

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

F. N. Yousif, V. K. Tondon,* and G. C. Shukla

Department of Physics, Basrah University, Basrah, Iraq

(Received 9 August 1977)

Expressions for multipole polarizabilities and shielding of the hydrogen atom have been obtained by generalizing the scheme worked out by Weiner and Askar based on the hydrodynamic analogy to quantum mechanics. Our expressions, for the dipole case, reduce to those of Weiner and Askar and for the zero-frequency limit to those of Dalgarno. Our calculated resonance frequencies are in much better agreement with the exact values than those reported by the variational approach.

Recently¹ (paper I) we formulated a differential equation and its variational analog using the hydrodynamic analogy to quantum mechanics in order to study the multipoles of the hydrogen atom. The differential equation for the multipole L [Eq. (3.3) of paper I] is

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

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

In paper I, we solved the variational analog of Eq. (1) [Eq. (3.10) of paper I] and found expressions for the multipole polarizabilities and shielding factors of the hydrogen atom following Askar and Demiralp.² In the present paper, we generalize the scheme developed by Weiner and Askar³ to study the multipole polarizabilities and shielding factors of the hydrogen atom.

The scheme essentially consists in solving differential equation (1) by considering a solution of the type

$$F_L(R) = E \sum_{k=0}^{\infty} \omega^{2k} F_k, \tag{3}$$

and requiring the solution to hold for all values of ω^2 . One obtains the following set of equations:

$$D_{R,L}^2 F_0 = LR^{L-1}$$

and

$$D_{R,L}^2 F_k = F_{k-1}, \quad k = 1, 2, \dots \tag{4}$$

We now consider a solution of the Frobenius type,

$$F_k = R^S \sum_{n=1}^{\infty} a_{k,n} R^n, \quad k = 0, 1, 2, \dots, \tag{5}$$

S being the index of the power series. The indicial equation gives four values for S : $L-1$, $-L-2$, $L+1$, $-L$. Out of these only $S=L-1$ yields a physically appropriate solution consistent with the boundary condition that $\Psi_0 F_L(R)$ remains bounded at $R=0$ and vanishes at $R=\infty$.

The following set of algebraic equations result by substitution of Eq. (5) into Eq. (4) with $S=L-1$:

$$B_2 a_{k,2} - C_1 a_{k,1} = 0,$$

$$B_3 a_{k,3} - C_2 a_{k,2} + D_1 a_{k,1} = 0,$$

$$B_4 a_{k,4} - C_3 a_{k,3} + D_2 a_{k,2} = 0,$$

$$B_{n+4} a_{k,n+4} - C_{n+3} a_{k,n+3} + D_{n+2} a_{k,n+2} = a_{k-1,n},$$

$$n = 1, 2, \dots, N_k - 4$$

where

$$B_n = \frac{1}{4} [(n+L-1)(n+L) - L(L+1)] \\ \times [(n+L-2)(n+L-3) - L(L+1)],$$

$$C_n = \frac{1}{2} (n+L-1) \\ \times [(n+L-1)(n+L-2) + (n+L)(n+L-3)] \\ - L(L+1)(n+L-2),$$

$$D_n = (n+L-1)(n+L-2), \tag{6}$$

and

$$N_k = 2k + 2. \tag{7}$$

The solution for F_k is a finite series³ with the highest power of R equal to $2k+2$. To calculate $a_{k,n}$, we use the recursion relationship

$$a_{k,n} = (a_{k-1,n-2} + C_{n+1} a_{k,n+1} - B_{n+2} a_{k,n-2}) / D_n,$$

$$n = N_k, N_k - 1, \dots, 2$$

with

$$a_{k,n} = 0, \quad n > N_k, \quad a_{k-1,n-2} = 0, \quad n = 2$$

$$a_{k,1} = (B_2 / C_1) a_{k,2}. \tag{8}$$

For $k=0$, we get

$$D_2 a_{0,2} = L \tag{9}$$

and

$$a_{0,1} = (B_2 / C_1) a_{0,2},$$

yielding

$$a_{0,1} = 1/L, \quad a_{0,2} = 1/(L+1). \quad (10)$$

Hence for $k=0$, we have

$$F_0 = (1/L)R^L + [1/(L+1)]R^{L+1}. \quad (11)$$

It can be easily seen that above general expressions, for multipole L , reduce to those of Weiner and Askar³ for the special case of a dipole ($L=1$). If we substitute Eq. (11) in Eq. (3), we get the same expression for $F_L(R)$ as was obtained earlier by a variational approach [Eq. (4.7) of paper I].

The multipole polarizabilities α_{2L} and shielding factors Y_{2L} are given by¹

$$\alpha_{2L} = \frac{8}{2L+1} \int_0^\infty e^{-2R} F_L(R) R^{L+2} dR, \quad (12)$$

and

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

Substituting for $F_L(R)$ and integrating we get

$$\alpha_{2L}(\omega^2) = \sum_{k=0}^\infty \alpha_k \omega^{2k},$$

and

$$Y_{2L}(\omega^2) = \sum_{k=0}^\infty \gamma_k \omega^{2k}, \quad (13)$$

where α_k and γ_k are Cauchy's coefficients and are given as

$$\alpha_k = \frac{8}{2L+1} \sum_{n=1}^{Nk} a_{k,n} I_n, \quad k=0, 1, 2, \dots$$

with

$$I_n = (n+2L+1)!/2^{n+2L+2}, \quad (14)$$

and

$$\gamma_k = \frac{8}{2L+1} \sum_{n=1}^{Nk} a_{k,n} H_n, \quad k=0, 1, 2, \dots \quad (15)$$

with

$$H_n = n!/2^{n+1}.$$

Using the above equations, the static multipole polarizability $\alpha_{2L}(0)$ and the static shielding factor $Y_{2L}(0)$ become

$$\alpha_{2L}(0) = \frac{8}{2L+1} (a_{0,1} I_1 + a_{0,2} I_2) = \frac{(2L+2)!(L+2)}{2^{2L+1} L(L+1)} \quad (16)$$

and

TABLE I. Numerical values for Cauchy moments of multipole polarizabilities α_k , multipole shielding factors γ_k , and calculated resonance frequencies for $L=1$ to 6. The notation $a b$ represents $a \times 10^b$.

$L=1$; exact $\omega_p = 0.375000$				$L=2$; exact $\omega_p = 0.444444$			
k	α_k	γ_k	ω_{Calc}	k	α_k	γ_k	ω_{Calc}
0	4.5	1	...	0	15	0.33333	...
1	2.65833	1	0.411435	1	4.99791	6.12037	-1 0.547837
2	1.72188	2	0.392919	2	1.91422	1.80480	0 0.510972
3	1.16209	3	0.384930	3	7.94155	6.49067	0 0.490957
4	8.01016	3	0.380890	4	3.46578	2.59413	1 0.478687
5	5.58684	4	0.378649	5	1.56519	1.10511	2 0.470561
6	3.92395	5	0.377330	6	7.24240	4.90892	2 0.464882
7	2.76786	6	0.376521	7	3.41146	2.24464	3 0.460755
8	1.95771	7	0.376009	8	1.62872	1.04807	4 0.457664
9	1.38713	8	0.375678	9	7.85712	4.97052	4 0.455293
10	9.83990	8	0.375460	10	3.82142	2.38547	5 0.453439
11	6.98554	9	0.375314	11	1.87073	1.15548	6 0.451966
12	4.96177	10	0.375216	12	9.20623	5.63811	6 0.450780
13	3.52556	11	0.375150	13	4.55001	2.76729	7 0.449815
14	2.50567	12	0.375104	14	2.25672	1.36473	8 0.449022
15	1.78112	13	0.375072	15	1.12257	6.75674	8 0.448364
16	1.26623	14	0.375051	16	5.59780	3.35606	9 0.447815
17	9.00263	14	0.375035	17	2.79715	1.67145	10 0.447353
18	6.40102	15	0.375025	18	1.40014	8.34327	10 0.446963
19	4.55141	16	0.375017	19	7.01892	4.17260	11 0.446632
20	3.23634	17	0.375012	20	3.52306	2.09016	12 0.446349
21	2.30129	18	0.375009	21	1.77028	1.04845	13 0.446107
22	1.63642	19	0.375006	22	8.90365	5.26537	13 0.445899
23	1.16365	20	0.375004	23	4.48172	2.64697	14 0.445719
24	8.27471	20	0.375003	24	2.25748	1.33182	15 0.445563
25	5.88417	21	0.375002	25	1.13780	6.70612	15 0.445429

TABLE I. (Continued)

$L=3$; exact $\omega_r=0.468750$				$L=5$; exact $\omega_r=0.486111$			
k	α_k	γ_k	ω_{Calc}	k	α_k	γ_k	ω_{Calc}
0	1.31250 2	1.66666 -1	...	0	5.45736 4	6.66666 -2	...
1	3.32817 2	1.74411 -1	0.627981	1	1.04440 5	3.24127 -2	0.722867
2	9.81656 2	3.32948 -1	0.582268	2	2.31223 5	3.35467 -2	0.672077
3	3.18889 3	8.36027 -1	0.554829	3	5.68172 5	5.05280 -2	0.637934
4	1.10699 4	2.45112 0	0.536718	4	1.50961 6	9.53303 -2	0.613489
5	4.031983 4	7.93065 0	0.523979	5	4.26161 6	2.08978 -1	0.595176
6	1.52258 5	2.74527 1	0.514599	6	1.26556 7	5.09812 -1	0.580980
7	5.91278 5	9.97812 1	0.507450	7	3.89038 7	1.34712 0	0.569677
8	2.34766 6	3.76198 2	0.501854	8	1.23842 8	3.78652 0	0.560482
9	9.48996 6	1.45909 3	0.497377	9	4.05157 8	1.11792 1	0.552869
10	3.89298 7	5.78754 3	0.493731	10	1.35671 9	3.43494 1	0.546471
11	1.61665 8	2.33758 4	0.490718	11	4.63498 9	1.09085 2	0.541028
12	6.78306 8	9.58280 4	0.488197	12	1.61123 10	3.56167 2	0.536346
13	2.87103 9	3.97724 5	0.486064	13	5.68686 10	1.19063 3	0.532282
14	1.22437 10	1.66795 6	0.484242	14	2.03429 11	4.06159 3	0.528724
15	5.25536 10	7.05699 6	0.482674	15	7.36414 11	1.41009 4	0.525588
16	2.26853 11	3.00843 7	0.481315	16	2.69428 12	4.97134 4	0.522804
17	8.84077 11	1.29091 8	0.480128	17	9.95181 12	1.77657 5	0.520320
18	4.28747 12	5.57089 8	0.479086	18	3.70757 13	6.42550 5	0.518091
19	1.87518 13	2.41607 9	0.478167	19	1.39204 14	2.34901 6	0.516081
20	8.22933 13	1.05243 10	0.477352	20	5.26361 14	8.67031 6	0.514262
21	3.62250 14	4.60209 10	0.476626	21	2.00314 15	3.22807 7	0.512608
22	1.59895 15	2.01933 11	0.475977	22	7.66829 15	1.21130 8	0.511100
23	7.07495 15	8.88767 11	0.475396	23	2.95145 16	4.57777 8	0.509719
24	3.13739 16	3.92246 12	0.474872	24	1.14165 17	1.74129 9	0.508452
25	1.39405 17	1.73539 13	0.474400	25	4.43638 17	6.66296 9	0.507285
$L=4$; exact $\omega_r=0.480000$				$L=6$; exact $\omega_r=0.489795$			
0	2.12625 3	0.1	...	0	2.02702 6	4.76190 -2	...
1	4.56231 3	6.85304 -2	0.682676	1	3.56735 6	1.73226 -2	0.753800
2	1.13814 4	9.36179 -2	0.633130	2	7.21529 6	1.41135 -2	0.703146
3	3.14694 4	1.78031 -1	0.601388	3	1.61803 7	1.73453 -2	0.667780
4	9.37292 4	4.10941 -1	0.579437	4	3.92879 7	2.74110 -2	0.641747
5	2.95256 5	1.07664 0	0.563426	5	1.01607 8	5.13423 -2	0.621821
6	9.71526 5	3.08286 0	0.551280	6	2.76585 8	1.08702 -1	0.606106
7	3.30981 6	9.42509 0	0.541783	7	7.85443 8	2.52432 -1	0.593412
8	1.15993 7	3.02949 1	0.534176	8	2.31120 9	6.30050 -1	0.582959
9	4.16123 7	1.01290 2	0.527965	9	7.00963 9	1.66608 0	0.574211
10	1.52241 8	3.49577 2	0.522810	10	2.18198 10	4.61902 0	0.566790
11	5.66345 8	1.23824 3	0.518473	11	6.94735 10	1.33195 1	0.560422
12	2.13715 9	4.48198 3	0.514781	12	2.25623 11	3.97057 1	0.554903
13	8.16510 9	1.65219 4	0.511607	13	7.45653 11	1.21773 2	0.550077
14	3.15336 10	6.18609 4	0.508855	14	2.50281 12	3.82739 2	0.545825
15	1.22943 11	2.34743 5	0.506449	15	8.51812 12	1.22896 3	0.542053
16	4.83359 11	9.01218 5	0.504331	16	2.93542 13	4.02103 3	0.538687
17	1.91457 12	3.49536 6	0.502456	17	1.02302 14	1.33769 4	0.535666
18	7.63422 12	1.36789 7	0.500787	18	3.60183 14	4.51655 4	0.532941
19	3.06233 13	5.39598 7	0.499294	19	1.27996 15	1.54531 5	0.530472
20	1.23503 14	2.14371 8	0.497951	20	4.58729 15	5.35074 5	0.528227
21	5.00517 14	8.57076 8	0.496740	21	1.65689 16	1.87284 6	0.526176
22	2.03743 15	3.44628 9	0.495642	22	6.02740 16	6.61984 6	0.524297
23	8.32713 15	1.39290 10	0.494644	23	2.20722 17	2.36090 7	0.522571
24	3.41592 16	5.65612 10	0.493734	24	8.13215 17	8.48913 7	0.520978
25	1.40600 17	2.30654 11	0.492902	25	3.01316 18	3.07546 8	0.519507

$$Y_{2L}(0) = 2/L(L+1). \quad (17)$$

Equations (16) and (17) represent the exact values for the static multipole polarizabilities and shielding

factor of the hydrogen atom. These formulas are identical to those obtained by Dalgarno⁴ by the usual perturbation method and also to Eqs. (4.18) and (4.19) of paper I.

We have computed the values of $a_{k,n}$ for $k = 0, 1, \dots, 25$ and $n = 1, 2, \dots, 52$ for the first six multipoles,⁵ $L = 1$ to $L = 6$. Our values of $a_{k,n}$ for the dipole case for $k = 0, \dots, 14$ are the same as those given by Weiner and Askar.³ In Table I, we give the computed values of the Cauchy coefficients γ_k and α_k , and of the resonance frequency ω_r along with its exact values for all six cases, $L = 1$ to 6. The resonance frequencies are calculated by utilizing the radius-of-convergence criterion for the power series for $\alpha_{2L}(\omega^2)$:

$$\omega_r^2 = \lim_{k \rightarrow \infty} (\alpha_{k-1}) / \alpha_k. \quad (18)$$

We can compute ω_r to arbitrary accuracy by utilizing the values of α_k and α_{k-1} for different values of k . For the dipole case, by taking k as large as 25, we have been able to get better than 0.001% agreement for the resonance frequency. For the quadrupole resonance frequency, the agreement is within 1%, whereas for $L = 6$ our calculated value is as much as 6% off. Obviously, for higher multipoles one needs to include $a_{k,n}$ far beyond $k = 25$ to get good agreement. However, our calculated values of resonance frequencies for all multipoles are much closer to the exact values than those obtained by a variational approach.^{1,2,6} The reason lies in realizing that the resonance frequency is governed by the choice of G and convergence in it. Earlier^{1,2,6} we had taken a simple choice for G .

In Table II we have tabulated resonance frequencies for such a choice: they are inferior to present estimates. It should be added that recently⁷ we have used a better G function, obtaining resonance

TABLE II. Comparison of multipole resonance frequencies for the hydrogen atom (in a.u.).

L	Present	Exact	Previous (Refs. 1 and 6)
1	0.375 002	0.375 000	0.471 404
2	0.445 429	0.444 444	0.632 455
3	0.474 400	0.468 750	0.717 137
4	0.492 902	0.480 000	0.769 800
5	0.507 285	0.486 111	0.805 822
6	0.519 507	0.489 795	0.832 050

character in it. However, convergence is slow because for the dipole case, even with solving an 8×8 determinantal equation, we get a dipole resonance frequency of 0.398. Moreover, in the present case, we have a clear-cut prescription for computing ω_r for all multipoles to any arbitrary accuracy.

Finally, we add that calculations of Cauchy's coefficients are important in the study of multipole-multipole dispersion interactions⁸ when one member of the interacting pair or triplet is the hydrogen atom or another neutral atom or molecule.

ACKNOWLEDGMENTS

The authors take this opportunity to thank Professor A. Dalgarno of MIT and Professor R. M. Sternheimer of BNL for their interest in this work and for making their expert opinion available to us.

The authors thank Dr. R. AL Rashid for his encouragement during the course of this work.

*Present address: Dept. of Physics, Roorkee Univ., India.

¹G. C. Shukla and M. Barbaro, Phys. Rev. A 15, 23 (1977). There are three misprints in this paper; namely, in Eq. (2.7) the last term is $-1/R^2$ (not $1/R^3$), in the integral of Eq. (4.15) there should be division by R^{L-1} (not R^{L+1}), and $\omega_L = [(L+2/L)(1+1/2L)]^{-1/2}$ [Eq. (5.10)].

²A. Askar and M. Demiralp, J. Chem. Phys. 60, 2762 (1974).

³J. H. Wiener and A. Askar, J. Chem. Phys. 54, 1108

(1971).

⁴A. Dalgarno, Adv. Phys. 2, 281 (1962).

⁵The complete tables for $a_{k,n}$ for $L = 1$ to $L = 6$ are not presented here for economy of space. These will be given in M. Sc. thesis of one of the authors (F.N.Y.).

⁶G. C. Shukla and M. Barbaro, Instituto Superiore Di Sanita, Laboratorio de Fisica Report No. ISSP 75/15, 1975 (unpublished).

⁷F. N. Yousif and G. C. Shukla (to be published).

⁸P. W. Lianghoff and M. Karplus, J. Chem. Phys. 53, 233 (1970).