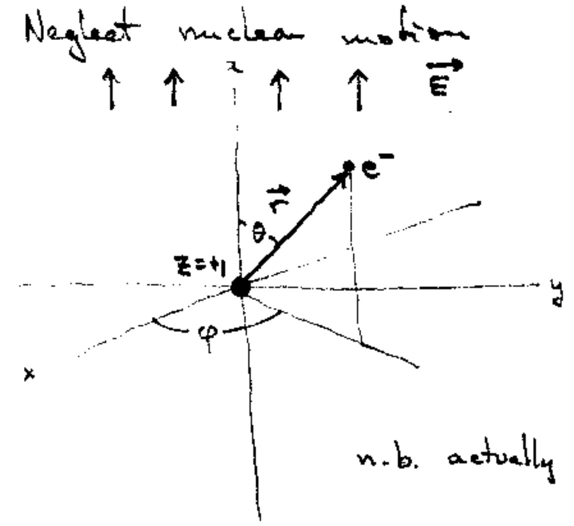
e.g.s of perturbation theory problems 2^{nd} order Stark effect

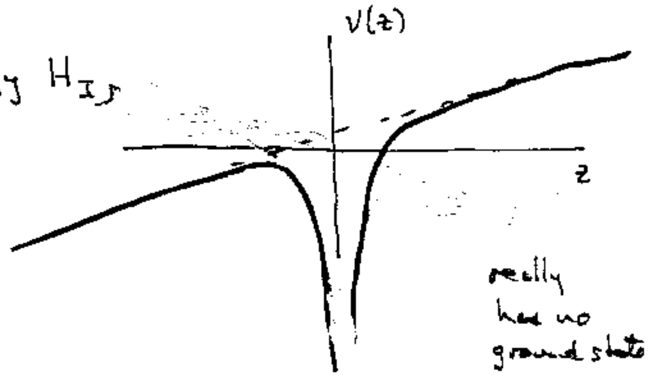
1. H atom in external electric field
$\vec{E} = E\hat{z}$, calculate the induced dipole moment $\vec{d}$ (in the H atom ground state) to leading nonzero order.

Neglect nuclear motion



$$H = \underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{\hbar c\alpha}{r}\psi}_{H_0} + \underbrace{eEz}_{\sum_i q_i\phi(\vec{r}_i)} \to H_I$$

n.b. actually this is a crazy H_I,



really has no ground state! ∴ Electron will eventually escape from the nucleus with any nonzero constant $\vec{E}$.

Anyway, proceed perturbatively.

Unperturbed ground state is

$$|\phi_0\rangle = \eta_{1s} e^{-r/a_0} Y_{00}(\Omega) \qquad a_0 = \frac{\hbar}{\alpha m c} = \text{Bohr radius} \cong 0.529\,\text{Å}$$

$$E(0) = -\frac{1}{2} mc^2\alpha^2 \qquad \eta_{1s} = \frac{2}{a_0^{3/2}}$$

To calculate the expected dipole moment $\langle \vec{d}\rangle = -e\langle \vec{r}_{e^-}\rangle = -e\hat{z}\langle z\rangle$ we 1^{st} have to calculate the change in the ground state $|\psi\rangle$ due to the perturbation H_I. The first order correction $|\phi_1\rangle$ is

$$|\phi_1\rangle = \sum_n{}' \frac{\langle n|H_I|\phi_0\rangle}{E(0)-E_n(0)}\,|n\rangle,$$

where the $\{|n\rangle\}$ are a complete set of eigenstates of H_0. For Hydrogen atom <u>bound states</u> these are labelled by orbital angular momentum

L_z quantum number

$|N, \underbrace{l, m}\rangle$

from $Y_{lm}(\hat{r})$ angular dependence

princ. quant. number

In principal could calculate $|\phi_1\rangle$ from overlap integrals

$$\langle n | H_I | \phi_0 \rangle = \langle N, l, m | (+eEr\cos\theta) \underbrace{|\phi_0\rangle}_{\text{1S wavefunction}}$$

$$\phi_0(\vec{x}) = \eta_{1s} e^{-r/a_0} Y_{00}(\hat{r})$$

+ we have simple restriction that $\cos\theta = \sqrt{\frac{4\pi}{3}}\, Y_{10}(\Omega)$, so only $l=1$, $m=0$ states mix in at $|\phi_1\rangle$ level,

$$|\phi_1\rangle = \sum_n{}' \frac{\langle n | H_I | \phi_0 \rangle}{E(0) - E_n(0)} |n\rangle ,$$

but have all radial excitations N present, so this gets very complicated. Much easier way is not to use eigen mode expansion but instead to solve for $|\phi_1\rangle$ directly:
recall $|\phi_1\rangle$ $\mathcal{O}(\lambda)$ eqn,

$$[E(0) - H_0] |\phi_1\rangle = P H_I |\phi_0\rangle$$

as differential operators,

$$\left[E(0) - \left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{\alpha\hbar c}{r} \right) \right] \phi_1(\vec{x}) = P \cdot \underbrace{(+eEr\cos\theta)\,\phi_0(r)}_{}$$

$\propto Y_{10}(\Omega)$ so is independent of ϕ_0 + can drop P,

$$\left[E(0) - \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{\alpha\hbar c}{r}\right)\right]\phi_1(r)\,Y_{10}(\Omega) = +eE\sqrt{\frac{4\pi}{3}}\,r\phi_0(r)\,Y_{10}(\Omega)$$

Now use simple result

$$\nabla^2 f(r) Y_{\ell m}(\Omega) = \left[\frac{d^2 f}{dr^2} + \frac{2}{r}\frac{df}{dr} - \frac{\ell(\ell+1)}{r^2} f\right] Y_{\ell m}(\Omega)$$

So that

$$\left[E(0)\phi_1 - \left(-\frac{\hbar^2}{2m}\left(\phi_1'' + \frac{2}{r}\phi_1' - \frac{2}{r^2}\phi_1\right) - \frac{\alpha\hbar c}{r}\phi_1\right)\right]\cancel{Y_{10}(\hat{\Omega})}$$

$$= +eE\sqrt{\frac{4\pi}{3}}\,r\phi_0(r)\,\cancel{Y_{10}(\hat{\Omega})}$$

Now $\phi_0(r) = \frac{\eta_{1s}}{\sqrt{4\pi}}\,e^{-r/a_0}$, most obvious guess for $\phi_1(r)$ is a polynomial $\mathbb{P}(r)$ times e^{-r/a_0}, so the e^{-r/a_0} can be eliminated throughout:

$$\phi_1 = \mathbb{P}e^{-r/a_0} \qquad \phi_1' = \left(\mathbb{P}' - \frac{\mathbb{P}}{a_0}\right)e^{-r/a_0}$$

$$\phi_1'' = \left(\mathbb{P}'' - \frac{2\mathbb{P}'}{a_0} + \frac{\mathbb{P}}{a_0^2}\right)e^{-r/a_0}$$

$$\left[E(0)\mathbb{P} + \frac{\hbar^2}{2m}\left(\mathbb{P}'' - \frac{2}{a_0}\mathbb{P}' + \frac{1}{a_0^2}\mathbb{P} + \frac{2}{r}\mathbb{P}' - \frac{2}{a_0 r}\mathbb{P} - \frac{2}{r^2}\mathbb{P}\right)\right.$$

$$\left. + \frac{\alpha\hbar c}{r}\mathbb{P}\right] = -eE\frac{\eta_{1s}}{\sqrt{3}}\,r$$

Suppose polynomial $\mathbb{P} = a_m r^m + a_{m-1} r^{m-1} + \dots + a_n r^n$

if $m > 1$,

leading terms are $(\mathcal{O}(r^m))$ $\quad \underbrace{E(0)}\,a_m r^m + \underbrace{\frac{\hbar^2}{2ma_0^2}}\,a_m r^m = 0$

$$a_m r^m\left[-\frac{1}{2}m\alpha^2c^2 + \frac{\hbar^2}{2m}\cdot\left(\frac{\alpha mc}{\hbar}\right)^2\right] = 0$$

Assume a series expansion $\mathbb{P}(r) = \sum_k A_k r^k$,
+ derive recursion relation
for the coeffts A_k from the coeff of r^k. This is

$$\boxed{(k^2+3k)\,A_{k+1} = \frac{2}{a_0} k A_k + \frac{eE}{\sqrt{3}} \eta_{1s}\, \delta_{k,2} \cdot \frac{2m}{\hbar^2}}$$

Only terminates (+ hence really is a polynomial) if r.h.s. = 0 at k=2,
so $A_3=0$, hence $\mathbb{P}$ is just quadratic.

This leads to $\quad A_2 = \frac{-eE}{\sqrt{3a_0}} \cdot \frac{m}{\hbar^2}, \quad A_1 = 2a_0 A_2, \quad A_0 = 0$, so

$$\phi_1(\vec{x}) = \frac{-eEm}{\hbar^2 \sqrt{3a_0}} \left(r^2 + 2a_0 r\right) e^{-r/a_0}\, Y_{10}(\Omega)$$

So now we can calculate the second-order energy using

$$E_0(2) = \langle \phi_0 | H_I | \phi_1 \rangle = +\int d\vec{x}\; \phi_0(\vec{x})^* \, eEr\cos\theta\, \phi_1(\vec{x})$$

using $a_0 = \frac{\hbar}{\alpha mc}$ and $\alpha = \frac{e^2}{\hbar c}$, $e^2 = \frac{\hbar^2}{ma_0}$

$$= -\frac{2E^2}{3a_0^3} \int_0^\infty (r^5 + 2a_0 r^4)\, e^{-2r/a_0}\, dr = -\frac{9}{4} E^2 a_0^3$$

∴ Energy of H atom $\psi_0(\vec{x})$ in static electric field is

$$E_0 = -\frac{1}{2} mc^2\alpha^2 - \frac{9}{4} E^2 a_0^3.$$

$a_0 = \frac{\hbar}{\alpha mc}$ = Bohr radius

(Of course linear correction to $E_0 = \langle \phi_0 | (+eEz\cos\theta) | \phi_0 \rangle \propto \int d\Omega \cos\theta = 0$.)

Finally, problem was to calculate expected dipole moment, $d = e\langle \psi_0 | z | \psi_0 \rangle$, can get this from Feynman-Hellman theorem,

$H_{(\lambda)} = H + \lambda\,\mathcal{O} + \ldots$

$E_0(\lambda) = E_0 + \lambda \langle \psi_0 | \mathcal{O} | \psi_0 \rangle$

$\therefore \langle \psi_0 | \mathcal{O} | \psi_0 \rangle = \left.\frac{\partial E_0(\lambda)}{\partial \lambda}\right|_{\lambda=0}$

small additional E field

$$H = H_{0,E} + \underbrace{H_{\delta E}}_{\boxed{+\, e \cdot \delta E \cdot z}}$$

so $\left.\frac{\partial E_0}{\partial \delta E}\right|_{\delta E = 0} = \langle \psi_0 | +ez | \psi_0 \rangle = +d$

$$E_0 = -\frac{1}{2} mc^2\alpha^2 - \frac{9}{4} E^2 a_0^3 - \frac{9}{2} E a_0^3\, \delta E + \mathcal{O}((\delta E)^2)$$

so

$$\boxed{d = \frac{9}{2} E a_0^3}$$

$= \langle ez \rangle$

$\therefore$ induced dipole moment $\propto$ displacement of electron $\propto$ E field.
It's also $\propto e$ (e^--E coupling), but that's hidden in $a_0^3 = \frac{\hbar^6}{m^3 e^6}$. Complicated because $V_{e^- z}$ is also $\propto e^2$, same coupling.

This also is used to define the "polarizability", α, in a system with an induced moment,

$$\boxed{\Delta \mathcal{E}nergy \equiv -\frac{1}{2}\alpha E^2}$$

electric field,

for hydrogen this case

$$\boxed{\boxed{\alpha = \frac{9}{2} a_0^3 .}}$$