Electric fields : Stark effect, dipole & quadrupole polarizability.

We are often interested in the effect of an external electric field on the energy levels and wavefunction of H and other one-electron atoms so lets consider the atom in a spatially constant electric field. The energy shift due to the electric field is called the Stark effect. If the atom is in an external electrostatic potential $\varphi(\vec{r})$ the Hamiltonian becomes

$$\left(-\frac{\hbar^2}{2m_t}\nabla^2_{cm} -\frac{\hbar^2}{2\mu}\nabla^2 -\frac{Ze^2}{4\pi\varepsilon_0 r} + Ze\varphi(\vec{r}_n) - e\varphi(\vec{r}_e) \right)\Psi = E\Psi$$

where $e > 0$ and the electric field $\vec{F} = -\nabla\varphi$. Since $\vec{F}$ is constant $\varphi = -\vec{r}\cdot\vec{F}$ up to an arbitrary constant, which we ignore. Converting $\vec{r}_e$ & $\vec{r}_n$ to $\vec{r}$ & $\vec{R}$ we have

$$(\hat{H}_{cm} + \hat{H}_{int})\Psi = E\Psi$$

where

$$\hat{H}_{cm} = -\frac{\hbar^2}{2m_t}\nabla^2_{cm} + e\vec{F}\cdot\vec{R}(1-Z)$$

and

$$\hat{H}_{int} = -\frac{\hbar^2}{2\mu}\nabla^2 -\frac{Ze^2}{4\pi\varepsilon_0 r} + e\vec{F}\cdot\vec{r}(1+(Z-1)(m_e/m_t))$$

Since the center of mass and the internal motion are independent the wave function $\Psi(\vec{R},\vec{r}) = \phi(\vec{R})\psi(\vec{r})$ factorizes into a product where

$$\left(-\frac{\hbar^2}{2m_t}\nabla^2_{cm} + e\vec{F}\cdot\vec{R}(1-Z) \right)\phi(\vec{R}) = E_{cm}\phi(\vec{R})$$

and

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + q\vec{F}\cdot\vec{r} \right)\psi(\vec{r}) = E_{int}\psi(\vec{r})$$

where $q = e(1+(Z-1)(m_e/m_t))$, an effective charge for $Z \neq 1$. The center of mass motion is considered latter and we now focus on the effect of the field on the internal motion of the electron. Before getting into any detail lets consider the order of magnitude of the internal electric field before applying the external field. This field at a distance r from the nucleus is given by $\frac{Ze}{4\pi\varepsilon_0 r^2}$ and after substituting the numerical values of the constants the field strength is $(1.4399649 \times 10^{11})\frac{Z}{r^2}\frac{volts}{m}$ with r in Å. The first Bohr orbit in H has a radius of 0.5291772Å so the field in H at that distance from the nucleus is $5.1422081 \times 10^{11}\frac{volts}{m}$. Laboratory fields vary widely but $10^7\frac{volts}{m}$ is reasonable and is smaller than the internal field by a factor of approximately 10^4 suggesting that perturbation theory will be adequate to estimate the change in energy of the one electron atom in typical laboratory fields.

The unperturbed internal Hamiltonian is

$$\hat{H}^0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

where

$$\hat{H}^0\psi^0_{nlm} = E^0_n\psi^0_{nlm}$$

and $E^0_n = \frac{-e^2 Z^2}{2(4\pi\varepsilon_0)a_\mu n^2}$

If we measure length in multiples of γa_0 and the energy in multiples of $\frac{e^2}{(4\pi\varepsilon_0)a_\mu}$ we have

$$\hat{H}^0 = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \text{ with } E^0_n = \frac{-Z^2}{2n^2}$$

Lets choose $\vec{F}$ to be along the z axis, $\vec{F} = F\hat{z}$

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + qFr\cos\theta = \hat{H}^0 + qFr\cos\theta = \hat{H}^0 + VF$$

where θ is the angle between the field and the position vector $\vec{r}$ and $\hat{V} = qr\cos\theta$. In these units F is measured in multiples of $\frac{e}{(4\pi\varepsilon_0)a_\mu^2}$ and $q = 1 + (Z-1)/\left(1 + \frac{1}{m_n}\right)$ with m_n in multiples of the electron mass.

Lets first consider the effect of the perturbation on the ground state wave-function $\psi_0 \equiv \psi_{100}$ with energy $E_0 = -\frac{Z^2}{2}$. Since the wave-function and energy in the field are solutions to

$$\left(\hat{H}^0 + \hat{V}F\right)\psi = E\psi$$

we may expand $E\,\&\,\psi$ in powers of F

$$\psi = \sum_{n=0}^{\infty}\psi_n F^n \text{ and } E = \sum_{n=0}^{\infty}E_n F^n$$

The Schrodinger equation becomes

$$\left(\hat{H}^0 + VF\right)\sum_{n=0}^{\infty}\psi_n F^n = \sum_{n=0}^{\infty}\psi_n F^n \sum_{m=0}^{\infty}E_m F^m$$

where $\psi_n\,\&\,E_n$ are the nth order corrections to the wave-function and energy.

We can write this equation as

$$\sum_{p=0}^{\infty}F^p\left(\hat{H}^0\psi_p + \left(1 - \delta_{p0}\right)\hat{V}\psi_{p-1} - \sum_{k=0}^{p}E_{p-k}\psi_k\right) = 0$$

and since it must be true for any F each coefficient of F^p must be zero. Accordingly we recover the usual Rayleigh-Schrodinger perturbation equations

$$\hat{H}^0\psi_p + \left(1 - \delta_{p0}\right)\hat{V}\psi_{p-1} = \sum_{k=0}^{p}E_{p-k}\psi_k$$

The first few equations are

p=0 $\hat{H}^0\psi_0 = E_0\psi_0$, the unperturbed equation

where $\psi_0 = \sqrt{\dfrac{Z^3}{\pi}}e^{-Zr}$ and $E_0 = -\dfrac{Z^2}{2}$

p=1; $(\hat{H}^0 - E_0)\psi_1 + (\hat{V} - E_1)\psi_0 = 0$, the first order equation

p=2; $(\hat{H}^0 - E_0)\psi_2 + (\hat{V} - E_1)\psi_1 = E_2\psi_0$, the second order equation

p=3; $(\hat{H}^0 - E_0)\psi_3 + (\hat{V} - E_1)\psi_2 = E_3\psi_0 + E_2\psi_1$, the third order equation

p=4; $(\hat{H}^0 - E_0)\psi_4 + \hat{V}\psi_3 = E_4\psi_0 + E_2\psi_2$

Note that since the energy cannot depend on the direction of the electric field all odd order corrections, $E_1, E_3, \cdots$ must be zero. We can verify this explicitly for E_1 as follows.

Multiply the first order equation by the ground state wave-function and integrate

$$\langle 0|(\hat{H}^0 - E_0)|1\rangle + \langle 0|(\hat{V} - E_1)|0\rangle = 0$$

Since $\hat{H}^0$ is Hermitian

$$\langle 0|(\hat{H}^0 - E_0)|1\rangle = \langle 1|(\hat{H}^0 - E_0)|0\rangle = 0$$

and so the first order correction to the energy is the average of the perturbation over the ground state wave-function which is zero by symmetry.

$$E_1 = \langle 0|\hat{V}|0\rangle = 2qZ^3 \int_0^\infty e^{-2Zr}r^3\,dr \int_0^\pi \cos(\theta)\sin(\theta)\,d\theta = 0$$

Consequently the first order equation becomes

$$(\hat{H}^0 - E_0)\psi_1 + \hat{V}\psi_0 = 0$$

It happens that one can solve the above perturbation equations exactly to determine $\psi_n \& E_n$ and we will do so before discussing the more common approach of expanding the functions ψ_n in terms of the eigenfunctions of $\hat{H}^0$.

We note that the atom in the field has cylindrical symmetry and look for a solution of the form

$$\psi_1 = g(r,\theta)\psi_0$$

Since

$$(\hat{H}^0 - E_0)g(r,\theta)\psi_0 = \psi_0\left(-\frac{1}{2}\frac{\partial^2 g}{\partial r^2} + \frac{\partial g}{\partial r}(Z-\frac{1}{r}) + \frac{\hat{L}^2 g}{2r^2}\right)$$

the first order equation becomes

$$\frac{\partial^2 g}{\partial r^2} - 2\frac{\partial g}{\partial r}(Z-\frac{1}{r}) - \frac{\hat{L}^2 g}{r^2} = 2qr\cos\theta$$

The most general form of $g(r,\theta)$ is

$$g(r,\theta) = \sum_{\ell=0}^{\infty} f_\ell(r)P_\ell(\cos\theta) \quad \text{where } P_\ell(\cos\theta) \text{ is a Legendre polynomial.}$$

Substituting this form into the differential equation for g and noting

$$\hat{L}^2 P_\ell(\cos\theta) = \ell(\ell+1)P_\ell(\cos\theta)$$

results in

$$\sum_{\ell=0}^{\infty} P_\ell\left(f_\ell'' + 2f_\ell'(\frac{1}{r}-Z) - \frac{\ell(\ell+1)}{r^2}f_\ell\right) = 2qrP_1$$

where we note that $\cos\theta = P_1$ and consequently only the term with $\ell=1$ contributes.

Accordingly we have

$$f'' + 2f'(\frac{1}{r}-Z) - \frac{2}{r^2}f = 2qr$$

The solution to which is

$$f = -\frac{q}{Z^2}\left(r + \frac{Zr^2}{2}\right)$$

and so

$$\psi_1 = -\frac{q}{Z^2}\left(r + \frac{Zr^2}{2}\right)P_1(\cos\theta)\psi_0$$

To find E_2 we multiply the second order equation by ψ_0 and integrate

$$\langle 0|(\hat{H}^0 - E_0)|2\rangle + \langle 0|\hat{V}|1\rangle = E_2$$

Since $\hat{H}^0$ is Hermitian

$$\langle 0|(\hat{H}^0 - E_0)|2\rangle = \langle 2|(\hat{H}^0 - E_0)|0\rangle = 0$$

we have

$$E_2 = \langle 0|\hat{V}|1\rangle$$

Doing the integration results in

$$E_2 = -\frac{9q^2}{4Z^4}$$

and since the dipole polarizability α is defined by $E_2 = -\frac{1}{2}\alpha F^2$ we have

$$\alpha = \frac{9q^2}{2Z^4}$$

To find E_4 we use the *p=4* equation

$$(\hat{H}^0 - E_0)\psi_4 + \hat{V}\psi_3 = E_4\psi_0 + E_2\psi_2$$

which after multiplying by ψ_0 and integrating results in

$$E_4 = \langle 0|\hat{V}|3\rangle - E_2\langle 0|2\rangle$$

Note that using the first order equation we can write

$$\langle 0|\hat{V}|3\rangle = -\langle 1|\hat{H}^0 - E_0|3\rangle$$

but from the *p=3* equation

$$\left(\hat{H}^0 - E_0\right)\psi_3 = E_2\psi_1 - \hat{V}\psi_2$$

which results in

$$\langle 0|\hat{V}|3\rangle = \langle 1|\hat{V}|2\rangle - E_2\langle 1|1\rangle$$

and finally

$$E_4 = \langle 1|\hat{V}|2\rangle - E_2\langle 0|2\rangle - E_2\langle 1|1\rangle$$

So the fourth order correction to the energy depends on the first and second order corrections to the wavefunction and since we have the first order we need the second order correction which we will get from the *p=2* equation

$$(\hat{H}^0 - E_0)\psi_2 + \hat{V}\psi_1 = E_2\psi_0$$

using

$$\psi_1 = -\frac{q}{Z^2}\left(r + \frac{Zr^2}{2}\right)P_1(\cos\theta)\psi_0 \ , \ \hat{V} = qr\cos\theta \ \text{ and } \ E_2 = -\frac{9q^2}{4Z^4}$$

and writing $\psi_2 = g(r,\theta)\psi_0$ results in

$$\frac{\partial^2 g}{\partial r^2} - 2\frac{\partial g}{\partial r}(Z - \frac{1}{r}) - \frac{\hat{L}^2 g}{r^2} + \frac{2q^2}{Z^2}\left(r^2 + \frac{Zr^3}{2}\right)\cos^2\theta = \frac{9q^2}{2Z^4}$$

using

$$g(r,\theta) = \sum_{\ell=0}^{\infty} f_\ell(r)P_\ell(\cos\theta)$$

results in

$$\sum_{\ell=0}^{\infty} P_\ell\left(f_\ell'' + 2f_\ell'(\frac{1}{r} - Z) - \frac{\ell(\ell+1)}{r^2}f_\ell\right) + \frac{2q^2}{Z^2}\left(r^2 + \frac{Zr^3}{2}\right)\cos^2\theta = \frac{9q^2}{2Z^4}$$

and since

$$\cos^2\theta = P_1^2 = \frac{2}{3}P_2 + \frac{1}{3}$$

only $\ell = 0 \,\&\, 2$ contribute. Letting $A = \dfrac{q^2}{Z^4}$ results in the two differential equations

$$f_2'' + 2f_2'(\frac{1}{r} - Z) - \frac{6}{r^2}f_2 + \frac{4AZ^2}{3}\left(r^2 + \frac{Zr^3}{2}\right) = 0$$

and

$$f_0'' + 2f_0'(\frac{1}{r} - Z) + \frac{2AZ^2}{3}\left(r^2 + \frac{Zr^3}{2}\right) = \frac{9A}{2}$$

The solutions being

$$f_2 = \frac{A}{24}\left(2Z^2 r^4 + 10Zr^3 + 15r^2\right) \text{ and } f_0 = \frac{A}{24}\left(Z^2 r^4 + 6Zr^3 + 18r^2\right) \text{ so}$$

$$\psi_2 = f_0\psi_0 + f_2 P_2(\cos\theta)\psi_0$$

As seen above

$$E_4 = \langle 1|\hat{V}|2\rangle - E_2\langle 0|2\rangle - E_2\langle 1|1\rangle$$

and doing the various integrations results in

$$\langle 1|\hat{V}|2\rangle = -\frac{2529}{32}\frac{q^4}{Z^{10}} \;,\; \langle 0|2\rangle = \frac{81}{16}\frac{q^2}{Z^6} \;,\; \langle 1|1\rangle = \frac{43}{8}\frac{q^2}{Z^6}$$

and finally

$$E_4 = -\frac{q^4}{Z^{10}}\frac{3555}{64}$$. Since the second hyper-polarizability γ is defined by

$$E = E_0 - \frac{1}{2}\alpha F^2 - \frac{1}{24}\gamma F^4 \text{ one has } \gamma = \frac{10665}{8}\frac{q^4}{Z^{10}}$$

With these results we can calculate the dipole moment μ of the one electron atom induced by the electric field since by definition

$$\mu = -\frac{dE}{dF} = \alpha F + \frac{1}{6}\gamma F^3$$

In addition to the dipole moment higher moments are induced by the field. For example the zz component of the induced quadrupole moment is given by

$$\Theta_{zz} \equiv \Theta = \frac{\langle \psi | r^2 P_2(\cos\theta) | \psi \rangle}{\langle \psi | \psi \rangle}$$

The numerator is

$$\langle \psi | r^2 P_2(\cos\theta) | \psi \rangle = \left(2\langle 0 | r^2 P_2 | 2 \rangle + \langle 1 | r^2 P_2 | 1 \rangle\right) F^2 +$$

and

$$\langle 0 | r^2 P_2 | 2 \rangle = \frac{117}{8} \frac{q^2}{Z^8} \quad \& \quad \langle 1 | r^2 P_2 | 1 \rangle = 24 \frac{q^2}{Z^8}$$

and since

$$\langle \psi | \psi \rangle = 1 + \left(2\langle 0 | 2 \rangle + \langle 1 | 1 \rangle\right) F^2 + \cdots$$

the induced quadrupole through order F^2 is simply the numerator

$$\Theta = \frac{213}{4} \frac{q^2 F^2}{Z^8}$$

What are these moments in the SI system?

Energy and electric field in the SI and au systems are related by $E_{SI} = \left(\dfrac{e^2}{4\pi\varepsilon_0 a_\mu}\right) E_{au}$

and $F_{SI} = \left(\dfrac{e}{4\pi\varepsilon_0 a_\mu^2}\right) F_{au}$ so if $E_{SI} = -\dfrac{1}{2}\alpha_{SI} F_{SI}^2$ then

$$E_{SI} = \left(\frac{e^2}{4\pi\varepsilon_0 a_\mu}\right) E_{au} = -\frac{1}{2}\alpha_{au} F_{au}^2\left(\frac{e^2}{4\pi\varepsilon_0 a_\mu}\right) = -\frac{1}{2}\alpha_{SI} F_{au}^2\left(\frac{e}{4\pi\varepsilon_0 a_\mu^2}\right)^2 \text{ and so}$$

$\alpha_{SI} = \alpha_{au} 4\pi\varepsilon_0 a_0^3$. The quantity $\dfrac{\alpha_{SI}}{4\pi\varepsilon_0}$ is usually reported and is called the

polarizability volume. Note it's $\alpha_{au} a_0^3 = 0.1481847 x 10^{-30} \alpha_{au} m^3$. The polarizability

volume of the H atom in the SI system is then $\dfrac{\alpha_{SI}}{4\pi\varepsilon_0} = 0.1481847 x 10^{-30} \left(\dfrac{9}{2}\right)\left(\dfrac{q_{au}}{Z^4}\right) m^3$.

The third order function is given by $\Phi_{100}^{(3)} = F^3\left(d P_1 + e P_3\right)\Phi_{100}^0$ where

$$d = \frac{1}{480}\left(6r^6 + 64r^5 + 344r^4 + 852r^3 + 1590r^2 + 3180r\right) \text{ and}$$

$$e = \frac{1}{240}\left(2r^6 + 18r^5 + 63r^4 + 8r^3\right)$$ and allows the energy to be calculated through 6th order or F^6.

Series solution for E_2

Usually one cannot solve the differential equations for the various perturbation corrections to the wavefunction and energy as we have done above and one calculates these corrections using the eigenfunctions and eigenvalues of the unperturbed Hamiltonian. For example when the perturbation is $\hat{V} = rF\cos\theta$ the second order change in the ground state energy of H is given by the general formula

$$E_{100}^{(2)} = \sum_{nlm}{}' \frac{V_{100,nlm} V_{nlm,100}}{E_{100} - E_{nlm}} \quad \text{where } V_{100,nlm} = \langle \psi_{100} | rF\cos\theta | \psi_{nlm} \rangle \text{ and } E_{nlm} = -\frac{1}{2n^2}$$

which assumes that the unperturbed functions are complete with respect to the perturbed solutions. There are two classes of eigenfunctions for the H atom, those that describe the bound states, $E < 0$, and those that describe the continuum states, $E > 0$. Since we have solved the differential equation exactly we know the exact second order energy, $E_{100}^{(2)} = -\frac{9}{4}F^2$, so lets see what the error is if we use only the bound wavefunctions to calculate the second order correction. Accordingly

$$E_{100}^{(2)} = \sum_{nlm} \frac{\left|\langle 100 | Fr\cos\theta | nlm \rangle\right|^2}{E_1^0 - E_n^0} = F^2 \sum_{nlm} \frac{\left|\langle 100 | r\cos\theta | nlm \rangle\right|^2}{E_1^0 - E_n^0} = 2F^2 \sum_{nlm} \frac{\left|\langle 100 | r\cos\theta | nlm \rangle\right|^2}{\left(-1 + \frac{1}{n^2}\right)}$$

The required matrix element is

$$\langle 100 | r\cos\theta | nlm \rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_0^0 \cos\theta\, Y_l^m \int_0^{\infty} dr\, R_{10}(r)\, r^3 R_{nl}(r)$$

and the angular factor can be easily evaluated by observing that $\cos\theta = \sqrt{\frac{4\pi}{3}} Y_1^0$ so

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_0^0 \cos\theta\, Y_l^m = \frac{1}{\sqrt{3}} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_1^0\, Y_l^m = \frac{1}{\sqrt{3}} \delta_{1l}\delta_{0m} \text{ so}$$

$$\langle 100 | r\cos\theta | nlm \rangle = \frac{1}{\sqrt{3}} \delta_{1l}\delta_{0m} \int_0^{\infty} dr\, R_{10}(r)\, r^3 R_{n1}(r) = \frac{1}{\sqrt{3}} \delta_{1l}\delta_{0m} \langle R_{10} | r | R_{n1} \rangle$$

$$E_{100}^{(2)} = -\frac{2}{3}F^2 \sum_{n=2}^{\infty} \frac{\left|\langle R_{10}|r|R_{n1}\rangle\right|^2}{\left(+1-\dfrac{1}{n^2}\right)}.$$ Note that only the np_z states contribute to the

summation.

The radial integral can be evaluated and the series summed (W. Gordon, *Annalen der Physik 1929*, **394**, 1031) resulting in

$$E_{1s}^{(2)} = -\frac{2^9}{3}F^2 \sum_{n=2}^{\infty} \frac{n^9 (n-1)^{2n-6}}{(n+1)^{2n+6}} = -1.8225F^2$$

Since the exact $E_{1s}^{(2)} = -\frac{9}{4}F^2$ the bound state wave-functions then account for ~81%

of the exact result, a significant error! The need to include the continuum solutions in the expansion makes sense physically because in the electric field the electron

feels the potential $-\frac{1}{r} + Fr\cos\theta$ and if $\cos\theta < 0$ the perturbation will eventually

overwhelm the Coulomb term and instead of the potential going to zero at large r it will eventually become lower than the $1s$ energy and the electron will be able to tunnel into the continuum. This is illustrated in the following figure with $F = 1/20\,au$