Mass defect effects in atomic clocks

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Abstract
We consider some implications of the mass defect on the frequency of atomic transitions. We have found that some well-known frequency shifts (the gravitational shift and motion-induced shifts such as quadratic Doppler and micromotion shifts) can be interpreted as consequences of the mass defect in quantum atomic physics, i.e. without the need for the concept of time dilation used in special and general relativity theories. Moreover, we show that the inclusion of the mass defect leads to previously unknown shifts for clocks based on trapped ions.

Keywords: atomic clocks, frequency shifts, mass defect, special relativity

1. Introduction

At the present time, atomic clocks are extremely precise scientific devices. The operating principle of these quantum instruments is based on modern methods from laser physics and high-precision spectroscopy. In this way, an unprecedented value of fractional instability and uncertainty, at the level of 10−18, has already been achieved with the goal of 10−19 on the horizon [1]. Frequency measurements at such a level could have a huge influence on further developments in fundamental and applied physics. In particular, we can foresee tests of quantum electrodynamics and cosmological models, searches for drift of the fundamental constants, new types of chromometric geodesy, and so on (see, for example, review [2]). However, this level of experimental accuracy requires a comparable level of theoretical support, which would account for systematic frequency shifts of atomic transitions due to different physical effects. Thus, modern atomic clocks are at the point of interweaving different areas of theoretical physics.

In this letter we develop the mass defect concept with respect to atomic clocks. Historically, considerations of the mass defect have been primarily connected with nuclear physics where the mass defect explains the huge energy emitted due to different nuclear reactions. However, a quite unexpected result is that this effect is directly related to frequency standards, where it leads to the different shifts in the frequencies of atomic transitions.

The main idea of our approach is the following. Let us consider an arbitrary atomic transition between two states |g⟩ and |e⟩ with unperturbed frequency \( \omega_0 = (E_e^{(0)} - E_g^{(0)})/\hbar \), where \( E_g^{(0)} \) and \( E_e^{(0)} \) are the unperturbed energies of the corresponding states (see figure 1). Using Einstein’s famous formula, \( E = Mc^2 \), which links the mass \( M \) and energy \( E \) of a particle (\( c \) is the speed of light), we can find the rest masses of our particle, \( M_g \) and \( M_e \), for the states |g⟩ and |e⟩, respectively: \( E_g^{(0)} = M_g c^2 \) and \( E_e^{(0)} = M_e c^2 \). The fact that \( M_g \neq M_e \) is the essence of the so-called mass defect (or mass difference). In our case, the connection between \( M_g \) and \( M_e \) is the following:

\[
M_e c^2 = M_g c^2 + \hbar \omega_0 \quad \Rightarrow \quad M_e = M_g + \frac{\hbar \omega_0}{c^2}. \tag{1}
\]

Note that several years ago an idea about direct measurement of the mass difference \( \delta M = M_e - M_g \) under emission of gamma rays (from nuclei) was actively discussed (e.g. see [3]).

In this letter we show that the relationship (1) allows us to reinterpret some well-known systematic frequency shifts (such as the so-called time dilation effects [4–6]) in atomic
we can write the well-known expression (in the case of $|\varphi/c^2| \ll 1$):
\[
\frac{\omega(r_1) - \omega(r_2)}{\omega(r_1)} = \frac{|\varphi(r_1) - \varphi(r_2)|/c^2}{1 + |\varphi(r_1)/c^2|} \approx \frac{\varphi(r_1) - \varphi(r_2)}{c^2},
\]
which connects the fractional shift $\Delta \omega/\omega$ with the difference of gravitational potentials $|\varphi(r_1) - \varphi(r_2)|$ between emitter (coordinate $r_2$) and observer (coordinate $r_1$).

Note that equation (3) was derived without including the gravitational time dilation, which is taken as a basis of Einstein’s theory of general relativity [5]. Therefore, the mass defect approach (see also [9]) can be considered to be a ‘quasi-classical’ explanation of the gravitational shift.

3. Motion-induced shifts for a free atom

As a second example, we will perform an exact quantum-relativistic calculation of the frequency of transition under one-photon absorption and emission by a free-moving atom. We assume that the energy and momentum of the atom–photon system are conserved. Considering the law of energy conservation for absorption/emission of a photon with frequency $\omega$, the following relativistic relationship results:
\[
h\omega = \sqrt{c^2p_e^2 + M_e^2c^4} - \sqrt{c^2p_g^2 + M_g^2c^4},
\]
where $p_e$ and $p_g$ are the momenta of an atom in the internal states $|e\rangle$ and $|g\rangle$, respectively.

Let us first consider the absorption of a photon with momentum $\hbar k = n\hbar\omega/c$, where the unit vector $n = k/|k|$ is directed along the wave vector $k$. We assume that initially the atom is in the lower state $|g\rangle$ and has the momentum $p_g$. Then, in accordance with conservation of momentum, we find the atomic momentum in the excited state $|e\rangle$ after absorption of the photon to be: $p_e = p_g + n\hbar\omega/c$. In this case, equation (6) has the following form:
\[
h\omega = \sqrt{c^2(p_g + n\hbar\omega/c)^2 + M_e^2c^4} - \sqrt{c^2p_g^2 + M_g^2c^4},
\]
which should be considered as an equation for the unknown frequency $\omega$. Taking into account (1), the exact solution of equation (7) can be written as:
\[
\omega = \sqrt{\frac{\omega_0^2 + \omega_0^{(rec)}}{1 + \frac{\omega_0^{(rec)}}{c^2} - (n \cdot v_g)/(M_gc)}}.
\]

Thus, the combination of special relativity ($E = Mc^2$) and quantum mechanics (the definition of the frequency of atomic transition) leads to a formally noncontradictory explanation of the gravitational shift (3), which describes different experiments (e.g. see [6–8]) with atomic clocks in a spatially non-uniform gravitational potential $\varphi(r)$. Indeed, using equation (3)
Let us now calculate the frequency of a photon emitted along the line of $\mathbf{n}$ by the moving atom, which was initially in the upper level $|e\rangle$ and had momentum $p_e$. In this case, the momentum of the atom in the lower level $|g\rangle$ after emission of the photon becomes $p_g = p_e - n/m\omega/c$. Solving equation (6), we obtain the following result:

$$\omega = \frac{\omega_0 - \omega_e^{(rec)}}{\sqrt{1 + p_e^2/(M_e c^2)} - (n \cdot p_e)/(M_e c)} = \frac{\omega_0 - \omega_e^{(rec)}}{\sqrt{1 - v_e^2/c^2} - (n \cdot v_e)/c^2}. \quad (10)$$

where $\omega_e^{(rec)} = \hbar \omega_e^2/(2M_e c^2)$ is the correction due to the recoil, and the velocity $v_e$ and momentum $p_e$ are connected by the relationship: $p_e = M_e v_e/\sqrt{1 - v_e^2/c^2}$.

For comparison, let us consider the absorbing/emitting classical oscillator with eigenfrequency $\omega_0$, which moves with velocity $v$ relative to the laboratory system of coordinates. In this case, using the Lorentz transformations, we obtain the following well-known expression for the frequency of the electromagnetic wave under absorption/emission along the line $n$:

$$\omega = \frac{\omega_0 \sqrt{1 - v^2/c^2}}{1 - (n \cdot v)/c}. \quad (11)$$

Comparing equation (11) with formulas (9) and (10), we see that the quantum-relativistic calculation significantly differs from the classically-relativistic version. Formally this can be seen as a renormalization of the eigenfrequency $\omega_0$: $\omega_0 \rightarrow \omega_0 + \omega_e^{(rec)}$ in the case of absorption (see equation (9)); and $\omega_0 \rightarrow \omega_0 - \omega_e^{(rec)}$ in the case of emission (see equation (10)).

Note that the interrelation of the second-order Doppler shift and the mass defect in the context of a free-moving object was previously shown for the $M$ and the mass defect in the context of a free-moving object was previously shown for the $M$ and the mass defect in the context of a free-moving object was previously shown for the $M$ and the mass defect in the context of a free-moving object was previously shown for the $M$ and the mass defect in the context of a free-moving object was previously shown for the $M$. However, the derivation in [11] is not quite suitable for atomic clocks, because it did not include the nonzero recoil shift (see $\omega_g^{(rec)}$ in the exact expressions (9) and (10)), which is very important for frequency standards based on free atoms. Our formulas (9) and (10) coincide with equation (11) in the limit $M_g \rightarrow \infty$, when $\omega_g^{(rec)} \rightarrow 0$.

We have shown above that for one-photon transition the Doppler formula (11), based on the Lorentz transformations and time delay concept, does not coincide with the exact quantum-relativistic expressions (8)–(10) based on the mass defect concept. This occurs because the velocities in the ground and exited states are not equal to each other, $v_g \neq v_e$, due primarily to the recoil effect. Consequently, a unique inertial reference frame, which can be unambiguously associated with the moving atom, does not exist. Moreover, let us now show that even in the total absence of the recoil effect for two-photon transition, formed by two counter-propagating waves with the same frequency $\omega \approx \omega_0/2$ (i.e. a standing wave), the well-known formula based on the Lorentz transformations:

$$\omega = \frac{\omega_0}{\sqrt{1 - v^2/c^2}}, \quad (12)$$

is also not exact. Indeed, in the absence of the recoil effect, the momenta in the ground and exited states are the same, $p_g = p_e = p$. Nevertheless, using relativistic expressions:

$$p = \frac{M_j v_j}{\sqrt{1 - v^2/c^2}} \Rightarrow v_j = \frac{p/M_j}{\sqrt{1 + p^2/(M_j c^2)}}, \quad (j = g, e), \quad (13)$$

we see that the velocities are not the same, $v_g \neq v_e$, due to the mass defect ($M_g \neq M_e$). Therefore, the use of equation (12) leads to the ambiguity:

$$\omega(1) = \frac{\omega_0}{2\sqrt{1 + p^2/(M_g c^2)}}, \quad \omega(2) = \frac{\omega_0}{2\sqrt{1 + p^2/(M_e c^2)}}. \quad (14)$$

However, the exact result can be expressed as the following:

$$2\hbar \omega = \sqrt{c^2 p^2 + M_g^2 c^4} - \sqrt{c^2 p^2 + M_e^2 c^4}, \quad (15)$$

where we have used energy conservation and the mass defect.

4. Motion-induced shifts for atoms (ions) trapped in a confining potential

A third example concerns frequency shifts for trapped atoms (ions) in an external confining potential. In this case, the conservation of energy and momentum does not exist. Therefore, the above consideration for free atoms is not valid, and the implementation of the mass defect concept requires other approaches, which are developed below.

For simplicity, we will consider a stationary confining potential $U(r)$, which we take to be the same for both states $|g\rangle$ and $|e\rangle$. Such a situation can occur both for clocks based on neutral atoms in an optical lattice and for those based on trapped ions. In this case, we use the standard formalism that quantizes the energy levels with translational degrees of freedom:

$$\hat{H}_j |\psi_{j,\alpha}(r)\rangle = \varepsilon_{j,\alpha}^{(vib)} |\psi_{j,\alpha}(r)\rangle, \quad \hat{H}_j = \frac{\hat{p}^2}{2M_j} + U(r), \quad (16)$$

where the Hamiltonian $\hat{H}_j$ describes the translational motion of the particle in the $j$th internal state $|j\rangle$ ($j = g, e$), the wavefunction $|\psi_{j,\alpha}(r)\rangle$ corresponds to the $\alpha$th vibrational level ($\alpha = 0, 1, 2, \ldots$) of the $j$th internal state $|j\rangle$, and $r$ is the coordinate of the atomic center of mass. Thus, taking into account the translational motion, the atomic wave function is described by the pair products $|j\rangle \otimes |\psi_{j,\alpha}(r)\rangle$. Because of the mass defect ($M_e \neq M_g$), the energy levels for the lower and upper states differ: $\varepsilon_{e,\alpha}^{(vib)} \neq \varepsilon_{g,\alpha}^{(vib)}$. Consequently, the frequency $\omega_{\alpha\alpha}$ between corresponding levels of the trapped particle is different from the unperturbed frequency, $\omega_0$ (see figure 1), with a value $\Delta \omega$ (see figure 1):

$$\Delta \omega_{\alpha\alpha} = \omega_{\alpha\alpha} - \omega_0 = \left(\varepsilon_{e,\alpha}^{(vib)} - \varepsilon_{g,\alpha}^{(vib)}\right)/\hbar. \quad (17)$$
Let us now estimate this value. For this purpose, we write the Hamiltonian for the upper state \( \hat{H}_e \) in the following form:

\[
\hat{H}_e = \hat{H}_e + \Delta \hat{H}; \quad \Delta \hat{H} = \frac{\hat{p}^2}{2M_e} - \frac{\hat{p}^2}{2M_e} = \frac{\hbar}{2} \frac{\hat{p}^2}{2M_e},
\]

where the operator \( \Delta \hat{H} \) can be considered as a small perturbation. In this case, using standard perturbation theory, the energy \( E^{(\text{ vib})}_{\epsilon, \alpha} \) can be written as a series \( E^{(\text{ vib})}_{\epsilon, \alpha}(0) + \Delta E^{(\text{ vib})}_{\epsilon, \alpha}(1) + \Delta E^{(\text{ vib})}_{\epsilon, \alpha}(2) + \ldots \), where \( E^{(\text{ vib})}_{\epsilon, \alpha}(0) = E^{(\text{ vib})}_{\epsilon, \alpha} \), and the first correction is determined as the average value \( \Delta E^{(\text{ vib})}_{\epsilon, \alpha}(1) = \langle \Psi_{\epsilon, \alpha} | \Delta \hat{H} | \Psi_{\epsilon, \alpha} \rangle \). Using equation (18) and taking into account \( M_e \approx M_g \), we obtain the following estimate of the relative value of shift (17):

\[
\frac{\Delta \omega_{\epsilon \alpha}}{\omega_0} \approx \left( \frac{2}{c^2} \right) \frac{M_g M_e}{M_e M_g} \approx \frac{1}{2} \frac{\langle \Psi_{\epsilon, \alpha} | \hat{p}^2 | \Psi_{\epsilon, \alpha} \rangle}{\langle \Psi_{\epsilon, \alpha} | \hat{p}^2 | \Psi_{\epsilon, \alpha} \rangle}.
\]

We note that this expression coincides with a well-known relativistic correction, which is the quadratic Doppler shift due to the time dilation effect for a moving particle [6]. We see this correspondence if we consider the conventional explanation for this effect. In agreement with special relativity, the tick rate \( \Delta t' \) in the moving (with velocity \( \mathbf{v} \)) coordinate system changes with respect to the tick rate \( \Delta t \) in the motionless (laboratory) coordinate system according to the law: \( \Delta t = \Delta t' \sqrt{1 - \mathbf{v}^2/c^2} \). As a result, an atomic oscillation with eigenfrequency \( \omega_0 \) is perceived by an external observer to be shifted to: \( \omega = \omega_0 \sqrt{1 - \mathbf{v}^2/c^2} \). In the nonrelativistic limit, \( (\mathbf{v}^2/c^2 \ll 1) \), we have: \( \omega \approx \omega_0 (1 - \mathbf{v}^2/(2c^2)) = \omega_0 (1 - (\mathbf{p}/M)^2/(2c^2)) \) (where \( \mathbf{p} \) is the momentum of the particle). Then, if we take into account quantum considerations through the replacement \( \mathbf{p} \rightarrow -i\hbar \nabla \), we obtain the expression (19) for the frequency shift.

Thus, the conventional explanation formally requires the use of the proper (internal) time of the atom. However, because of the wave nature of quantum objects and the probabilistic interpretation of quantum mechanics, a notion of the proper time (as some continuum) of a quantum particle, spatially localized in a confined potential, seems unclear and even contradictory. In this context, an approach based on the mass defect concept has no internal logical contradictions and comes from the canonical quantum-mechanical scheme (i.e. Hamiltonians, eigenvalues, eigenfunctions), which does not require the notion of the proper time of a quantum particle. Note also that, due to the mass defect, a general definition of the atomic velocity operator \( \hat{v} \) does not exist at all. Indeed, using the following quantum-relativistic formulas

\[
\hat{p} = \frac{M_j \hat{v}}{\sqrt{1 - \hat{v}^2/c^2}} \Rightarrow \hat{v} = \frac{\hat{p} / M_j}{\sqrt{1 + \hat{p}^2/(M_j c^2)}},
\]

we can rigorously determine only the particular velocity operator \( \hat{v} \), which is associated with only the selected atomic energy state \( |j\rangle \) (with the mass \( M_j \)).

To define more precisely the frequency shift for trapped atoms (ions), we need to find the stationary states from the Klein–Gordon equation (for \( J_\xi = 0 \rightarrow J_\zeta = 0 \) clock transition):

\[
\{ [\mathcal{E}^{(\text{tot})}_{j \xi} - U(\mathbf{r})]^2 - \mathcal{E}^2 - M^2 c^4 \} |\Psi_j\rangle = 0,
\]

\[
\mathcal{E}^{(\text{tot})}_{j \xi} = \mathcal{E}^{(0)}_{j \xi} + \mathcal{E}^{(\text{ vib})}_{j \xi}, \quad (j = g, e),
\]

in the confining potential \( U(\mathbf{r}) \). Note that the resulting shift \( \Delta \omega/\omega_0 \) will not be equal to the well-known phenomenological expression (see [6]):

\[
\frac{\Delta \omega}{\omega_0} = \left( \frac{1}{(1 - v||/c) / \sqrt{1 - \mathbf{v}^2/c^2}} \right) - 1, \quad (v|| = (\mathbf{n} \cdot \mathbf{v})).
\]

In the general case, the shift obtained from equation (22) will coincide with the exact shift obtained from equation (21) only in the second order Doppler term.

In the case of dynamic confinement of an ion (with charge \( eZ_i \)) in the time-dependent electric potential \( \phi(t, \mathbf{r}) \) of an rf Paul trap (see [2, 12]):

\[
\phi(t, \mathbf{r}) = V_{\text{dc}} a(\mathbf{r}) + V_{\text{rf}} b(\mathbf{r}) \cos(f t),
\]

where \( a(\mathbf{r}) \) and \( b(\mathbf{r}) \) describe spatial dependencies, the mass defect concept is also applicable and can explain, in particular, the frequency shift, which is usually interpreted as the micro-motion shift. Indeed, in the case of relatively high rf frequency \( f \) in the Paul trap, there is a good working approximation of the so-called pseudopotential, which can be expressed for the \( j \)th internal state \( |j\rangle \) (in the context of the mass defect) as the following sum:

\[
U^{(\text{ pseudo})}_{j}(r) = eZ_i V_{\text{dc}} a(\mathbf{r}) + W_{\text{rf}}(\mathbf{r}) + \frac{e^2 Z_i^2 V_{\text{rf}}^2}{4f^2} (\nabla b(\mathbf{r}))^2,
\]

where the first term is connected with the static electric potential and the second term is produced by the rf oscillating potential (see in equation (23)) and is related to the micro-motion (\( \nabla \) is the gradient operator). Note that the pseudopotential approach equation (24) is valid for description of the lower vibrational levels: \( \mathcal{E}^{(\text{ vib})}_{j \epsilon, \alpha} \ll \hbar f \).

As we see, the second term in equation (24) is mass-dependent. In this case, the total Hamiltonian for the upper state, \( \hat{H}^{(\text{eff})}_{\epsilon, \alpha} = \hat{p}^2/(2M_e) + U^{(\text{ eff})}_{\epsilon, \alpha}(\mathbf{r}) \), can be written in the following form:

\[
\hat{H}^{(\text{eff})}_{\epsilon, \alpha} = \hat{H}^{(\text{dc})}_{\epsilon, \alpha} + \Delta \hat{H}^{(\text{eff})}_{\epsilon, \alpha},
\]

\[
\Delta \hat{H}^{(\text{eff})}_{\epsilon, \alpha} = \left( \frac{1}{M_e} - \frac{1}{M_g} \right) \frac{\hat{p}^2}{2} + W_{\text{rf}}(\mathbf{r}) = -\frac{\hbar \omega_0}{M_g M_e c^2} \frac{\hat{p}^2}{2} + W_{\text{rf}}(\mathbf{r}).
\]

where the operator \( \Delta \hat{H}^{(\text{eff})}_{\epsilon, \alpha} \) can be considered to be a small perturbation. Consequently, we have the frequency shift:

\[
\frac{\Delta \omega_{\epsilon \alpha}}{\omega_0} \approx \left( -\frac{1}{2} \frac{\langle \Psi_{\epsilon, \alpha} | \hat{p}^2 | \Psi_{\epsilon, \alpha} \rangle}{M_g M_e c^2} + \langle \Psi_{\epsilon, \alpha} | W_{\text{rf}}(\mathbf{r}) | \Psi_{\epsilon, \alpha} \rangle \right)
\approx \frac{1}{2} \frac{\langle \Psi_{\epsilon, \alpha} | \hat{p}^2 | \Psi_{\epsilon, \alpha} \rangle}{M_g} - \frac{\langle \Psi_{\epsilon, \alpha} | W_{\text{rf}}(\mathbf{r}) | \Psi_{\epsilon, \alpha} \rangle}{M_g^2 c^2}.
\]

where the first contribution coincides with equation (19), and can be considered as a secular-motion-induced shift.
The second term in equation (26) can be interpreted as a micromotion shift. Note that both these shifts have comparable values, in the general case.

In the case of a purely rf Paul trap with $V_{dc} = 0$ in equation (24), we have the following relationships for Hamiltonians, vibrational energies and eigenfunctions:

$$\hat{H}_e = \frac{M_e}{M} \hat{H}_e^{(eff)}, \quad \hat{E}_{vib} = \frac{M_e}{M} \hat{E}_{vib}^{(e)}, \quad \psi_{e,o}(r) = \psi_{e,o}(r),$$

leading to the total fractional frequency shift:

$$\frac{\Delta \omega_{\alpha \alpha}}{\omega_0} = - \frac{\epsilon_{e}^{(vib)}}{M e c^2} \approx - \frac{\epsilon_{e}^{(vib)}}{M e c^2},$$

which contains both secular-motion and micromotion contributions (see equation (26)).

Note that in a similar way we can consider the mass defect effects in the case of several ions confined in the same trap.

5. Previously unconsidered field-induced shifts for trapped ions

Besides the reinterpretation of some well-known shifts, the mass defect concept predicts additional contributions for field-induced shifts that have not been previously discussed in the scientific literature. We emphasize that these additional shifts are associated with translational degrees of freedom and they vanish if we do not take into account the mass defect.

We will consider a trapped ion (with charge $eZ_j$) in the presence of an additional weak electric field with potential $\varphi_{add}(r)$, which describes all controlled and uncontrolled fields except the trapping potential $U(r)$ from the previous section 3.

Let us show how an additional potential $\varphi_{add}(r)$ will perturb the vibrational structure formed by $U(r)$. For this purpose we will use vibrational eigenfunctions $|\psi_{g,o}(r)\rangle$ and $|\psi_{e,o}(r)\rangle$, which describe a spatial localization of the ion in the internal states $|g\rangle$ and $|e\rangle$ due to the trap potential $U(r)$, as a basis for perturbation theory on the small additional interaction $U_{add}(r) = eZj \varphi_{add}(r)$. This addition describes an interaction of the point charge $Zj$ with the potential $\varphi_{add}(r)$.

The center of the ion localization $r_0$ in the trap is determined by averaging: $r_0 = \langle \psi_{g,o}(r) | r | \psi_{g,o} \rangle$. In this case, we will use the following Taylor series of the additional operator $U_{add}(r)$ at the point of ion localization $r_0$:

$$U_{add}(r) = eZj \varphi_{add}(r) = eZj \varphi_{add}(r_0 + (r - r_0))$$

$$= eZj \left[ \varphi_{add}(r_0) - ((r - r_0) \cdot \mathbf{E}_{add}(r_0)) + \sum_{q'd=1} G_{q'q}^{(norm)} \psi_{q'}^{(add)}(r_0) + \ldots \right]$$

$$= eZj \varphi_{add}(r_0) - \left[ \mathbf{d}^{(cloud)} \cdot \mathbf{E}_{add}(r_0) \right] + \left[ \mathbf{Q}^{(cloud)} \psi^{(add)}(r_0) \right] + \ldots$$

where $\mathbf{E}_{add}(r_0) = - \nabla_r \varphi_{add}(r_0)r_0$ and $\mathbf{W}^{(add)}(r_0) = W_{qq}^{(add)}(r_0)$ are the electric vector and electric tensor, respectively, at the point $r_0$. Operators $\mathbf{d}^{(cloud)}$ and $\mathbf{Q}^{(cloud)}$ describe the mesoscopic dipole and quadrupole moments, respectively, of the ion cloud:

$$\mathbf{d}^{(cloud)} = eZj(r - r_0),$$

$$\mathbf{Q}^{(cloud)} = q_{qq}^{(cloud)} = eZj \left\{ (r - r_0)_q (r - r_0)_q' - \delta_{qq'} (r - r_0)^2 \right\}$$

where $(r - r_0)_q$ is the $q$th Cartesian coordinate of the vector $(r - r_0)$. The first term in the last line of equation (29) is unimportant, and we can use the following condition: $\varphi_{add}(r_0) = 0$ (we assume, for simplicity, that $r_0$ is the same for all states $|\psi_{g,o}(r)\rangle$). The obtained results can be reproduced in the general case of a four-vector $\{ \varphi_{add}(t,r), A_{add}(t,r) \}$. Note also that the approach developed above is suitable if the size of the spatial nonuniformity (e.g. wavelength $\lambda$) of the additional field is much more than the size of the ion cloud:

$$R_{cloud} = \sqrt{\langle \psi_{g,o}(r_0) | r - r_0 | ^2 \psi_{g,o}(r) \rangle},$$

which is a typical size of the wavefunctions $|\psi_{g,o}(r)\rangle$.

Thus, we have shown that apart from the well-known electronic dipole and quadrupole moments a trapped ion has additional mesoscopic dipole and quadrupole moments, which describe an interaction of the ion cloud (formed by the trapping potential $U(r)$) with weak external fields. This interaction involves only translational degrees of freedom (r) and it leads to a perturbation (i.e. frequency shifts) of the vibrational structure in trapped ions. However, to see the manifestation of these shifts in atomic clocks we need to take into account the mass defect concept, because without mass defect these shifts will not lead to a shift of the clock transitions.

As a first example, let us consider the first-order shift, $\Delta \omega_{10} = \langle \psi_{j,o} | U_{add}(r) | \psi_{j,o} \rangle / \hbar$. Because $\langle \psi_{j,o} | \mathbf{d}^{(cloud)} | \psi_{j,o} \rangle = 0$ (see equation (30)), we obtain:

$$\Delta \omega_{10} = \langle \psi_{j,o} | U_{add}(r) | \psi_{j,o} \rangle / \hbar,$$

$$\langle \mathbf{Q}^{(cloud)} | j, o \rangle = \langle \psi_{j,o} | \mathbf{Q}^{(cloud)} | \psi_{j,o} \rangle, \quad (j = g, e).$$

Consequently, we have the following residual shift of the clock transition $|g\rangle \leftrightarrow |e\rangle$:

$$\Delta \omega_{10} = \Delta \omega_{10} - \Delta \omega_{10} = \Delta \omega_{10} \mathbf{Q}^{(m-def)} W_{add}(r_0) / \hbar,$$

where $\Delta \omega_{10}^{(m-def)}$ is a residual quadrupole moment:

$$\Delta \omega_{10}^{(m-def)} = \langle \psi_{g,o} | \mathbf{Q}^{(cloud)} | \psi_{g,o} \rangle - \langle \psi_{g,o} | \mathbf{Q}^{(cloud)} | \psi_{g,o} \rangle,$$

which can be nonzero, because $|\psi_{g,o}(r)\rangle \neq |\psi_{e,o}(r)\rangle$ in the general case due to the mass defect. Let us estimate an order of $\Delta \omega_{10}^{(m-def)}$:

$$\Delta \omega_{10}^{(m-def)} \approx \langle \psi_{g,o} | \mathbf{Q}^{(cloud)} | \psi_{g,o} \rangle \hbar \alpha_0 \approx eZj R_{cloud}^2 / M e c^2,$$

where $R_{cloud}$ is the size of the ion cloud (see in equation (31)), and $M \approx M_{e,g}$. Though the expression (35) contains a very small multiplier, $\hbar \alpha_0 / M e c^2 \ll 1$, the size of the ion localization $R_{cloud}$ significantly exceeds the Bohr radius $\alpha_0$. Indeed, $R_{cloud} \approx (10^{-2} - 10^{-3}) \alpha_0$ even for an ion which has been deeply cooled to the lowest vibrational level in the confined potential $U(r)$ (i.e. for the quantum limit of cooling),
and $R_{\text{cloud}} \sim 10^4 a_0$ for the upper vibrational states, which are populated if the ion is laser-cooled to the usual so-called Doppler temperature (mK range). As a result, the quadrupole shift of the clock transition, modified by the mass defect, can be metrologically significant for modern and future optical frequency standards. For example, let us consider an atomic clock based on the transition $^1S_0 \rightarrow ^3P_0$ in the ion $^{27}\text{Al} + [13]$. Because of the zero electronic angular momentum for the clock transition, $J_g = J_e = 0$, the quadrupole moment, associated with internal degrees of freedom, is very small ($|\Delta Q| \sim 10^{-9} e a_0^2$, see [14]). However, on the basis of formula (35), we estimate $|\Delta Q| \sim 10^{-5} e a_0^2$ for $R_{\text{cloud}} \sim (10^2-10^4)a_0$. As another example, let us consider the so-called nuclear clock, based on the intranuclear transition in $^{239}\text{Th}^{1+} + [15]$. In [15], the quadrupole moment (associated with internal degrees of freedom) for the clock transition was estimated to be $|\Delta Q| \sim 10^{-5} e a_0^2$. Using now our formula (35), we find $|\Delta Q| \sim (10^{-2}-10^{-6}) e a_0^2$ for $R_{\text{cloud}} \sim (10^2-10^4)a_0$. Such values of the quadrupole moment may be important for atomic clocks with fractional uncertainty at the level of $10^{-18}-10^{-19}$. However, for more accurate estimates, it is necessary to know the wave functions on the translational degrees of freedom $|\Psi_{j\alpha}(r)\rangle$ ($j = g, e$). In particular, this quadrupole shift is absent for spherically-symmetrical states $|\Psi_{j\alpha}(r)\rangle = |\Psi_{j\alpha}(r - r_0)\rangle$, when $\langle \Psi_{g\alpha}|\hat{Q}^{(\text{cloud})}|\Psi_{g\alpha}\rangle = 0$ and $\langle \Psi_{e\alpha}|\hat{Q}^{(\text{cloud})}|\Psi_{e\alpha}\rangle = 0$. The residual quadruple moment (34) also vanishes for a purely rf Paul trap, because of $\langle \Psi_{g\alpha}|\hat{Q}^{(\text{cloud})}|\Psi_{e\alpha}\rangle$ (see equation (27)).

To see another manifestation of mass defect, let us consider a previously unknown contribution to the ac-Stark shift in the presence of weak external low-frequency field, $E(t) = (E_0 e^{-i\omega t} + E_0' e^{i\omega t})$. Here we will investigate only shifts of the quantum levels $E_{\pm\alpha}$ and $\xi^{(\text{vib})}_{\pm\alpha}$ on the translational degrees of freedom of the trapped ion (see figure 1).

This shift exists because some nondiagonal elements of the dipole moment between two different vibrational states $\alpha$ and $\alpha'$ can be nonzero: $d^{(2)}_{\alpha\alpha'}(\nu) = \langle \Psi_{j\alpha}(r)|\hat{e}_{\nu}^{(\text{cloud})}|\Psi_{j\alpha'}(r)\rangle \neq 0$ ($\alpha \neq \alpha'$). In this case, the expression for the shift of the $\alpha$th vibrational level $E_{\alpha}$ in the internal state $|j\rangle$ has the following standard form:

$$\Delta E_{\alpha} = \frac{1}{h} \sum_{\nu} \left[ \frac{|E_0|^2}{h^2} \frac{|d_{\alpha\alpha'}^{(2)}|^2}{|\xi_{j\alpha}|^2} + \frac{|E_0'|^2}{h^2} \frac{|d_{\alpha\alpha'}^{(2)}|^2}{|\xi_{j\alpha'}|} \right], \quad (j = g, e).$$

(36)

Note that the square of the ion-cloud dipole moment has order of magnitude $|d_{\alpha\alpha'}^{(2)}|^2 \sim e^2 Z_c R_{\text{cloud}}^2$, which is many orders greater than the square of the atomic dipole moment $e^2 a_0^2$ because $R_{\text{cloud}} \gg a_0$. Thus, the vibrational levels of a trapped ion are very sensitive even to weak external fields. However, because $\Delta E_{\alpha}$ and $\Delta E_{\alpha}$ are slightly different only due to the mass defect, we find and estimate the differential shift of the clock transition $|g\rangle \leftrightarrow |e\rangle$:

$$\delta_{\alpha}^{(2)} = \Delta E_{\alpha} - \Delta E_{\alpha}, \quad \bar{\delta}_{\alpha}^{(2)} \sim \Delta E_{\alpha} \frac{\hbar \omega}{MC^2}.$$

(37)

which can exceed the ac-Stark shift connected with low-frequency polarizability, which is associated with internal (electronic) degrees of freedom. In a similar way, we can find new contributions to the black body radiation shift, linear and quadratic Zeeman shifts, and so on. Note that we have formulated here only a general qualitative approach to the description of previously unknown shifts, which require more detailed consideration in further investigations.

6. Conclusion

We have considered some manifestations of the mass defect in atomic clocks. As a result, some well-known systematic shifts, previously interpreted as time dilation effects in the framework of special and general relativity theories, can be considered as a consequence of the mass defect in quantum mechanics. In particular, we have derived previously unknown exact quantum-relativistic formulas (8)–(10) and (15) for one-photon and two-photon transitions for free atoms. We have also obtained previously unknown analytical expression for the micromotion shift (26) for an ion trapped in an rf Paul trap. Furthermore, our approach has predicted a series of previously unknown field-induced shifts for ion clocks. These results are important for high-precision atomic clocks and could be interesting for theoretical quantum physics.

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