Effect of atomic electric quadrupole moment on positron binding

C. Harabati, V. A. Dzuba, and V. V. Flambaum
School of Physics, University of New South Wales, Sydney 2052, Australia

Effect of the electric quadrupole moment, $Q$, is studied for positron-atom bound systems. It is demonstrated that for $Q > 50$ a.u. the electric quadrupole potential is sufficiently strong to bind positron (or electron) even in the absence of the dipole polarization potential. Such large values of $Q$ are not known for atomic ground states, however, they exist in molecules and excited atoms. In the state $2s2p^3 P^o_2$ of beryllium, the quadrupole contribution makes difference between stable bound state and decay to Be$^+$ ion and positronium. In a majority of atoms the quadrupole contribution is small and can be neglected.

PACS numbers: 36.10.-k

I. INTRODUCTION

Unperturbed central potential of an atom is positive on all distances and can not bind positron. Only when correlations between positron and atomic electrons are taken into account, positron can be bound to a majority of atoms [1] (see also [2]–[10] and references therein). A simple explanation of the positron binding is polarization of the atom by positron field. Electron-positron attraction shifts the electron cloud towards the positron producing electric dipole moment of the atom. This induced electric dipole moment creates polarization potential which on large distances behaves like $-\alpha/2r^4$, where $\alpha$ is static dipole polarizability of the atom. However, many atoms also have a static quadrupole moment which produces a long-range potential which decays slower ($\sim 1/r^3$) than the polarization potential ($\sim 1/r^4$). Therefore, it looks interesting to investigate the role of the quadrupole potential in the positron binding.

There are many different techniques used to calculate positron binding energy to atoms. The variational and configuration interaction calculations may easily include the quadrupole contribution. In other calculations based on the correlation potential [8–10] and coupled-cluster single-double [11, 12] approaches the quadrupole potential contribution was not included since the positron was assumed to be in s-wave. Note, that assuming positron being in s state does not mean that contribution of higher angular momenta are totally neglected. For example, in the case of correlation potential method [8–10] binding energy is related to the expectation value of the correlation potential $\hat{\Sigma}$: $\epsilon \sim \langle s|\hat{\Sigma}|s \rangle$, where $s$ is the positron wave function and higher values of both electron and positron angular momenta are included into the perturbation theory calculation of $\hat{\Sigma}$. Therefore, the effect of the virtual positron formation is taken into account (see, e.g. [8, 9, 11]).

In spite of the fact that many calculations do include the quadrupole contribution, it was never presented separately. However, it is useful to know it to judge whether it can be at least partly responsible for the difference in results in different calculations. It is also important to know whether that contribution can be large enough to provide the difference between binding and not binding. In this paper we study the quadrupole contribution using simple variational approach.

II. VARIATIONAL ENERGY OF A POSITRON IN AN ATOM

Positron trial wave function in the presence of electric dipole and quadrupole potentials is taken in the form

$$\Psi(r, \theta) = A(r-a) e^{-\kappa r} \sqrt{1 - \beta^2} Y_{00} + \beta Y_{20}$$

where $A$ is the normalization constant, $Y_{lm}(\theta, \phi)$ are spherical harmonics, $\kappa$ and $\beta$ are variational parameters, and $a$ is a cut-off distance from the nucleus. It is assumed that the wave function is zero at $r < a$. The potential energy of the positron for $r > a$ is

$$V(r, \theta) = \frac{e^2 \alpha}{2r^4} + \frac{eQ P_2(\cos \theta)}{r^3}$$

where $\alpha$ is the polarizability of the atom, $Q$ is its quadrupole moment, and $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is Legendre polynomial. There is also additional infinite potential barrier at $r = a$ which simulates the effect of positron repulsion from the positive electrostatic potential inside the atom. The mixing of $s$ and $d$ waves provides localisation of the positron wave function in equatorial or polar areas depending on the sign of $Q$.

Using Schrödinger equation positron energy can be written as

$$E(\kappa, \beta) = \frac{\int d^3 r \left( \frac{\hbar^2}{2m} \nabla \Psi^* \cdot \nabla \Psi + \Psi^* V \Psi \right)}{\int d^3 r \Psi^* \Psi}$$

Substituting (1) into (3) leads to explicit form of $E(\kappa, \beta)$:

$$\frac{4ma^2}{\hbar^2} E(\kappa, \beta) = \delta(x, \beta) = \frac{x^2 f(x, \beta)}{x^2 + 6x + 12}$$

where $x = 2a\kappa$ is a dimensionless variational parameter and $\delta(x, \beta)$ is the dimensionless variational energy. The
function \( f(x, \beta) \) can be written in the form
\[
f(x, \beta) = -\Omega x^3 + (1/2 - \Omega - \Lambda \xi)x^2 + \alpha x + (\Omega x^3 + (2\Omega + \Lambda \xi)x^3)xe^x - E_1(x) \tag{5}
\]
where
\[
\Omega = \frac{me^2 \alpha}{\hbar^2 a^2}, \tag{6}
\]
\[
\Lambda = 2 \frac{meQ}{\hbar^2 a}, \tag{7}
\]
\[
\xi = \beta \sqrt{\frac{1 - \beta^2}{5}} + \frac{\beta^2}{3}, \tag{8}
\]
and
\[
E_1(x) = \int_x^\infty dt \frac{e^{-t}}{t} \tag{9}
\]
is the exponential integral [12].

Variation of the energy [3] with respect of the parameters \( x \) and \( \beta \) requires that
\[
\frac{\partial \mathcal{E}(x, \beta)}{\partial x} = 0, \quad \frac{\partial \mathcal{E}(x, \beta)}{\partial \beta} = 0.
\]

Solving these equations for \( x \) and \( \beta \) would lead to the ground state energy \( \mathcal{E}(x_0, \beta_0) \) of the positron in an atom specified by three parameters, the cut-off parameter \( a \), the polarizability \( \alpha \), and quadrupole moment \( Q \).

Partial derivative of the energy [4] with respect to \( \beta \) leads to
\[
\frac{\partial \mathcal{E}}{\partial \beta} = \Lambda \frac{\partial \xi}{\partial \beta} (xe^x E_1(x) - 1)x^2 + x + 24\beta = 0. \tag{10}
\]

This equation can be used to express \( \beta \) in terms of the other parameter \( x \),
\[
\beta = \pm \sqrt{(1 \pm \lambda(x))/2}, \tag{11}
\]

where \( \lambda(x) \) is a simple function of \( x \):
\[
\lambda(x) = \left[ 1 - \frac{1}{1 + x + 5 \left( \frac{\hbar^2}{2m} \frac{\alpha}{Q} \sqrt{g(x)} + \frac{\beta}{5} \right)} \right]. \tag{12}
\]
The function \( g(x) = (xe^x E_1(x) - 1)x^2 + x \) is the same as the \( x \)-dependent part of the equation [10], it is positive for all \( x > 0 \) and \( g(x) \sim 2 \) asymptotically at \( x \to \infty \).

We substitute the expression [11] for \( \beta \) into second variational equation \( \frac{\partial \mathcal{E}}{\partial x}(x, \beta(x)) = 0 \). For each root \( x_0 \) of this equation there are four different values of \( \beta \) found from Eq. [11].

Final equation to solve for the extrema of the energy, which depends only on \( x \) after substituting \( \beta(x) \), has the form
\[
-(\Omega/2)x^4 + (1 - 4\Omega - 5\Lambda \xi)x^3 + (1 - 12\beta^2 + 3\Lambda \xi)x^2 + (4 + 3\beta^2)x + (6\Omega x^4 + 5(2\Omega + \Lambda \xi)x^3)xe^x E_1(x) =
\]
\[
-\Omega x^5 + (1/2 - \Omega - \Lambda \xi)x^4 + (1 + \Lambda \xi)x^3 + 2(1 + 6\beta^2)x^2 + (\Omega x^5 + (2\Omega + \Lambda \xi)x^4)xe^x E_1(x) =
\]
\[
-x^2 + 4x + 6
\]
\[
x^2 + 6x + 12 \tag{13}
\]

This equation is to be solved numerically for the roots \( x = x_0 \) if they exist.

### III. RESULTS AND DISCUSSION

To use Eq. [13] for calculation of the positron energy we need to know atomic polarizability \( \alpha \), atomic quadrupole moment \( Q \) and the value of the cut-off parameter \( a \) of the trial positron wave function [1]. For polarizabilities and quadrupole moments we use the values which can be found in the literature (either experimental or theoretical) and we treat the cut-off parameter \( a \) as a fitting parameter. We choose its value to fit the most accurate calculations of the positron energy. The value of the quadrupole contribution is found as a difference between the energy at given value of the quadrupole moment and the value found at \( Q = 0 \).

In cases when atomic polarizability or quadrupole moment cannot be found in the literature we calculate them using the configuration interaction (CI) technique [21, 22]. Static scalar polarizability of an atom in a state \( \gamma \) is given by
\[
\alpha_\gamma = \frac{2}{3(2J_\gamma + 1)} \sum_n \frac{(\gamma||D||n)^2}{E_\gamma - E_n}, \tag{14}
\]
TABLE I: Energy shift, $\Delta E$ of a bound positron in an atom due to the electric quadrupole moment $Q$ of the atom. $J$ is the ionization energy and $\alpha$ is the static dipole polarizability of the atomic state. The parameter $a$ included in the positron trial function shows the minimal distance between the positron and the nucleus. $E$ is the positron energy without quadrupole contribution except Be atom case where the quadrupole effect has already been included in the positron energy. [19]

| $Z$ | Atom | state | $I^z$ (eV) | $\alpha^a$ (a.u.) | $a$ (a.u.) | $Q$ (a.u.) | $E^b$ (meV) | $\Delta E$ (meV) |
|-----|------|-------|------------|----------------|-----------|-----------|-----------|-------------|
| 66  | Dy   | $4f_{10} 6s^2 \ 5I_s$ | 5.939      | 162.02        | 2.587     | 0.0234    | -1438     | -5.36$x10^{-4}$ |
| 68  | Er   | $4f_{12} 6s^2 \ 3H_6$ | 6.107      | 150.12        | 2.530     | 0.0139    | -1346     | -1.98$x10^{-4}$ |
| 77  | Ir   | $5d^7 6s^2 \ 2F_{9/2}$ | 8.967      | 50.26         | 1.8606    | 0.75      | -101      | -0.6549     |

| Ground states | Excited states |
|---------------|----------------|
| 4 Be 2s2p 3P_2 | 6.597 38.33 1.60774 4.28 -236 | -41.98 |
| 13 Al 3s^2 3p 2P^o | 5.972 44.97 1.81304 5.6, 5.06 | -0 | -28.67 |
| 49 In 5s^2 5p 2F^o | 5.512 67.45 2.13042 5.88 | -114 | -23.15 |

$\alpha^a = \sqrt{\frac{\langle \gamma \parallel r^2 \parallel \gamma \rangle}{\langle \gamma \parallel J \parallel J \rangle}}(2J + 1)(2J_i + 1)$ (15)

Here $|\gamma\rangle$ and $|n\rangle$ are many-electron states found in the CI calculations.

About half of all atoms do not have quadrupole moments in the ground state due to small value of the total angular momentum $J$ (one needs $J \geq 1$). Atoms with open $d$ or $f$ shells have large angular momenta. In Table I we present three such examples, Dy, Er, and Ir atoms. Polarizabilities $\alpha$ are taken from Ref. [13], quadrupole moments $Q$ are calculated using the CI technique, the cut-off parameter $a$ is chosen to fit calculated positron energies presented in Ref. [1]. Since the calculations in [1] are done under assumption that the positron is in s wave and therefore cannot interact with the atomic quadrupole moment the fitting is done for $Q = 0$. After the cut-off parameter $a$ is found, Eq. (13) with values of $Q$ from the table is used to calculate new bound energies. The resulting energy shift $\Delta E$ is the quadrupole contribution to the energy. We see that it is small in all three cases. This justifies neglecting the quadrupole contribution in calculations of Ref. [1].

Small value of the quadrupole contribution means that it can be treated by means of the perturbation theory. The first-order contribution for positron in s wave is zero, therefore expansion starts from the second order and quadrupole contribution is proportional to the square of the quadrupole moment. Using Ir atom as a reference point we can estimate the quadrupole contribution to the positron energy level for any atom with a small quadrupole moment:

$$\Delta E = -0.6549 \left( \frac{Q}{0.75} \right)^2 \text{meV}, \quad (16)$$

where $Q$ is in atomic units ($ea_0^3$). The values given by this formula differ from those presented in Table I by 13% for Er and 19% for Dy. We expect similar accuracy for other atoms with small quadrupole moments.

In Table I we also present three other results for the quadrupole contribution to the positron energy. We consider excited state of Be atom for which accurate calculations of the positron energy is available [19] and we consider upper $(2P_3/2)$ components of the fine structure doublets of the ground $p$ state of Al and In. In all these cases the value of the quadrupole moment is relatively large. So is the quadrupole shift. The case of Be atom is interesting because the quadrupole contribution makes important difference for the positron energy. The calculated energy [19] (-236 meV) relative to the atom plus free positron does include the quadrupole contribution. However, if this contribution is neglected, the system becomes unstable against emission of positronium ($\text{Be}+e^+ \rightarrow \text{Be}^+ + \text{Ps}$).

In some excited atomic states the polarizability may be very small or even negative [22]. Therefore, it is interesting to check if the quadrupole alone (for $a = 0$) may provide the positron binding. We use Eq. (13) to estimate what value of the quadrupole moment is needed to provide the positron binding. Fig. I shows a plot of the quadrupole moment corresponding to the $-100$ meV positron energy as a function of the cut-off parameter $a$. We use an estimation $a \sim 1/I$ to find reasonable range of values for $a$. Here $I$ is ionization potential, and both values $a$ and $I$ are in atomic units. We see that required
values of the quadrupole moments are large. No atom in the ground state has so large quadrupole moment. However, quadrupole moment can be large in excited state, $Q \sim \nu^4$, where $\nu$ is the effective principle quantum number ($E = -1/(2\nu^2)$). Large values of $Q$ proportional to their squared size may also exist in molecules.

IV. CONCLUSION

A simple quantum mechanical variational method is used to estimate the contribution of the positron interaction with atomic quadrupole moment to the positron energy in an atom. It is found that the contribution is small for the binding in the ground state. This validates the calculations in which this contribution is neglected. The quadrupole contribution can be significant in excited states. For example, in excited state of beryllium it makes a difference between a bound state and decay into beryllium positive ion and positronium.

Quadrupole contribution can probably play important role in positron binding to molecules which have large quadrupole moments.

Acknowledgments

This work was funded by the Australian Research Council.

[1] C. Harabati, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A 89, 022517 (2014).
[2] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B: At. Mol. Opt. Phys. 35, R81 (2002).
[3] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and C. Harabati, Phys. Rev. A 86, 032503 (2012).
[4] G. G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. 79, 4124 (1997).
[5] K. Strasburger and H. Chojnacki, J. Chem. Phys. 108, 3218 (1998).
[6] J. Mitroy, J. Y. Zhang, M. W. J. Bromley, and S. I. Young, Phys. Rev. A 78, 012715 (2008).
[7] M. W. J. Bromley and J. Mitroy, Phys. Rev. A 81, 052708 (2010).
[8] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, Phys. Rev. A 52, 4541 (1995).
[9] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and C. Harabati, Phys. Rev. A 60, 3641 (1999).
[10] V. A. Dzuba, V. V. Flambaum, and C. Harabati, Phys. Rev. A 62, 042504 (2000).
[11] V. A. Dzuba, V. V. Flambaum, W. A. King, B. N. Miller, and O. P. Sushkov, Phys. Scr. T46, 248 (1993).
[12] M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions: with Formulas, Graphs, and Mathematical Tables, (Dover, New York, 1972), Chap. 5.
FIG. 1: The required electric quadrupole moment $Q$ versus the small distance cut-off parameter of the positron wave function, $a$, in a.u., to get a bound state with the energy $E = -100$ meV. The dipole polarizability is assumed to be zero, $\alpha = 0$. 