Ionization energies of hydrogenlike atoms in intense electromagnetic fields

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An analytic expression is derived for the energy spectrum of hydrogenlike atoms in an intense radiation field, which is valid up to intensities for which $R_0 \ll$ a Bohr radius, where R_0 is the amplitude of the classical displacement of a free electron in the radiation field.

Since the advent of the laser, there has been considerable interest in multiphoton processes. Most attention has been given to the calculation of transition probabilities. However, most of these calculations did not include the change of the energies of both the bound and continuum electrons—which we will refer to as ΔE_b and ΔE_c, respectively—due to the intense field. For example, Keldysh[1] included ΔE_c but not ΔE_b, whereas, as we shall see, the latter is always the most important. Henneberger[2] was the first to draw attention to the importance of ΔE_b. Recently,[3] ΔE_I (the change in the ionization energy, which in essence is $\Delta E_c - \Delta E_b$) has been calculated numerically for the *ground* states of hydrogen and helium. It is our purpose here to derive an analytic expression for ΔE_I for the *complete spectrum* of hydrogenlike atoms, which is valid up to intensities for which $R_0/\langle r\rangle \ll 1$, where R_0 is the amplitude of the classical displacement $\vec{R}$ of a free electron in the radiation field and $\vec{r}$ is the coordinate of the electron in the absence of the field.

To avoid the use of conventional perturbation theory, many papers[4] have used the momentum-translation approximation of Reiss,[5] but recent objections[6,7] have made it clear that this may not always be a reliable method for general use. We feel that the most elegant approach is to use the Kramers-Henneberger unitary transformation of the wave function.[8] The problem then reduces,[2] in the nonrelativistic dipole approximation, to the motion of an electron in a time-dependent potential $V(\vec{r}-\vec{R})$.

At first glance, it might appear that the effect of a time-dependent radiation field is simply to cause transitions. Thus, how real are the energy shifts? As real as the Lamb shift! In fact, our method of calculation is similar to that used by Welton,[9] who showed that the zero-point fluctuations of the electromagnetic field can account for Bethe's nonrelativistic result for the Lamb shift. Our calculation differs from that of Welton in two respects: (a) We consider a single frequency (and thus do not encounter divergence problems), and (b) the direction of $\vec{R}$ is fixed in space, in contrast to the random fluctuations produced by the zero-point oscillations (and thus we get contributions to other than $l=0$ levels).

As a preliminary, we note that Welton's calculation does not concern itself explicitly with ΔE_c. This is because such a term also appears as a part of ΔE_b—it is the (infinite) change in the kinetic energy of the electron due to the zero-point fluctuations. The same remark applies to our calculation (except that ΔE_c is finite here), and so we will concern ourselves directly with ΔE_I (this was also done implicitly by Henneberger and coworkers[2,3]). However, as ΔE_c has been used in many calculations instead of ΔE_I, we will later calculate it explicitly for comparison with ΔE_I.

Consider a hydrogenlike atom of nuclear charge Z in the field of a monochromatic plane wave of angular frequency ω. Then, in the dipole approximation, we have (in atomic units)

$$\vec{E} = \vec{E}_0 \sin\omega t, \tag{1}$$

with $E_0 = \alpha\omega A_0$, where $\vec{E}$, $\vec{A}$, and α are the electric field, vector potential, and fine-structure constant, respectively. It follows that $R_0 = E_0/\omega^2 = \alpha A_0/\omega$. We recall that the atomic units of electric field and angular frequency are 5.1×10^9 V/cm, and 27 eV/$\hbar$, respectively.

In addition, we define the unit of intensity as 7×10^{16} W/cm^2, corresponding to an electric field whose rms value is equal to 5.1×10^9 V/cm. Hence

$$R_0^2 = 2\omega^{-4} I. \tag{2}$$

As with Welton,[9] we expand the potential, take the time average and find, to lowest order, that the effective static potential may be written as $V(\vec{r}) + \Delta V(\vec{r})$, where

$$\Delta V(\vec{r}) = \tfrac{1}{4}(\vec{R}_0\cdot\vec{\nabla})^2 V(\vec{r}). \tag{3}$$

Thus, for $V(\vec{r}) = -Z/r$, we obtain

$$H' \equiv \Delta V(\vec{r}) = \tfrac{1}{4} Z\{\tfrac{4}{3}\pi R_0^2 \delta(\vec{r}) + (R_0^2/r^3)[1-3\cos^2\theta]\}, \tag{4}$$

where θ is the angle between $\vec{R}_0$ and $\vec{r}$.

It follows that the total Hamiltonian is invariant under rotations about the z axis and under parity,

and hence the corresponding eigenvalues, m and $\pm$, are constants of the motion. In addition, consistent with our perturbation expansion, we can neglect inter-n perturbations so that n can also be regarded as a good quantum number. However, l is not a good quantum number because H' connects states for which $\Delta l \equiv l - l' = 0, \pm 2$.

Thus we have a situation similar to that which occurs for the quadratic Zeeman effect.[10] For $n=1$ and 2, the perturbed energy levels are simply the expectation values of H' for the corresponding states. However, in general ($n>2$), for given values of n and m, it is necessary to diagonalize the matrix of H'.

We assume intensities of sufficient magnitude that the effect of H' dominates over spin-orbit and relativistic effects.

Now, labeling the unperturbed states $|nlm\rangle$, we have

$$\langle nlm|\cos^2\theta|nlm\rangle = \frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)} + \frac{(l+m)(l-m)}{(2l+1)(2l-1)} \tag{5}$$

and

$$\langle nlm|r^{-3}|nlm\rangle = \frac{2(Z/n)^3}{l(l+1)(2l+1)}. \tag{6}$$

It follows directly, from Eqs. (4)–(6), that

$$\langle n00|H'|n00\rangle = (Z^4/3n^3)R_0^2 \quad (\text{for } n=1 \text{ or } 2) \tag{7}$$

and

$$\langle 21m|H'|21m\rangle = (Z^4/240)R_0^2(3m^2-2). \tag{8}$$

In particular, for the ground state of hydrogen, we obtain $E_b = -\frac{1}{2}$ and $-\Delta E_I = \frac{1}{3}R_0^2$, which is consistent with the results of Ref. 3 for small values of R_0. Using Eq. (2), we note that, for a given intensity, $-\Delta E_I$ is proportional to the fourth power of the wavelength. In addition, from Eq. (2), we note that for, say, $\hbar\omega = 2.7$ eV, $R_0^2 \leq 1$ for I values as high as 3.6×10^{12} W/cm^2.

To return to the general case of given but arbitrary values of n and m, we denote the matrix elements $\langle nlm|H'|nl'm\rangle$ by $H'_{ll'}$. For large n values it is apparent that diagonalization of the $(n-|m|)$ squared matrix should be carried out numerically. However, as an alternative, we can use an ingenious method due to Schiff and Snyder.[10] The latter authors pointed out that the energy levels are so close together that one simply observes a single broadened line resulting from all transitions between the $l=0$ ground state and the $l=1$ component (allowed transitions) of the group of states that are obtained by diagonalization of $H'_{ll'}$. Then, neglecting the dependence of the dipole radiation transition probability on energy over the small range of energies involved in this group of states, it follows[10] that the center of gravity of the group of lines is given by $E_{\rm av} \equiv H'_{11}$. Now, for the problem under discussion, we recall that we are considering radiation with polarization parallel to z and so we must restrict attention to the group of final states for which $m=0$. It follows that

$$E_{\rm av} \equiv \langle n10|H'|n10\rangle = -(Z^4/15n^3)R_0^2. \tag{9}$$

We turn now to the effect of the radiation on the free electron, and our solution is simply the nonrelativistic dipole limit of the Volkov wave function.[11] This can be written in the form[12]

$$\psi = \exp[i\vec{P}\cdot(\vec{r}-\vec{R})] \times \exp[-i(\tfrac{1}{2}P^2 + \Delta E_c)t - i(\Delta E_c/2\omega)\sin 2\omega t], \tag{10}$$

where

$$\Delta E_c = \tfrac{1}{4}\alpha^2 A_0^2. \tag{11}$$

It is clear that ΔE_c is simply the classical oscillation energy of an electron in an electromagnetic wave. We also see immediately that

$$\Delta E_c = \tfrac{1}{4}R_0^2\omega^2. \tag{12}$$

Whereas the presence of the latter term has been noted by many authors in various contexts,[1,12] its relevance for the problem at hand has generally given rise to a lot of confusion. As already pointed out, it can be removed completely from consideration by essentially a renormalization. Now, from Eqs. (7) and (12), we have that

$$\Delta E_c/|\Delta E_I| \sim \omega^2 n^3/Z^4. \tag{13}$$

Hence, for optical frequencies ($\omega \sim 0.1$), and even for $Z=1$, we see that, except for large n, $\Delta E_c \ll |\Delta E_I|$. In other words, the use of ΔE_c (as in Ref. 1, for example) *increases* the ionization energies by a relatively small amount, whereas the correct result is that the ionization energies can be either *increased or decreased* by the relatively large amount $|\Delta E_I|$.

The above calculation treated the case of linearly polarized radiation but it is readily seen that, within the framework of our perturbation expansion, the same results ensue for the case of circularly polarized radiation.

It is apparent that these results may be used also as the basis of a calculation of multiphoton absorption transition probabilities in an intense field. However, in this connection, we should note that for low frequencies and high intensities, tunneling may become the dominant effect.[1]

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[1]L. V. Keldysh, Zh. Eksp. Teor. Fiz. 47, 1945 (1964) [Sov. Phys.—JETP 20, 1307 (1965)].
[2]W. C. Henneberger, Phys. Rev. Lett. 21, 838 (1968).
[3]C. C. Choi, W. C. Henneberger, and F. C. Sanders, Phys. Rev. A 9, 1895 (1974).
[4]See Ref. 7 for a detailed bibliography.
[5]H. R. Reiss, Phys. Rev. A 1, 803 (1970).
[6]C. Cohen-Tannoudji, J. Dupont-Roc, C. Fabre, and G. Grynberg, Phys. Rev. A 8, 2747 (1973).
[7]A. Decoster, Phys. Rev. A 9, 1446 (1974).
[8]The origin of this particular transformation has been attributed (see Refs. 3 and 9) to Kramers. However, Henneberger (Ref. 2) was the first to realize its potentiality for intense-field problems.
[9]T. Welton, Phys. Rev. 74, 1157 (1948).
[10]L. I. Schiff and H. Snyder, Phys. Rev. 55, 59 (1939).
[11]D. M. Volkov, Z. Phys. 94, 250 (1935); V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Relativistic Quantum Theory* (Addison-Wesley, Reading, Mass., 1971), p. 123.
[12]J. H. Eberly, *Progress in Optics* (North-Holland, Amsterdam, 1969), Vol. VII, p. 361.