac{2me\mathcal{E}}{\hbar^2} r\cos\vartheta$$

$$\psi_{100}(r) = N e^{-r/a_0} \Rightarrow \frac{\vec{\nabla}\psi_{100}}{\psi_{100}} = -\frac{\vec{\nabla} r}{a_0} = -\frac{\vec{e}_r}{a_0}$$

$\Rightarrow$ We need

$$\nabla^2\Omega_0 - \frac{2}{a_0}\partial_r\Omega_0 = \frac{2me\mathcal{E}}{\hbar^2} r\cos\vartheta$$

Shankar gives $\boxed{\Omega_0 = -\frac{me\mathcal{E}a_0}{\hbar^2}\left(\frac{r^2\cos\vartheta}{2} + a_0 r\cos\vartheta\right)}$

as solution. Let's check it:

$$\nabla^2\Omega_0 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\left(-\frac{me\mathcal{E}a_0}{\hbar^2}\right)\left(\frac{z}{2}\sqrt{x^2+y^2+z^2} + az\right)$$

$$= -\frac{me\mathcal{E}a_0}{\hbar^2}\left(\frac{z}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) r + \frac{\partial}{\partial z}\underbrace{\left(\frac{1}{2} r + \frac{z}{2}\partial_z r\right)}_{\frac{\partial}{\partial z}\left(\frac{zr}{2}\right)} + 0\right)$$

$$= -\frac{me\mathcal{E}a_0}{\hbar^2}\left(\frac{z}{2}\underbrace{\nabla^2 r}_{2/r} + \frac{z}{r}\right) = -\frac{me\mathcal{E}a_0}{\hbar^2}\frac{2z}{r} = -\frac{2me\mathcal{E}a_0}{\hbar^2}\cos\vartheta$$

$$-\frac{2}{a_0}\partial_r\Omega_0 = +\frac{2me\mathcal{E}}{\hbar^2}\left(r\cos\vartheta + a_0\cos\vartheta\right) = \frac{2me\mathcal{E}}{\hbar^2} r\cos\vartheta + \frac{2me\mathcal{E}a_0\cos\vartheta}{\hbar^2}$$

Adding these gives the desired result.

Plugging this into the result at the bottom of p. (40):

$$E^2_{100} = \langle 100|\hat{H}'\hat{\Omega}_0|100\rangle - \underbrace{\langle 100|\hat{H}'|100\rangle}_{=0}\langle 100|\hat{\Omega}_0|100\rangle$$

$$= -\frac{me^2\mathcal{E}^2 a_0}{\hbar^2}\left\langle 100\left|\hat{Z}\left(\frac{\hat{R}\hat{Z}}{2} + a_0\hat{Z}\right)\right|100\right\rangle \qquad \left(\frac{me^2}{\hbar^2} = \frac{1}{a_0}\right)$$

$$\left(\hat{Z}^2 \to \tfrac{1}{3}\hat{R}^2\right)$$

$$= -\frac{1}{3}\mathcal{E}^2\left(\int d^3r\, \psi^2_{100}(r)\left(\frac{r^3}{2} + a_0 r^2\right)\right)$$

$$= -\frac{1}{3}\mathcal{E}^2\left\langle \underbrace{\frac{r^3}{2}}_{\frac{15}{4}a_0^3} + \underbrace{a_0 r^2}_{3a_0^3}\right\rangle = -\frac{9}{4}a_0^3\mathcal{E}^2$$

This is the exact result. Since $-\frac{9}{4} = -\frac{8}{3}\cdot\frac{27}{32} = 0.84\cdot\left(-\frac{8}{3}\right)$ it falls roughly in the middle between 0.55 and 1 times $-\frac{8}{3}$ derived as upper and lower limits for E^2_{100} above.

So there is no energy shift at first order: A spherical electron cloud interacting with a constant electric field has zero total interaction energy. But the field polarizes the cloud, leading a first-order change in the ground state wavefunction, corresponding to an electric dipole moment. E^2_{100} at second order is the interaction energy of that dipole with the electric field.

So how large is the induced dipole moment?

We write $\vec{p}_e = \alpha\vec{E}$ and the work done by the electric

field in separating the electron charge density from the proton as

$$dW = -\mathcal{E}\, dq = -\alpha \mathcal{E}\, d\mathcal{E} \quad \Rightarrow \quad W = -\frac{\alpha}{2}\mathcal{E}^2$$

Identifying $W = E_{100}^2$ we get

$$\boxed{\alpha = \frac{18}{4} a_0^3 \approx \frac{18}{4}(0.53\text{Å})^3 \approx 0.67\,\text{Å}^3} \quad (\text{exp: } 0.68\,\text{Å}^3)$$

for the polarizability α of the hydrogen atom in its ground state. The induced dipole moment is then obtained from

$$\vec{p_e} = \alpha \vec{E}$$