Electric polarizability of hydrogen atom: a sum rule approach

published: in Eur. J. Phys. 17 (1996) 30

Marco Traini a,b

^aDipartimento di Fisica, Università degli Studi di Trento, I-38050 Povo (Trento), Italy

^band Istituto Nazionale di Fisica Nucleare (INFN), G.C., Trento

Abstract

The sum rules technique is introduced in the context of the interaction of atoms with the electromagnetic radiation and used to study rigorous bounds to the electric dipole polarizability of the hydrogen atom.

(pacs: 32.60.+i; 35.10.Di)

(ICSU-AB: 32.60S; 35.10.D)

riassunto: La tecnica delle regole di somma viene introdotta nel contesto dell'interazione degli atomi con la radiazione elettromagnetica ed utilizzata per studiare dei limiti rigorosi per la polarizzabilià elettrica di dipolo dell'atomo di idrogeno.

1 Introduction

Hydrogen atom is traditionally a privileged system to be used for pedagogical introduction to the classical or quantum description of many microscopic phenomena. The response of an atom to a static electric field is one of these phenomena and represents a first example of linear response of a system to an external probe leading to the concept of electric polarizability. A classical estimate of this quantity can be obtained approximating the effect of the external electric field by a rigid shift of the electron cloud and would give (e.g. ref.[1]) $\alpha = R^3$ where R is the radius of the uniform electron density (gaussian units are used).

In quantum mechanics the calculation of α is connected to the change of the energy levels of the hydrogen caused by the uniform electric field of strength \mathcal{E} and is called *Stark effect*. The general framework to evaluate these changes is the (stationary) perturbation theory applied to the Hamiltonian

$$H(\mathcal{E}) = H_0 + H'(\mathcal{E}) = H_0 - \mathcal{E} D_z = \frac{\mathbf{p}^2}{2m_e} - \frac{e^2}{r} + e \mathcal{E} z , \qquad (1)$$

where the polar axis and the electric field \mathcal{E} are in the positive z-direction, e is the absolute value of the electron charge, m_e the electron mass, $D_z = -ez$ the induced electric dipole moment and \mathbf{r} the relative coordinate of the electron with respect to the atomic nucleus [2]. The (negative) lower order correction to the energy of the hydrogen ground state is quadratic in the perturbative electric field and defines the electric polarizability

$$\lim_{\mathcal{E}\to 0} \left\langle \mathcal{E} \right| H_0 + H'(\mathcal{E}) \left| \mathcal{E} \right\rangle = E_0 - \frac{1}{2} \alpha \mathcal{E}^2 , \qquad (2)$$

where $|\mathcal{E}\rangle$ is the ground state of $H(\mathcal{E})$, and $E_0 = -e^2/2a_0$ is the ground state energy value of the unperturbed Hamiltonian H_0 ($a_0 \equiv$ Bohr radius).

The polarizability α can be equivalently defined from the induced electric dipole moment as in the classical case, namely

$$\alpha = \lim_{\mathcal{E} \to 0} \frac{\langle \mathcal{E} | D_z | \mathcal{E} \rangle}{\mathcal{E}} .$$
(3)

Both eqs.(2) and (3) lead to the well know perturbative expression (we remind that $\langle 0|D_z|0\rangle = 0$ because of parity invariance)

$$\alpha = 2 \sum_{n \neq 0} \frac{|\langle n | D_z | 0 \rangle|^2}{E_n - E_0} .$$

$$\tag{4}$$

The explicit evaluation of eq.(4) involves the sum over the continuous part of the spectrum which accounts for approximately one-third of the value of α [3]. An elegant alternative solution for eq.(4) has been proposed by Dalgarno and Lewis in 1955 [4] by looking for an operator F which fulfills the requirement $\langle n|D_z|0\rangle/(E_n - E_0) = \langle n|F|0\rangle$ (for a detailed discussion and a complete list of references on the solution of eq.(4) see [3, 5]). The exact (analytic) value of α results

$$\alpha = \frac{9}{2}a_0^3 \ . \tag{5}$$

However in order to compare the previous result with the classical prediction $\alpha = R^3$ one has to note that the hard sphere radius R cannot be identified with the Bohr radius. Assuming a hard distribution which reproduces the root-mean-square radius of the hydrogen atom ($\langle \mathbf{r}^2 \rangle = 3a_0^2$) one obtains $R^2 = 5a_0^2$, and $\alpha = 5^{3/2}a_0^3$ which is (approximately) a factor 2.5 larger than the exact result. The remaining difference can be attributed (from a semiclassical point of view) to the deformation induced on the electron cloud by the external electric field.

Aim of the present paper is the introduction of the sum rule technique in the context of the interaction of the (hydrogen) atom with the electromagnetic radiation, a path which has also hystorical basis. However, in order to give a feeling of the power of the method, a specific problem will be investigated: the electric polarizability of the hydrogen atom. Since the solution of that problem is already well known within alternative and simple approaches (namely perturbative and variational), one can appreciate the peculiarity of the sum rule technique. Many aspects of the paper have a general validity and are not restricted to hydrogen which repesents an illustrative example. In order to make clear the distinction of what is true in general and what is special to the hydrogen atom, each section is splitted in two parts: General Results and Application to the hydrogen.

2 Electric dipole strength distribution, photoabsorption cross section and sum rules

2.1 General Results

Given a system governed by a Hamiltonian H_0 , the action of a perturbing external probe coupled to the system by the operator D_z can be generally written in terms of the so-called *response* or *strength distribution function* of the system

$$R^{D}(\omega) = \sum_{n=0}^{\infty} |\langle n|D_{z}|0\rangle|^{2} \,\delta(\omega - \omega_{n0}) \,\,, \tag{6}$$

where $|n\rangle$ and $E_n = \hbar \omega_n$ are the eigenstates and eigenvalues of the Hamiltonian H_0 , $(E_{n0} = \hbar \omega_{n0} = E_n - E_0)$, and $\hbar \omega$ is the energy transferred to the system. If the state $|n\rangle$ is in the continuum, the sum must be replaced by an integral together with an appropriate density of states.

Interpreting the operator D_z as the electric dipole moment induced by an external electromagnetic field, eq.(6) describes the strength distribution of the system to an external radiation of frequency ω in the long- wavelength approximation where the wavelength of the incident light is assumed to be large compared with the linear dimensions of the absorbing system. The δ -function in eq.(6) reflects the frequency condition originally postulated by Bohr $\hbar \omega = E_n - E_0$ (energy conservation). The total photoabsorption cross section (in long-wavelength or dipole approximation) can be written in terms of the distribution function (6) in a rather simple way [6]

$$\sigma^{D}(\omega) = \frac{4\pi^{2}}{\hbar c} \omega \sum_{n=0}^{\infty} |\langle n|D_{z}|0\rangle|^{2} \,\delta(\omega - \omega_{n0}) , \qquad (7)$$

where the polarization vector of the external field has been assumed in the z-direction [7].

Particularly interesting are the integral properties (or moments) of the strength distribution, defined by

$$m_p = \int_0^\infty d\omega \,(\hbar\omega)^p \,R^D(\omega) = \sum_{n=0}^\infty \,|\langle n|D_z|0\rangle|^2 \,E_{n0}^p \,\,, \tag{8}$$

where p is an integer number. In fact, the use of the closure property

$$\sum_{n=0}^{\infty} |n\rangle\langle n| = \mathbf{1}$$
(9)

leads to

$$m_p = \langle 0 | D_z^{\dagger} (H_0 - E_0)^p D_z | 0 \rangle .$$
 (10)

The application of the closure property has washed out all the complications of the excited states and left one with quantities which are connected with basic features of the dynamics of the system (ground state and Hamiltonian) and of the kind of reaction (coupling operator D_z).

Relation (10), when $p \ge 0$, is called sum rule (SR) of order p for the operator D_z (for reviews see refs. [8]). For Hermitian operators (as in the dipole case) the evaluation of a SR can be easier because one can write

$$m_{0} = \int d\omega R^{D}(\omega) = \frac{1}{2} \langle 0 | \{D_{z}, D_{z}\} | 0 \rangle$$

$$m_{1} = \int d\omega \hbar \omega R^{D}(\omega) = \frac{1}{2} \langle 0 | [D_{z}, [H_{0}, D_{z}]] | 0 \rangle$$

$$m_{2} = \int d\omega (\hbar \omega)^{2} R^{D}(\omega) = \frac{1}{2} \langle 0 | \{[D_{z}, H_{0}], [H_{0}, D_{z}]\} | 0 \rangle$$

$$m_{3} = \int d\omega (\hbar \omega)^{3} R^{D}(\omega) = \frac{1}{2} \langle 0 | [[D_{z}, H_{0}], [H_{0}, [H_{0}, D_{z}]]] | 0 \rangle$$
etc... (11)

The odd sum rules involve only commutators [,], while the even ones involve anticommutators $\{, \}$ as well. The presence of commutators simplifies the calculation for systems with many degrees of freedom like the many-body systems.

As an additional remark one notices that the moments m_p of the dipole strength distribution can be related to the moments of the dipole cross section $\sigma_p^D = \int d\omega (\hbar \omega)^p \sigma^D(\omega)$, one gets (cfr. eq.(7) and (8))

$$\sigma_p^D = \frac{4\pi^2}{\hbar^2 c} m_{p+1} .$$
 (12)

2.2 Application to the hydrogen

The hydrogen is a particularly simple and instructive example where the calculation of the sum rules introduced in the previous section can be performed rather easily not only for the odd moments which depend on commutators, but for the even moments also, although they require the evaluation of anticommutators.

Let us now calculate the first few sum rules for the dipole operator:

$$D_{z} = \sum_{k} e_{k} z_{k} = -e (z_{e} - z_{p}) = -e z$$
(13)

where z is the relative distance (in the direction of the external field) of the electron with respect to the proton.

i) m_0 gives the total integrated response function

$$m_0 = \frac{1}{2} \langle 0 | \{ D_z, D_z \} | 0 \rangle = e^2 \langle 0 | z^2 | 0 \rangle = e^2 a_0^2 , \qquad (14)$$

and is related to the rms radius of the hydrogen $(3 \langle z^2 \rangle = \langle \mathbf{r}^2 \rangle = 3 a_0^2);$

ii) m_1 is probably the most popular SR and is known as the Thomas-Reiche-Kuhn sum rule [9]. It relates the total integrated photoabsorption cross section (in long-wavelength approximation) to the classical radius of the electron $r_0 = e^2/m_ec$. In fact one has

$$m_1 = \frac{1}{2} \langle 0 | [D_z, [H_0, D_z]] | 0 \rangle = \frac{1}{2} e^2 \langle 0 | \left[z, \left[\frac{\mathbf{p}^2}{2m_e}, z \right] \right] | 0 \rangle = \frac{\hbar^2 e^2}{2m_e} \left[\equiv \frac{e^4 a_0}{2} \right]$$
(15)

where the result

$$[H_0, D_z] = -e \left[\frac{\mathbf{p}^2}{2m_e}, z\right] = -\frac{e}{2m_e} \left\{ p_z \left[p_z, z \right] + \left[p_z, z \right] p_z \right\} = -\frac{e}{m_e} i \hbar p_z \quad (16)$$

has been used. The simplicity of the previous commutators has basically due to the fact that the Coulomb potential commutes with the dipole operator, and the use of the canonical commutation relations yields the result (16).

The connection of the first moment with the photoabsorption cross section is obtained using (12), one gets

$$\sigma_0^D = \frac{4\pi^2}{\hbar^2 c} m_1 = 2\pi^2 \frac{e^2}{m_e c} . \tag{17}$$

For more complex atoms eq.(17) still holds becoming $\sigma_0^D = 2\pi^2 Z e^2/m_e c$ where Z is the atomic number. The last relation (in square-brackets in the eq.(15) and in the equations (18) and (19)) is obtained by using the definition of the Bohr radius $a_0 = \hbar^2/e^2 m_e$.

iii) Also m_2 and m_3 are rather easily calculated by noting that $[H_0, D_z] = [\mathbf{p}^2/2m_e, D_z]$. One obtains

$$m_2 = \frac{1}{2} \langle 0 | \{ [D_z, H_0], [H_0, D_z] \} | 0 \rangle$$

$$= e^{2} \frac{\hbar^{2}}{m_{e}^{2}} \langle p_{z}^{2} \rangle = \frac{2}{3} e^{2} \frac{\hbar^{2}}{m_{e}} \langle \frac{\mathbf{p}^{2}}{2m_{e}} \rangle$$
$$= e^{2} \frac{\hbar^{4}}{3m_{e}^{2}a_{0}^{2}} \left[\equiv \frac{e^{6}}{3} \right] , \qquad (18)$$

and

$$m_{3} = \frac{1}{2} \langle 0| \left[\left[D_{z}, H_{0} \right], \left[H_{0}, \left[H_{0}, D_{z} \right] \right] \right] | 0 \rangle$$

$$= \frac{1}{2} e^{2} \frac{\hbar^{2}}{m_{e}^{2}} \langle \left[p_{z}, \left[H_{0}, p_{z} \right] \right] \rangle = \frac{1}{2} e^{2} \frac{\hbar^{2}}{m_{e}^{2}} \left\langle \left[p_{z}, \left[-\frac{e^{2}}{r}, p_{z} \right] \right] \right\rangle$$

$$= e^{2} \frac{\hbar^{4}}{2m_{e}^{2}} \left\langle \nabla_{z}^{2} \left(-\frac{e^{2}}{r} \right) \right\rangle = e^{2} \frac{\hbar^{4}}{2m_{e}^{2}} \frac{1}{3} \left\langle \vec{\nabla}^{2} \left(-\frac{e^{2}}{r} \right) \right\rangle = e^{4} \frac{\hbar^{4}}{6m_{e}^{2}} \left\langle 4\pi\delta(\mathbf{r}) \right\rangle$$

$$= \frac{2}{3} e^{4} \frac{\hbar^{4}}{m_{e}^{2}} \frac{1}{a_{0}^{3}} \left[\equiv \frac{2}{3} \frac{e^{8}}{a_{0}} \right] .$$
(19)

To calculate the m_3 sum rule a point like proton has been assumed. More generally $m_3 = -4\pi e^2 (\hbar^4/6m_e^2) \int d^3r \rho_p(r)\rho_e(r)$ where ρ_p and ρ_e are the proton and electron charge densities respectively $(\int d^3r \rho_p(r) = -\int d^3r \rho_e(r) = e)$. Higher SR $(m_4, m_5 \text{ etc.})$ would diverge if the proton is again assumed point like (see Jackiw in ref.[8]).

3 Bounds on the electric polarizability

3.1 General Results

For p < 0 relation (10) has only a formal meaning, nevertheless inverse energy-weighted sum rules may also have interesting applications and indeed one can easily check that for p = -1 eq.(8) leads to (cfr. also eq.(4))

$$m_{-1} = \int d\omega \, \frac{R^D(\omega)}{\hbar \omega} = \sum_{n \neq 0} \frac{|\langle n | D_z | 0 \rangle|^2}{E_n - E_0} \equiv \frac{1}{2} \, \alpha \,, \qquad (20)$$

showing that the electric polarizability is related to a particular moment of the dipole strength distribution, namely m_{-1} . Such a moment cannot be written, in general [10], in a closed form as it is for the $p \ge 0$ moments. However general inequalities and upper and lower bounds to m_{-1} (and consequently on α) can be established and they are founded on the positivity of the distribution function $R^D(\omega)$. In the following we will discuss few examples.

i) Since $R^{D}(\omega)$ is a positive defined function the following inequality

$$\int_0^\infty d\omega \, \frac{R^D(\omega)}{\hbar\omega} \, (1+\beta \, \hbar\omega)^2 \, \ge \, 0 \tag{21}$$

holds for any real number β . As a consequence one gets

$$m_{-1} \ge -(2\beta m_0 + \beta^2 m_1) ,$$
 (22)

where the definition of the moments (8) has been used. Now one can vary the parameter β in order to maximize the right-hand-side of eq.(22) obtaining $\beta = -m_0/m_1$ and consequently

$$m_{-1} \ge \frac{m_0^2}{m_1}$$
, (23)

which establishes a lower bound for the inverse moment.

In a similar way one can find an upper bound to m_{-1} considering that the first excited dipole state has energy $E_1 = \hbar \omega_1$ and consequently $\hbar \omega \ge \hbar \omega_{10} = E_1 - E_0$ in the definition of m_{-1} (see eq.(20)). One can, thus, write

$$\int_{0}^{\infty} d\omega \, \frac{R^{D}(\omega)}{\hbar\omega} \, \le \int_{0}^{\infty} d\omega \, \frac{R^{D}(\omega)}{\hbar\omega_{10}} \tag{24}$$

which implies

$$m_{-1} \le \frac{m_0}{\hbar\omega_{10}} \ . \tag{25}$$

The lower bound (23) is often called Feynmann approximation because he applied it to the excitations of the superfluid helium, the upper bound (25) represents the most intuitive way of approximating α and is discussed in many text books (e.g. [11]).

ii) The bounds previously discussed have been recently generalized to include additional sum rules, by Dalfovo and Stringari [12] for the study of the static response function in superfluid helium. Following these authors one could define the following inequality

$$\int_0^\infty d\omega \, \frac{R^D(\omega)}{\hbar\omega} \, (1 + \beta \, \hbar\omega + \gamma \, \hbar^2 \omega^2)^2 \, \ge \, 0 \tag{26}$$

valid for any real β and γ . As before one can write eq.(26) as a lower bound for m_{-1} and vary the parameters β and γ . One gets:

$$m_{-1} \ge \frac{(m_0)^2/m_1}{1 - \Delta/\Gamma}$$
, (27)

where

$$\Delta = \frac{m_2}{m_1} - \frac{m_1}{m_0} \tag{28}$$

and

$$\Gamma = \left[\frac{m_3}{m_1} + \left(\frac{m_1}{m_0}\right)^2 - 2\frac{m_2}{m_0}\right] \left(\frac{m_2}{m_1} - \frac{m_1}{m_0}\right)^{-1} .$$
(29)

As to the upper bound one generalizes eq.(24) in the following way

$$\int_0^\infty d\omega \, \frac{R^D(\omega)}{\hbar\omega} \, (1+\epsilon\,\hbar\omega)^2 \le \int_0^\infty d\omega \, \frac{R^D(\omega)}{\hbar\omega_{10}} \, (1+\epsilon\,\hbar\omega)^2 \,, \tag{30}$$

or, equivalently,

$$m_{-1} \le \frac{m_0}{\hbar\omega_{10}} + 2\,\epsilon \left[\frac{m_1}{\hbar\omega_{10}} - m_0\right] + \epsilon^2 \left[\frac{m_2}{\hbar\omega_{10}} - m_1\right] \,, \tag{31}$$

and minimizing with respect to ϵ the right-hand side, one has

$$m_{-1} \le \frac{m_0}{\hbar\omega_{10}} \left[1 - \frac{m_0}{m_1} \left(\frac{m_1}{m_0} - \hbar\omega_{10} \right)^2 \left(\frac{m_2}{m_1} - \hbar\omega_{10} \right)^{-1} \right] .$$
(32)

iii) An additional way of estimating the inverse moment m_{-1} , founded again on the positivity of the strength distribution, is based on the Schwartz inequality and makes use of ratios of different SR. Let us first consider the expression $m_1/m_0 = \int d\omega \, \hbar \omega \, R^D(\omega) / \int d\omega \, R^D(\omega) \equiv \bar{E}_{1,0}$, this ratio defines a mean value of the excitation energy. Other mean values can be defined making use of different energy-weighted SR: $\bar{E}_{3,2} = m_3/m_2$; $\bar{E}_{2,1} = m_2/m_1$, or inverse energy-weighted sums: $\bar{E}_{-1,-2} = m_{-1}/m_{-2}$; $\bar{E}_{0,-1} = m_0/m_{-1}$, etc. They fulfill the following properties:

$$\frac{m_3}{m_2} \ge \frac{m_2}{m_1} \ge \frac{m_1}{m_0}...$$
(33)

and, equivalently,

$$\frac{m_1}{m_0} \ge \frac{m_0}{m_{-1}} \ge \frac{m_{-1}}{m_{-2}}....$$
(34)

The previous inequalities collapse to identity in the case of a very narrow spectrum only, i.e. when one state exhausts all the strength.

Among other possible inequalities, one can write [13]

$$\frac{m_{k+2}}{m_k} \ge \frac{m_k}{m_{k-2}} \quad ; \quad \bar{E}_{k+2,k}^2 \ge \bar{E}_{k,k-2}^2 \tag{35}$$

which evaluated for k = -1 and k = 1 lead to a further estimate of the electric polarizability, namely

$$2\frac{m_1^2}{m_3} \le \alpha \le 2\sqrt{m_1 m_{-3}} . (36)$$

Eq.(36) contains the inverse cubic moment

$$m_{-3} = \sum_{n \neq 0} \frac{|\langle n | D_z | 0 \rangle|^2}{(E_n - E_0)^3} , \qquad (37)$$

which has no closed form in terms of commutators and anticommutators. Nevertheless, because of the rather large value of the exponent in the denominator, it can be easily estimated including the first excited state only: $m_{-3} \approx |\langle 1|D_z|0\rangle|^2/(E_1 - E_0)^3$.

3.2 Application to the hydrogen

The three examples of bounds to the inverse-energy-weighted sum m_{-1} or, equivalently, to the polarizability $\alpha = 2 m_{-1}$ discussed in the previous section can be rather easily applied to the hydrogen atom to check the degree of approximation they imply in comparison with the exact quantum prediction (5). In order to obtain numerical estimates one has to use the sum rule calculation of section(II B) for m_0, m_1, m_2 and m_3 . i) A first example is given by the bounds (23) and (25), namely

$$2\frac{m_0^2}{m_1} \le \alpha \le 2\frac{m_0}{\hbar\omega_{10}}$$
, (38)

where $\hbar\omega_{10} = E_1 - E_0 = 3e^2/8a_0$ from the energy spectrum of the hydrogen. By using results of section(II B) one gets

$$4 a_0^3 \le \alpha \le \frac{16}{3} a_0^3 . \tag{39}$$

Both the bounds are rather simple and surprisingly good. In particular the lower bound has an elegant interpretation because it is related to a variational wave function approach. One can, in fact, demonstrate that approximating the perturbed ground state $|\mathcal{E}\rangle$ of eq.(2) by applying on the unperturbed ground state $|0\rangle$ a simple transformation of the form

$$|\mathcal{E}\rangle \approx (1 + a D_z) |0\rangle \tag{40}$$

and minimizing the energy variation with respect the parameter a, one gets $\alpha = 4 a_0^3$ exactly corresponding to the lower bound due to Feynmann. The most simple, semiclassical, interpretation is that the deformation induced by the external electric field on the electron cloud is nicely approximated by the eq.(40) [14].

ii) The bounds (38) can be improved by means of the generalization discussed by Dalfovo and Stringari [12] and summarized in the equations (27) and (32) leading to the inequalities

$$\frac{33}{8}a_0^3 \le \alpha \le \frac{100}{21}a_0^3.$$
(41)

The lower bound is improved only slightly, but the upper bound is significantly decreased in much better agreement with the exact result.

iii) As third example one can apply the inequalities (36). Within this approximation one gets

$$\frac{3}{4}a_0^3 \le \alpha \le 4.59a_0^3.$$
(42)

The upper bound is particularly good, while the lower value is rather unsatisfactory. The reason is related to the use of moments like m_1 and m_3 which emphasize the role of the high energy part of the excitation spectrum, while m_{-1} is connected to the low- ω properties of the distribution function. A different way of understanding that is, again, connected with the variational approaches. The prediction $\alpha = 3/4 a_0^3$ corresponds to the variational wave function [14]

$$|\mathcal{E}\rangle \approx e^{-i\,a\,p_z}\,|0\rangle\tag{43}$$

which assumes that the global effect of the external electric field is only a rigid translation of the electron cloud (driven by the translational operator p_z) without any additional deformation. Such an assumption reproduces the actual effect rather poorly and the resulting polarizability is quite low.

4 Conclusions

The calculation of the electric polarizability of the hydrogen is a classical problem in quantum mechanics. Most of the textbooks discuss it as an example of perturbative calculation. Aim of the present paper is emphasizing the fact that the polarizability is also connected to the moments of the dipole strength distribution function entering the cross section for absorption and stimulated emission of electromagnetic radiation. A point of view which has also an historical basis since the sum rule technique has been introduced for the study of the interaction of the light with the atoms. The aspect which makes the hydrogen a privileged system to introduce and evaluate the sum rules lies in the simplicity of calculating commutators and anticommutators for one-electron atom. In addition the value of its electric polarizability is well known and can be used to asses the inequalities which fix rigorous bound to the inverse energy-weighted moments.

References

- Berkeley physics course (vol.2) 1965 *Electricity and magnetism* (New York: McGraw-Hill Book Company) p. 309
- [2] For sake of simplicity we will assume infinite proton mass. In order to account for the motion of the atomic nucleus one should substitute, in the expressions of the present paper, the electron mass m_e with the reduced mass μ_e and the Bohr radius $a_0 = \hbar^2/m_e e^2$ with $a_\mu = \hbar^2/\mu_e e^2$.
- [3] Bethe H A and Salpeter E E 1977 The Quantum Mechanics of one-and two-electron atoms (New York: Plenum)
- [4] Dalgarno A and Lewis J T 1955 Proc. Roy. Soc. (London) A233 70
- [5] Schiff L I 1968 *Quantum Mechanics* (McGraw-Hill Book Company)
- [6] Merzbacher E 1970 Quantum Mechanics (New York: John Wiley & Sons, Inc.)
- [7] To be more precise eq.(7) can be interpreted as the photoabsorption cross section if the hydrogen atom is at zero temperature (T = 0). In a more general case eq.(7) represents the difference between the cross section for absorption and stimulated emission (e.g. cfr.[6] p. 467).
- [8] Jackiw R 1967 Phys. Rev. 157 1220; Leonardi R and Rosa-Clot M 1971 Rivista Nuovo Cimento 1 1; Bohigas O, Lane A M and Martorell J 1979 Phys. Rep. 51 267; Lipparini E and Stringari S 1989 Phys. Rep. 175 103; Orlandini G and Traini M 1991 Rep. Prog. Phys. 54 257
- [9] This sum rule (often called oscillator-strength sum rule in atomic physics) had originally been proven before the advent of wave mechanics and its exsistence led Heisenberg to believe that the canonical commutator between position and momentum to be valid. For the original references and

an historical introduction cfr. Slater J C 1960 Quantum theory of atomic structure (New York: McGraw-Hill Book Company) p. 157. For more recent discussions see Fano U and Cooper J W 1968 Rev. Mod. Phys. **40** 441 and ref.[11]. Quite recently the TRK sum rule received new attention and the small corrections due to the motion of the proton have been discussed: Baxter C 1994 Phys. Rev. A **50** 875 and reference therein.

- [10] This statement should be taken with some caution. In fact just in the case of the dipole operator m_{-1} can be written in a closed form because the solution due to Dalgarno and Lewis is based on the equation $[H_0, F]|0\rangle = D_z|0\rangle$ and the operator F is found to be $F = -m_e E a_0/\hbar^2 (r^2/2 + a_0 r) \cos \theta$. As a consequence the inverse-energy weighted sum takes the form $m_{-1} = \langle 0|D_z F|0\rangle$ (cfr.[6] and Schwartz C 1959 Ann. Phys. (N.Y.) **6** 156.
- [11] Brandsen B H and Joachain C J 1983 The Physics of atoms and molecules (London: Longman Scientific and Technical)
- [12] Stringari S 1992 Phys. Rev. B 46 2974; Dalfovo F and Stringari S 1992 Phys. Rev. B 46 13991
- [13] Traini M and Leonardi L 1994 Phys. Lett. B 334 7
- [14] Traini M 1995 preprint