

Theory of Random Noise (Gordon and Breach, Science Publishers, Inc., New York, 1963), Vol. I.

³¹W. E. Lamb, Jr., in Quantum Optics and Electronics, edited by C. deWitt, A. Blandin, C. Cohen-Tannoudji (Gordon and Breach, Science Publishers, Inc., New York, 1965), p. 377

³²B. Picinbono and E. Boileau, *J. Opt. Soc. Am.* **58**, 785 (1968).

³³See for example, E. F. Keller, *Phys. Rev.* **139**, B202 (1965).

³⁴L. Mandel, in Progress in Optics, edited by E. Wolf

(North-Holland Publishing Company, Amsterdam, 1963), Vol. II, p. 181. See also Proceedings of the Symposium on Modern Optics (Polytechnic Press of the Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1967), Vol. XVII, p. 143.

³⁵See for example C. L. Mehta, Lectures in Theoretical Physics, edited by Wesley E. Brittin *et al.* (University of Colorado Press, Boulder, Colorado, 1965), Vol. VII C p. 345.

³⁶L. Mandel and E. Wolf, *Rev. Mod. Phys.* **37**, 231 (1965).

Perturbation Study of Some Excited States of Two-Electron Atoms

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A perturbation study of the NP states of two-electron atoms has been made. In particular, oscillator strength values for the (1^1S , 2^1P) and (2^3S , 2^3P) transitions are obtained. The 2^1P and 2^3P states are studied through ninth and tenth order, respectively. In addition, the N^1P and N^3P states are studied in first order through the $10P$ member of the series. Perturbation energy coefficients and other expectation values for several important operators have been computed. Perturbation energy coefficients for the 1^1S state (through 25th order) and 2^3S state (through 17th order) are also reported. Where comparison is possible, these results are in satisfactory agreement with the results obtained from variational calculations by C. L. Pekeris and co-workers. The variational-perturbation method for excited states requires auxiliary conditions on the perturbation wave functions. The condition on the n th-order wave function is derived here. This is a generalization of the first-order condition given by Sinanoğlu.

I. INTRODUCTION AND PROCEDURE

This study was undertaken in order to apply the variational-perturbation methods previously developed¹ to a study of the oscillator strengths in the 2^1P to 1^1S and the 2^3P to 2^3S transitions for the helium isoelectronic series. This task necessitated the construction of accurate $2P$ perturbation wavefunctions through high orders, and, concomitantly, the availability of 1^1S and 2^3S wave functions of comparable accuracy and order. For reasons of computational convenience, a new 1^1S ground-state wave function was determined, although similar wave functions already are in existence. In addition the $2P$ perturbation wave functions are themselves of interest, and a study has been made of their eigenvalues, expectation values with certain operators, etc. The perturbation energy coefficients for the 1^1S and 2^3S

states are also reported. The S state calculations were regarded as of secondary interest, and no detailed study of them is presented. Further, first-order studies of the NP states, N from 3 to 10, were completed, and are briefly reported.

1. Notation

The notation used here is as follows. Let the Hamiltonian be given in atomic units² by

$$H = H_0 + H_1 = H_0 + 1/Zr_{12}, \quad (1)$$

where Z is the nuclear charge and $1/Zr_{12}$ is regarded as the perturbation. Then a solution $\Psi^{(M)}$ for the M th state can be written

$$\Psi^{(M)} = \sum_n Z^{-n} \psi_n^{(M)}, \quad (2)$$

with eigenvalue

$$E^{(M)} = \sum_n Z^{-n} \epsilon_n^{(M)}. \quad (3)$$

The $\psi_n^{(M)}$ and $\epsilon_n^{(M)}$ are the n th-order perturbation expansion coefficients for the wave function and eigenvalue of the M th state. (In the following, the index M is suppressed when not explicitly required.) The ψ_0 and corresponding ϵ_0 and ϵ_1 are exactly known from elementary theory.³ An n th-order variational-perturbation procedure as usually applied furnishes simultaneously approximations for the ψ_i and the ϵ_j through $i=n$ and $j=2n+1$. Let Ω be any operator. Define

$$\langle i | \Omega | j \rangle = \int d\tau \psi_i^* \Omega \psi_j, \quad (4)$$

$$\langle i | j \rangle = \int d\tau \psi_i^* \psi_j. \quad (5)$$

In these terms, the expectation value of an operator Ω is given by

$$\langle \Omega \rangle = \sum_p Z^{-p} \langle \Omega \rangle_p, \quad (6)$$

$$\text{where } \langle \Omega \rangle_p = \sum_{m+n=p} \langle m | \Omega | n \rangle. \quad (7)$$

An interesting and useful pair of relations,

$$\langle r_1^{-1} + r_2^{-1} \rangle_p = (p-2)\epsilon_p, \quad (8a)$$

$$\langle r_{12} \rangle_p = (p+1)\epsilon_{p+1}, \quad (8b)$$

may be deduced, respectively, from the virial theorem and from the perturbation equations plus the requirement of orthonormality.

2. Oscillator Strengths

Oscillator strengths (f values) for the electric-dipole transitions obtained from time-dependent perturbation theory may be calculated by means of three alternative, but exactly equivalent, expressions; the dipole "length," "velocity," and "acceleration" formulas⁴:

$$f_L = 2(E^{(NP)} - E^{(MS)}) \times |\langle \Psi^{(NP)} | z_1 + z_2 | \Psi^{(MS)} \rangle|^2, \quad (9a)$$

$$f_V = 2(E^{(NP)} - E^{(MS)}) - 1 \times |\langle \Psi^{(NP)} | \partial/\partial z_1 + \partial/\partial z_2 | \Psi^{(MS)} \rangle|^2, \quad (9b)$$

$$f_A = 2(E^{(NP)} - E^{(MS)}) - 3 \times |\langle \Psi^{(NP)} | z_1/r_1^3 + z_2/r_2^3 | \Psi^{(MS)} \rangle|^2. \quad (9c)$$

The integral whose magnitude squared appears above is called the matrix element of the operator.

The three expressions above will give identical f values provided exact wave functions are used. Usually only approximate wave functions are available and three different f values are obtained. The velocity form of the operator generally gives the most accurate value when used with a variationally obtained wave function.

Equations (9) of course are also expressible as power series in Z^{-1} :

$$f = \sum_n Z^{-n} \langle f \rangle_n. \quad (10)$$

Order by order the agreement among the $\langle f \rangle_n$ should be exact.

3. Procedure

The form of the trial wave functions is⁵

$$\Phi_n = F_n r_1 \cos\theta_1 + \bar{F}_n r_2 \cos\theta_2 \quad (11)$$

for NP states, and

$$\Phi_n = F_n + \bar{F}_n \quad (12)$$

for NS states, where

$$\bar{F}_n(r_1, r_2, \cos\theta_{12}) = \pm F_n(r_2, r_1, \cos\theta_{12}).$$

The upper sign corresponds to a singlet, the lower sign to a triplet.

The F_n were taken as 100-term expansions of the form

$$F_n = (A + Br_{12}) \exp[-K_n(r_2 + N^{-1}r_1)], \quad (13)$$

with A and B both of the form

$$\sum_{a,b,l} \chi_{a,b,l} \binom{n}{a+l} r_1^{a+l} r_2^{b+l} P_l(\cos\theta_{12}). \quad (14)$$

The P_l are the Legendre polynomials.

The ratio of orbital exponents in Eq. (13) is the same ratio as for the zero-order wave functions (hydrogenic ratio). This preselection of ratio leaves only one over-all scale factor as our remaining nonlinear parameter. The effectiveness of this choice was tested by comparing the results for the ψ_1 with those from fully optimized two nonlinear parameter, 200-term wave functions for the $2P$ states. The choice made here is a practical compromise between utility and accuracy, and becomes progressively better for larger N .

4. Results

The 2^1P and 2^3P wave functions were determined through ninth order (19th order in energy) and tenth order (21st order in energy), respectively. The energy coefficients are listed in Table I. Total energies computed from the coefficients for

the first-few members of the helium isoelectronic sequence are tabulated in Table II. Tables III and IV present the perturbation operator expansion coefficients, [the $\langle \Omega \rangle_P$ of Eq. (7)], for various operators over these states. In these and the following tables it is convenient to use the definitions

$$r^n = r_1^n + r_2^n; \quad \omega = \cos\theta_{12}. \quad (15)$$

In Table V the ϵ_n calculated directly from the perturbation equations are compared with those calculated indirectly from Eqs. (8). Table VI provides a comparison of several total expectation values as given here with those calculated variationally by C. L. Pekeris *et al.*⁶ These $2P$ results are also compared in Table VII with the calculations of Machacek, Sanders, and Scherr⁷ and of Knight and Scherr.⁸ The results of the first-order calculations on the NP states ($N=3$ to 10) are collected in Tables VIII, IX, and X. Table XI presents a comparison, in first order, of the ϵ_1 similar to that of Table V.

The ϵ_n for the 1^1S and 2^3S states are tabulated in Tables XII and XIII. Table XII also compares the ϵ_n for 1^1S case with those previously calculated by Scherr and Knight¹ and by Mitdal.⁹ Total energies for the 2^3S state of two-electron atoms are presented in Table XIV.

The transitions of interest here are ($1^1S, N^1P$) and ($2^3S, N^3P$). The expansion coefficients for

TABLE I. The ϵ_n in atomic units.

n	2^1P	2^3P
0	-0.625 000 0	-0.625 000 00
1	0.259 868 9	0.225 727 79
2	-0.157 028 3	-0.072 998 91
3	0.026 105 0	-0.016 585 44
4	0.005 788 8	-0.010 353 09
5	-0.005 041 3	-0.005 424 84
6	-0.007 066 6	-0.002 020 80
7	-0.001 259 5	0.000 238 27
8	0.003 405 1	0.001 610 32
9	0.001 920 9	0.002 269 62
10	-0.001 608 7	0.002 361 71
11	-0.001 878 5	0.002 024 55
12	0.000 602 1	0.001 401 32
13	0.001 811 8	0.000 636 60
14	0.000 409 0	-0.000 136 89
15	-0.001 141 2	-0.000 800 33
16	-0.000 536 4	-0.001 257 41
17	0.001 368 1	-0.001 465 40
18	0.000 702 7	-0.001 363 56
19	-0.001 361 4	-0.000 996 01
20		-0.000 309 63
21		0.000 488 73

TABLE II. The total energies in atomic units.

Z	2^1P	2^3P
1	-0.499 939 5 ^a	-0.501 953 41 ^a
2	-2.123 842 3	-2.133 163 82
3	-4.993 350 6	-5.027 715 53
4	-9.110 771 3	-9.174 973 05
5	-14.477 283 0	-14.573 137 61
6	-21.093 332 0	-21.221 710 63
7	-28.959 116 1	-29.120 501 68
8	-38.074 735 0	-38.269 422 65
9	-48.440 244 0	-48.668 427 23
10	-60.055 676 5	-60.317 488 76

^aThe $Z=1$ sums have still not converged in 19th (2^1P) and 21st (2^3P) order.

the oscillator strengths of these transitions are listed in Table XV for $N=2$, and Table XVI for $N=3$ to 10. Table XVII tabulates the total oscillator strengths obtained from these $\langle f \rangle_n$ for transitions from the $2P$ states. For the helium atom case ($Z=2$) it is possible to compare these f values with those found¹⁰ by Schiff and Pekeris (Table XVIII). All calculations were performed in "double precision" (28 decimal figure arithmetic) on the CDC 6600 located on this campus.

II. DISCUSSION

1. The $2P$ States

A discussion of the convergence of variational-perturbation calculations must recognize two types of convergence: the perturbational convergence of the entire perturbation series, and the variational convergence of each term in the series. The most striking feature of the present calculations is the perturbational convergence of the $2P$ states energy coefficients as displayed in Fig. 1. For comparison, Fig. 2 shows similar curves (on a different scale) for the 1^1S and 2^3S states. The ϵ_n for the $2P$ states fall off sufficiently fast to permit a satisfactory estimate of the energy sum for all members of the helium isoelectronic sequence except H^- ($Z=1$). In this case we are interested in determining whether the ion is bound - i. e., whether the energy value sums to less than - 0.5 a. u. The truncated energy sums computed through each order are shown in Fig. 3. Although the perturbation series seems to be convergent for both these states, the truncation of the series is clearly premature. However, both states appear to be approaching final values close to - 0.5 a. u.

For all other values of Z , the accuracy with which these energy values can be obtained is limited by the variational convergence of the ϵ_2 's. The degree of convergence to be attributed to these ϵ_2 's may be estimated by comparing them

TABLE III. The $\langle \Omega \rangle_p$ in atomic units -the 2^1P state.

Ω/p	1	2	3	4	5	6	7	8	9
$\pi\delta(\tilde{r})$	0.02183	-0.04862	-0.01131	0.05083	0.03632	-0.03392	-0.04609	0.00838	0.04577
$\pi\delta(\tilde{r}_{12})$	-0.03993	0.07559	-0.06491	0.01600	0.00802	0.00222	-0.00421	-0.00512	0.00028
$r_1^{-1}r_2^{-2}$	-0.2681580	0.0171113	0.0320781	-0.0030068	-0.0333304	-0.0222890	0.0140523	0.0236526	-0.0020155
r^{-1}/r_{12}	-0.489573	0.185085	0.023095	-0.043021	-0.063263	-0.002688	0.041690	0.020121	-0.026865
r^{-1}	-0.2598688	-0.0000009	0.0261249	0.0115472	-0.0150271	-0.0284010	-0.0062454	0.0203043	0.0135447
r_{12}^{-1}	-0.3140567	0.0783138	0.0231571	-0.0252174	-0.0423925	-0.0088195	0.0272432	0.0173234	-0.0162280
ω/r_{12}	-0.1816427	0.1485681	0.0155463	-0.0457468	-0.0329039	0.0179891	0.0339485	-0.0013525	-0.0300977
r/r_{12}	-0.6139236	0.2527918	0.0750987	-0.0844994	-0.1175254	-0.0025935	0.0861748	0.0326801	-0.0624976
ω	-0.2651903	0.1448163	0.1444562	-0.0232910	-0.1026597	-0.0241176	0.0683071	0.0418654	-0.0472569
$r\omega/r_{12}$	-0.75359	0.47660	0.14905	-0.09473	-0.18813	-0.00027	0.14239	0.04951	-0.10687
r	5.388425	5.284844	4.545080	4.098365	4.502119	5.213106	5.362283	4.961962	4.754984
r_{12}	5.6284	5.0068	4.3769	4.0502	4.6671	5.2743	5.2571	4.8810	4.8219
r^2/r_{12}	4.023895	5.723702	4.879816	4.026459	4.213140	5.119541	5.532491	5.091039	4.647848
$r\omega$	-1.3278724	0.2494423	0.8702112	0.2814484	-0.4257796	-0.3391280	0.2180392	0.3564512	-0.0693630
$r_1r_2\omega/r_{12}$	-0.8023	0.3584	0.2515	-0.0119	-0.2270	-0.0774	0.1377	0.1050	-0.0870
$r^2\omega/r_{12}$	-1.7550	0.9412	0.4256	0.2153	-0.4535	-0.2019	0.2808	0.2654	-0.1378
r^2	64.6888	97.3899	121.3102	140.9646	166.4682	200.1513	234.5490	263.6892	290.6381
r_{12}^2	67.9496	97.7290	119.1181	139.4334	167.0903	201.3365	234.4110	262.6443	290.3967
r^3/r_{12}	60.9116	97.8250	122.5851	141.4202	165.8468	199.5911	234.8202	264.2462	290.6004
$r_1r_2\omega$	-1.630382	-0.169545	1.096090	0.765624	-0.311036	-0.592615	0.068979	0.522466	0.120732
$r^2\omega$	-4.24403	-1.51188	1.96444	1.98658	-0.46144	-1.59055	-0.21757	1.18352	0.54840
$r^3\omega/r_{12}$	-3.357	3.828	2.561	4.319	1.404	1.257	2.762	3.537	2.712
r^3	678.337	1379.995	2225.787	3178.294	4303.045	5682.219	7317.978	9153.411	11165.281
$r^3\omega$	-17.01	-18.83	-8.23	2.01	-6.14	-14.38	-13.24	-30.88	141.67

TABLE IV. The $\langle Q \rangle_p$ in atomic units—the 2^3P state.

Ω/p	1	2	3	4	5	6	7	8	9	10
$\pi\delta(\bar{r})$	-0.085 93	0.121 04	0.026 46	-0.066 13	-0.023 35	-0.029 66	-0.027 76	-0.020 35	-0.009 60	0.002 05
$r_1^{-1}r_2^{-1}$	-0.198 087 778	-0.029 449 117	-0.036 537 066	-0.023 259 255	-0.009 185 641	0.003 365 661	0.013 252 606	0.019 525 668	0.021 692 072	0.019 707 120
r^{-1}/r_{12}	-0.265 760 1	-0.029 849 0	-0.043 553 0	-0.024 311 7	-0.005 664 0	0.010 091 3	0.021 627 0	0.027 909 3	0.028 573 1	0.023 866 5
r^{-1}	-0.225 727 75	-0.000 000 13	-0.016 582 07	-0.020 705 44	-0.016 262 41	-0.008 078 95	0.001 190 51	0.009 641 37	0.015 866 37	0.018 844 99
r_{12}^{-1}	-0.145 997 8	-0.049 756 5	-0.041 412 4	-0.027 125 3	-0.012 126 7	0.001 666 0	0.012 882 2	0.020 426 2	0.023 622 9	0.022 271 7
ω/r_{12}	-0.000 587 1	0.009 585 2	-0.002 717 1	-0.005 604 9	-0.005 927 3	-0.004 618 7	-0.002 373 0	0.000 240 1	0.002 646 3	0.004 463 8
r/r_{12}	-0.116 069 77	-0.062 627 37	-0.063 563 51	-0.053 040 59	-0.036 086 58	-0.016 032 18	0.004 048 01	0.021 380 99	0.033 554 26	0.039 027 21
ω	0.045 492 43	0.066 764 39	0.026 953 28	-0.002 194 04	-0.019 594 44	-0.027 415 07	-0.027 582 65	-0.021 877 22	-0.012 335 91	-0.000 925 02
$r\omega/r_{12}$	-0.014 25	0.065 46	-0.007 21	-0.023 31	-0.038 91	-0.037 11	-0.027 78	-0.012 78	0.002 87	0.018 86
r	3.910 606	3.951 611	4.543 673	5.161 472	5.652 695	5.966 905	6.085 280	6.010 315	5.766 460	5.398 616
r_{12}	3.670 32	3.775 25	4.484 54	5.130 88	5.669 59	6.007 81	6.139 14	6.063 86	5.811 45	5.424 11
r^2/r_{12}	3.648 018	3.941 868	4.512 012	5.089 059	5.564 757	5.888 775	6.034 630	5.996 515	5.790 897	5.455 619
$r\omega$	0.060 311 3	0.342 180 9	0.225 706 3	0.062 378 8	-0.057 956 2	-0.124 793 2	-0.144 421 9	-0.126 255 1	-0.081 090 9	-0.020 764 4
$r_1^2\omega/r_{12}$	-0.011 15	0.083 31	0.013 74	-0.020 91	-0.052 42	-0.059 52	-0.052 25	-0.033 67	-0.010 28	0.015 75
$r^2\omega/r_{12}$	-0.004 1	0.352 8	0.076 3	0.049 7	-0.063 0	-0.097 2	-0.104 2	-0.080 4	-0.046 5	0.008 0
r^2	47.083 28	67.428 69	94.489 53	126.690 51	162.649 13	201.065 58	240.547 84	279.653 93	317.039 78	351.616 17
r_{12}^2	47.271 73	66.583 31	93.686 27	126.326 47	162.690 61	201.371 86	240.968 78	280.060 51	317.333 19	351.734 17
r^3/r_{12}	46.230 61	67.516 27	94.655 90	126.684 78	162.492 27	200.842 91	240.339 90	279.519 51	317.012 69	351.704 52
$r_1^3\omega$	-0.089 227	0.422 693	0.396 630	0.182 015	-0.020 740	-0.153 139	-0.210 468	-0.203 293	-0.146 708	-0.059 003
$r^2\omega$	-0.615 628	0.521 893	0.513 832	0.073 869	-0.340 260	-0.581 787	-0.635 293	-0.527 804	-0.302 153	-0.011 832
$r^3\omega/r_{12}$	0.906	2.950	2.205	2.677	2.437	2.469	2.512	2.609	2.668	2.777
r^3	499.158	921.224	1534.543	2374.721	3470.428	4843.282	6505.407	8457.880	10 690.534	13 133.149
$r^3\omega$	-6.66	-4.42	-4.67	-8.16	-10.71	-14.12	-14.86	-19.35	-8.08	-15.04

TABLE V. The ϵ_n calculated three ways.

n	2^1P			2^3P		
	Via Eq. (8a)	Via Eq. (8b)	Directly	Via Eq. (8a)	Via Eq. (8b)	Directly
1	0.259 868 8		0.259 868 9	0.225 727 75		0.225 727 79
2		-0.157 028 338 2	-0.157 028 338 2		-0.072 998 914 04	-0.072 998 914 04
3	0.026 124 9	0.026 104 6	0.026 105 0	-0.016 582 07	-0.016 585 50	-0.016 585 44
4	0.005 773 6	0.005 789 3	0.005 788 8	-0.010 352 72	-0.010 353 10	-0.010 353 09
5	-0.005 009 0	-0.005 043 5	-0.005 041 3	-0.005 420 80	-0.005 425 05	-0.005 424 84
6	-0.007 100 2	-0.007 065 4	-0.007 066 6	-0.002 019 74	-0.002 021 12	-0.002 020 80
7	-0.001 249 1	-0.001 259 9	-0.001 259 5	0.000 238 10	0.000 238 00	0.000 238 27
8	0.003 384 1	0.003 405 4	0.003 405 1	0.001 606 89	0.001 610 28	0.001 610 32
9	0.001 935 0	0.001 924 8	0.001 920 9	0.002 266 62	0.002 269 58	0.002 269 62
10		-0.001 622 8	-0.001 608 7		0.002 362 29	0.002 361 71

TABLE VI. A comparison with the results of Pekeris. For each operator, the first line contains the results obtained in the present paper, the second line contains the results obtained by B. Schiff, H. Lifson, C. L. Pekeris, and P. Rabinowitz (Ref. 6).

$\langle \Omega \rangle$	2^1P He	2^1P Li ⁺	2^3P He
E	-2.123 842 3 -2.123 843 085 800	-4.993 350 6 -4.993 351 074 6	-2.133 163 82 -2.133 164 190 534
$\pi \langle \delta(\vec{r}) \rangle$	8.007 12 8.007 247 060	27.058 58 27.058 985 77	7.909 70 7.909 653 61
$\pi \langle \delta(\vec{r}_{12}) \rangle$	0.002 33 0.002 31 102	0.030 95 0.030 922 40	
$\langle r^{-1} \rangle$	2.246 368 0 2.246 355 019 4	3.493 161 1 3.493 159 082	2.266 462 33 2.266 484 844 8
$\langle r_{12}^{-1} \rangle$	0.245 008 4 0.245 023 869	0.492 775 9 0.492 775 102	0.266 626 5 0.266 641 309
$\langle r \rangle$	5.818 686 5.821 368 46	3.043 831 3.043 864 02	5.345 595 5.345 792 322
$\langle r_{12} \rangle$	5.135 6 5.138 328 1	2.592 2 2.592 468 7	4.697 41 4.699 954 93
$\langle r^2 \rangle$	31.434 9 31.531 302	8.082 7 8.083 254 2	26.322 97 26.423 478 6
$\langle r_{12}^2 \rangle$	31.502 1 31.598 508	8.073 7 8.074 208	26.542 34 26.642 791

with the results of the 200-term calculations and by an examination of the $-\langle r^{-1} \rangle_1$ of Table V. It should be noted that the extent of agreement between $-\langle r^{-1} \rangle_1$ and ϵ_2 , rather than directly reflecting the accuracy of the first-order wave function, is influenced to some extent by the care with which the scale factors have been obtained. It can be concluded that the 200-term ϵ_2 's are correct to at least seven and eight decimal places for the 2^1P and 2^3P states,¹¹ respectively. If

this is correct, then the 100-term ϵ_2 's are converged to within three units in the seventh decimal place for the 2^1P state and six units in the eighth decimal place for the 2^3P state. The ϵ_n of Table I and the total energies of Table II have accordingly been rounded off to seven and eight decimal places for the singlet and triplet states, respectively. The validity of this procedure is borne out by a comparison (in Table VI) with the total energies for the $2P$ states computed by

TABLE VII. A comparison of the results of the present paper (PP), arbitrarily truncated to six decimal figures, with the results of Machacek, Sanders, and Scherr (MSS, Ref. 7) and of Knight and Scherr (KS, Ref. 8).

$\langle \Omega \rangle_p$	2^1P			2^3P		
	PP	MSS	KS	PP	MSS	KS
ϵ_2	-0.157 028	-0.157 023	-0.157 021	-0.072 999	-0.072 997	-0.072 992
ϵ_3	0.026 105	0.026 06	0.026 124	-0.016 585	-0.016 61	-0.016 558
ϵ_4	0.005 789	0.006 1	0.006 046 ^a	-0.010 353	-0.010 13	
ϵ_5	-0.005 041	-0.006	-0.004 429 ^a	-0.005 425	-0.006 5	
ϵ_6	-0.007 067	-0.006	-0.004 777 ^a			
$\pi \langle \delta(\vec{r}) \rangle_1$	0.021 832		0.021 140	-0.085 931		-0.087 287
$\pi \langle \delta(\vec{r}_{12}) \rangle_1$	-0.039 931		-0.039 811			
$\langle r^{-1} \rangle_1$	-0.259 869	-0.264 064	-0.259 865	-0.225 728	-0.225 0	-0.225 724
$\langle r^{-1} \rangle_2$	-0.000 001	-0.001 0		-0.000 000	0.001 4	
$\langle r^{-1} \rangle_3$	0.026 125	0.032 08		-0.016 582	-0.029 0	
$\langle r_{12}^{-1} \rangle_1$	-0.314 057	-0.314 34	-0.314 042	-0.145 998	-0.144 7	-0.145 985
$\langle r_{12}^{-1} \rangle_2$	0.078 314	0.078 7		-0.049 757	-0.049 0	
$\langle r_{12}^{-1} \rangle_3$	0.023 157	0.013 1		-0.041 412	-0.051 8	
$\langle \omega \rangle_1$	-0.265 190		-0.265 194	0.045 492		0.045 474
$\langle r \rangle_1$	5.388 425	5.428	5.387 978	3.910 606	3.938	3.910 008
$\langle r \rangle_2$	5.284 844	4.600		3.951 611	3.362	
$\langle r_{12} \rangle_1$	5.628 437	5.633	5.594 593	3.670 319	3.677	3.647 599
$\langle r_{12} \rangle_2$	5.006 811	4.41		3.775 250	3.20	
$\langle r^2 \rangle_1$	64.688 850	65.92	64.678 840	47.093 281	47.98	47.080 533
$\langle r^2 \rangle_2$	97.389 904	74.6		67.428 692	49.6	
$\langle r_{12}^2 \rangle_1$	67.949 614	69.2		47.271 735	48.2	
$\langle r_{12}^2 \rangle_2$	97.728 995	75.2		66.583 306	48.7	
$\langle r_1 r_2 \omega \rangle_1$	-1.630 382		-1.630 300	-0.089 227		-0.089 078

^aR. E. Knight and C. W. Scherr, unpublished material.

TABLE VIII. Perturbation energy coefficients in atomic units.

N	N^1P		N^3P	
	ϵ_2	ϵ_3	ϵ_2	ϵ_3
3	-0.060 750 9	-0.000 279 8	-0.041 856 07	-0.003 351 84
4	-0.032 975 6	-0.000 667 2	-0.025 643 48	-0.001 323 27
5	-0.020 764 5	-0.000 467 1	-0.017 158 79	-0.000 671 90
6	-0.014 261 4	-0.000 426 5	-0.012 242 25	-0.000 424 41
7	-0.010 379 3	-0.000 491 2	-0.009 155 61	-0.000 302 36
8	-0.007 890 5	-0.000 417 5	-0.007 094 35	-0.000 239 89
9	-0.006 205 9	-0.000 371 7	-0.005 658 53	-0.000 209 86
10	-0.005 016 1	-0.000 232 9	-0.004 619 86	-0.000 120 34

Pekeris and co-workers.⁶ These highly accurate variational calculations are based on 560-term expansion approximations (364 terms for the Li⁺ case). A similar procedure has been applied to the $\langle \Omega \rangle_p$ of Tables III and IV. For operators such as r^2 , whose total expectation values receive significant contributions from higher-order terms not considered here, the comparisons of Table VI are not useful.

Machacek, Sanders, and Scherr⁷ have computed variational energies and expectation values for the $2P$ states of the helium isoelectronic sequence. They have recovered the first-few coefficients of the perturbation sequence from their data via a "differencing technique." Their results, together with the first-order results of Knight and Scherr,⁸ are compared with the present data in Table VII.

TABLE IX. The $\langle \Omega \rangle_1$ in atomic units—the N^1P states.

Ω/N	3	4	5	6	7	8	9	10
$\pi\delta(\vec{r}_1)$	0.00077	0.00009	0.00009	0.00021	0.00101	-0.00091	0.00015	-0.00004
$\pi\delta(\vec{r}_{12})$	-0.01138	-0.00468	-0.00231	-0.00125	-0.00073	-0.00046	-0.00031	-0.00022
$r_1^{-1}r_2^{-1}$	-0.1138350	-0.0633698	-0.0403824	-0.0279547	-0.0204963	-0.0156648	-0.0123680	-0.0101424
r^{-1}/r_{12}	-0.172429	-0.087263	-0.052379	-0.034738	-0.024639	-0.018362	-0.014220	-0.011347
r^{-1}	-0.1133575	-0.0633605	-0.0404208	-0.0280153	-0.0205554	-0.0157226	-0.0124138	-0.0100497
r_{12}^{-1}	-0.1215017	-0.0659513	-0.0415290	-0.0285227	-0.0207587	-0.0157810	-0.0124117	-0.0100322
ω/r_{12}	-0.0418736	-0.0163629	-0.0080766	-0.0045336	-0.0027150	-0.0016994	-0.0010958	-0.0007514
r/r_{12}	-0.1996115	-0.1039494	-0.0644007	-0.0438124	-0.0315571	-0.0237259	-0.0184535	-0.0148451
ω	-0.0488265	-0.0180702	-0.0088137	-0.0051038	-0.0033880	-0.0023021	-0.0017449	0.0011270
$r\omega/r_{12}$	0.42018	-0.08095	0.16085	-0.20045	0.06185	0.00022	0.08983	-0.00641
r	12.961524	23.589779	37.217221	53.840309	73.484554	96.117876	121.807467	150.416078
r_{12}	11.7608	23.5652	36.8048	54.1530	73.3188	96.0822	121.6093	150.4065
r^2/r_{12}	12.554083	23.379221	37.086896	53.751373	73.419935	96.068713	121.769696	150.390133
$r\omega$	-0.2780126	-0.1362968	-0.0840798	-0.0547858	-0.0512052	-0.0001294	-0.1787385	0.1859676
$r_1r_2\omega/r_{12}$	0.3967	-0.0930	0.1410	-0.2008	0.0506	-0.0068	0.0802	-0.0082
$r^2\omega/r_{12}$	4.0547	-0.1999	1.3747	-1.3286	0.5212	0.0909	0.5384	0.1697
r^2	373.9515	1231.9322	3059.9961	6399.9938	11919.9920	20395.8365	32755.3899	49967.8302
r_{12}^2	374.7110	1232.3703	3060.2864	6400.2038	11920.1462	20395.9421	32755.9882	49967.1286
r^3/r_{12}	372.7760	1231.2686	3059.5643	6399.6889	11919.7667	20395.6709	32755.0026	49968.1101
$r_1r_2\omega$	-0.379776	-0.219054	-0.145185	-0.104988	-0.077101	-0.052808	-0.299138	0.350824
$r^2\omega$	-1.98549	-1.94073	-2.03485	-1.49646	-4.31749	7.92557	-26.61649	27.57670
$r^3\omega/r_{12}$	28.895	9.580	24.581	18.492	35.538	56.484	38.196	102.718
r^3	8638.140	51748.647	200771.419	604578.342	1532881.928	3425636.145	6964887.054	13114397.676
$r^3\omega$	-24.12	-45.17	-81.69	-28.18	-583.95	1484.47	-4066.36	4567.98

TABLE X. The $\langle \Omega \rangle_1$ in atomic units—the $N^3 P$ states.

Ω/N	3	4	5	6	7	8	9	10
$\pi\delta(\vec{r}_1)$	-0.01047	-0.00414	-0.00211	-0.00081	0.00002	-0.00120	-0.00041	-0.00034
$r_1^{-1}r_2^{-1}$	-0.098484564	-0.057474689	-0.037485562	-0.026314363	-0.019460882	-0.014948308	-0.011835888	-0.009605558
r^{-1}/r_{12}	-0.1217805	-0.0677950	-0.0428929	-0.0294658	-0.0214383	-0.0162523	-0.0127385	-0.0102585
r^{-1}	-0.10429382	-0.05967211	-0.03856294	-0.02694965	-0.01988709	-0.01527752	-0.01210148	-0.00982711
r_{12}^{-1}	-0.0837121	-0.0512870	-0.0343176	-0.0244845	-0.018311	-0.0141887	-0.0113171	-0.0092397
ω/r_{12}	-0.0036850	-0.0019492	-0.0010880	-0.0006505	-0.0003949	-0.0002197	-0.0001069	-0.0000464
r/r_{12}	-0.10347832	-0.06823292	-0.04713237	-0.03424357	-0.02589052	-0.02018095	-0.01614542	-0.01321305
ω	-0.00217668	-0.00232542	-0.00148543	-0.00100108	-0.00075695	-0.00056543	-0.00049857	0.00167500
$r\omega/r_{12}$	-0.98988	-0.20760	0.01476	-0.16653	0.03527	0.00318	0.06490	-0.00441
r	10.899432	20.870362	33.836888	49.801291	68.760756	90.721543	115.713648	143.643859
r_{12}	12.87683	21.16517	33.73976	50.06923	68.65717	90.68735	115.56833	143.63379
r^2/r_{12}	10.653650	20.715393	33.732713	49.726789	68.704799	90.677887	115.678600	143.619411
$r\omega$	-0.1713520	-0.1117652	-0.0748736	-0.0520279	-0.0454081	-0.0118299	-0.1444317	0.1611806
$r_1r_2\omega/r_{12}$	-1.01159	-0.22489	-0.00352	-0.17122	0.02381	-0.00473	0.05514	-0.00719
$r^2\omega/r_{12}$	-7.1569	-1.4018	0.1802	-1.1570	0.2873	0.0699	0.3724	0.1480
r^2	313.95684	1088.92272	2781.02046	5919.36817	1152.37129	19249.55818	31113.58395	47714.06400
r_{12}^2	314.69986	1089.39561	2781.33732	5919.59248	1152.55042	19249.62713	31114.17208	47713.42475
r^3/r_{12}	313.01767	1088.32607	2780.61685	5919.07913	1152.14816	19249.41703	31113.20611	47714.31481
$r_1r_2\omega$	-0.371508	-0.236443	-0.158427	-0.112154	-0.089563	-0.034478	-0.294070	0.319625
$r^2\omega$	-2.073454	-2.048830	-2.053656	-1.810148	-3.492947	4.592311	-21.453824	23.823900
$r^3\omega/r_{12}$	-35.772	1.272	16.241	17.051	32.700	50.372	39.226	95.616
r^3	7431.725	45768.113	182556.888	559434.925	1434450.388	3233613.556	6616070.732	12523109.970
$r^3\omega$	-26.54	-46.53	-76.86	-69.64	-420.87	968.96	-3272.43	3947.95

TABLE XI. The ϵ_1 calculated two ways.

N	N^1P		N^3P	
	Via Eq. (8a)	Directly	Via Eq. (8a)	Directly
3	0.113 357 5419	0.113 357 5439	0.104 293 8229	0.104 293 8232
4	0.063 360 4550	0.063 360 4710	0.059 672 1061	0.059 672 1050
5	0.040 420 8139	0.040 420 8752	0.038 562 9352	0.038 562 9851
6	0.028 015 2955	0.028 015 2948	0.026 949 6502	0.026 949 5099
7	0.020 555 3777	0.020 555 4712	0.019 887 0927	0.019 887 8230
8	0.015 722 6108	0.015 722 7077	0.015 277 5162	0.015 276 9524
9	0.012 413 8349	0.012 413 8342	0.012 101 4796	0.012 101 4926
10	0.010 049 7292	0.010 049 4420	0.009 827 1149	0.009 822 1224

TABLE XII. The ϵ_n in atomic units – the 1^1S state. Comparison of the results of the present paper (PP) with those of Scherr and Knight (SK, Ref. 1) and the 203-term results of J. Mitdal (JM, Ref. 9).

n	PP	SK	JM
0	-1.000 000 00	-1.000 000 00	-1.000 000 00
1	0.625 000 00	0.625 000 00	0.625 000 00
2	-0.157 666 38	-0.157 666 41	-0.157 666 24
3	0.008 698 97	0.008 698 99	0.008 698 50
4	-0.000 888 50	-0.000 888 59	-0.000 888 05
5	-0.001 036 35	-0.001 036 37	-0.001 036 86
6	-0.000 612 73	-0.000 612 92	-0.000 612 70
7	-0.000 372 04	-0.000 372 19	-0.000 372 25
8	-0.000 242 75	-0.000 242 87	-0.000 242 86
9	-0.000 165 58	-0.000 165 65	-0.000 165 66
10	-0.000 116 12	-0.000 116 16	-0.000 116 18
11	-0.000 083 26	-0.000 083 28	-0.000 083 30
12	-0.000 060 85	-0.000 060 87	-0.000 060 88
13	-0.000 045 21	-0.000 045 21	-0.000 045 23
14	-0.000 034 06		-0.000 034 08
15	-0.000 025 98		-0.000 025 99
16	-0.000 020 02		-0.000 020 03
17	-0.000 015 58		-0.000 015 58
18	-0.000 012 22		-0.000 012 22
19	-0.000 009 66		-0.000 009 66
20	-0.000 007 68		-0.000 007 69
21	-0.000 006 15		-0.000 006 15
22	-0.000 004 95		
23	-0.000 004 00		
24	-0.000 003 25		
25	-0.000 002 65		

2. Oscillator Strengths

The zero-order energies for the 2^3P and 2^3S states are the same. Thus the lead coefficient in the length expansion vanishes. If identical expansions are to be obtained from each of the three forms of the operator, the first *two* terms of the velocity expansion, and the first *four* terms of the acceleration expansions must also vanish.

Since the leading (zero-order) coefficients in the corresponding matrix element expansions for the velocity and acceleration forms are both rigorously zero, it follows that the first *two* f coefficients for both these forms are also rigorously zero. However, the second matrix element expansion coefficient for the acceleration form and hence the third and fourth f expansion coefficients must be computed to be zero from the

TABLE XIII. The ϵ_n in atomic units – the 2^3S state.

n	ϵ_n
0	-0.625 000 00
1	0.187 928 67
2	-0.047 409 27
3	-0.004 872 43
4	-0.003 457 57
5	-0.002 030 06
6	-0.001 287 02
7	-0.000 871 45
8	-0.000 617 90
9	-0.000 454 12
10	-0.000 343 38
11	-0.000 265 65
12	-0.000 209 38
13	-0.000 167 54
14	-0.000 133 73
15	-0.000 097 89
16	-0.000 044 08
17	0.000 048 21

approximate wave functions. In the present case, the third expansion coefficient for the acceleration form of the operator was 10^{-8} and the fourth coefficient was 10^{-4} .

TABLE XIV. The total energies in atomic units—the 2^3S state. Comparison of the results of the present paper (PP) with the extrapolated results of Pekeris (P) Phys. Rev. 126, 1470 (1962); and 126, 143 (1962).

Z	PP	EP
1	-0.499 284 59	-0.499 3
2	-2.175 229 36	-2.175 229 38
3	-5.110 727 36	-5.110 727 37
4	-9.297 166 58	
5	-14.733 897 33	
6	-21.420 755 88	
7	-29.357 681 72	
8	-38.544 647 30	
9	-48.981 638 30	
10	-60.668 646 56	

The f expansion coefficients for the (1^1S , 2^1P) and the (2^3S , 2^3P) transitions, presented in Table XV, and the total oscillator strengths furnished by the truncated perturbation sums, shown in Table XVII, show a satisfactory degree of consistency. For a proper comparison, it should be borne in mind that the (2^3S , 2^3P) total oscillator strength sums have been truncated at widely different points for the three forms of the operator

TABLE XV. The $\langle f \rangle_n$ in atomic units.

n	$(1^1S, 2^1P)$			$(2^3S, 2^3P)$		
	Length	Velocity	Acceleration	Length	Velocity	Acceleration
0	0.832 393 4360	0.832 393 4360	0.832 393 4360	0.	0.	0.
1	-1.068 552	-1.068 491	-1.068 734	0.680 384	0.	0.
2	-0.334 404	-0.334 209	-0.333 685	0.572 321	0.680 386	0.
3	0.392 916	0.393 193	0.392 248	0.414 668	0.572 338	-0.000 481
4	0.319 247	0.318 963	0.320 638	0.221 902	0.414 735	0.682 669
5	-0.163 645	-0.164 139	-0.166 487	0.008 914	0.222 063	0.563 913
6	-0.276 357	-0.277 273	-0.280 672	-0.203 524	0.009 049	0.413 123
7	0.083 525	0.083 593	0.083 082	-0.394 358	-0.204 538	0.239 757
8	0.327 886	0.328 290	0.314 556	-0.624 501	-0.376 310	0.027 832
9	0.113 510	0.113 864	0.145 743			

TABLE XVI. First-order f (velocity) expansion coefficients.^a

N	$(1^1S, N^1P)$		$(2^3S, N^3P)$	
	$\langle f \rangle_0$	$\langle f \rangle_1$	$\langle f \rangle_0$	$\langle f \rangle_1$
3	0.158 203 1250	-0.066 620	0.434 865 4387	-0.667 372
4	0.057 982 0585	-0.010 792	0.102 764 6217	-0.095 601
5	0.027 876 6878	-0.002 398	0.041 930 0729	-0.030 990
6	0.015 598 9854	-0.000 522	0.021 629 3335	-0.014 325
7	0.009 627 9016	-0.000 014	0.012 740 3828	-0.008 067
8	0.006 366 8546	-0.000 121	0.008 180 5578	-0.005 106
9	0.004 432 2176	-0.000 146	0.005 583 0816	-0.003 571
10	0.003 210 7346	-0.000 140	0.003 988 2514	-0.002 620

^aSimilar coefficients for the length and acceleration forms are available upon request.

TABLE XVII. Total f values in atomic units.

Z	Length	$(1^1S, 2^1P)$		$(2^3S, 2^3P)$		
		Velocity	Acceleration	Length	Velocity	Acceleration
2	0.276 113	0.276 182	0.276 012	0.540 553	0.543 145	0.549 327
3	0.456 585	0.456 631	0.456 578	0.307 965	0.308 075	0.308 108
4	0.551 524	0.551 555	0.551 515	0.213 137	0.213 151	0.212 850
5	0.608 893	0.608 914	0.608 881	0.162 625	0.162 629	0.162 307
6	0.647 051	0.647 068	0.647 038	0.131 381	0.131 383	0.131 063
7	0.674 185	0.674 198	0.674 172	0.110 177	0.110 178	0.109 858
8	0.694 439	0.694 450	0.694 426	0.094 854	0.094 855	0.094 531
9	0.710 121	0.710 131	0.710 109	0.083 266	0.083 267	0.082 937
10	0.722 617	0.722 625	0.722 606	0.074 198	0.074 199	0.073 863

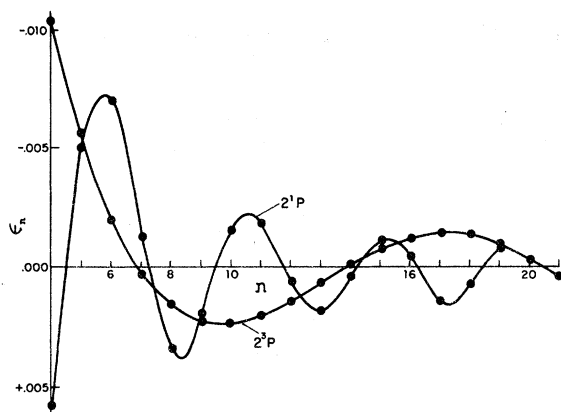
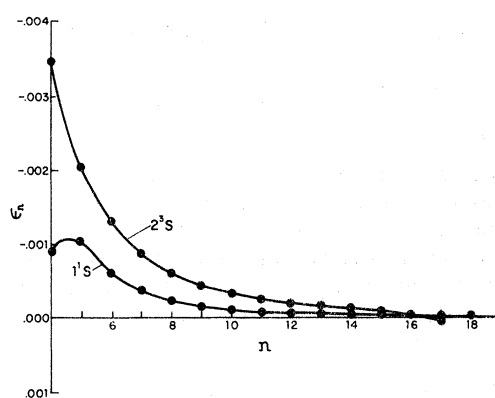
TABLE XVIII. Total f values for the case $Z=2$.

Form of f	$(1^1S, 2^1P)$		$(2^3S, 2^3P)$	
	PP ^a	SP ^b	PP ^c	SP ^b
length	0.276 113	0.276 102	0.540 553	0.539 086
velocity	0.276 182	0.276 163	0.543 145	0.539 087
acceleration	0.276 012	0.276 036	0.549 327	0.537 977

^aPresent paper. Computed through ninth order in wave function, and hence through ninth order in the f -series summation.

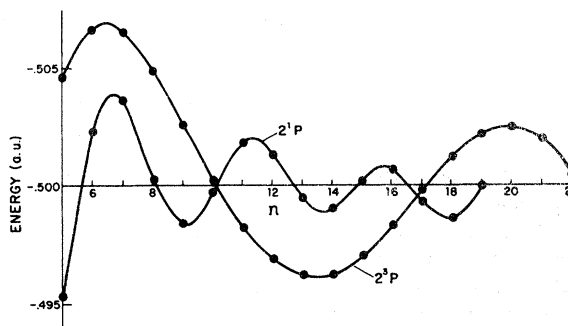
^bB. Schiff and C. L. Pekeris (Ref. 10); their 220-term results.

^cPresent paper. Computed through eighth order in wave function and hence through eighth, seventh, and fifth order in the f -series summation for the length, velocity, and acceleration forms, respectively. Although six figures are reported, the sums were still being affected in the third significant figure at truncation.

FIG. 1. The ϵ_n in atomic units – the $2P$ states.FIG. 2. The ϵ_n in atomic units – the 1^1S and 2^3S states.

(at 8th, 7th, and 5th order for the length, velocity, and acceleration forms, respectively).

In Table XVII the total oscillator strengths computed for the helium atom case ($Z=2$) are compared with the values obtained by Schiff and Pekeris¹⁰ for the same systems from total variational wave function calculations based on 220-term expansion approximations. In the case of the $(1^1S, 2^1P)$ transition, the present total oscillator strengths agree to five significant figures with their results. The internal consistency of the three sets of oscillator strengths obtained is also almost quantitatively the same as that of

FIG. 3. The total energies for the $2P$ states of the H^- ion.

Pekeris's data. Thus, as an example, the absolute difference of the velocity and length values from Pekeris's data is 0.000 061, from the present data 0.000 069 units.

In the (2^3S , 2^3P) transition, only the length form of the operator has been summed to a sufficiently high order to begin to reflect the true accuracy of the present calculations. Thus the degree of inconsistency between the three forms in the present results is predominately due to the effects of truncation, rather than to the inaccuracies in the expansion coefficients themselves.

APPENDIX

The Orthogonality Conditions In n th Order

Since the variational theorem is used to obtain the variational-perturbation equations (Ref. 1), it is sufficient to require that the $\Psi^{(M)}$ be orthogonal to all energetically lower states:

$$\langle \Psi^{(M)} | \Psi^{(K)} \rangle = 0. \quad (\text{A. 1})$$

Here and in all that follows, K takes on the values 1, 2, ..., $M-1$. Inserting Eq. (2) into the above expression, we obtain

$$\sum_{n=0}^{\infty} \sum_{i=0}^n \langle \psi_i^{(M)} | \psi_{n-i}^{(K)} \rangle Z^{-n} = 0. \quad (\text{A. 2})$$

The above equation can be satisfied only if

$$\sum_{i=0}^n \langle \psi_i^{(M)} | \psi_{n-i}^{(K)} \rangle = 0; \quad n=0, 1, 2, \dots \quad (\text{A. 3})$$

However, because of the nature of the Hamiltonian, the exact total wave functions satisfy Eq. (A. 1) and thus Eq. (A. 3). This is generally not the case for the approximate variational-perturbation wave functions, $\Phi_n^{(M)}$. It is necessary to construct the $\Phi_n^{(M)}$ so that they satisfy the analog of Eq. (A. 3),

$$\sum_{i=0}^{n-1} \langle \psi_i^{(M)} | \psi_{n-i}^{(K)} \rangle + \langle \Phi_n^{(M)} | \psi_0^{(K)} \rangle = 0; \quad n=0, 1, 2, \dots; \quad (\text{A. 4})$$

where the $n-1$ lower-order wave functions are assumed to be known exactly. But, by Eq. (A. 3), the condition on $\Phi_n^{(M)}$ is then, simply,

$$\langle \Phi_n^{(M)} | \psi_0^{(K)} \rangle = \langle \psi_n^{(M)} | \psi_0^{(K)} \rangle. \quad (\text{A. 5})$$

From the general perturbation equation

$$(H_0 - \epsilon_0)\psi_n + (H_1 - \epsilon_1)\psi_{n-1} = \sum_{i=0}^{n-2} \epsilon_{n-i} \psi_i,$$

it follows that Eq. (A. 5) can be written as

$$\begin{aligned} \langle \Phi_n^{(M)} | \psi_0^{(K)} \rangle &= [\langle \psi_{n-1}^{(M)} | H_1 | \psi_0^{(K)} \rangle \\ &\quad - \sum_{i=1}^{n-1} \epsilon_{n-i} \langle \psi_i^{(M)} | \psi_0^{(K)} \rangle] \\ &\quad \times (\epsilon_0^{(M)} - \epsilon_0^{(K)})^{-1}; \end{aligned} \quad (\text{A. 6})$$

where the expression on the right is now an exactly known quantity. Thus a suitable choice for a properly orthogonalized wave function, $\Phi_n^{(M)}$, is given by

$$\Phi_n^{(M)} = \sum_{K=1}^{M-1} \chi_K^{(n)} \psi_0^{(K)} + \phi_n^{(M)}, \quad (\text{A. 7})$$

where $\phi_n^{(M)}$ is a function which satisfies Eq. (11) or Eq. (12), and where¹²

$$\begin{aligned} \chi_K^{(n)} &= [\langle \psi_{n-1}^{(M)} | H_1 | \psi_0^{(K)} \rangle \\ &\quad - \sum_{i=1}^{n-1} \epsilon_{n-i} \langle \psi_i^{(M)} | \psi_0^{(K)} \rangle] \\ &\quad \times (\epsilon_0^{(M)} - \epsilon_0^{(K)})^{-1} - \langle \phi_n^{(M)} | \psi_0^{(K)} \rangle. \end{aligned} \quad (\text{A. 8})$$

Equation (A. 8) is the generalization to n th order of Sinanoğlu's condition on first-order wave functions.¹³

¹C. W. Scherr and R. E. Knight, Rev. Mod. Phys. 35, 436 (1963).

²Units of length Za_0 and units of energy $2RhcZ^2$ are used throughout the text; in the tables, however, units of length a_0 and of energy $2Rhc$ are used. The a_0 is the Bohr radius, the R is the infinite mass rydberg.

³F. C. Sanders and C. W. Scherr [compare J. Chem. Phys. 42, 4314 (1965)] have given extensive numerical tables of ϵ_1 for the helium isoelectronic series. A copy

of these tables has been deposited as Document No. 8267 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints, or \$1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

⁴See H. Bethe and E. E. Salpeter, in *Handbuch der*

Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, part 1, pp. 334 ff.

⁵G. Breit, *Phys. Rev.* **35**, 569 (1930). It is necessary to apply orthogonality conditions in all orders. The general procedure developed here is shown in Appendix I.

⁶B. Schiff, H. Lipson, C. L. Pekeris, and P. Rabinowitz, *Phys. Rev.* **140**, A1104 (1965).

⁷M. Machacek, F. C. Sanders, and C. W. Scherr, *Phys. Rev.* **136**, A680 (1964); **137**, A1066 (1965).

⁸R. E. Knight and C. W. Scherr, *Rev. Mod. Phys.* **35**, 431 (1963).

⁹J. Mitdal, *Phys. Rev.* **138**, A1012 (1965).

¹⁰B. Schiff and C. L. Pekeris, *Phys. Rev.* **134**, A638

(1964). Also see L. C. Green, N. C. Johnson, and E. K. Kolchin, *Astrophys. J.* **144**, 369 (1966).

¹¹The 200-term results are: $\epsilon_2(2^1P) = -0.157\,028\,645$, $\epsilon_2(2^3P) = -0.072\,998\,980$; $\epsilon_3(2^1P) = 0.026\,106\,210$, $\epsilon_3(2^3P) = -0.016\,585\,304$.

¹²It should be noted that if a trial wave function of the form A.7 is used directly in the variational-perturbation equations (i.e., with the $\chi_K^{(n)}$ regarded as variational parameters) that the so obtained $\chi_K^{(n)}$ will be the same as the values given by Eq. (A.8).

¹³O. Sinanoğlu, *Phys. Rev.* **122**, 49 (1961). Also see W. H. Miller, *J. Chem. Phys.* **45**, 2198 (1966).

Analytically Solvable Problems in Radiative Transfer. I

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As is well known, the transfer of radiation in a medium is described by an integral equation, first given by Biberman and Holstein. They assumed that the emission coefficient is proportional to the absorption coefficient. After a discussion of the relation of this type of radiative transfer to Brownian motion, we solve the integral equation for a slab and for all line shapes of interest with and without hyperfine structure in the limit of high optical depth.

INTRODUCTION

The theory of imprisonment of resonance radiation is of fundamental importance for many problems in low-density plasmas. Compton¹ tried to use it to explain the behavior of low-voltage arcs.² He seems to have been the first who noticed a certain, perhaps only formal, analogy between the phenomenon of repeated absorption and re-emission, from which the effect stems, and Brownian Motion, and it was his suggestion that the phenomenon could be described by a diffusion equation. A few years later the diffusion equation was derived rigorously by Milne³ from the basic equations of radiative transfer with the tacit assumption that the frequencies of the absorbed and re-emitted quanta are the same. It was shown that the predictions of the theory were not in agreement with the experiments.⁴ Attention, therefore, remained focused on the problem. The notion that the phenomenon should be described by a diffusion equation even misled an author who had written down the correct initial equations.⁵ Kenty⁶ seems to have been the first

who succeeded in solving the discrepancy between theory and experiment by taking into account the shape of the spectral line. He calculated an effective diffusion constant for the Doppler profile that was substantially in agreement with the experiment. The formulation of the problem in terms of an integral equation by Biberman⁷ and Holstein⁸ about 15 years later was physically much simpler and led to an expression for the Doppler profile that was in fair agreement with the one found by Kenty. Holstein⁸ calculated the lowest eigenvalue of the integral equation for a number of line shapes and volumes by a variational procedure. Later on the Russian literature⁹ showed progress towards an analytical approach. Hearn, Hummer and others,¹⁰ following a different, but equivalent formulation of the problem common among astrophysicists,¹¹ calculated some interesting quantities numerically for a slab and Doppler or Voigt profiles, for instance, the line shape of the radiation emitted by a slab. In the meantime many experiments¹² were performed, mostly with the purpose of verifying the dependence of the lowest eigenvalue on the num-