Application: The Stark effect in hydrogen atoms

If an external electric field \( \vec{E} \) is applied, it generates an additional term in \( H \) given by:

\[
\hat{V} = - \hat{\vec{d}} \cdot \vec{E}
\]

where \( \hat{\vec{d}} = \text{electric dipole operator} \)

\[
\hat{\vec{d}} = -e \hat{r}
\]

Then

\[
\hat{V} = e \hat{r} \cdot \vec{E} = eEz = eErcos\theta \quad \text{for} \quad \vec{E} = E\hat{z}
\]

"along \( \hat{z} \)"

To understand the effect of this external field on the atom, we have to realize that

\[ \rightarrow \text{ground state is not degenerate} \]

\[ \rightarrow \text{All other levels are degenerate so we need to treat these two cases separately} \]

Ground State: We will ignore spin interactions, relativity

\[
\hat{H}_0 \rightarrow \hat{H}
\]

\[
\hat{H} = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{e^2}{r} \right) + eE\hat{z}
\]

\[
\text{replace in S.I. units}
\]

\[
\text{where } a_B = \frac{\hbar^2}{me^2} = \frac{\hbar^2}{m_e e^2} \quad \text{Bohr radius}
\]

\[
\text{Here } m_e \text{ electron mass}
\]

\[
\frac{m}{m + m_p} \quad \text{mass}
\]

So we know the unperturbed ground state is

\[
E^{(0)}_{1s} = -\frac{e^2}{2a_B}
\]

\[ \Rightarrow \text{The unperturbed wavefunction is:} \]
\[ \psi_{1s}^{(0)}(\mathbf{r}) = \frac{U_{1s}(r)}{r} Y_{00}(\theta, \phi) \]

with \[ U_{1s}(r) = a^{-\frac{1}{2}} \left( \frac{2r}{a} \right)^{-r/a} \]

Here the 1st order correction vanishes (by parity)

i.e. \[ \langle 1s | eE r \cos \theta | 1s \rangle = 0 \]

The leading order energy correction comes from second order perturbation theory

\[ E_{1s}^{(2)} = -\frac{1}{2} \langle 1s | \frac{1}{2} | E^2 \rangle, \quad \text{where} \quad \langle 1s | \frac{1}{2} | E^2 \rangle = 2e^2 \sum_{n,m} \frac{\langle 1s | \cos \theta | n,m \rangle \langle n,m | \cos \theta | 1s \rangle}{E_n - E_{1s}} \]

To evaluate this quantity we observe that \([L_z, V] = 0\) but \([L^2, V] \neq 0\)

Only \(m_s\) remains a good quantum number exactly for this case (note however that this will not be the case if we include spin-orbit interactions but we will ignore them for the moment).

Note that \( V = eE r \cos \theta = eE \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} Y_{10}(\theta, \phi) \)

Also note \( Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \). Then we have

\[ \langle n1m1 | eE r \cos \theta | 1s \rangle = eE \left( \frac{4\pi}{3} \right)^{\frac{1}{2}} \frac{1}{\sqrt{4\pi}} \int_0^\infty r^2 R_n(r) \times R_{10}(r) \, dr \]

Therefore by selection rules only the \( l=1 \) states contribute to the sum at second order. It is a sum over all bound
states (n) plus continuum states \( \sum_n E_n^{(\infty)} \)

\[
E_{1s}^{(\infty)} = \sum_{n=2}^{\infty} \frac{|\langle n,1,0 | eEz | 1s \rangle|^2}{E_{1s} - E_{n,1,0}} + \int_0^\infty \frac{dE}{E_{1s} - E} \ \langle 1s | eEz | 1s \rangle^2
\]

Here \( n = 1,0 \): energy normalized continuum (scattering) state.

To estimate the value of this infinite sum + integral note that:

\[
E_{n,1,0}^{(\infty)} > E_{2,1,0}^{(\infty)}
\]

and therefore

\[
E_{1s}^{(\infty)} > E_{n,1,0}^{(\infty)} - E_{1s}^{(\infty)} \ 	ext{thus}
\]

\[
\frac{1}{E_{1s}^{(\infty)} - E_{2,1,0}^{(\infty)}} > \frac{1}{E_{1s}^{(\infty)} - E_{n,1,0}^{(\infty)}}
\]

\[
E_{1s}^{(\infty)} > \frac{1}{E_{1s}^{(\infty)} - E_{2,1,0}^{(\infty)}} \langle 1s | eEz | n,1,0 \rangle \langle n,1,0 | eEz | 1s \rangle
\]

and therefore completeness of eigenstates

\[
E_{1s}^{(\infty)} > \frac{1}{E_{1s}^{(\infty)} - E_{2,1,0}^{(\infty)}} \langle 1s \rangle (eEz)^2 | 1s \rangle = -\frac{8}{3} a_b^3 E^2 = -\frac{1}{2} \omega_{app} E^2
\]

where \( \omega_{app} = \frac{16 a_b^3}{3} \) \( \approx \) Exact

**Exact Solution for the Polarizability of Hydrogen**

Dalgarno - Lewis Method


The basic trick is to rewrite the polarizability in the weak field limit as

\[
\alpha_{1s} = 2 e^2 \langle 1s | r \cos \theta \hat{e} r \cos \theta | 1s \rangle
\]

\[
= 2 \langle 1s | \hat{W} \hat{e} \hat{W} | 1s \rangle \ 
\hat{W} = e r \cos \theta
\]
\[ \hat{\mathbf{G}} = \sum_{n,m} \frac{\ln \xi \eta}{E_{n}^{\omega} - E_{m}^{\omega}} \]

\[ \hat{\mathbf{G}} \text{ obeys: } (\hat{\mathbf{h}}_{0} - E_{is}^{(\omega)}) \hat{\mathbf{G}} = \hat{\mathbf{1}} \]

or in position representation:

\[ \langle \mathbf{r} | \hat{\mathbf{G}}(\mathbf{r}') \rangle = \mathbf{G}(\mathbf{r}, \mathbf{r}') \]

\[ \langle \mathbf{r} | \hat{\mathbf{1}} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') \]

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} - E_{is}^{(\omega)} \right] G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \]

Key idea: Dalgarno + Lewis noticed that if we define an auxiliary function \( | \psi \rangle = 6W|1s\rangle \)

Then \( | \psi \rangle \) obeys an inhomogeneous Sch. Equation:

\[ (\hat{\mathbf{h}}_{0} - E_{is}^{(\omega)}) | \psi \rangle = W|1s\rangle \]

This method recasts the evaluation of the sum into a different problem: solution of an inhomogeneous differential equation.

Once we know \( | \psi \rangle \), the polarizability is just

\[ \alpha_{1s} = 2 \langle 1s | W | \psi \rangle \]

In the present problem, the spherical symmetry of \( \alpha \) allows us to reduce this to the solution of a radial differential equation using

\[ \alpha_{1s} = 2e^2 \left| \langle 1s | \cos \theta | 1s \rangle \right|^2 \left( \frac{\hat{\mathbf{r}}^2}{\hbar^2} + \frac{\hat{\mathbf{r}}}{\hbar} \right) \left( \frac{\langle 5l | 110 \rangle \langle 110 | r 1s \rangle}{E_{1s}^{(\omega)} - E_{is}^{(\omega)}} \right) \]
Only the $l=1,m=0$ contribute along with the continuum

Let's us then apply the Dalgarno-Lewis “trick” to the radial wave function

$$\hat{G}_{l=1} = \sum_{\ell} \frac{|n\ell\ell><n\ell\ell|}{E_{n\ell\ell} - E^{(3)}}$$

For simplicity let's use from now on atomic units

\( \hbar = e = m = 1 \)

The radial Green function obeys:

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell (\ell + 1)}{2r^2} - \frac{1}{r} - E^{(3)} \right) \hat{G}_{l=1}(r,r') = \delta(r-r')
\]

\[
\hat{G}(r) = \int_0^r dr' \hat{G}_{l=1}(r,r') r' U_{13}(r') = \frac{2r e^{-r}}{E^{(3)} - \frac{1}{2}} \ln a.u.
\]

The inhomogeneous radial equation is:

\[
-\frac{1}{2} \hat{G}'' + \left( \frac{1}{r^2} - \frac{1}{r} + \frac{1}{2} \right) \hat{G}(r) = 2r^2 e^{-r}
\]

As a guess or ansatz to solve this, we can try a solution of the form:

\[
\hat{G}(r) = e^{-r} r^2 y(r)
\]

where \(e^{-r}\) is expected: large \(r\) behavior
and \(r^2\) “““ small \(r\) behavior

Plugging this and simplifying now gives

\[-\frac{1}{2} r r''(r) + (r-2) y'(r) + y(r) = 2r\]

This can be exactly (try, e.g., a power series) solved
to give \( y(r) = 2 + r \) (confirm by your self)

when by \( \Phi(r) = (2r^2 + r^3) e^{-r} \)

Then finally \( L_{1s} = 2 \left( \frac{\langle 1s | \cos \theta | 1s \rangle}{\langle 1s | 1s \rangle} \right)^{1/3} \frac{27/4}{27/4} \)

which gives \( L_{1s} = \frac{9}{2} a_B^3 \) atomic hydrogen

Compared with priorly derived approximate expression \( L_{1s} \approx \frac{16}{3} a_B^3 = 5.333 a_B^3 \)

Remark: This concept of polarizability is useful only at low field strengths where 2nd-order perturbation theory is valid, and higher order corrections can be neglected.

• **Excited State Stark Effect:**

Here we need to apply degenerate perturbation theory.

Treat for example the \( n=2 \) levels

\( 12 \ell m^s = 12, \ell, 12, 0, 0 \), \( 12, \ell, -1, 12, 1, 0, 0 \), \( 12, 0, 0, 12, 0, 0 \)

⇒ Since \( [L_z, V] = 0 \) we can treat the different \( m \) manifolds separately

The only non-zero element induced by the electric field is in the \( m=0 \) sector

\( \langle 210 | eE_z | 220 \rangle = U_{10} \)
\( \langle 200 | eE_z | 210 \rangle = U_{01} \)
If you work out the integral $V_{01} = V_{10} = -3eEg_0$

(\text{using } \int_0^R r_2,_{r=1}(r) \sqrt{r_2,_{r=0} r^2 dr} = -3g_0 \sqrt{3})

For $m=\pm 1$ the 1st order correction vanishes

$E_{2,\pm 1}^{(1)} = E_{2,\pm 1}^{(0)} + O(F^2)$

For $m=0$, we need to diagonalize the matrix

$$\mathbf{H} = \begin{bmatrix} E_2^{(0)} & V_{01} \\ V_{10} & E_2^{(0)} \end{bmatrix}$$

And the eigenvalues are

$$E_{\pm} = E_2^{(0)} \pm 3eEg_0$$

The corresponding eigenstates are $\frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ \pm 1 \end{array} \right)$

i.e. $|\pm_{\pm 1}, m=0 \rangle = \frac{|\psi_{2,01}^{(0)} \rangle \pm |\psi_{2,01}^{(0)} \rangle}{\sqrt{2}}$

Visually the unperturbed zero-th order states are

\[ \text{S} \quad \text{P} \rightarrow \text{S} \]

where as the perturbed states are
$\Psi_-$

Higher energy state

$\Psi_+$

Lower energy state: e$^-$ move in opposite direction to F.