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

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...

$$\rightarrow V_{nk} = e\vec{\mathcal{E}}\cdot\langle n|\vec{r}|k\rangle = e\mathcal{E}z_{nk}, \text{ w/ } z_{nk} = \langle n|z|k\rangle. \qquad (27)$$

The states $|k\rangle$ are eigenstates of the unperturbed hydrogen atom, which have definite parity [$P = (-)^{l}$ 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

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

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

We can actually evaluate the sum here, explicitly.

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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

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

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

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

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

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

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...

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

... but : $\mathcal{H}_0 = -\frac{\hbar^2}{2mr^2}\Big[\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \hat{\Lambda}\Big] - \frac{e^2}{r}$, per Davydov Eq. (34.2)... ↖ $\measuredangle$ operator [Davydov Eq. (16.18)]

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

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

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

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left to problem ◯) with the result that...

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

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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

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

All we have to do to get the complicated sum is to evaluate two trivial matrix elements, 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

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

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: $\mathcal{E}_M = |E_0^{(0)}|/ea = 2.6\times10^9$ Volts/cm, which is ~ enormous.

END of ASIDE