5. Influence of External (Static) Electric Field

(1) Stark Effect: The influence of an external electric field on atomic spectra was discovered by J. Stark in 1913 and is known as the stark effect. Stark's discovery was made on the Balmer series of hydrogen. Before that in 1899, Voigt gave attention to the electric perturbation of atoms and came to the conclusion that the effects would be very small. This is because only hydrogen-like atoms/ions have significant linear Stark effects, while other atoms usually have very small quadratic Stark effects, when the external electric field is small.

(2) Quadratic Stark Effect:

The Stark effect is the splitting and shifting of atomic levels under the interaction of an external electric field.

The energy of an atom in a homogeneous electric field is equal to the scalar product of the strength of the electric field $\vec{E}$ and the electric dipole moment of the atom $\vec{D}$ taken with negative sign. In other words, the Hamiltonian operator $\Delta\hat{H}e$ in a homogeneous static electric field is given by

$$\Delta\hat{H}e = -\hat{\vec{D}}\cdot\hat{\vec{E}} = e\sum_i \hat{\vec{r}}_i \cdot \hat{\vec{E}}$$

where $\hat{\vec{D}} = -e\sum_i \vec{r}_i$ is the electric dipole moment of the atomic system, and $\vec{E}$ is the electric field strength.

Change the SI unit to atomic unit, then

$$\Delta\hat{H}e = -\hat{\vec{D}}\cdot\hat{\vec{E}} = \sum_i \hat{\vec{r}}_i \cdot \hat{\vec{E}} \ (a.u.)$$

One a.u. $\vec{E}$ is $\frac{e^2}{2a_0^2} = 8.576\times10^6$ (e.s.u) $= 2.572\times10^9$ V/cm

When the electric field $\vec{E}$ is weak, $\Delta\hat{H}_e$ is regarded as a perturbation to the original Hamiltonian operator. Thus, we can use perturbation theory to derive the energy correction.

Notice that the matrix elements of $\hat{\vec{D}}$ connecting states of the same parity, including the diagonal matrix elements, are zero: $\langle \psi_i | \Delta\hat{H}_e | \psi_i \rangle \equiv \langle \Delta\hat{H}_e \rangle = 0$.

This is because $\Delta\hat{H}_e$ has the following symmetry under spatial inversion: $\Delta\hat{H}_e(-\vec{r}) = -\Delta\hat{H}_e(\vec{r})$.

$$\therefore \langle \psi_i | \Delta\hat{H}_e | \psi_i \rangle = -\langle \psi_i | \Delta\hat{H}_e | \psi_i \rangle = 0.$$

Therefore, the first-order perturbation does not lead to any change in the atomic energy. The splitting of levels is determined by second-order corrections.

Let us choose the z-axis along the direction of the external field $\vec{E}$. $\Delta\hat{H}_e = -E\hat{D}_z$, where $\hat{D}_z$ is the projection of $\hat{\vec{D}}$ along z direction. For an energy state $|\alpha J M\rangle$ (where α represents the quantum numbers other than J, M, e.g., n, L, S), the 2nd order perturbation theory gives the energy correction as:

$$\Delta E_e = E^2 \sum_{\alpha' J'} \frac{|\langle \alpha J M | \hat{D}_z | \alpha' J' M' \rangle|^2}{E_{\alpha J} - E_{\alpha' J'}}$$

where the sum is taken for $\alpha' \neq \alpha$, $J' \neq J$.

Because $\hat{D}_z$ and $\hat{J}_z$ are commute, i.e., $[\hat{D}_z, \hat{J}_z] = 0$, only the $M' = M$ matrix elements are non-zero.

The nature of this second-order correction to the energy level is that the atom does not have intrinsic electric dipole moment, but the external field induced some electric dipole moment, i.e., induced electric dipole moment: $\vec{D} \propto \vec{E}$

$\therefore$ the energy correction $\Delta E_e \propto E^2$.

i.e., proportional to the square of electric field strength.

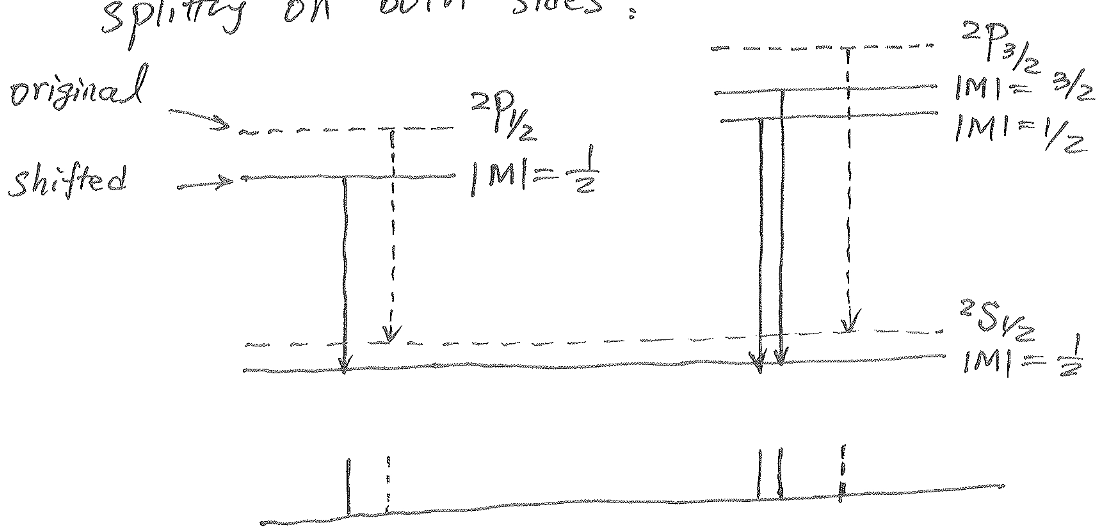
— So-called quadratic Stark effect.

Features of quadratic Stark effect:

① Energy levels with the same $|M|$ are degenerate.

— When reverse the $\vec{E}$ direction, the energy doesn't change.

② Energy shifts to one direction, instead of symmetric splitting on both sides:



(3) Linear Stark Effect.

The above quadratic Stark effect equations are valid as long as the corrections to the energy are small in comparison with the initial splitting $E_{\alpha J} - E_{\alpha' J'}$. In the general case it is necessary to treat, at the same time, the interaction with the external field $\Delta \hat{H}e$ and the interaction $\hat{H}'$ that is responsible for the splitting of the levels αJ and $\alpha' J'$, like spin-orbital coupling.

Let us consider one pair of energy levels, they are separated by a splitting δ when $E = 0$. Let

$$E_{\alpha J} = E_0 + \tfrac{1}{2}\delta, \qquad E_{\alpha' J'} = E_0 - \tfrac{1}{2}\delta.$$

$$\frac{\delta}{2} = \langle \alpha J M | \hat{H}' | \alpha J M \rangle = - \langle \alpha' J' M | \hat{H}' | \alpha' J' M \rangle$$

Here, E_0 is the initial energy levels when J and J' are degenerate, and $\hat{H}'$ is the interaction that causes the splitting of J and J'.

With external electric field,

$$\Delta \hat{H} = \hat{H}' + \Delta \hat{H}e$$

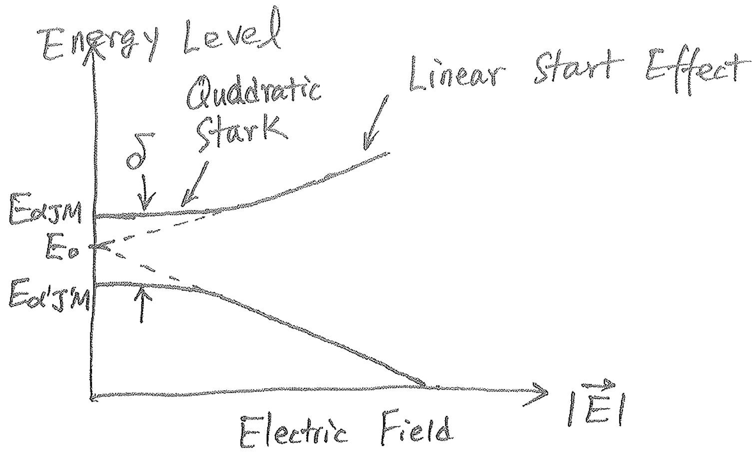
From perturbation theory, we have the energy correction

$$\Delta E = \pm \sqrt{\left(\frac{\delta}{2}\right)^2 + |\langle \alpha J M | \hat{D}_z | \alpha' J' M \rangle|^2 E^2}$$

When $|E|$ is very small, $\Delta E \simeq \pm \left[\frac{\delta}{2} + \frac{|\langle \alpha J M | \hat{D}_z | \alpha' J' M \rangle|^2 E^2}{\delta} \right]$

When $|E|$ is very large,

$$\Delta E \simeq \pm |\langle \alpha J M | \hat{D}_z | \alpha' J' M \rangle| \, |E|$$



If $\delta = 0$ from the beginning, i.e., two levels are degenerate, then only linear Stark effect will show up.

(4) Hydrogen's Stark effect.

It turns out that the Stark effect in H-atom is exceptionally large, especially in the Balmer series.

For $n=2$, $^2P_{1/2}$ and $^2S_{1/2}$ are nearly degenerate, except the small relativity fine structure correction.

Thus, its linear Stark effect is strong, which enabled Stark to observe the effect in 1913.

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	Angular Momentum		Magnetic Moment
Electron orbital motion $\longrightarrow$	$\hat{\vec{l}}$, $\lvert\hat{\vec{l}}\rvert = \sqrt{l(l+1)}\,\hbar$	$\longrightarrow$	$\hat{\vec{\mu}}_l = -g_l\sqrt{l(l+1)}\,\mu_B$
Electron Spin motion $\longrightarrow$	$\hat{\vec{S}}$, $\lvert\hat{\vec{S}}\rvert = \sqrt{S(S+1)}\,\hbar$	$\longrightarrow$	$\hat{\vec{\mu}}_S = -g_S\sqrt{S(S+1)}\,\mu_B$
Nuclear Spin $\longrightarrow$	$\hat{\vec{I}}$, $\lvert\hat{\vec{I}}\rvert = \sqrt{I(I+1)}\,\hbar$	$\longrightarrow$	$\hat{\vec{\mu}}_N = g_I\sqrt{I(I+1)}\,\mu_N = g_I'\sqrt{I(I+1)}\,\mu_B$

$$\boxed{\mu_B = \frac{e\hbar}{2m_e}} \qquad (g_l = 1) \qquad (g_S = 2).$$

$$\boxed{\mu_N = \frac{e\hbar}{2m_p}} \qquad \frac{g_I'}{g_I} = \frac{m_e}{m_p}$$

$$\left.\begin{matrix}\hat{\vec{l}} \\ \hat{\vec{S}}\end{matrix}\right\} \Rightarrow \left.\begin{matrix}\hat{\vec{j}} = \hat{\vec{l}} + \hat{\vec{S}} \\ \hat{\vec{I}}\end{matrix}\right\} \Rightarrow \hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{j}}$$

$$\left.\begin{matrix}\hat{\vec{\mu}}_l \\ \hat{\vec{\mu}}_S\end{matrix}\right\} \Rightarrow \left.\begin{matrix}\hat{\vec{\mu}}_j = \dfrac{(\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_S)\cdot\hat{\vec{j}}}{\hat{\vec{j}}^{\,2}}\,\hat{\vec{j}} \\ \hat{\vec{\mu}}_I\end{matrix}\right\} \Rightarrow \hat{\vec{\mu}}_F = \frac{(\hat{\vec{\mu}}_j + \hat{\vec{\mu}}_I)\cdot\hat{\vec{F}}}{\hat{\vec{F}}^{\,2}}\,\hat{\vec{F}}$$

(Please refer to the Vector Models in Appendix)

$$\hat{\vec{\mu}}_F = -g_F \sqrt{F(F+1)}\, \mu_B . \qquad \boxed{\mu_B = \frac{e\hbar}{2m_e}} \qquad |\hat{\vec{F}}| = \sqrt{F(F+1)}\, \hbar$$

$$\hat{\vec{\mu}}_j = -g_j \sqrt{j(j+1)}\, \mu_B . \qquad |\hat{\vec{j}}| = \sqrt{j(j+1)}\, \hbar$$

$$\hat{\mu}_{F,z} = \hat{\vec{\mu}}_F \cdot \hat{\vec{e}}_B = -g_F m_F \mu_B , \qquad m_F = F,\ F-1, \dots, -F$$

$$\hat{\mu}_{j,z} = \hat{\vec{\mu}}_j \cdot \hat{\vec{e}}_B = -g_j m_j \mu_B , \qquad m_j = j,\ j-1, \dots, -j .$$

Meaning of $n,\ l,\ s,\ j,\ I,\ F,\ m_l,\ m_s,\ m_j,\ m_I,\ m_F$.

n:	energy is quantized
l, s, I, j, F:	angular momentum is quantized
m_l, m_s, m_I, m_j, m_F:	angular momentum is spatially quantized.

$$g_J = g_{j_1} \frac{J(J+1) + j_1(j_1+1) - j_2(j_2+1)}{2J(J+1)} - g_{j_2} \frac{J(J+1) + j_2(j_2+1) - j_1(j_1+1)}{2J(J+1)}$$

Atomic Structure vs. Interactions

$$\left(\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137}\right)$$

Quantum Number — Atomic Structure

1. Coulomb Force (Electrostatic Interaction between nucleus and electron) $\longrightarrow$ principale n $\longrightarrow$ main structure

$$\left(E_n = -\frac{\mu z^2 e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2}\right) = -\frac{\alpha^2 z^2 \mu c^2}{2n^2}$$

$n = 1, 2, 3, 4$

or $n = 3, 4, 5, \cdots$

2. Relativity mass correction $\left(m = m_0 / \sqrt{1 - v^2/c^2}\right)$

$$\longrightarrow \Delta E_m = -\frac{\alpha^4 z^4 \mu c^2}{2n^3}\left[\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right]$$

Darwin term (relativity)

$$\longrightarrow \Delta E_d = \begin{cases} 0, & l \neq 0 \\ \dfrac{\alpha^4 z^4 \mu c^2}{2n^3}, & l = 0 \end{cases}$$

$l - s$ (spin-orbit) coupling

$$\longrightarrow \Delta E_{ls} = \begin{cases} \dfrac{\alpha^4 z^4 \mu c^2}{4n^3} \cdot \dfrac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, & l = 0 \end{cases}$$

$\Rightarrow$ Fine structure ${}^{2S+1}L_J$

$$\Rightarrow \Delta E_{fine} = \Delta E_m + \Delta E_d + \Delta E_{ls}$$

$$= -\frac{\alpha^4 z^4 \mu c^2}{2n^3}\left[\frac{1}{j+1/2} - \frac{3}{4n}\right]$$

(for $S = 1/2$ single electron)

Electron $\rightarrow$ [Orbital angular momentum l; Spin angular momentum s; total angular momentum j]

$l \leq n-1$

$m_l = l, l-1, \cdots, -l$

s

$m_s = s, s-1, \cdots, -s$

$j = l+s, l+s-1, \cdots, |l-s|$

$m_j = j, j-1, \cdots, -j$

	Quantum Number	Atomic Structure
3. Nuclear $\vec{I}$ and electron $\vec{\hat{J}}$ coupling $\longrightarrow$	Total angular momentum F	Hyperfine structure
Nuclear Q and electric field gradient interaction $\Longrightarrow$	$\Delta E = A \cdot \frac{F(F+1) - J(J+1) - I(I+1)}{2} + B \cdot \frac{\frac{3}{2}K(K+1) - 2I(I+1)J(J+1)}{4I(2I-1)J(2J-1)}$	$F = J+I,\ J+I-1, \cdots, \lvert J-I \rvert$.
4. External magnetic field. $-\vec{\hat{\mu}} \cdot \vec{\hat{B}}$ (Zeeman Effect). $\longrightarrow$	m_j, m_l, m_s, or m_F, m_j, m_I.	Zeeman Splitting
	$\Delta E = g_j m_j \mu_B B$.	$l_z = m_l \hbar$
	$\Delta E = (g_l m_l + g_s m_s) \mu_B B$.	$l_z = m_l \hbar$
	$\Delta E = -\frac{\delta E}{2(2I+1)} - m_F g_I' \mu_B B \pm \frac{\delta E}{2}\sqrt{1 + \frac{4m_F}{2I+1}x + x^2}$	$j_z = m_j \hbar$
	(Breit – Rabi formular) ("+" for $F = I + \frac{1}{2}$; "−" for $F = I - \frac{1}{2}$)	$S_z = m_s \hbar$

Review on Atomic Structure and QM

Atomic Structure	$\xrightarrow[QM]{QED}$	Energy Eigenvalues angular momentum of single atom	$\rightarrow$ Resonance freq.
Radiative Transition	$\xrightarrow[QM]{QED}$	Transition probability Selection rules of single atom	$\rightarrow$ Polarization, Direction Intensity
Statistical Interaction of an atom ensemble with radiation	$\xrightarrow[\text{+ statistical physics}]{QM}$	Statistical behavior of atom ensemble	$\rightarrow$ Shape, width Intensity.

* Atomic energy levels are negative energy, which is determined by the potential energy format:

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

The $V(r)$ expression already means that $V(r) = 0$ @ $r \to \infty$.

Under such $V(r)$ condition,

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(r) = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

can only have negative energy E_n as quantized energy.

If $E > 0$, then it is continuous value that satisfies the the radial direction equation $R(r)$.

* The potential energy between nucleus and electron in H

is $V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_1}$

The total energy of H in ground state is

$$E_n = -\frac{\mu Z^2 e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}.$$

Recall $a_1 \equiv r_1 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \Rightarrow \frac{1}{r_1} = \frac{\mu e^2}{4\pi\varepsilon_0\hbar^2}$

$$\therefore E_n = -\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_1}\cdot\frac{1}{n^2}$$

$$\therefore E_1 = -\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_1} = +\frac{1}{2}V(r)$$

This is due to the kinetic energy that the electron has compensating half of the potential energy.