The Quadratic Stark Effect on the Ground State of H

$$H_0 = \frac{p^2}{2\mu} - \frac{e^2}{r}$$

$$\lambda V = e\mathcal{E} z \qquad (e > 0)$$

The electric field is parallel to the z-axis.

The mean value of z vanishes in the spherically symmetric ground state

$$\langle 100 | z | 100 \rangle = 0$$

so to first order in $e\mathcal{E}$ the energy of the ground state does not change

$$\Delta_1^1 = e\mathcal{E} \langle 100 | z | 100 \rangle = 0,$$

To second order in $e\mathcal{E}$, the change in the energy is

$$\Delta_{100}^2 = e^2\mathcal{E}^2 \sum_{\substack{n \neq 1 \\ \ell m}} \frac{|\langle n\ell m | z | 100 \rangle|^2}{E_1^0 - E_n^0} < 0$$

in which $E_n^0 = -E_I/n^2 = -\frac{1}{2}\mu c^2 \alpha^2/n^2$.

What is the electric dipole moment of this H-atom? To lowest order in $e\mathcal{E}$,

$$\vec{d} = \langle \psi | -e\vec{r} | \psi \rangle$$

in which since

$$|n^0\rangle + \lambda |n^1\rangle = |n^0\rangle + \lambda \frac{\phi_n}{E_n^0 - H_0} V |n^0\rangle$$

$$|\psi\rangle = |100\rangle + e\mathcal{E} \sum_{\substack{n \neq 1 \\ l, m}} \frac{|nlm\rangle \langle nlm | z | 100\rangle}{E_1^0 - E_n^0}.$$

So

$$\vec{d} = -e \langle 100 | \vec{r} | 100\rangle$$

$$-e^2 \mathcal{E} \sum_{\substack{n \neq 1 \\ l m}} \frac{\langle 100 | \vec{r} | nlm\rangle\langle nlm | z | 100\rangle + \langle 100 | z | nlm\rangle\langle nlm | \vec{r} | 100\rangle}{E_1^0 - E_n^0}$$

Now

$\langle nlm | z | 100\rangle = 0$ unless $m = 0$ and $l = 1$,

because

$$z \propto Y_1^0.$$

Also, x & y are proportional to linear combinations of $Y_1^{\pm 1}$ so

$$\langle n10|x|100\rangle = 0 = \langle n10|y|100\rangle.$$

So $\vec{d} = d\hat{z}$ with

$$d = -e^2 \mathcal{E} \sum_{n\neq 1} \frac{|\langle n10|z|100\rangle|^2}{E_1^0 - E_n^0}.$$

The linear electric susceptibility χ is given by

$$d = \chi \mathcal{E}$$

so χ is

$$\chi = -2e^2 \sum_{n>1} \frac{|\langle n10|z|100\rangle|^2}{E_1^0 - E_n^0}.$$

Now $E_1^0 - E_n^0 = -\frac{1}{2}\mu c^2 \alpha^2 \left(1 - \frac{1}{n^2}\right)$ so

$$\chi = \frac{4e^2}{\mu c^2 \alpha^2} \sum_{n>1} \frac{|\langle n10|z|100\rangle|^2}{1 - \frac{1}{n^2}}$$

$$= \frac{4e^2 \hbar^2 c^2}{\mu c^2 e^4} \sum_{n>1} \frac{|\langle n10|z|100\rangle|^2}{1 - \frac{1}{n^2}}$$

$$= \frac{4\hbar^2}{\mu e^2} \sum_{n>1} \frac{|\langle n10|z|100\rangle|^2}{1 - \frac{1}{n^2}}$$

Now for $n>1$

$$\frac{1}{1-\frac{1}{n^2}} \le \frac{1}{1-\frac{1}{4}} = \frac{4}{3}$$

so

$$\chi_{1s} \le \frac{4\hbar^2}{\mu e^2}\,\frac{4}{3}\sum_{n>1} \langle 100|z|n10\rangle\langle n10|z|100\rangle.$$

But the states $|n10\rangle$ are the only ones that do not vanish in the above sum. Thus

$$\chi_{1s} \le \frac{16}{3}\frac{\hbar^2}{\mu e^2}\sum_{n\ell m}\langle 100|z|n\ell m\rangle\langle n\ell m|z|100\rangle$$

$$\le \frac{16}{3}\frac{\hbar^2}{\mu e^2}\langle 100|z^2|100\rangle.$$

$$\le \frac{16}{3}a_0\,\langle 100|z^2|100\rangle$$

where $a_0 = \hbar^2/(\mu e^2)$ is the Bohr radius, $a_0 \sim 0.53\,\mathring{A}$.

Now

$$\langle 100|z^2|100\rangle = \frac{1}{3}\langle 100|\vec{r}^{\,2}|100\rangle = \frac{1}{3}\int_0^\infty r^2 dr\, R_{10}^2(r)\, r^2$$

$$= \frac{4}{3}a_0^{-3}\int_0^\infty dr\, r^4 e^{-2r/a_0} = \left(\frac{a_0}{2}\right)^5 \frac{4}{3}a_0^{-3}\int_0^\infty dx\, x^4 e^{-x} = \frac{4}{3}4!\,\frac{a_0^2}{2^5}$$

$$= \frac{4\cdot 4\cdot 3\cdot 2}{3\cdot 4\cdot 4\cdot 2}a_0^2 = a_0^2$$

So the linear electric susceptibility of the ground state of hydrogen is bounded by

$$\chi_{1s} \le \frac{16}{3} a_0^3 \approx 5.3 a_0^3 .$$

The exact value is

$$\chi_{1s} = 4.5 a_0^3 .$$