# Electric polarizability of the hydrogen atom: classical variational approaches

#### Notes by:

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#### Abstract

A simple variational approach to the electric polarizability of the hydrogen atom is discussed within a classical picture. The deformation of the electron cloud can be discussed in detail and compared with quantum mechanical results. Step by step the approach is applied to simple rigid sphere cloud and developed to include radial dependence and deformation. If applied consistently to the electron cloud as it emerges from quantum calculations, the exact predictions for the electric polarizability are reproduced within 3% of accuracy. Also the deformations induced by the external field are quite close to the exact results.

## 1 Introduction

The electric polarizability  $\alpha$  of a system measures *how easily* an electric dipole moment can be induced on that system by an external (static) electric field and represents one of its fundamental (electromagnetic) properties. In particular *how easily* means how much work is needed to induce the dipole moment and is related to the basic features of the model description of the system.

A classical exercise is the evaluation of  $\alpha$  for the simplest atom: the hydrogen, and it represents a first example of *linear* response of a system to an external field. Many textbooks (e.g ref.[1]) discuss a classical approach to  $\alpha$  assuming that the hydrogen can be approximated by a static charge distribution where the electron density is spherically symmetric and uniform within a radius R, and the pointlike proton occupies, in absence of external field, the equilibrium position at the center. Assume that when the external field  $\mathcal{E}$  is applied (in the positive z-direction) the electron cloud is merely displaced (keeping its form and density) in such a way that the nucleus occupies a new equilibrium position at a relative distance  $\xi$  with respect the center of the homogeneous sphere [2]. A simple calculation of the forces acting on the positive charge gives  $\alpha = R^3$  (Gaussian units are used).

The same example could be discussed from a variational point of view considering the work made to induce the electric dipole moment or, equivalently, the variation of the total energy  $\Delta E(\xi)$  due to the presence of the electric field. One can write

$$\Delta E(\xi) = E_{\text{tot}} - E_0 = L(\xi) + E_{\text{int}}(\xi) \tag{1}$$

where  $L(\xi)$  is the work done to shift the relative position of the positive charge e of a quantity  $\xi$ ,

$$L(\xi) = \int_0^{\xi} \frac{e^2}{R^3} r \, dr = \frac{1}{2} \frac{e^2}{R^3} \xi^2 \,, \qquad (2)$$

and  $E_{\text{int}}(\xi)$  the interaction energy of the *polarized* hydrogen ( $D_z$  is the induced dipole moment) with the external field

$$E_{\rm int}(\xi) = -D_z \mathcal{E} = -e\,\xi\,\mathcal{E} \ . \tag{3}$$

 $E_0$  is the energy of the isolated hydrogen [3].

The minimum value of the total energy is obtained for  $dE_{\text{tot}}(\xi)/d\xi = 0$ which gives

$$\xi_{\rm eq} = \frac{R^3}{e} \mathcal{E} \tag{4}$$

for the equilibrium value of  $\xi$ . Consequently the induced dipole moment and the total energy result

$$D_z = e \xi_{eq} = R^3 \mathcal{E} \equiv \alpha \mathcal{E}$$
  

$$E_{tot} = E_0 + E_{int}(\xi_{eq}) + L(\xi_{eq}) = E_0 - \frac{1}{2}R^3 \mathcal{E}^2 \equiv E_0 - \frac{1}{2}\alpha \mathcal{E}^2 \qquad (5)$$

which define the electric polarizability

$$\alpha = R^3 . (6)$$

Even if it has been demonstrated in this particular example, the result that the total energy is lowered by the interaction with the external field (cfr.Eq.(5)) is quite general. However the use of a restricted class of deformation induced by the electric field (namely the assumption of a rigid shift of the electron cloud) makes the variational calculation an approximation which leads to an upper limit for the energy variation and, consequently, the estimated polarizability  $\alpha$  represents a lower bound to the exact value.

Moreover the simple result (6) does not take into account two relevant facts, namely: i) the electron density distribution is not uniform; ii) it can be deformed (with respect its spherical shape) under the influence of the external field.

# 2 Classical variational approaches

In order to introduce a more flexible and general formalism including the contributions due to the density diffuseness and to the induced deformations, let me assume that the electron density is described by a function  $\rho_0(\mathbf{r})$  for  $\mathcal{E} = 0$  (no external electric field) and  $\rho_{\mathcal{E}}(\mathbf{r})$  when  $\mathcal{E} \neq 0$ . The total energy of the system will result [4]

$$E_{\text{tot}} = \int d\mathbf{r} \, \frac{e}{r} \, \varrho_{\mathcal{E}}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \, \frac{\varrho_{\mathcal{E}}(\mathbf{r}) \, \varrho_{\mathcal{E}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \mathcal{E} \int d\mathbf{r} \, z \, \varrho_{\mathcal{E}}(\mathbf{r})$$
  
=  $E_1 + E_2 + E_{\text{int}} , \qquad (7)$ 

where the first term  $(E_1)$  embodies the interaction energy between the pointlike proton and the electron density, the second contribution  $(E_2)$  is the work done to build up the electron cloud, and the last contribution  $(E_{int})$  is the interaction with the external field of the induced dipole moment  $D_z = \int d\mathbf{r} z \, \varrho_{\mathcal{E}}(\mathbf{r})$ . (Since  $\varrho_0(\mathbf{r})$ , is spherically symmetric,  $\int d\mathbf{r} z \, \varrho_0(\mathbf{r}) = 0$ ).

In order to discuss first the effects of the electron density diffuseness let me assume  $\rho_{\mathcal{E}}(\mathbf{r})$  being still spherically symmetric and that the effect of the external field is again approximated by a rigid shift of the electron cloud. As a consequence the electron density, in the presence of the external field, is described by  $\rho_{\mathcal{E}}(\mathbf{r}) = \rho_0(\mathbf{r} + \xi \hat{z})$  and the total energy variation can be written

$$\Delta E(\xi) = e \int d\mathbf{r} \left[ \frac{\varrho_{\mathcal{E}}(\mathbf{r})}{r} - \frac{\varrho_0(\mathbf{r})}{r} \right] - \mathcal{E} \int d\mathbf{r} \, z \, \varrho_{\mathcal{E}}(\mathbf{r}) \,. \tag{8}$$

The first term is the variation of the interaction energy between the pointlike proton and the electron cloud, and the last term is the contribution due to the interaction of the system with the external field. It should be stressed that the  $E_2$  term of Eq.(7) does not contribute to the energy variation (8). In fact if the effect of the external field is approximated by a rigid displacement, no additional work is needed to deform the electron cloud. For small  $\xi$  the following expansion up to second order holds

$$\varrho_{\mathcal{E}}(\mathbf{r}) = \varrho_0(\mathbf{r} + \xi \,\hat{z}) = \varrho_0(r) + \xi \nabla_z \varrho_0(r) + \frac{1}{2} \xi^2 \nabla_z^2 \varrho_0(r) , \qquad (9)$$

and consequently one gets

$$\Delta E(\xi) = \Delta E_1(\xi) + \Delta E_{\text{int}}(\xi) = \frac{1}{6} e \xi^2 \int d\mathbf{r} \frac{1}{r} \nabla^2 \varrho_0(r) - \xi \mathcal{E} \int d\mathbf{r} \, z \, (\nabla_z \varrho_0(r)) \\ = -\frac{1}{6} e \, \xi^2 4 \pi \varrho_0(0) - e \, \xi \, \mathcal{E} \, , \qquad (10)$$

where the relation  $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$  have been used together with the assumption of spherical symmetry for  $\rho_0(r)$ . Once again minimizing the total energy variation (10) one obtains the equilibrium parameter  $\xi_{\rm eq}$  and the polarizability

$$\alpha = -\frac{3}{4\pi} \frac{e}{\varrho_0(0)} \,. \tag{11}$$

The results (11) generalizes Eq.(6) and reduces to  $\alpha = R^3$  in the limiting case of constant density ( $\rho_0(r) = \rho_0(0) = -e 3/4\pi R^3$ ). Assuming for the functional form of the electron density the quantum solution  $\rho_0(r) =$  $(-e/\pi a_0^3) \exp(-2r/a_0)$ , one has  $\rho_0(0) = -e/\pi a_0^3$  and, consequently,

$$\alpha = \frac{3}{4}a_0^3 \ . \tag{12}$$

The previous result is quite far from the exact quantum mechanical prediction [5]

$$\alpha_{\text{exact}} = \frac{9}{2}a_0^3 \ . \tag{13}$$

and the discrepancy cannot be ascribed to the fact that one did not make use of quantum mechanics, but to the neglected deformation of the electronic density. Indeed the same prediction (12) can obtained within a rigorous quantum framework assuming a rigid shift of the spherical electron density [6].

#### 2.1 Effects of the density deformation

In order to introduce the effects due to the density deformation induced by the external field one can make the assumption

$$\varrho_{\mathcal{E}}(\mathbf{r}) = \frac{1}{N} \left[ 1 + aF(\mathbf{r}) \right]^2 \varrho_0(\mathbf{r}) \tag{14}$$

with  $\int d\mathbf{r} \rho_0(\mathbf{r}) = \int d\mathbf{r} \rho_{\mathcal{E}}(\mathbf{r}) = -e$  and consequently  $N = \int d\mathbf{r} [1+aF(\mathbf{r})]^2 \rho_0(\mathbf{r}) = 1 + a^2 \langle F^2 \rangle$  where  $\langle F^2 \rangle = \int d\mathbf{r} F^2(\mathbf{r}) \rho_0(\mathbf{r})$  and  $\int d\mathbf{r} F(\mathbf{r}) \rho_0(\mathbf{r}) = 0$  [7]. Eq.(14) is assumed to be valid up to second order corrections in the variational parameter a, and therefore

$$\varrho_{\mathcal{E}}(\mathbf{r}) = \left\{ 1 + 2aF(\mathbf{r}) + a^2 \left[ F^2(\mathbf{r}) - \langle F^2 \rangle \right] \right\} \varrho_0(\mathbf{r}) \\
= \varrho_0(\mathbf{r}) + \delta \varrho_{\mathcal{E}}(\mathbf{r}) .$$
(15)

The total energy variation and the induced dipole moment can be written (cfr. Eq.(7))

$$\Delta E_{\text{tot}} = \int d\mathbf{r} \, \frac{e}{r} \, \delta \varrho_{\mathcal{E}}(\mathbf{r}) + \int \frac{d\mathbf{r} \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \left[ \varrho_0(\mathbf{r}) \delta \varrho_{\mathcal{E}}(\mathbf{r}') + \frac{1}{2} \delta \varrho_{\mathcal{E}}(\mathbf{r}) \delta \varrho_{\mathcal{E}}(\mathbf{r}') \right] - \mathcal{E} \int d\mathbf{r} \, z \, \delta \varrho_{\mathcal{E}}(\mathbf{r}) = \Delta E_1 + \Delta E_2 + \Delta E_{\text{int}} , \qquad (16)$$

and

$$D_z = \int d\mathbf{r} \, z \, \delta \varrho_{\mathcal{E}}(\mathbf{r}) \, . \tag{17}$$

The internal energy variation  $(\Delta E_1 + \Delta E_2)$  must result quadratic in the variational parameter a. In fact  $\rho_0(\mathbf{r})$  is the equilibrium density for  $\mathcal{E} = 0$  and consequently the minimum value of  $\Delta E_1 + \Delta E_2$  must be recovered at a = 0. In contrast the variation of the interaction energy will be linear in the same parameter. This feature is common to all the variational calculations of the form (14) and leads to

$$\Delta E_{\text{tot}} = \frac{a^2}{2} C_{aa} - 2 \, a \, \mathcal{E} \, C_a \, . \tag{18}$$

Minimizing the energy variation one finally gets

$$\alpha = 4 \frac{C_a^2}{C_{aa}} . \tag{19}$$

In the following I will discuss results obtained for different choices of  $F(\mathbf{r})$ . i)  $F(\mathbf{r}) = z = rP_1(\cos\theta)$ . In this case

$$\delta \varrho_{\mathcal{E}}(\mathbf{r}) = \left\{ 2az + a^2 \left[ z^2 - a_0^2 \right] \right\} \varrho_0(\mathbf{r}) \tag{20}$$

and one gets (the appendix contains the relevant formulas needed for the evaluation of the  $\Delta E_2$  contribution)

$$\Delta E_1 = \frac{1}{2}a^2 e^2 a_0; \quad \Delta E_2 = a^2 e^2 a_0 \left[ -\frac{3}{16} + \frac{7}{48} \right]; \quad \Delta E_{\text{int}} = 2 \, a \, \mathcal{E} \, e \, a_0^2 \, . \tag{21}$$

and the polarizability

$$\alpha = \frac{48}{11} a_0^3 , \qquad (22)$$

a result which improves the prediction (12) (which neglects the deformation induced on the electron cloud) by almost a factor 6, and is only 10% larger than the quantum calculation obtained imposing the same deformation [6].

ii)  $F(\mathbf{r}) = rz = r^2 P_1(\cos \theta)$ . In this case

$$\delta \varrho_{\mathcal{E}}(\mathbf{r}) = \left\{ 2 \, a \, r \, z + a^2 \left[ r^2 \, z^2 - \frac{15}{2} a_0^2 \right] \right\} \varrho_0(\mathbf{r}) \tag{23}$$

and one obtains

$$\Delta E_1 = 5 a^2 e^2 a_0^3; \quad \Delta E_2 = a^2 e^2 a_0^3 \left[ -\frac{585}{256} + \frac{185}{384} \right]; \quad \Delta E_{\text{int}} = 5 a \mathcal{E} e a_0^3$$
(24)

Table 1: Summary of the contributions to the energy variation coming from the various terms of Eq.(16) and for different choices of the deformation operator  $F(\mathbf{r})$ . The  $\Delta E_2$  part has been separated in the two contributions as in Eq.(16).

	$F(\mathbf{r}) = z$	$F(\mathbf{r}) = r z$	$F(\mathbf{r}) = r^2 z$	$F(\mathbf{r}) = r^3 z$
$\Delta E_1/a^2$	$\frac{1}{2}e^2a_0$	$5 e^2 a_0^3$	$\frac{315}{4}e^2a_0^5$	$1890  e^2 a_0^7$
$\Delta E_2/a^2$	$ \begin{pmatrix} -\frac{3}{16} + \\ +\frac{7}{48} \end{pmatrix} e^2 a_0 $	$ \begin{pmatrix} -\frac{585}{256} + \\ +\frac{185}{384} \end{pmatrix} e^2 a_0^3 $	$ \begin{pmatrix} -\frac{40635}{1024} + \\ +\frac{165}{64} \end{pmatrix} e^2 a_0^5 $	$\begin{array}{l} \left(-\frac{4119255}{4096} + \right. \\ \left. +\frac{41685}{2048}\right) e^2 a_0^7 \end{array}$
$\Delta E_{\rm int}/a\mathcal{E}$	$2 e a_0^2$	$5 e a_0^3$	$15  e  a_0^4$	$\frac{105}{2} e a_0^5$
$lpha/a_0^3$	$\frac{48}{11}$	$\frac{1920}{491}$	$\frac{7680}{2843}$	$\frac{53760}{35291}$

and the polarizability

$$\alpha = \frac{1920}{491} a_0^3 . \tag{25}$$

iii) The values (22) and (25) represent rather good lower bound to the exact result and one can guess that increasing the power of r would improve the agreement. Assume then  $F(\mathbf{r}) = r^n z = r^{n+1} P_1(\cos \theta)$ . The results are summarized in table 1. The closest predictions with respect to the exact result are obtained for n = 0 and n = 1 (i.e. for the choices discussed in i) and ii)), while for larger values of n the polarizability is strongly underestimated.

iv) As final example a linear combination of the most favorable assumptionsi) and ii) can be made, namely

$$a F(\mathbf{r}) \to az + b rz$$
, (26)

where a and b are variational parameters. The generalization of Eq.(18) for the total energy variation reads

$$\Delta E_{\text{tot}} \equiv \Delta E_1 + \Delta E_2 + \Delta E_{\text{int}} = \frac{a^2}{2} C_{aa} + \frac{b^2}{2} C_{bb} + ab C_{ab} - 2\mathcal{E} \left[ a C_a + b C_b \right] .$$
(27)

Minimizing the total energy variation (27) with respect to both the parameters a and b, one finds the equilibrium values

$$a_{eq} = 2 \frac{C_a C_{bb} - C_b C_{ab}}{C_{aa} C_{bb} - C_{ab}^2} \mathcal{E}$$
  

$$b_{eq} = 2 \frac{C_b C_{aa} - C_a C_{ab}}{C_{aa} C_{bb} - C_{ab}^2} \mathcal{E} , \qquad (28)$$

which leads to the polarizability

$$\alpha = \frac{2}{\mathcal{E}} \left( a_{\rm eq} \, C_a + b_{\rm eq} \, C_b \right) \ . \tag{29}$$

In our particular case one obtains

$$\Delta E_{1} = e^{2} \left[ \frac{1}{2} a^{2} a_{0} + 5 b^{2} a_{0}^{3} + \frac{4}{3} a b a_{0}^{2} \right]$$

$$\Delta E_{2} = e^{2} \left[ \left( -\frac{3}{16} + \frac{7}{48} \right) a^{2} a_{0} + \left( -\frac{585}{256} + \frac{185}{384} \right) b^{2} a_{0}^{3} + \left( -\frac{43}{192} + \frac{77}{96} \right) a b a_{0}^{2} \right]$$

$$\Delta E_{\text{int}} = e \left[ 2 a a_{0}^{2} + 5 b a_{0}^{3} \right] \mathcal{E}$$
(30)

and for the polarizability

$$\alpha = \frac{126080}{27117} a_0^3 \approx 4.65 a_0^3 . \tag{31}$$

The result (31) is the (classical) counterpart of the quantum exact prediction and it differs from that by 3% only. In fact the quantum value (13) can be found also within quantum variational approach which assumes a density deformation of the form given in Eq.(26) [8]. However the equilibrium values of the variational parameters as well as the normalization coefficient N differ in quantum and classical calculations. Specifically in the quantum calculation one gets

$$a_{\rm eq} = -a_0 \frac{\mathcal{E}}{e}$$
 and  $b_{\rm eq} = -\frac{1}{2} a_0 \frac{\mathcal{E}}{e}$ , (32)

and

$$\varrho_{\mathcal{E}}(\mathbf{r}) = -\frac{1}{N} \left[ 1 - \frac{\mathcal{E}}{e} \left( a_0 + \frac{1}{2} r \right) z \right]^2 \varrho_0(\mathbf{r}) , \qquad (33)$$

where  $N = 1 + \frac{43}{8} \left(\frac{\mathcal{E}}{e}\right)^2 a_0^4$ .

In the classical calculation the same parameters result

$$a_{\rm eq} = -\frac{39680}{27117} a_0 \frac{\mathcal{E}}{e} \approx -1.463 a_0 \frac{\mathcal{E}}{e} \quad \text{and} \quad b_{\rm eq} = -\frac{9344}{27117} \frac{\mathcal{E}}{e} \approx -0.345 a_0 \frac{\mathcal{E}}{e} ,$$
(34)

and

$$\varrho_{\mathcal{E}}(\mathbf{r}) = -e|\phi_{\mathcal{E}}(\mathbf{r})|^2 = \frac{1}{N} \left[ 1 - \frac{\mathcal{E}}{e} \left( 1.463 \, a_0 + 0.345 \, r \right) z \right]^2 \varrho_0(\mathbf{r}) \,, \qquad (35)$$

respectively. In the present case  $N = 1 + 5.553 \left(\frac{\varepsilon}{e}\right)^2 a_0^4$ .

Of course if one assume for the classical density the deformation obtained from the quantum calculation, one would reproduce exactly the prediction (13). However one cannot expect to reproduce the same value when the energy variation is evaluated classically. The reason has to do with the different assumptions on the kinetic energy variation. In fact the classical model is static and does not consider the motion of the electron, on the contrary the quantum calculation includes kinetic energy variations due to the deformation of the electron density (or wave function) [9].

#### 2.2 Charge density distribution

The differences (and analogies) between the classical and quantum results can be better appreciated comparing the charge density distribution of the electron as predicted in the two cases. The classical solution (35) for the deformed electron density and the analogous quantum result (33) differ only slightly as can be seen from Figs. 1, where the polar plots ( $\mathcal{P}_{\mathcal{E}}(r,\theta),\theta$ ) for both classical and quantum solutions, are compared with the analogous results for the spherical unperturbed solution  $\mathcal{P}_0(r)$  for  $r = \sqrt{3}/2 a_0$ ,  $r = \sqrt{3} a_0$ ,  $r = 2\sqrt{3} a_0$ , and  $r = 3\sqrt{3} a_0$ (note that  $\sqrt{\langle r^2 \rangle} = \sqrt{3} a_0$ ).  $\mathcal{P}_0(r)$  represents the one-dimensional density probability

$$\mathcal{P}_0(r) = \left(\frac{1}{-e}\right) 4\pi r^2 \varrho_0(r) .$$
(36)

Normalization is such that  $\int \mathcal{P}_0(r) \frac{d\Omega}{4\pi} dr = 1$ , and  $\mathcal{P}_{\mathcal{E}}(r,\theta)$  is its deformed analogous

$$\mathcal{P}_{\mathcal{E}}(r,\theta) = \left(\frac{1}{-e}\right) \, 4 \, \pi \, r^2 \, \varrho_{\mathcal{E}}(r,\theta) \tag{37}$$

normalized in the same way  $\int \mathcal{P}_{\mathcal{E}}(r,\theta) \frac{d\Omega}{4\pi} dr = 1$ . In order to show clearly the effects of deformations,  $\mathcal{P}_{\mathcal{E}}(r,\theta)$  is calculated assuming a rather strong external electric field, which, however, still fulfills the requirement of perturbation theory. In practice the typical value of the energy interaction  $\mathcal{E} D_z \equiv e \mathcal{E} a_0$  must be much less than the total unperturbed ground state energy  $e^2/2a_0$ . The choice of Fig. 1 is  $e \mathcal{E} a_0 = 0.1 \times e^2/2a_0 = 0.1 \times 13.6 \, eV$  which defines the value of the electric field  $\mathcal{E}$ .

In Fig. 2 the spherical probability density  $\mathcal{P}_0(r)$  is also shown to visualize the points of the polar plots (asterisks).

One can easily conclude that the classical (and quantum) solutions are more and more deformed increasing the radial distance, and that the classical calculation approximate the quantum exact solution in a quite good way.

# Appendix

In order to evaluate the term

$$\Delta E_2 = \int \frac{d\mathbf{r} \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \left[ \varrho_0(\mathbf{r}) \, \delta \varrho_{\mathcal{E}}(\mathbf{r}') + \frac{1}{2} \delta \varrho_{\mathcal{E}}(\mathbf{r}) \, \delta \varrho_{\mathcal{E}}(\mathbf{r}') \right] \tag{1}$$

of Eq.(16) one should use the expansion

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r} \sum_{n=0}^{\infty} \left(\frac{r'}{r}\right)^n P_n(\cos\theta) P_n(\cos\theta') \quad \text{if } r > r'$$
$$= \frac{1}{r'} \sum_{n=0}^{\infty} \left(\frac{r}{r'}\right)^n P_n(\cos\theta) P_n(\cos\theta') \quad \text{if } r' > r ,$$

the integral properties of the Legendre polynomials  $P_n(u)$ 

$$\int_{-1}^{+1} du P_n(u) P_m(u) = \delta_{nm} \frac{2}{2n+1}$$
(2)

and the equalities

$$z = r P_1(\cos \theta); \quad P_1^2(u) = \frac{1}{3} \left[ 2 P_2(u) + 1 \right] .$$
 (3)

An example

$$\Delta E_2^{(1)} = \int \frac{d\mathbf{r} \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \, \varrho_0(\mathbf{r}) \, \delta \varrho_{\mathcal{E}}(\mathbf{r}') \, . \tag{4}$$

Only the second order terms in  $\delta \varrho_{\mathcal{E}}(\mathbf{r})$  will contribute and one gets:

$$\Delta E_2^{(1)} = a^2 \left(\frac{-e}{\pi a_0^3}\right)^2 (2\pi)^2 \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} e^{-2r/a_0} e^{-2r'/a_0} \times \left[\frac{2}{3}r^2 P_2(\cos\theta) - \left(a_0^2 - \frac{1}{3}r'^2\right)\right] d(\cos\theta) d(\cos\theta') r^2 dr r'^2 dr'$$

$$= a^{2} \left(\frac{-e}{\pi a_{0}^{3}}\right)^{2} (2\pi)^{2} \left[ -4 \int_{0}^{\infty} r^{2} dr e^{-2r/a_{0}} \int_{0}^{r} r'^{2} dr' \frac{1}{r} e^{-2r'/a_{0}} \left(a_{0}^{2} - \frac{1}{3}r'^{2}\right) -4 \int_{0}^{\infty} r^{2} dr e^{-2r/a_{0}} \int_{r}^{\infty} r'^{2} dr' \frac{1}{r'} e^{-2r'/a_{0}} \left(a_{0}^{2} - \frac{1}{3}r'^{2}\right) \right]$$

$$= -\frac{1}{2} a^{2} e^{2} a_{0} \left[ \int_{0}^{\infty} x dx e^{-x} \int_{0}^{x} dx' e^{-x'} \left( x'^{2} - \frac{1}{12} x'^{4} \right) + \int_{0}^{\infty} x^{2} dx e^{-x} \int_{x}^{\infty} dx' e^{-x'} \left( x' - \frac{1}{12} x'^{3} \right) \right] .$$

The integrals are analytic and, for this simple case, can be easily performed obtaining

$$\Delta E_2^{(1)} = -\frac{1}{2} a^2 e^2 a_0 \left[\frac{3}{8}\right] \tag{5}$$

In the more complicate case of  $a F(\mathbf{r}) = a z r^n$  or  $a F(\mathbf{r}) \rightarrow a z + b z r$  a symbolic Mathematica code has been used.

### References

- Purcel E M 1965 Berkeley physics course (vol.2) Electricity and magnetism (New York: McGraw-Hill Book Company) p. 309
- [2] In the following the mass of the (pointlike) proton will be supposed much larger than the electron mass  $(m_e/m_p \rightarrow 0)$  in such a way that the center of mass of the system can be localized at the proton position.
- [3] Since we assumed pointlike proton  $E_0$  is not well defined. If one calculates the integral  $\int d\mathbf{r} \mathcal{E}^2/8\pi$  and subtracts the (infinite) contribution due to the pointlike charge  $\int d\mathbf{r} e^2/(8\pi r^2)$ , one gets  $E_0 = -9e^2/10R$  which is just the sum of the work done to build the electron distribution  $(3e^2/5R)$  and the interaction energy between the point-like proton and the electron cloud  $(-3e^2/2R)$ .
- [4] The infinite self-energy due to the assumed point-like structure of the proton has been subtracted.

- [5] Schiff L I 1968 Quantum Mechanics (McGraw-Hill Book Company), p. 263 267
- [6] Traini M 1996 Eur. J. Phys., 17, 30
- [7]  $F(\mathbf{r})$  can be written as  $F(\mathbf{r}) = f(r)P_1(\cos\theta)$  where  $P_1$  is the Legendre polynomial of order 1.
- [8] Pauling L and Wilson E B 1935 Introduction to Quantum Mechanics (McGraw-Hill Book Comp.) p. 180-206. More precisely the quantum deformation has to be associated with the perturbed wave function.
- [9] Classical and quantum variational results are identical if the assumed deformation does not change the mean value of the kinet energy as in the case of a rigid displacement of the electron cloud as described by Eq.(9).



Figure 1: Polar plots of the one-dimensional densities of Eq.(35). The deformed classical (continuous blue lines) solutions are compared with the spherical unperturbed results (dashed green lines) for radial distances :  $r = \sqrt{3}/2 a_0$  (a),  $r = \sqrt{3} a_0$  (b),  $2\sqrt{3} a_0$  (c) and  $3\sqrt{3} a_0$  (d).



Figure 2: Polar plots of the one-dimensional densities of Eq.(33). The deformed quantum solutions (continous red lines) are compared with the spherical unperturbed results (dashed green lines) for radial distances :  $r = \sqrt{3}/2 a_0$  (a),  $r = \sqrt{3} a_0$  (b),  $2\sqrt{3} a_0$  (c) and  $3\sqrt{3} a_0$  (d).



Figure 3: The radial one-dimensional density of Eq.(36) as function of the radial distance. The asterisks indicate the points of the polar plots (a, b, c, d) of Figs.(1),(2)