The Quadratic Stark Effect on the Ground State of H

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

\[ \Delta V = e^3 z \quad (z \geq 0) \]

The electric field is parallel to the z-axis.

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

\[ \langle 100|z|1100\rangle = 0 \]

so to first order in \( e^3 \) the energy of the ground state does not change

\[ \Delta_1 = e^3 \langle 100|z|1100\rangle = 0. \]

To second order in \( e^3 \), the change in the energy is

\[ \Delta_2 = e^2E^2 \sum_{n=1}^{\infty} \frac{|\langle nm\lambda m121100\rangle|^2}{E_0 - E_n} < 0 \]

in which \( E_0 = -E_\perp/n^2 = -\frac{1}{2}\mu c^2 \alpha^2/m^2 \).
What is the electric dipole moment of this H-atom? To lowest order in $e^2$, 

$$d = \langle \hat{r}^2 \rangle$$

In which case, since

$$|m^0\rangle + e |m^1\rangle = |m^0\rangle + e \sum_{\eta, \ell, m} \frac{\phi_{\eta, \ell, m}}{E^0_{\eta, \ell, m} - E^0} |m^0\rangle$$

$$|\psi\rangle = |1100\rangle + e \sum_{\eta, \ell, m} \frac{\phi_{\eta, \ell, m}}{E^0_{\eta, \ell, m} - E^0} |\phi_{\eta, \ell, m}\rangle$$

So

$$d = -e \langle 1001 \mid \hat{r} \mid 1100 \rangle - e^2 \sum_{\eta, \ell, m} \frac{\phi_{\eta, \ell, m}}{E^0_{\eta, \ell, m} - E^0}$$

Now

$$\langle n \ell m \mid \hat{r} \mid 1100 \rangle = 0$$

unless $m = 0$ and $\ell = 1$, because

$$\hat{r} \propto Y^0_1$$

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

$<n101z1100> = 0 = <n101y1100>$. 

So $d = d^2$ with

$$d = -c^2E \sum_{m \neq 1} \frac{|<n101z1100>|^2}{E_1^0 - E_m^0}.$$ 

The linear electric susceptibility $\chi$ is given by

$$d = \chi E$$

so $\chi$ is

$$\chi = -2e^2 \sum_{m \neq 1} \frac{|<n101z1100>|^2}{E_1^0 - E_m^0}.$$ 

Now $E_1^0 - E_m^0 = -\frac{1}{2} \mu c^2 d^2 \left(1 - \frac{1}{m^2}\right)$ so

$$\chi = \frac{4e^2}{mc^2 d^2} \sum_{m \neq 1} \frac{|<n101z1100>|^2}{1 - \frac{1}{m^2}}.$$ 

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$$= \frac{4e^2}{mc^2} \sum_{m \neq 1} \frac{|<n101z1100>|^2}{1 - \frac{1}{m^2}}.$$
Now for \( n > 1 \)

\[
\frac{1}{1 - \frac{1}{m^2}} < \frac{1}{1 - \frac{1}{4}} = \frac{4}{3}
\]

so

\[
\chi_{1s} \leq \frac{4 \hbar^2}{m e^2} \frac{4}{3} \sum_{n \geq 1} \langle 1001z^2 | m_1 \otimes m_1 \otimes m_1 \otimes 1100 \rangle,
\]

But the states \( 1m_1m_1 \rangle \) are the only ones that do not vanish in the above sum. Thus

\[
\chi_{1s} \leq \frac{16 \hbar^2}{3 m e^2} \sum_{m_1} \langle 1001z \otimes m_1 \otimes m_1 \otimes 1100 \rangle
\]

\[
\leq \frac{16 \hbar^2}{3 m e^2} \langle 1001z^2 | 1100 \rangle
\]

\[
\leq \frac{16 a_0}{3} \langle 1001z^2 | 1100 \rangle
\]

where \( a_0 = \frac{\hbar^2}{m e^2} \) is the Bohr radius, \( a_0 \sim 0.53 \text{Å} \).

Now

\[
\langle 1001z^2 | 1100 \rangle = \frac{1}{2} \langle 1001z^2 | 1100 \rangle = \frac{1}{3} \int_0^\infty r^2 e^{-2r/a_0} \mathcal{R}_{10}(r) r^2 \, dr
\]

\[
= \frac{4}{3} a_0^{-3} \int_0^\infty r^4 e^{-2r/a_0} \, dr = \left( \frac{a_0}{2} \right)^3 \frac{4}{3} a_0^{-3} \int_0^\infty x^4 e^{-x} \, dx = \frac{4}{3} \left( \frac{4 a_0^2}{25} \right)
\]

\[
= \frac{4 \cdot 4 \cdot 3 \cdot 2}{3 \cdot 4 \cdot 4 \cdot 2} a_0^2 = a_0^2
\]
So the linear electric susceptibility of the ground state of hydrogen is bounded by

\[ \chi_{1s} \leq \frac{16}{3} a_0^3 \approx 5.3 a_0^3. \]

The exact value is

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