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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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