Perturbations to 2nd order [$\theta(V^2)$].

5) We have the first-order [i.e. $\theta(V)$, same as $\theta(\lambda)$] energy corrections $E_k^{(1)} = V_{kk}$ and amplitudes $a_{nk}^{(1)} = V_{nk}/(E_k^{(0)} - E_n^{(0)})$ from Eqs. (17). And we have shown that we can choose $a_{kk}^{(\sigma)} = 0$ for all $\sigma \geq 1$, which simplifies the proceedings.

Now go after second-order corrections. Like this:

In Eq. (16), choose $\nu = 1$ ($\Rightarrow$ working to $\theta(V^2)$, 2nd order pert$^{\underline{b}}$n theory).

$$\xrightarrow{\text{So}}(E_k^{(0)} - E_m^{(0)})a_{mk}^{(2)} + E_k^{(2)}\delta_{mk} = \sum_n{}' V_{mn}a_{nk}^{(1)} - E_k^{(1)}a_{mk}^{(1)}. \tag{26}$$

1. $m \neq k$, (26) $\Rightarrow$ $(E_k^{(0)} - E_m^{(0)})a_{mk}^{(2)} = \sum_n{}' V_{mn}a_{nk}^{(1)} - V_{kk}a_{mk}^{(1)}$,

but $a_{nk}^{(1)} = \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}$, so

$$\boxed{a_{mk}^{(2)} = \frac{1}{E_k^{(0)} - E_m^{(0)}}\sum_{n\neq k}(V_{mn} - V_{kk}\delta_{mn})\frac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}}. \tag{26a}$$

Then: $\psi_k = \psi_k^{(0)} + \sum_m{}' a_{mk}^{(1)}\psi_m^{(0)} + \sum_m{}' a_{mk}^{(2)}\psi_m^{(0)} + \ldots$ Gets pretty messy!

2. $m = k$, (26) $\Rightarrow$ $0 + E_k^{(2)} = \sum_n{}' V_{kn}a_{nk}^{(1)} - 0$

but $a_{nk}^{(1)} = \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}}$,

$$\boxed{E_k^{(2)} = \sum_{n\neq k} V_{kn}V_{nk}/(E_k^{(0)} - E_n^{(0)})}. \tag{26b}$$

Now: $E_k = E_k^{(0)} + V_{kk} + \sum_{n\neq k}\dfrac{V_{kn}V_{nk}}{E_k^{(0)} - E_n^{(0)}} + \ldots$ to $\theta(V^2)$. Fairly compact!

REMARKS on 2nd order results.

(a) The iteration can be continued ($\nu = 2, 3$, etc.), but ψ_k up thru $\psi_k^{(1)}$ and E_k up thru $E_k^{(2)}$ are sufficient for most problems.

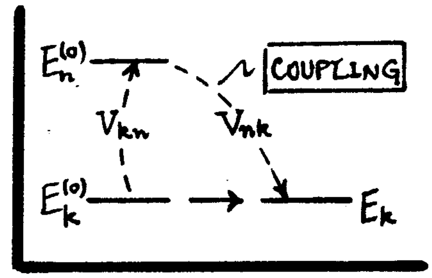
(b) E_k up thru $E_k^{(2)}$ [i.e. $\theta(V^2)$] can be calculated from ψ_k up thru $\psi_k^{(1)}$ [i.e. $\theta(V)$] by evaluating: $E_k = \langle\psi_k|\mathcal{H}|\psi_k\rangle / \langle\psi_k|\psi_k\rangle$. Do as exercise.

(c) Both $a_{mk}^{(2)}$ & $E_k^{(2)}$ are 2nd order in V, and the smallness conditions in Eqs. (17) (e.g. $|V_{nk}| \ll |E_k^{(0)} - E_n^{(0)}|$) ensure $|E_k^{(2)}| \ll |E_k^{(1)}|$, etc.

$\boxed{\text{REMARKS}}$ (cont'd)

(d) Since V is a Hermitian perturbation, then $V_{kn} = V_{nk}^*$, and Eq. (26b) reads $\underline{E_k^{(2)} = \sum_{n\neq k} |V_{nk}|^2/(E_k^{(0)} - E_n^{(0)})}$; the numerator is +ve definite. If $k=0$ is the ground state of the system, then $E_0^{(2)} = (-)\sum_{n>0} |V_{n0}|^2/(E_n^{(0)} - E_0^{(0)})$. When $V_{00}=0$, the perturbed ground state $E_0 = E_0^{(0)} + E_0^{(2)} + \ldots$ is driven <u>downward</u>, so -- curiously enough -- the applied V (usually) <u>increases</u> the binding.

(e) Notice the way that "coupling" works in forming the energy shift $E_k^{(2)} = \sum_{n\neq k} V_{kn} V_{nk}/(E_k^{(0)} - E_n^{(0)})$. The matrix element V_{kn} mixes $k\to n$, then V_{nk} takes that contribution $n \to k$ back to the (perturbed) state k, weighted by the energy denominator $(E_k^{(0)} - E_n^{(0)})$. $E_k^{(2)}$ is formed by state k "exploring" all possible intermediate states n ($^{w/}V_{kn}\neq 0$) in this way.



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6) $\boxed{\text{EXAMPLE}}$ <u>Stark Effect on ground state of atomic hydrogen.</u>

Let: $V(\vec{r}) = +e\vec{\mathcal{E}}\cdot\vec{r}$, for interaction of $(-)e$ $^{w/}$ cnst external field $\vec{\mathcal{E}}$.

Choose $\vec{\mathcal{E}}$ along z-axis. $\vec{\mathcal{E}}$ is cnst over atomic dimensions, so...

$$\rightarrow V_{nk} = e\vec{\mathcal{E}}\cdot\langle n|\vec{r}|k\rangle = e\mathcal{E}z_{nk}, \quad ^{w/}\; z_{nk} = \langle n|z|k\rangle. \tag{27}$$

The states $|k\rangle$ are eigenstates of the unperturbed hydrogen atom, which have definite parity [$P = (-)^\ell$ for ∡ momentum ℓ]. So $z_{nk}\equiv 0$ for states of the same parity; in particular $z_{kk}=0$ for the $k=0$ ground state. So

$$\rightarrow E_0 \simeq E_0^{(0)} - e^2\mathcal{E}^2 \sum_{n>0} |z_{n0}|^2/(E_n^{(0)} - E_0^{(0)}), \tag{28}$$

is the perturbed energy to $\Theta(\mathcal{E}^2)$ [the $\Theta(\mathcal{E})$ correction $\equiv 0$].

We can actually evaluate the sum here, explicitly.

Stark Effect in H groundstate

$\boxed{\text{ASIDE}}$: Evaluation of sum $S_z = \sum_{n>0} |z_{n0}|^2/(E_n^{(0)} - E_0^{(0)})$ in Eq. (28).

(1) Suppose we can find an operator F with the "magical" property that

$$\rightarrow z|0\rangle = (F\mathcal{H}_0 - \mathcal{H}_0 F)|0\rangle = [F, \mathcal{H}_0]|0\rangle \int \begin{matrix} |0\rangle = \text{H-atom groundstate} \\ \mathcal{H}_0 = \text{unperturbed Ham}^{\underline{n}} \end{matrix} \qquad (28a)$$

then, $z_{n0} = \langle n|F\mathcal{H}_0 - \mathcal{H}_0 F|0\rangle = (E_0^{(0)} - E_n^{(0)})\langle n|F|0\rangle$,

and $S_z = (-)\sum_{n>0} \dfrac{\langle 0|z|n\rangle\langle n|z|0\rangle}{E_0^{(0)} - E_n^{(0)}} = -\sum_{n>0} \langle 0|z|n\rangle\langle n|F|0\rangle$

$$= -\Big\{ \sum_{\text{all } n} \langle 0|z|n\rangle\langle n|F|0\rangle - \cancelto{0}{\langle 0|z|0\rangle}\langle 0|F|0\rangle \Big\}$$

$$= -\langle 0|z\underbrace{\Big(\sum_n |n\rangle\langle n|\Big)}_{\equiv 1, \text{ by completeness}}F|0\rangle = -\langle 0|zF|0\rangle. \qquad (28b)$$

So S_z is reduced to one term here. Now we must find the "magic" F.

(2) From Eq. (28a), F is defined by $z|0\rangle = [F, \mathcal{H}_0]|0\rangle$. Since $\mathcal{H}_0|0\rangle = E_0^{(0)}|0\rangle$, with $E_0^{(0)} = -e^2/2a$ $(a = \hbar^2/me^2)$ in the ground state, we have...

$$\rightarrow z|0\rangle = FE_0^{(0)}|0\rangle - \mathcal{H}_0(F|0\rangle) \qquad (28c)$$

∡ operator [Davydov Eq. (16.18)]

... but : $\mathcal{H}_0 = -\dfrac{\hbar^2}{2mr^2}\Big[\dfrac{\partial}{\partial r}\Big(r^2\dfrac{\partial}{\partial r}\Big) + \hat{\Lambda}\Big] - \dfrac{e^2}{r}$, per Davydov Eq. (34.2)...

... and : $|0\rangle = \mathcal{N}e^{-r/a}$, for ground state (norm $\mathcal{N}$ unimportant)...

$$\overset{\text{So}}{\rightarrow} z|0\rangle = \Big(-\frac{e^2}{2a} + \frac{e^2}{r}\Big)F|0\rangle + \frac{\hbar^2}{2mr^2}\Big[\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \hat{\Lambda}\Big]F|0\rangle. \qquad (28d)$$

This is a differential eqtn for F, which will generally depend on r and θ, since $[F, \mathcal{H}_0] = z = r\cos\theta$. It can be solved straightforwardly (details are left to problem (32)) with the result that...

$$\left[\!\left[F(r,\theta) = -\frac{ma}{2\hbar^2}(r+2a)z \right. \right.$$ $\int^{\text{w}}$ $a = \hbar^2/me^2$ (Bohr radius), $z = r\cos\theta$. (28e)

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(3) According to Eq. (28b), the perturbation sum is...

$$\rightarrow S_z = -\langle 0|zF|0\rangle = +\frac{ma}{2\hbar^2}\langle 0|(r+2a)r^2\cos^2\theta|0\rangle. \tag{28f}$$

But, w.r.t. a spherically symmetric state like $|0\rangle$, have $\langle\cos^2\theta\rangle = \frac{1}{3}$, so

$$S_z = \frac{ma}{2\hbar^2}\cdot\frac{1}{3}\langle 0|r^3+2ar^2|0\rangle. \quad \boxed{\text{NOTE}}\ \frac{ma}{2\hbar^2} = \frac{1}{2e^2}. \tag{28g}$$

<u>All we have to do to get the complicated sum is to evaluate two trivial matrix elements</u>, viz. $\langle r^3\rangle$ & $\langle r^2\rangle$. It is easy to show:

$$\langle 0|r^n|0\rangle = \frac{1}{\pi a^3}\int_{4\pi} d\Omega \int_0^\infty r^{n+2}e^{-2r/a}dr = \frac{(n+2)!}{2^{n+1}}a^n; \tag{28h}$$

so/ $\langle 0|r^3|0\rangle = \frac{5!}{2^4}a^3$, and: $\langle 0|r^2|0\rangle = \frac{4!}{2^3}a^2$.

Then we have S_z in (28g) as...

$$\rightarrow S_z = \frac{1}{2e^2}\cdot\frac{1}{3}\left(\frac{5!}{16}a^3 + 2a\cdot\frac{4!}{8}a^2\right) = \frac{9}{4}(a^3/e^2). \tag{28i}$$

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(4) The Stark-perturbed energy in Eq. (28) is now written succinctly as...

$$E_0 = E_0^{(0)} - e^2\mathcal{E}^2 S_z = E_0^{(0)} - \frac{9}{4}a^3\mathcal{E}^2, \quad ^{\text{w/}}\ E_0^{(0)} = -\frac{e^2}{2a^2},$$

so/ $$\boxed{E_0 = E_0^{(0)}\left[1+\frac{9}{8}\left(\frac{e\mathcal{E}a}{E_0^{(0)}}\right)^2\right]}, \text{ to } \theta(\mathcal{E}^2). \tag{28j}$$

This approxn is good so long as: $e\mathcal{E}a \ll |E_0^{(0)}| = 13.6$ eV, i.e. for electric fields $\mathcal{E}$ up to: <u>$\mathcal{E}_m = |E_0^{(0)}|/ea = 2.6\times10^9$ Volts/cm</u>, which is ~ enormous.

$\boxed{\text{END of ASIDE}}$