Nalanda Open University

M.SC Part-1

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Topic- Atomic and Molecular Physics (Stark Effect)

Stark Effect

The Stark effect is the electric analogue to the Zeeman effect, i.e., a particle carrying an electric dipole moment, like the H-atom, will get a splitting of its energy levels when subjected to an exterior electric field. The Hamiltonian of the H-atom thus has (another) additional term, the ***Stark term*** H_{Stark}, which is perturbing the Coulomb Hamiltonian

$$H_{\text{Stark}} = -\vec{\mathcal{E}}\,\vec{\mu}_{\text{el}} = -\underbrace{q}_{-|e|}\,\vec{\mathcal{E}}\,\vec{x} = |e|\,\mathcal{E}\,z\,, \qquad (1)$$

where $\vec{\mathcal{E}}$ denotes the external electric field which, without loss of generality, we choose along the z-direction, and $\vec{\mu}_{\text{el}}$ is the electrical dipole moment. For the simple case of an electron of charge $-|e|$ placed at a distance $\vec{x}$ of the oppositely charged proton, resting at the origin, the electric dipole moment reduces to $\vec{\mu}_{\text{el}} = -|e|\vec{x}$.

To calculate the energy corrections of first and second order , we need to consider expectation values or scalar products of the Stark term in the Coulomb states of the form $|\,n,\,l,\,m_l\,\rangle$. This is, however, more complicated than the situation we studied before. To make the problem more precise, let us calculate the following scalar product, where we already know that L_z and z commute

$$\langle\,n,\,l,\,m_l\,|\,\underbrace{[\,L_z\,,\,z\,]}_{=0}\,|\,n',\,l',\,m_l'\,\rangle = (m_l - m_l')\,\langle\,n,\,l,\,m_l\,|\,z\,|\,n',\,l',\,m_l'\,\rangle = 0\,. \qquad (2)$$

Since the commutator of L_z and z is zero we can conclude that the states $|\, n,\, l,\, m_l \rangle$ and $z\,|\, n',\, l',\, m_l' \rangle$ must be orthogonal for $m_l \neq m_l'$, and since we are only interested in nonzero matrix elements we choose

$$m_l \equiv m_l' \,. \tag{3}$$

At the same time, however, for the scalar product to be nonzero, we have to require that the azimuthal quantum numbers be unequal, i.e. $l \neq l'$. The reason for this is the parity of the z operator.

Therefore, if the functions $\psi_{\mathrm{n},\, l,\, \mathrm{m}_l}$ and $\psi_{\mathrm{n}',\, l',\, \mathrm{m}_l}$ have the same azimuthal quantum number, i.e. parity, their product has parity $+1$. The z operator however changes its sign under a spatial inversion and the integration of the scalar product vanishes, because

$$\int_{-a}^{+a} dx\, \underbrace{f(x)}_{\text{even}}\, \underbrace{g(x)}_{\text{odd}} \equiv 0 \,. \tag{4}$$

We can then assume that

$$l' = l \pm 1 \,, \tag{5}$$

which is a reasonable choice since the electric dipole interacts with the electric field by exchanging photons of spin 1, so the angular momentum of the electron must decrease or increase by 1. The Stark effect will therefore only occur for matrix elements of the form

$$\langle\, n,\, l,\, m_l |\; z\; |\, n',\, (l \pm 1),\, m_l \rangle \neq 0 \,. \tag{6}$$

Let us now consider the energy correction for the ground state of the hydrogen atom, the first order correction is

$$E^{(1)}_{1,0,0} = |e|\,\mathcal{E}\,\langle 1,\,0,\,0|\,z\,|1,\,0,\,0\rangle = 0\,. \tag{7}$$

It vanishes due to the requirement of Eq. (5) and we thus see that there is no linear Stark effect for the hydrogen ground state. The effect of second order is of the form

$$E^{(2)}_{1,0,0} = e^2\,\mathcal{E}^2 \sum_{n=2}^{\infty} \frac{|\langle n,\,1,\,0|\,z\,|1,\,0,\,0\rangle|^2}{E^{(0)}_1 - E^{(0)}_n}\,, \tag{8}$$

where the unperturbed energy levels $E^{(0)}_n$ are given by following . This expression can be calculated using perturbative methods, which leads to the result

$$E^{(2)}_{1,0,0} = -\frac{9}{4}\,\frac{\hbar^2}{m_e\,e^2}\,\mathcal{E}^2 = -\frac{9}{4}\,r_B\,\mathcal{E}^2\,, \tag{9}$$

where r_B is the Bohr radius

The first excited state, in contrast to the ground state, is four-fold degenerate, i.e. there are 4 states $|2,\,0,\,0\rangle$, $|2,\,1,\,1\rangle$, $|2,\,1,\,0\rangle$ and $|2,\,1,\,-1\rangle$, that belong to the principal quantum number $n = 2$. In this case one has to consider degenerate perturbation theory, which leads to calculating the eigenvalues of a non-diagonal matrix.

Because of the requirement of Eq. (3) we only consider elements with equal magnetic quantum number, which is only the case for the states $|2,0,0\rangle$ and $|2,1,0\rangle$. It leaves us a 2×2 matrix to diagonalize. The second requirement (Eq. (5)) rids us of the diagonal elements of the matrix. The remaining nonzero off-diagonal elements are

$$\langle 2,1,0|\,z\,|2,0,0\rangle = \langle 2,0,0|\,z\,|2,1,0\rangle\ . \qquad (10)$$

The nonzero eigenvalues can thus be easily calculated and we conclude that the excited state has a linear Stark effect correction with the result

$$E^{(1)}_{2,l,m_l} = \pm|e|\,r_{\mathrm{B}}\,\mathcal{E}\ . \qquad (11)$$

Further splitting of the excited hydrogen energy levels can be seen in Fig. (1)

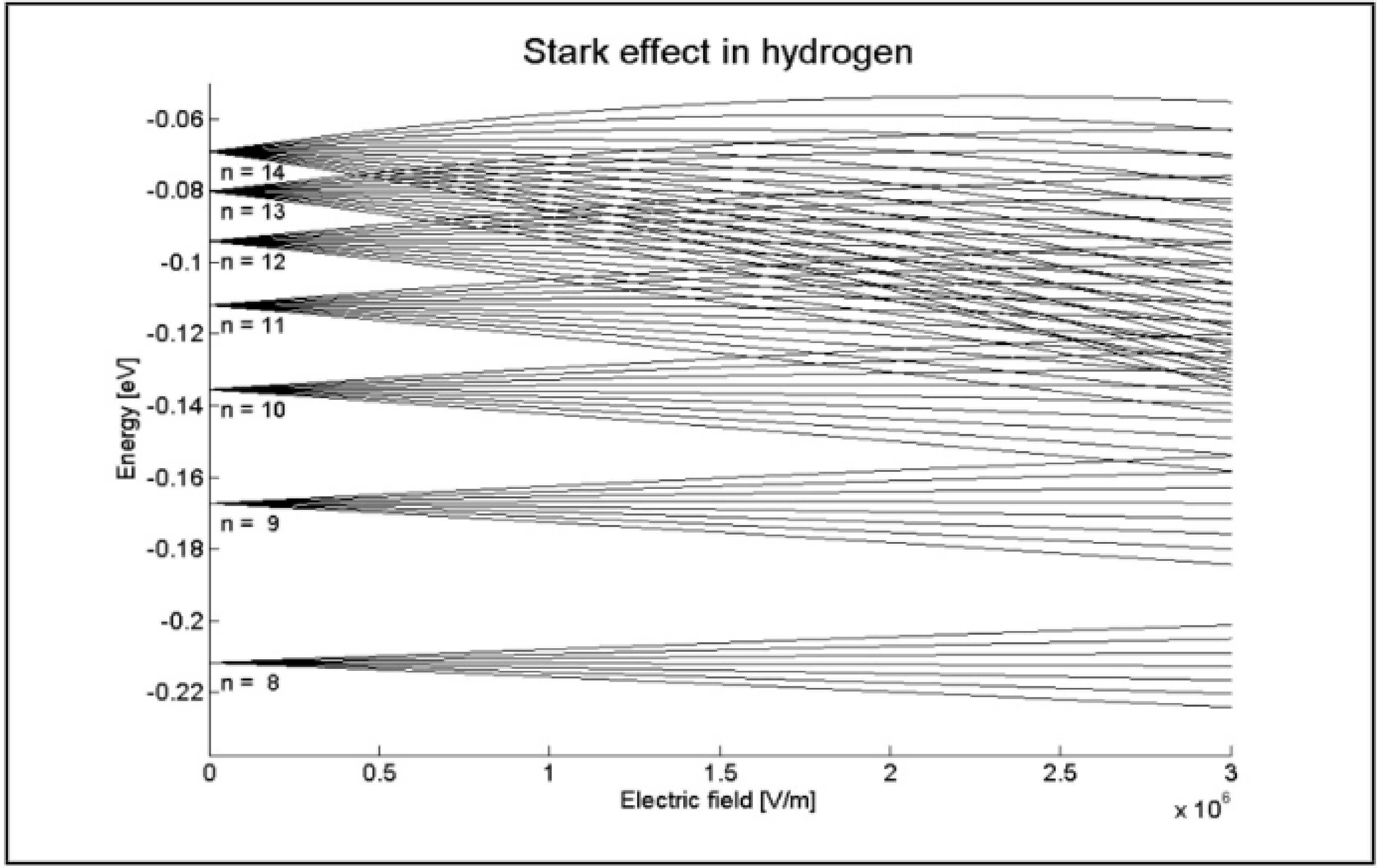

Figure (1) : Stark Effect in Hydrogen: The until then degenerate excited energy levels are split up if an exterior electric field is applied.