PHYSICAL REVIEW A VOLUME 15, NUMBER 1 JANUARY 1977

Multipole polarizabilities and shielding factors of the hydrogen atom from the hydrodynamic analogy to quantum mechanics

G. C. Shukla*† and M. Barbaro
Physics Laboratory, Istituto Superiore di Sanità, Roma, Italy

(Received 12 November 1975)

Expressions have been obtained for the multipole polarizabilities and shielding factors of the hydrogen atom by application of the time-dependent perturbation scheme developed by Wiener, Aşkar, and Demiralp utilizing a hydrodynamic analogy to quantum mechanics. Our expressions reduce to the exact values in the zero-frequency limit, obtained by Dalgarno with conventional perturbation theory.

I. INTRODUCTION

The hydrodynamic analogy[1] to quantum mechanics follows by considering the equation for the amplitude $A(x,t)$ and phase $s(x,t)$ of the complex wave function $\Psi(x,t)$ instead of the Schrödinger equation and then making suitable physical identifications. The resulting equation becomes nonlinear, reminiscent of those encountered in classical hydrodynamic. However, it is possible to linearize the equation with the acoustic approximation.

Wiener and Aşkar[2] have worked out a scheme using the hydrodynamic analogy to quantum mechanics to discuss the time-dependent perturbation of real bound states. They have applied it to derive the dipole polarizability of atomic hydrogen, reproducing the exact series solution in agreement with previous solutions obtained by different methods.[3,4,5] Recently, Aşkar and Demiralp[6] derived a variational analog to the differential equation of an earlier work and applied it to a derivation of the dipole polarizability of atomic hydrogen.

The purpose of the present paper is to examine the differential equation and its variational analog following earlier papers,[2,6] for a study of the multipoles of hydrogen atom. We use the notation $2L$ for 2^L multipoles following Dalgarno.[7] The dipole case corresponds to $L=1$. We present in Sec. II the main outline of earlier approaches[2,6] for the sake of completeness. We derive in Sec. III the differential equation and its variational analog to discuss the multipole polarizabilities and shielding factors of atomic hydrogen. Sec. IV is devoted to the solution of the variational analog (equation) and in it we obtain the expressions for multipole polarizabilities and shielding factors. In Sec. V we elaborate on the dipole case and draw our conclusions.

II. MAIN OUTLINE OF EARLIER APPROACHES

First, we point out the general perturbation technique developed by Wiener and Aşkar[2] utilizing the hydrodynamics analogy to quantum mechanics. They added a small time-dependent perturbation (potential) to the unperturbed Hamiltonian. Then they assumed that the bound state was real and such that $\Psi_0(x)=A_0(x,0)$, where $A(x,t)$ denotes the amplitude function of the Schrödinger equation. Use of the acoustic approximation

$$A(x,t)=A_0(x)\left[1+\epsilon(x,t)\right], \tag{2.1}$$

where $\epsilon=O(\lambda)$ and λ is an arbitrary parameter, led them to the linearized equation

$$(D^2-\omega^2)=D\Phi' , \tag{2.2}$$

where

$$D=\tfrac{1}{2}\nabla^2+(\nabla A_0/A_0)\nabla , \tag{2.3}$$

and Φ' is the spatial dependence of the perturbing potential.

Now we turn to the development of Aşkar and Demiralp,[6] which is simply a variational analog of the linearized equation (2.2). It reads[8]

$$\delta\int_v A_0^2\left[\tfrac{1}{2}\nabla S'\cdot\nabla S'+2\omega^2\epsilon'\Phi'+\tfrac{1}{2}\omega^2\nabla\epsilon'\cdot\nabla\epsilon' +2\omega^2\epsilon'S'\right]dv=0, \tag{2.4}$$

where S' denotes the spatial dependence of the amplitude of $\Psi(x,t)$. In order to discuss the dipole polarizability of the hydrogen atom we define

$$\begin{aligned}&\Phi'=-ER\cos\theta, \quad \Psi_0=e^{-R}/\sqrt{\pi} ,\\ &\epsilon'=F(R)\cos\theta, \quad S'=G(R)\cos\theta .\end{aligned} \tag{2.5}$$

Then the differential equation (2.2) becomes[2]

$$(D_R^2-\omega^2)F(R)=E , \tag{2.6}$$

$$D_R=\frac{1}{2R^2}\frac{d}{dR}R^2\frac{d}{dR}-\frac{d}{dR}+\frac{1}{R^2} . \tag{2.7}$$

Its variational analog equation (2.4)[6,8] is

$$\delta\int_0^\infty e^{-2R}\left\{\left[R^2\left(\frac{dF}{dR}\right)^2+2F^2+4FGR^2-4FR^3E\right]\omega^2 +\left[R^2\left(\frac{dG}{dR}\right)^2+2G^2\right]\right\}dR=0. \tag{2.8}$$

The Euler equation for arbitrary variation of F and G becomes

$$D_R F = -RE + G\,, \tag{2.9}$$

$$D_R G = F\omega^2\,. \tag{2.10}$$

The substitution of (2.10) into (2.9) results in Eq. (2.6) and shows the equivalence of the differential equation (2.6) and its variational analog (2.8).

III. DIFFERENTIAL EQUATIONS AND THEIR VARIATIONAL ANALOG FOR THE MULTIPOLE POLARIZABILITIES AND SHIELDING FACTORS OF THE HYDROGEN ATOM

In this section we derive the differential equations and their variational analogs needed to discuss the multipoles of atomic hydrogen. For multipoles of atomic hydrogen the spatial dependence of $\epsilon'(R,\theta)$ and $\Phi'(R,\theta)$ are

$$\epsilon'(R,\theta) = F_L(R)\,P_L(\cos\theta)\,, \tag{3.1}$$

$$\Phi'(R,\theta) = -ER^L P_L(\cos\theta)\,. \tag{3.2}$$

The ground state eigenfunction Ψ_0 is given by Eq. (2.5). The substitution of (3.1), (3.2), and (2.5) with (2.2) results in the following equation:

$$(D^2_{R,L} - \omega^2)F_L = ELR^{L-1}\,, \tag{3.3}$$

with

$$D_{R,L} = \frac{1}{2R^2}\frac{d}{dR}R^2\frac{d}{dR} - \frac{d}{dR} - \frac{L(L+1)}{2R^2}\,, \tag{3.4}$$

where L stands for the multipole. For $L=1$, the dipole case, it reduces to the earlier equation (2.6).

Now, we derive the variational analog of the differential equation (3.3); we choose for $S'(R,\theta)$

$$S'(R,\theta) = G_L(R)\,P_L(\cos\theta)\,. \tag{3.5}$$

Substitution of (3.1) into (3.3) and (2.5) in Eq. (2.4) results in the following equation:

$$\delta\int_{R=0}^{\infty}\int_{\theta=0}^{\pi} e^{-2R}R^2\left\{\left[\left(\frac{dF_L}{dR}\right)^2 P_L^2(\cos\theta) + F_L^2P_L'^2(\cos\theta)\sin^2\theta + 4F_LG_LP_L^2(\cos\theta) - 4F_L\,ER^LP_L^2(\cos\theta)\right]\omega^2 + \left(\frac{dG_L}{dR}\right)^2 + G_L^2P_L'^2(\cos\theta)\sin^2\theta\right\}\sin\theta\,d\theta\,dR = 0\,. \tag{3.6}$$

With $x=\cos\theta$, the equation is transformed into

$$\delta\int_0^{\infty}\int_{-1}^{1} e^{-2R}R^2\left\{\left[\left(\frac{dF_L}{dR}\right)^2 P_L^2(x) + F_L^2P_L'^2(x)\,(1-x^2) + 4F_LG_LP_L^2(x) - 4F_LR^LEP_L^2(x)\right]\omega^2 + \left(\frac{dG_L}{dR}\right)^2 P_L^2(x) + G_L^2P_L'^2(x)\,(1-x^2)\right\}dR\,dx = 0\,. \tag{3.7}$$

We use the following relations:

$$\int_{-1}^{1}P_L^2(x)\,dx = \frac{2}{2L+1}\,, \tag{3.8}$$

$$\int_{-1}^{1}P_L'^2(x)\,(1-x^2)\,dx = \frac{2L(L+1)}{2L+1}\,. \tag{3.9}$$

Integrating (3.7) with respect to x, and making use of relations (3.8) and (3.9), we obtain

$$\delta\int_0^{\infty} e^{-2R}\left\{\left[R^2\left(\frac{dF_L}{dR}\right)^2 + L(L+1)F_L^2 + 4F_LG_LR^2 - 4F_LR^{L+2}E\right]\omega^2 + R^2\left(\frac{dG_L}{dR}\right)^2 + L(L+1)\,G_L^2\right\}dR = 0\,. \tag{3.10}$$

Equation (3.10) is the variational analog of Eq. (3.3). It is easily shown to be equivalent to it by writing down the Euler equations for arbitrary variation of $F_L(R)$ and $G_L(R)$, namely,

$$D_{R,L}F_L = G_L - R^LE\,, \tag{3.11}$$

$$D_{R,L}G_L = F_L\omega^2\,. \tag{3.12}$$

IV. MULTIPOLE POLARIZABILITIES AND SHIELDING FACTORS OF HYDROGEN ATOM

In this section we solve the variational equation (3.9) to determine the multipoles of hydrogen atom. We choose the following simple function for $F_L(R)$ and $G_L(R)$:

$$F_L(R)=(C_{1L}R^L+C_{2L}R^{L+1})E\,, \tag{4.1}$$

$$G_L(R)=(C_{3L}R^L)E\,. \tag{4.2}$$

The substitution of (4.1) and (4.2) into (3.10) yields the following equations for $C_{iL}, i=1,2,3$:

$$\begin{bmatrix} L & (L+1)L & L+1 \\ 2L & (2L+1)(L+1) & 2L+3 \\ 2(L+1)\omega^2 & (2L+3)(L+1)\omega^2 & 2L \end{bmatrix} \begin{bmatrix} C_{1L} \\ C_{2L} \\ C_{3L} \end{bmatrix} = \begin{bmatrix} L+1 \\ 2L+3 \\ 0 \end{bmatrix}\,. \tag{4.3}$$

The solutions of (4.3) are

$$C_{1L}=\frac{1}{L}\left[1-\left(1+\frac{2}{L}\right)\left(1+\frac{1}{2L}\right)\omega_L^2\right]^{-1}, \tag{4.4}$$

$$C_{2L}=\frac{1}{L+1}\left[1-\left(1+\frac{2}{L}\right)\left(1+\frac{1}{2L}\right)\omega_L^2\right]^{-1}, \tag{4.5}$$

$$C_{3L}=-\omega_L^2\left(1+\frac{2}{L}\right)\left(1+\frac{1}{2L}\right)\times\left[1-\left(1+\frac{2}{L}\right)\left(1+\frac{1}{2L}\right)\omega_L^2\right]^{-1}. \tag{4.6}$$

We have added the suffix L to ω occurring in Eqs. (4.4), (4.5), and (4.6) to distinguish between the different multipoles. For $\omega_L=0$, $C_{1L}=1/L$, $C_{2L}=1/(L+1)$, and $C_{3L}=0$, so that

$$F_L(R)=\left(\frac{1}{L}R^L+\frac{1}{L+1}R^{L+1}\right)E, \quad G_L(R)=0\,. \tag{4.7}$$

For $L=1$, (4.7) is equivalent to the result obtained earlier.

The multipole polarizabilities α_{2L} and shielding factors γ_{2L}, produced by the applied electric field $\hat{E}=Ee_n\cos\omega t$ are given by the following expressions:

$$\alpha_{2L}=\langle\Psi|P_L(\cos\theta)R^L|\Psi\rangle \tag{4.8}$$

$$\approx 2\langle\Psi_0|P_L(\cos\theta)R^L|\epsilon'\Psi_0\rangle\cos\omega t\,, \tag{4.9}$$

$$\gamma_{2L}=\langle\Psi|\frac{P_L(\cos\theta)}{R^{L+1}}|\Psi\rangle \tag{4.10}$$

$$\approx 2\langle\Psi_0|\frac{P_L(\cos\theta)}{R^{L+1}}|\Psi_0\epsilon'\rangle\cos\omega t\,. \tag{4.11}$$

Therefore, if we let ϵ' correspond to the case $E=1$, the multipole polarizabilities and multipole shielding factors are given by

$$\alpha_{2L}=2\langle\Psi_0|P_L(\cos\theta)R^L|\Psi_0\epsilon'\rangle\,, \tag{4.12}$$

$$\gamma_{2L}=2\langle\Psi_0|\frac{P_L(\cos\theta)}{R^{L+1}}|\Psi_0\epsilon'\rangle\,. \tag{4.13}$$

Substituting the values of ϵ' and Ψ_0 and integrating, it becomes

$$\alpha_{2L}=\frac{8}{2L+1}\int_0^\infty e^{-2R}F_L(R)R^{L+2}dR\,, \tag{4.14}$$

$$\gamma_{2L}=\frac{8}{2L+1}\int_0^\infty e^{-2R}\frac{F_L(R)}{R^{L+1}}dR\,. \tag{4.15}$$

Substituting the value of $F_L(R)$ from Eqs. (4.1), (4.4), and (4.5) we obtain

$$\alpha_{2L}(\omega^2)=\alpha_{2L}[1-(1+2/L)(1+1/2L)\omega_L^2]^{-1}, \tag{4.16}$$

$$\gamma_{2L}(\omega^2)=\gamma_{2L}[1-(1+2/L)(1+1/2L)\omega_L^2]^{-1}, \tag{4.17}$$

where

$$\alpha_{2L}^{7}=\frac{(2L+2)!\,(L+2)}{2^{2L+1}L(L+1)}\,, \tag{4.18}$$

$$\gamma_{2L}^{7}=2/L(L+1)\,. \tag{4.19}$$

V. DIPOLE CASE AND RESULTS

We discuss the dipole case in detail. Putting $L=1$ in (4.16) and (4.17) we obtain the dipole polarizability and shielding factor of atomic hydrogen

$$\alpha_2(\omega^2)=\tfrac{9}{2}(1-\tfrac{9}{2}\omega^2)^{-1}, \tag{5.1}$$

$$\gamma_2(\omega^2)=(1-\tfrac{9}{2}\omega^2)^{-1}. \tag{5.2}$$

For $\omega=0$ we get the exact expression. Formulas (4.18) and (4.19) represent the exact values for the static multipole polarizabilities and shielding factors of the hydrogen atom. If we had chosen for the ground-state wave function $\Psi_0=e^{-ZR}Z^{3/2}/\sqrt{\pi}$, then additional multiplication factors in Z automatically enter in the expressions (4.18) and (4.19) making them equivalent to Eqs. (4.6) and (4.7) of the earlier reference.

From Eqs. (5.1) and (5.2) it follows that resonance frequency for the dipole case occurs at $\omega=0.471$. This is the result of Aşkar and Demiralp.[6] The exact value for the resonance frequency is 0.375. This can be achieved by solving Eq. (2.6) numerically. We note that the choice for the function $F(R)$ in the variational equation (2.8) is guaranteed by the indicial equation of the differential equation (2.6) with the boundary conditions that $\Psi_0F(R)$ is bounded for $R=0$ and vanishes at $R=\infty$. This suggests the choice of

$$F(R)=\left(\sum_{L=1}^{\infty}C_iR^i\right)E\,. \tag{5.3}$$

This is also our choice for $F_L(R)$ for general L. The Euler equations (2.9) and (2.10), (3.11), and (3.12) impose a boundary condition on G_L, namely,

$G_L = 0$ for $\omega_L = 0$. As for $\omega_L = 0$, we have $C_{3L} = 0$, from Eq. (4.6), implying that $G_L(R) = 0$ for all L. For the dipole case we make the following alternative choices for $F(R)$ and $G(R)$

$$\text{Case I:}\quad F(R) = (C_1R + C_2R^2 + C_3R^3)E\,,\qquad G(R) = (C_4R)E\,; \tag{5.4}$$

$$\text{Case II:}\quad F(R) = (C_1R + C_2R^2 + C_3R^3 + C_5R^4)E\,,\qquad G(R) = (C_4R)E\,. \tag{5.5}$$

In both cases we find that the polarizability and shielding factor are given by (5.1) and (5.2). Thus the inclusion of higher-order terms of R^i in $F(R)$ only complicates the algebra without modifying the polarizability expression.

Thus the only way to modify the resonance frequency is through the function $G(R)$. Thus we discuss the third case:

$$\text{Case III:}\quad F(R) = (C_1R + C_2R^2)E\,,\qquad G(R) = (C_3R^2 + C_4R^3)E\,. \tag{5.6}$$

We find that dipole polarizability and dipole shielding factor take the forms

$$\alpha_2(\omega^2) = \frac{9 + 125\,\omega^2}{2 + 845\,\omega^2 - 4000\,\omega^4}\,, \tag{5.7}$$

$$\gamma_2(\omega^2) = \frac{6 + 800\,\omega^2}{3(2 + 845\,\omega^2 - 4000\,\omega^4)}\,. \tag{5.8}$$

For $\omega = 0$ the correct static case follows, as well as $G = 0$.

Further, the resonance frequency is given by

$$\omega_\gamma^2 = 0.2135\,, \quad \omega_\gamma = 0.462\,. \tag{5.9}$$

Thus the resonance frequency changes from 0.471 to 0.462 but remains far away from the exact value 0.375.

We summarize the result of the present calculations as follows. The method developed by Wiener, Aşkar, and Demiralp is interesting as an alternative procedure which is equivalent formally to the conventional method within the framework of the acoustic approximation. We have derived the differential equations and their variational analogs to determine the multipole polarizabilities and shielding factors of the hydrogen atom. Then by use of the variational equation we obtained an expression for the multipole polarizabilities and shielding factors of the hydrogen atom. For $\omega = 0$, they give the exact result obtained by Dalgarno[7] with conventional perturbation theory. Further we observe that the multipoles have the resonance frequencies given by

$$\omega_L = [(1 + 1/L)(1 + 1/2L)]^{-1/2}\,. \tag{5.10}$$

For the dipole case this is an approximation and with a different choice of $G(R)$, we could improve on this estimate.

ACKNOWLEDGMENTS

The authors extend their appreciations to Doctor F. Podo and Professor C. Frontali for their encouragement. Also, the hospitality of the Physics Laboratory of Istituto Superiore di Sanità is acknowledged. Further one of us (G. C. S.) is grateful to CNR Rome, for a research grant.

---

*Visiting scientist for one year at the Istituto Superiore di Sanità, Physics Laboratory financially supported by the Italian Research Council.

†Present address: Dept. of Physics, College of Science, Basrah University, Basrah, Iraq.

[1] See, for example, D. I. Blockhintsev, *The Philosophy of Quantum Mechanics* (Reidel, Dordrecht, Holland, 1968), Chap. 7; H. E. Wilhelm, Phys. Rev. D 1, 2778 (1970); T. Takabaysi, Prog. Theor. Phys. 8, 143 (1952); 9, 187 (1955); 14, 283 (1955).

[2] J. H. Wiener and A. Aşkar, J. Chem. Phys. 54, 1108 (1971).

[3] M. Karplus and H. J. Kolker, J. Chem. Phys. 39, 1943 (1963).

[4] A. Dalgarno and A. E. Kingston, Proc. R. Soc. Lond. A 259, 424 (1960).

[5] C. Mavroyannis and M. J. Stephens, Phys. 5, 629 (1962).

[6] A. Aşkar and M. Demiralp, J. Chem. Phys. 60, 2762 (1974).

[7] A. Dalgarno, Adv. Phys. 2, 281 (1962).

[8] Unfortunately many misprints have crept into this paper. Equation (2.4) is the corrected version for Eq. (4.3) of Ref. 6. We are also grateful to Professor Aşkar for discussion regarding this point.