SHIFT AND SPLITTING OF ATOMIC ENERGY LEVELS BY THE FIELD OF AN ELECTROMAGNETIC WAVE

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The nonstationary wave function of an electron which is in a Coulomb field and in the field of an electromagnetic wave can be described by its fundamental harmonic, accurate to terms $\sim \xi \equiv ea(2mI)^{-1/2} \ll 1$ (a is the amplitude of the potential of the wave and I is the ionization energy). The shift and splitting of the frequency of this harmonic are found, relative to the energy of the atomic level unperturbed by the wave. The formulas obtained determine the frequencies of the most intense spectral lines in the light emitted by atoms in the field of an electromagnetic wave. Experimental measurements of these frequencies can serve as a way of determining the amplitude of the field strength of the wave.

THE wave function of an electron in a Coulomb field and the field of an electromagnetic wave[1] satisfies the Schrödinger equation

$$i\frac{\partial\psi}{\partial t} = \left\{-\frac{1}{2m}\left(\frac{\partial}{\partial \mathbf{x}} - ie\mathbf{A}\right)^2 - \frac{\alpha Z}{r}\right\}\psi \equiv (H_0 + V)\psi,$$

$$H_0 = -\frac{1}{2m}\frac{\partial^2}{\partial \mathbf{x}^2} - \frac{\alpha Z}{r}, \quad V = \frac{ie}{m}\mathbf{A}\frac{\partial}{\partial \mathbf{x}} + \frac{e^2}{2m}\mathbf{A}^2 \quad (1)$$

and owing to the periodic time dependence of $\mathbf{A}$ it can be expanded in a Fourier series

$$\psi(x) = \sum_{s=-\infty}^{\infty} \psi_s(\mathbf{x})\, e^{-i(\epsilon + s\omega)t} \quad (2)$$

with the frequency spectrum $\epsilon + s\omega$, $s = 0, \pm 1, \pm 2, \ldots$. We shall call the frequency ϵ the "quasi-energy" of the state ψ (cf. the quasi-four-momentum in [1]).

Exact solution of Eq. (1) is not possible. If, however, the amplitude $\mathbf{a}$ of the potential of the wave satisfies the condition $e|\mathbf{a}| \ll \mathbf{p}$, where $\mathbf{p}$ is the characteristic momentum of the electron, then the interaction with the wave can be taken into account by perturbation theory. For a free electron this condition reduces to $ea/m \ll 1$,[1] and for an electron bound in an atom, to the condition $\xi = ea(2mI)^{-1/2} \ll 1$[2] [since $p_{eff} \sim (2mI)^{1/2}$, where I is the ionization energy].[2] If $\xi \ll 1$, then the order of magnitude of the Fourier coefficients in (2) will be $\psi_s \sim \xi^s$, so that $\psi(x)$ is essentially determined by the Fourier coefficient with $s = 0$: $\psi(x) \approx \psi_0(\mathbf{x})e^{-i\epsilon t}$. We shall find the function $\psi_0(\mathbf{x})$ and the frequency ϵ.

If we expand V(x) in a Fourier series:

$$V(x) = \sum_{k=0,\pm1,\pm2} V_k(\mathbf{x})\, e^{-ik\omega t},$$

the Schrödinger equation (1) can be put in the form

$$(\varepsilon + s\omega - H_0)\psi_s(\mathbf{x}) = \sum_k V_k(\mathbf{x})\psi_{s-k}(\mathbf{x}). \quad (3)$$

We get, up to small terms of second order, the Schrödinger equation for the function $\psi_0(\mathbf{x})$

$$(\varepsilon - H_0)\psi_0(\mathbf{x}) = \left[V_0 + \sum_{k=\pm1} V_k(\varepsilon - k\omega - H_0)^{-1}V_{-k}\right]\psi_0(\mathbf{x}) \quad (4)$$

with a perturbation U (the expression in square brackets) independent of the time, and can look for its solution in the usual way (cf. [3], Secs. 38 and 39) as an expansion in terms of the eigenfunctions $\varphi_k(\mathbf{x})$ of the operator H_0:

$$\psi_0(\mathbf{x}) = \sum_k c_k\varphi_k(\mathbf{x}), \quad H_0\varphi_k = E_k\varphi_k; \quad (5)$$

[1] A monochromatic wave $A = (2n_\gamma/\omega)^{1/2}\,\mathrm{Re}\,ee^{ikx}$ is characterized by the wave vector $k_\mu = (k, i\omega)$, the unit vector e of its polarization, and the energy density u or the photon number density $n_\gamma = u/\omega$. We are using units $\hbar = c = 1$, $e^2/4\pi = \alpha = 1/137$.

[2] The parameter ξ can also be written in the form $\xi = 2I\mathcal{E}/\omega\mathcal{E}_0$ [where $\mathcal{E}$ is the amplitude of the field strength of the wave and $\mathcal{E}_0 = 2I(2mI)^{1/2}/e$ is the characteristic field strength in the atom], or in the form $\xi = (e^2n_\gamma/mI\omega)^{1/2}$ for linearly polarized and $\xi = (e^2n_\gamma/2mI\omega)^{1/2}$ for circularly polarized waves.

k stands for the set of all quantum numbers characterizing the state of the electron. The result is that the "quasi-energy" ϵ and the function $\psi_0(\mathbf{x})$ corresponding to a nondegenerate unperturbed level E_n are given to the accuracy in question by the formulas

$$\varepsilon - E_n \equiv \Delta E_n = U_{nn}; \quad c_n = 1,$$

$$c_k = U_{kn} / (E_k - E_n), \quad k \neq n;$$

$$U_{kn} = \int \varphi_k^*(\mathbf{x}) \left[V_0 + \sum_{l=\pm 1} V_l (\varepsilon - l\omega - H_0)^{-1} V_{-l} \right] \varphi_n(\mathbf{x}) d^3x, \tag{6}$$

and in U_{kn} we can set $\epsilon = E_n$. The "quasi-energy" ϵ corresponding to a degenerate unperturbed level E_n is found from the secular equation

$$|U_{nn^*} - (\varepsilon - E_n)\delta_{nn^*}| = 0, \tag{7}$$

where n and n* denote states belonging to the degenerate level E_n being considered. For each E_n Eq. (7) will in general give several values of ϵ, i.e., it determines not only a shift but also a splitting of the ϵ relative to E_n. For each ϵ the coefficients c_k are found in the usual way (cf. [3], Sec. 39) and determine the corresponding correct zeroth-approximation function and the correction to it in order $\sim \xi^2$.

For present laser beams the wavelength is much larger than the size of the atom, and a fortiori larger than the Compton wavelength, i.e., $\omega \ll (2mI)^{1/2} \ll m$. In this case the shift ϵ relative to a corresponding nondegenerate level E_n is given by

$$\Delta E_n = \frac{e^2 n_\gamma}{2m\omega} \left\{ 1 + \frac{1}{m} \times \sum_{n'} \left[\frac{|\mathbf{p}e_{n'n}|^2}{E_n - E_{n'} + \omega} + \frac{|\mathbf{p}e_{n'n^*}|^2}{E_n - E_{n'} - \omega} \right] \right\}, \tag{8}$$

where $\mathbf{p} \cdot \mathbf{e}_{n'n}$ is the matrix element of the operator $\mathbf{p} \cdot \mathbf{e}$ between the states φ_n and $\varphi_{n'}$; the summation is taken over all states of the discrete and continuous spectra.

In what follows we shall consider only hydrogenlike atoms, whose energy levels are degenerate. Furthermore, in order not to complicate the problem with the solution of secular equations we shall confine ourselves to the treatment of the shift and splitting of the first two levels, i.e., the levels with principal quantum numbers n = 1, 2, for which, as can be shown, the matrix U_{nn^*} is diagonal, so that the shift of the level E_n is given by (8).

The first term in (8), which arises from the term $\mathbf{A}^2$ in the interaction of the electron with the wave, does not depend on the state of the electron and gives a correction to the mass of the free electron. The expression for this correction is valid so long as it is small in comparison with m, i.e., for ea/m $\ll$ 1. The other two terms depend essentially on the state of the electron in the Coulomb field and vanish if this field is turned off, since

$$|\mathbf{p}e_{n'n}|^2 \sim m(E_{n'} - E_n) \to 0.$$

These terms are correct for $\xi \ll 1$. For $\omega \sim$ I the expression in curly brackets is of the order of unity, so that

$$\sim e^2 n_\gamma / 2m\omega \sim \xi^2 I.$$

With present laser beams values $\xi \sim 0.01$–0.1 and even larger are achieved.

For what follows it is convenient to introduce instead of the square of the absolute value of the matrix element $p_{\alpha n'n}$ (α = x, y, z) the oscillator strength $f_{\alpha n'n}$, and also the average oscillator strength $f_{n'n}$:

$$f_{\alpha n'n} = \frac{2|\mathbf{p}_{\alpha n'n}|^2}{m(E_{n'} - E_n)}, \quad f_{n'n} = \frac{1}{2l+1} \sum_{m,m'} f_{\alpha n'n}.$$

We note that

$$f_{xn'n} = f_{yn'n} = \left[1 \pm \frac{3m(l'-l)}{l'+l+1} + \frac{3m^2 - l(l+1)}{(l'+l+1)(2l'+1)} \right] \frac{f_{n'n}\delta_{m'm\pm 1}}{2},$$

$$f_{zn'n} = \left\{ 1 - 2\frac{3m^2 - l(l+1)}{(l'+l+1)(2l'+1)} \right\} f_{n'n}\delta_{m'm}, \tag{9}$$

if the axis of quantization is chosen along the z axis (n $\equiv$ n, l, m, n' $\equiv$ n', l', m').

1. Linearly polarized wave. In this case the vector e is real, and choosing the z axis along e we get from (8):

$$\Delta E_n = \frac{e^2 n_\gamma}{2m\omega} \left\{ 1 - \sum_{n'} f_{n'n} \frac{\omega_{n'n}^2}{\omega_{n'n}^2 - \omega^2} \times 2[3m^2 - l(l+1)] \sum_{n'} \frac{f_{n'n}}{(l'+l+1)(2l'+1)} \frac{\omega_{n'n}}{\omega_{n'n}^2 - \omega^2} \right\}, \tag{10}$$

where $\omega_{n'n} = E_{n'} - E_n$. As should be true for reasons of symmetry, the level E_n is split into n(n + 1)/2 sublevels; the shift is the same for levels that differ only in the sign of m. In the general case the sums in the curly brackets cannot be expressed in explicit form in terms of n. Numerical calculation leads to the following values of the shift and splitting of the first two levels of hydrogen for the frequency of the ruby laser (ω = 1.788 eV):

$$\Delta E_{1s} = -\frac{e^2 n_\gamma}{2m\omega} 0.019. \quad \Delta E_{2s} = -\frac{e^2 n_\gamma}{2m\omega} 3.93,$$

$$\Delta E_{2pm} = -\frac{e^2 n_\gamma}{2m\omega}[6.28 - (3m^2 - 2)0.734].$$

For $\omega^2 \gg \omega_{n'n}^2$, setting $\omega_{n'n}^2/(\omega_{n'n}^2 - \omega^2) \approx -\omega_{n'n}^2/\omega^2$ and using the sum rules (see [4], Sec. 61, and [5]), we get

$$\Delta E_n = \frac{e^2 n_\gamma}{2m\omega}\left\{1 + \frac{16}{3n^3} \times\left[\delta_{l0} + \frac{3(3m^2 - l(l+1))}{l(l+1)(2l-1)(2l+1)(2l+3)}\right]\left(\frac{I}{\omega}\right)^2\right\}. \quad (10')$$

On the other hand, for $\omega^2 \ll \omega_{n'n}^2$, setting $\omega_{n'n}^2/(\omega_{n'n}^2 - \omega^2) \approx 1 + \omega^2/\omega_{n'n}^2$ and using the fact that $\sum_{n'} f_{n'n} = 1$, we have

$$\Delta E_n = -\frac{e^2 n_\gamma}{2m\omega}\left(\frac{\omega}{I}\right)^2\left\{\sum_{n'} f_{n'n}\frac{I^2}{\omega_{n'n}^2} - 2[3m^2 - l(l+1)]\sum_{n'}\frac{f_{n'n}}{(l'+l+1)(2l'+1)}\frac{I^2}{\omega_{n'n}^2}\right\}. \quad (10'')$$

The infinite sums in curly brackets in (10") (we denote them by a_{nl}, b_{nl}) have not been found in explicit form; they are of the order of unity, so that

$$\Delta E_n \sim -\frac{e^2 n_\gamma}{2m\omega}\left(\frac{\omega}{I}\right)^2 = -\frac{e^2 \mathscr{E}^2}{4mI^2},$$

where $\mathscr{E}$ is the amplitude of the field strength.

At first glance it seems that at small frequencies the shift and splitting of the levels in the field of the wave could be obtained from the appropriate Stark-effect formula, if in this formula we regard the field as varying according to the law $\mathscr{E}\sin\psi$ and average over ψ. For hydrogenlike atoms, however, such an averaging includes a nonadiabatic perturbation and therefore leads to incorrect results, for example to merging of part of the split levels, which is already impossible for general reasons of symmetry. Nevertheless, by means of the Stark-effect formula one can get the correct shift of the "center of gravity" of a system of levels with given values of the quantum numbers n, m. Therefore, if we fix n, m and average (10") over l, and the Stark-effect formula over n_1, n_2 and (after setting $\mathscr{E} \to \mathscr{E}\sin\psi$) over ψ, we get for the shift of the "center of gravity" of a system of levels with given n, m the result

$$\Delta E_{nm} \equiv \frac{1}{n - |m|}\sum_{l=|m|}^{n-1}\Delta E_{nlm} = -\frac{e^2\mathscr{E}^2}{4mI^2}\frac{1}{n-|m|}$$

$$\times\sum_{l=|m|}^{n-1}\left\{a_{nl} - 2[3m^2 - l(l+1)]b_{nl}\right\} = -\frac{e^2\mathscr{E}^2}{4mI^2}\frac{n^4[16n^2 + 2n|m| - 10m^2 + 20]}{32} \quad (11)$$

This relation does not completely determine a_{nl}, b_{nl}, and a numerical calculation is required to find these quantities finally. The results for the hydrogen levels we are considering are

$$a_{1s} = 9/8, \quad a_{2s} = 30, \quad a_{2p} = 44, \quad b_{2p} = 2.5.$$

2. Circularly polarized wave. In this case, choosing the z axis along the direction k in which the wave is propagated, we get $\mathbf{e} = (\mathbf{e}_x + i\mathbf{e}_y)/2^{1/2}$ for the right and left circularly polarized waves. It then follows from (8) that

$$\Delta E_n = \frac{e^2 n_\gamma}{2m\omega}\left\{1 - \sum_{n'} f_{n'n}\frac{\omega_{n'n}}{\omega_{n'n}^2 - \omega^2} - [3m^2 - l(l+1)]\cdot \times\sum_{n'}\frac{f_{n'n}}{(l'+l+1)(2l'+1)}\frac{\omega_{n'n}^2}{\omega_{n'n}^2 - \omega^2} \mp 3m\sum_{n'}\frac{(l'-l)f_{n'n}}{(l'+l+1)}\frac{\omega\omega_{n'n}}{\omega_{n'n}^2 - \omega^2}\right\}. \quad (12)$$

Accordingly, the level E_n is split into n^2 sublevels—the degeneracy is completely removed. The shift of the s level is the same as for the linearly polarized wave. For the frequency of the ruby laser the shift and splitting of the 2p level of hydrogen are given by

$$\Delta E_{2pm} = -\frac{e^2 n_\gamma}{2m\omega}[6.28 + (3m^2 - 2)0.367 \pm m\cdot 4{,}69].$$

For $\omega^2 \gg \omega_{n'n}^2$, using the same procedure as for the derivation of (10'), we have

$$\Delta E_n = \frac{e^2 n_\gamma}{2m\omega}\left\{1 + \frac{16}{3n^3} \times\left[\delta_{l0} - \frac{3(3m^2 - l(l+1))}{2l(l+1)(2l-1)(2l+1)(2l+3)}\right]\left(\frac{I}{\omega}\right)^2\right\} \quad (12')$$

For $\omega^2 \ll \omega_{n'n}^2$

$$\Delta E_n = \frac{e^2 n_\gamma}{2m\omega}\left\{\pm\frac{9mn^2}{8}\frac{\omega}{I} + [a_{nl} + (3m^2 - l(l+1))\,b_{nl}]\left(\frac{\omega}{I}\right)^2\right\}. \quad (12'')$$

The values of a_{nl} and b_{nl} for the hydrogen levels with n = 1, 2 have been given above.

We note that although the effect in question is caused by the external field, in a certain sense it is a differential form of the radiative displacement of the levels. In fact, the well known formula of Bethe[6] for the Lamb shift is obtained from (8) by replacing the number density n_γ of the incident photons by the number density $d^3k/(2\pi)^3$ of virtual photons and then integrating over the momenta $\mathbf{k}$ and summing over the polarizations $\mathbf{e}$. The first term in (8), which does not depend on the state of the electron, then leads to a divergent correction to the mass of the electron, which is included in the renormalized mass and therefore is not observed, and the second term is absent because there is no photon in the initial state. In the effect we are considering, on the other hand, the first term gives a finite correction to the mass of the electron, leading to the effective mass $m_* = m + e^2n_\gamma/2m\omega$,[3)] which is observed, for example, in the emission of radiation by the electron or in the production of a pair by a photon in the field of the wave.[1,7]

As long as $\xi \ll 1$ and in Eq. (2) we can neglect the harmonics $\psi_s(\mathbf{x})$ with $s \neq 0$, the "quasi-energy" ϵ plays the role of the ordinary energy and the spectrum of values of ϵ determines the frequencies of the most intense spectral lines in the light emitted by atoms in the field of an electromagnetic wave.[4)] Measurement of these frequencies can serve as a sensitive method for determining the field-strength amplitude of a wave, since the frequency shift relative to the unperturbed atomic frequency is proportional to $\xi^2 = (2I\mathscr{E}/\omega\mathscr{E}_0)^2$.

In conclusion I take pleasure in thanking V. L. Ginzburg and A. I. Nikishov for a discussion of this work.

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[3)] In the general case, when $e^2n_\gamma/2m\omega$ is not small in comparison with m, the value is $m* = (m^2 + e^2n_\gamma/\omega)^{1/2}$.

[4)] The intensity of lines due to harmonics with $s \neq 0$ will be diminished by at least a factor ξ^{2s}.