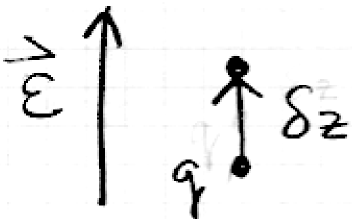
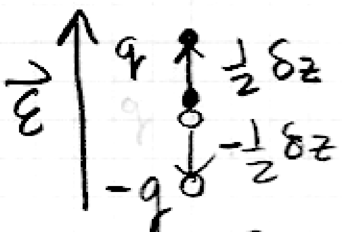
Energetics, Induced Dipole



if *you* move charge q a displacement δz (parallel to $\vec{E}$, but displacements $\perp$ to $\vec{E}$ don't change energy) you add energy

$$dW = -q\mathcal{E}\delta z$$

This creates no dipole moment.



$$dW = dW_+ + dW_-$$
$$= \left(-\tfrac{1}{2}q\mathcal{E}\delta z\right) + \left(-\tfrac{1}{2}(-q)\mathcal{E}(-\delta z)\right)$$
$$= -q\mathcal{E}\delta z$$

but now $\delta\mu = q\delta z$ $\Leftarrow$ increment in electric dipole moment

$$dW = -\mathcal{E}\,d\mu$$

Imagine: raising $\mathcal{E}$ from 0 to non-zero value, on a system that initially has no electric dipole moment

Assume: $\mu \propto \mathcal{E}$

$$\mu = \alpha\mathcal{E}$$
$$d\mu = \alpha\, d\mathcal{E}$$
$$dW = -\alpha\mathcal{E}\,d\mathcal{E}$$

then $W = \int_0^{\mathcal{E}} dW = -\alpha \int_0^{\mathcal{E}} \mathcal{E}' d\mathcal{E}'$

$$= -\frac{1}{2}\alpha \cancel{\mathcal{E}^2} = -\frac{27}{32}\frac{8}{3} a_0^3 \cancel{\mathcal{E}^2}$$

(note the $O(\mathcal{E}^2)$ on both sides...
on side classical
other side QM

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

Degenerate Perturbation Theory

What if $\underset{\sim}{H}^0$ had degeneracy ?

For example $E_n^0 = E_m^0$

then $\dfrac{\langle m^0 | \underset{\sim}{H}' | n^0 \rangle}{E_n^0 - E_m^0}$ ← This must go to 0!
← blows up.

How to make $\langle m^0 | \underset{\sim}{H}' | n^0 \rangle = 0$?

⇒ Diagonalize $\underset{\sim}{H}'$ inside the degenerate subspace of $\underset{\sim}{H}^0$.

$\underset{\sim}{H}^0 (\alpha |n^0\rangle + \beta |m^0\rangle)$

$$= \alpha E_n^0 |n^0\rangle + \beta E_m^0 |m^0\rangle$$

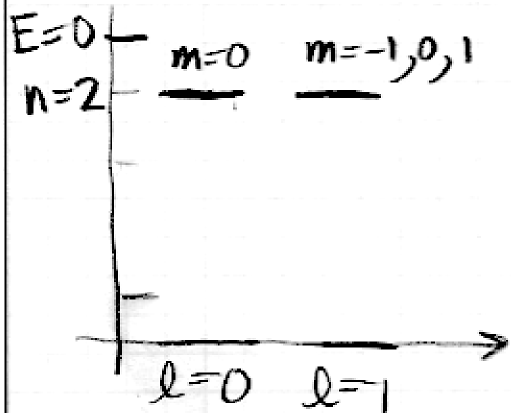
equal since degenerate

$$= E_n^0 (\alpha |n^0\rangle + \beta |m^0\rangle)$$

∴ $\alpha |n^0\rangle + \beta |m^0\rangle$ is still an eigenstate

Point.. can "re-shuffle" kets in $\underset{\sim}{H}^0$'s degenerate subspace to please $\underset{\sim}{H}^1$.

Example: $n=2$ levels of Hydrogen.



$$\underset{\sim}{H}' = e\mathcal{E}\underset{\sim}{z}$$

look at

$$\langle 2\ell' m' | \underset{\sim}{H}' | 2\ell m \rangle$$

① $= 0$ unless $\ell' \neq \ell$.

why? Parity.

Parity eigenvalue $\ell \Rightarrow (-1)^{\ell}$

$\ell' \Rightarrow (-1)^{\ell'}$

Parity of $\underset{\sim}{z} = -1$

$(-1)(-1)^{\ell+\ell'} = 1$ (or integral vanishes)

② $= 0$ unless $m' = m$: $[\underset{\sim}{L}_z, \underset{\sim}{H}'] = 0$

③ put them together: $m = m' = 0$

$$e\mathcal{E}\langle 210 | \underset{\sim}{z} | 200 \rangle$$

$$= e\mathcal{E}\int_0^{2\pi} d\phi \int_{-1}^{1} d\mu \int_0^{\infty} dr\, r^2 \underbrace{\left(\frac{1}{32\pi a_0^3}\right)^{1/2} \frac{r}{a_0} e^{-r/2a_0}\mu}_{\psi_{210}(\vec{x})} \times \underbrace{r\mu}_{z} \times \underbrace{\left(\frac{1}{32\pi a_0^3}\right)^{1/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}}_{\psi_{200}(\vec{x})}$$

$\mu = \cos\theta$

$$= e\mathcal{E}\left(\frac{1}{32\pi}\right) 2\pi \cdot a_0 \underbrace{\int_{-1}^{1} d\mu\, \mu^2}_{\frac{\mu^3}{3}\Big|_{-1}^{1}} \underbrace{\int_0^\infty d\rho\, \rho^4 (2-\rho) e^{-\rho}}_{2\cdot 4! - 5!} \qquad \rho = r/a_0,$$

$$= e\mathcal{E}\,\frac{1}{16}\cdot a_0 \times \frac{2}{3}\cdot 4\cdot 3\cdot 2\,(2-5)$$

$$\boxed{e\mathcal{E}\langle 210|z|200\rangle = -3e\mathcal{E}a_0}$$

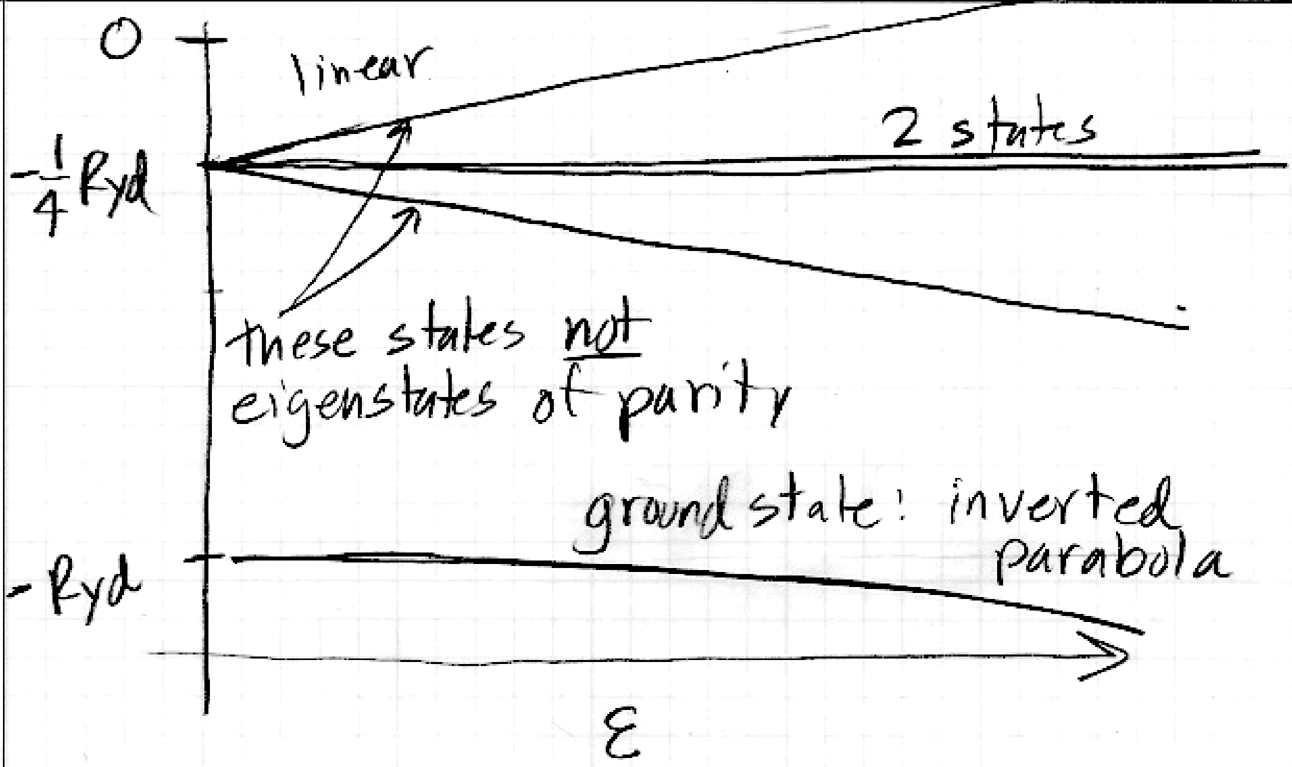
putting this in a table:

$n'l'm'$ \ nlm	200	210	211	21-1
200	0	$-3e\mathcal{E}a_0$	0	0
210	$-3e\mathcal{E}a_0$	0	0	0
211	0	0	0	0
21-1	0	0	0	0

eigenket: $\frac{1}{\sqrt{2}}\left[|200\rangle + |210\rangle\right]$ e.v. $= -3e\mathcal{E}a_0$

$\frac{1}{\sqrt{2}}\left[|200\rangle - |210\rangle\right]$ e.v. $= +3e\mathcal{E}a_0$

$|211\rangle$, $|21{-1}\rangle$ or any linear superposition are unperturbed.



Fine Structure:

Relativity

$$E = \sqrt{(mc^2)^2 + (cp)^2} \quad \text{Total Energy}$$

kinetic energy $= E - mc^2 \equiv T$

$$T = mc^2\left[1 + \frac{p^2}{m^2c^2}\right]^{1/2} - mc^2$$

$$\simeq \cancel{mc^2} + \frac{p^2}{2m} + \frac{(\frac{1}{2})(-\frac{1}{2})}{2}\frac{p^4}{m^3c^2} - \cancel{mc^2}$$

$$T \simeq \frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{m^3c^2}$$

perturbation $\underset{\sim}{H}_T = \frac{-1}{8}\frac{p^4}{m^3c^2}$