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Lamb Shift Excitation Energy in the Ground State of the Helium Atom[*]

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The evaluation of the Lamb shift excitation requires a knowledge of the oscillator strengths for transitions to all states which may be reached by dipole transitions from the ground state. The oscillator strengths for transitions to the continuum states $(1s,\epsilon p)$ and $(2s,\epsilon p)$ are calculated, using the 18-parameter ground-state wave function of Chandrasekhar and Herzberg. For the excited state in the continuum, a Hartree wave function is evaluated and used. It is shown that the error due to exchange and polarization in the f value for high excitation energy E of the p-state electron is only of relative order $1/E$, i.e., of absolute order of $E^{-9/2}$. The f values for transitions to states other than $(1s,\epsilon p)$ and $(2s,\epsilon p)$ are also considered.

An accurate value of the average excitation energy is obtained by combining these results with a method previously used by Pekeris. The value obtained by this method is 80.56 ± 0.90 ry, where the limits represent an estimate of the probable error. The corrections of order α^4 ry to the ionization energy are estimated roughly and are found to be -0.025 ± 0.01 cm^{-1}. When they are added to the radiative corrections of order α^3 ry evaluated by Kabir, Salpeter, Sucher, Dalgarno, and Stewart, the value of the Lamb shift becomes -1.361 ± 0.021 cm^{-1}, where the error is mainly due to the uncertainties in the estimate of corrections of order α^4 ry and the value of the average excitation energy. With this value of the Lamb shift correction, the theoretical ionization energy becomes 198310.665 cm^{-1}, compared with Herzberg's experimental value of 198310.8 ± 0.15 cm^{-1}.

I. INTRODUCTION

RECENT experimental measurements of the ionization potential of He initiated by Herzberg[1,2] have stimulated interest in accurate solutions of the wave equation for two-electron atoms. The best experimental value for the ionization potential of helium found by Herzberg[3] is

$$I_{\text{exp}}=198\,310.8\pm0.15\ \text{cm}^{-1}. \tag{1}$$

The best nonrelativistic eigenvalue obtained by Pekeris[4] is

$$I_{NR}=198\,317.3743\pm0.0221\ \text{cm}^{-1}. \tag{2}$$

The bulk in the uncertainty comes from the uncertainty of ±0.012 cm^{-1} in the present value of the Rydberg constant.[5] Adding the sum of the relativistic and mass polarization corrections as evaluated by Pekeris,[4] $\Delta I_R=5.3485\pm0.0005$ cm^{-1}, the theoretical value of the ionization energy becomes

$$I_{NR}+\Delta I_R=198\,312.026\pm0.023\ \text{cm}^{-1}. \tag{3}$$

The leading terms in the Lamb shift, to be added to the ionization potential, are represented[6] by

$$I_L=E_{L,1}-E_{L,2}-E_{L,2'}. \tag{4}$$

Here $E_{L,1}$ denotes the Lamb shift of the one-electron ion, and is given by

$$E_{L,1}=\frac{8}{3}z\alpha^3\frac{z^3}{\pi}\left[2\ln\frac{1}{z\alpha}-\ln\frac{K_0}{z^2\,\text{ry}}+\frac{19}{30}\right]\text{ry}, \tag{5}$$

where α is the fine structure constant, $1/137.036$. For helium, $E_{L,1}$ has the value 3.534 cm^{-1}. The second term on the right-hand side of (4) arises principally from the self-energy corrections and the change of energy arising from the polarization of the vacuum by the nuclear potential, giving

$$E_{L,2}=\frac{8}{3}z\alpha^3\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}\left[2\ln\frac{1}{\alpha}-\ln\frac{k_0}{\text{ry}}+\frac{19}{30}\right], \tag{6}$$

where $\langle\delta(r_1)+\delta(r_2)\rangle_{00}$ is the expectation value, in atomic units, of the operator $[\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)]$ for the ground state of the helium atom and k_0 is the average excitation energy defined by

$$\ln k_0=\int\omega_{n0}^2\ln\omega_{n0}df_{n0}\bigg/\int\omega_{n0}^2df_{n0},\quad \omega_{n0}\equiv E_n-E_0, \tag{7}$$

where the summation or integration extends over all states to which dipole transitions are possible from the ground state, and f_{n0}, defined by

$$f_{n0}=\tfrac{2}{3}|\langle n|\mathbf{p}_1+\mathbf{p}_2|0\rangle|^2/(E_n-E_0), \tag{8}$$

is the oscillator strength for transitions from the ground state to the state n. Here E_0 and E_n denote the energies of the initial state and of the nth excited state, respectively. Allowing an error of 0.01% in the expectation value of the operator $[\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)]$ evaluated by Pekeris,[4] $E_{L,2}$ has the value

$$E_{L,2}=5.009+0.823\delta\pm0.0005\ \text{cm}^{-1}, \tag{9}$$

where δ is defined by

$$\ln k_0=4.390+\delta, \tag{10}$$

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[6] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957). We shall sometimes abbreviate this reference K.S.

and is the error in Kabir and Salpeter's[6] value for $\ln k_0$. The third term of the expression (4) is

$$E_{L,2'}=(28/3)\alpha^3\langle\delta(\mathbf{r}_{12})\rangle_{00}\ln(1/\alpha)\text{ ry},\tag{11}$$

and has the value -0.2082 cm^{-1}.

Araki[7] and Sucher[8] have calculated the remaining corrections of order α^3 ry using the relativistic two-body equation, extended to the case where an external field is present. Sucher has evaluated these terms using the 39-parameter wave function of Kinoshita[9] and the six-parameter wave function of Hylleraas[10] and he finds an additional contribution of amount -0.072 cm^{-1}. An improved evaluation by Dalgarno and Stewart[11] gives -0.069, with an error presumably less than ± 0.001 cm^{-1}. Including this correction, the total Lamb shift correction becomes

$$I_L=1.336+0.823\delta+\eta\pm 0.00152\text{ cm}^{-1},\tag{12}$$

where η represents the contribution of the higher order radiative corrections, i.e., α^4 ry, etc.

The present uncertainty in the Lamb shift correction (12) stems primarily from the calculation of the excitation energy k_0 in (6) defined by (7). The calculation of $\ln k_0$ requires a knowledge of the oscillator strengths for transitions to all the excited states which may be reached by dipole transition from the ground state; Kabir and Salpeter,[6] making use of the approximate values of the oscillator strengths available at that time, arrived at an estimate of 4.39 for $\ln k_0$, with an estimated uncertainty of the order of ± 0.2. This leads to an uncertainty of the order of ± 0.2 cm^{-1} in the value of the Lamb shift and we see that a much better accuracy is needed before the Sucher's term can be compared with experiment. Incidentally, this is the only term which requires the use of the fully relativistic treatment of the two electrons in an external field and tests the Bethe-Salpeter equation in detail. The main objective of this paper is to evaluate $\ln k_0$ more accurately so that the Bethe-Salpeter equation may be put to a more severe test.

Most of the contribution to the numerator and the denominator in (7) comes from the oscillator strengths for the transitions to those states in which one of the electrons is in an s state and the other electron is in a p state. In Sec. II we describe in detail the calculation of the f values for transitions to $(1s,np)$, $(1s,\epsilon p)$, $(2s,np)$, and $(2s,\epsilon p)$ ^1P states and discuss qualitatively the order of magnitude of the oscillator strengths for transitions to all the other doubly excited states belonging to the class of (s,p) ^1P states.

In Sec. III, we expand the momentum space transition matrix element in a Born series and describe a method to obtain the first two terms of the asymptotic series for the oscillator strengths for transitions to $(ms,\epsilon p)$ states. We show that the sum of f values for transitions to all the $(ms,\epsilon p)$ and $(\epsilon' s,\epsilon p)$ ^1P states varies as

$$(512/3)E^{-7/2}(1-2\pi/(E)^{\frac{1}{2}}+\cdots)\langle\delta(\mathbf{r}_1)\rangle_{00}$$

with E the energy of the p electron when the p electron has high excitation energy.

Section IV deals with the evaluation of $\ln k_0$ defined by (7) and required for the calculation of Lamb shift. In addition to the usual method of evaluating $\ln k_0$, we shall make use of a slight extension of a method used by Pekeris[4] to obtain a more accurate value of $\ln k_0$. This section also contains a summary of results.

II. OSCILLATOR STRENGTHS FOR THE TRANSITIONS TO THE SINGLY AND DOUBLY EXCITED STATES

In this section we outline the calculation of the oscillator strengths for transitions to the singly and doubly excited states needed for the evaluation of $\ln k_0$ defined by (7). We need mainly the sums $\sum_n \omega_{n0}{}^2 f_{n0}$ and $\sum_n \omega_{n0}{}^2 \ln\omega_{n0} f_{n0}$ and will state the errors in the subsequent discussion for the sum $\sum_n \omega_{n0}{}^2 f_{n0}$.

The calculation of the average excitation energy k_0 requires a knowledge of the oscillator strengths for transitions to all the ^1P states which may be reached by dipole transition from the ground state ^1S. We shall discuss here only the oscillator strengths for transitions to those ^1P states in which one of the electrons is in an s state and the other electron is in a p state. The rest of the transitions have been discussed by Kabir and Salpeter and their arguments indicate that the contribution of these states to $\sum_n \omega_{n0}{}^2 f_{n0}$ is of the order of 1 or 2%.

We now discuss the contribution of the various groups of states belonging to the class of (s,p) ^1P states. Since the exact wave functions of helium are not known for any of the states, we are obliged to make use of oscillator strengths calculated with approximate wave functions.

(i) The oscillator strengths for the lowest two states of the principal series $(1s,np)$ ^1P were calculated using a 6-parameter Hylleraas wave function for the ground state and variational wave functions[12,13] for the excited states. Our f values (Table I) should be in error by less than ± 0.05 for $(1s,2p)$ and ± 0.02 for $(1s,3p)$ and agree with the values used by Dalgarno and Stewart[14] to much higher accuracy.

The f value for the transition to the $(1s,4p)$ ^1P state was calculated with a six-parameter wave function for the ground state and a product wave function of

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TABLE I. f values for transitions to $(1s,np)$ and $(2s,np)$ ^1P states.

n	$(1s,np)$ ^1P states (E_n-E_0) in ry	f_{n0}	$(2s,np)$ ^1P states (E_n-E_0) in ry	f_{n0}
2	1.5593	0.2717	4.5593	0.00503
3	1.6966	0.0706	4.6966	0.00039
4	1.7448	0.0329	4.7448	0.00020
5	1.7671	0.0177	4.7671	0.00010
6	1.7792	0.0115	4.7792	0.00007
7	1.7866	0.0080	4.7866	0.00005

hydrogen eigenfunctions with charge Z for the s electron and $Z-1$ for the p electron. From $n=8$ to $n=\infty$ we used the form $f_{n0}=C/n^3$. From requirements of continuity it follows that the constant C equals $2df/dE$ evaluated at the series limit. Our results (Table II) with an 18-parameter wave function for the ground state and Hartree wave function for the p electron in the continuum give $C=3.3792$. The f values for transitions to $(1s,np)$ ^1P states are given in Table I.

Our value for the contribution of the principal series to $\sum_n \omega_{n0}^2 f_{n0}$ is 1.176 ± 0.20 ry^2, compared with Kabir and Salpeters' 1.19 ry^2 and Dalgarno and Stewarts' value of 1.12 ry^2.

(ii) Our re-evaluation of the oscillator strengths for transitions to the $(2s,np)$ ^1P states is given in Table I. We used a six-parameter ground-state wave function, the variational excited state wave function given by Vinti[15] for $n=2$ and hydrogenic product wave function ($Z=2$ for $2s$, $Z=1$ for $3p$) for $n=3$. For $n\geq 8$ we again used the asymptotic form $f_{n0}=C/n^3$ and used interpolation for $n=4$ to 7. The contribution to $\sum_n \omega_{n0}^2 f_{n0}$ of transitions to states $(2s,np)$ is 0.128 ry^2 with an error of about ±0.10 ry^2. Previous values of Kabir and Salpeter[6] and Dalgarno and Stewart,[14] both based on an estimate by Vinti[15] for $(2s,2p)$, are about twice of ours.

TABLE II. f values for transitions to $(1s,\epsilon p)$ and $(2s,\epsilon p)$ ^1P states.

Energy of excitation in ry	$(1s,\epsilon p)$ ^1P states	$(2s,\epsilon p)$ ^1P states
0.0	1.6896	1.0426×10^{-2}
0.25	1.0392	9.0855×10^{-3}
0.50	0.70153	8.0245×10^{-3}
0.75	0.51070	7.1396×10^{-3}
1.0	0.39380	6.3849×10^{-3}
1.25893	0.31440	5.7077×10^{-3}
1.58489	0.24760	4.9810×10^{-3}
1.99526	0.19152	4.2238×10^{-3}
2.51189	0.14486	3.4660×10^{-3}
3.16228	0.10614	
3.98107	7.4758×10^{-2}	2.0774×10^{-3}
5.01185	5.0286×10^{-2}	
6.30958	3.2292×10^{-2}	1.0446×10^{-3}
7.94339	1.9836×10^{-2}	
10.0	1.1691×10^{-2}	4.3521×10^{-4}
12.5893	6.6589×10^{-3}	
15.8489	3.6840×10^{-3}	1.5177×10^{-4}
19.9526	1.9842×10^{-3}	
25.1189	1.0443×10^{-3}	4.5394×10^{-5}
31.6228	5.3829×10^{-4}	
39.8107	2.7280×10^{-4}	1.2105×10^{-5}
50.1185	1.3606×10^{-4}	
63.0958	6.6919×10^{-5}	2.9887×10^{-6}
79.4339	3.2541×10^{-5}	
100.0	1.5658×10^{-5}	7.0146×10^{-7}
125.893	7.4751×10^{-6}	
158.489	3.5375×10^{-6}	1.5884×10^{-7}
199.526	1.6644×10^{-6}	
251.189	7.7886×10^{-7}	3.5064×10^{-8}
316.228	3.6259×10^{-7}	
398.107	1.6806×10^{-7}	7.5814×10^{-9}
501.185	7.7577×10^{-8}	
630.958	3.5713×10^{-8}	1.6122×10^{-9}
794.339	1.6370×10^{-8}	
1000.0	7.5036×10^{-9}	

(iii) Using Vinti's[15] method, we estimate that the transition to (ms,np) ^1P states $(m>2)$ contribute to $\sum_n \omega_{n0}^2 f_{n0}$ approximately 0.054 ry^2.

(iv) We now outline the calculation of the oscillator strengths for the transitions to $(ns,\epsilon p)$ ^1P states.

The wave equation for the two electrons moving in the field of the helium nucleus has the form

$$\left[\tfrac{1}{2}(\nabla_1^2+\nabla_2^2)+E+\frac{z}{r_1}+\frac{z}{r_2}-\frac{1}{r_{12}}\right]\psi(\mathbf{r}_1,\mathbf{r}_2)=0, \quad (13)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the two electrons. If the p electron in the continuum has the wave number k and the electron in the ns state has the energy E_n, the total energy E is given by

$$E=E_n+\tfrac{1}{2}k^2. \quad (14)$$

In the Hartree approximation $\psi(\mathbf{r}_1,\mathbf{r}_2)$ is approximated by

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=u_n(\mathbf{r}_1)\left[\frac{1}{r}\chi_{\epsilon_n}(r_2)Y_1^m(\theta_2,\varphi_2)\right], \quad (15)$$

where $u_n(r_1)$ is simply the hydrogenic ns state wave function for $z=2$. The radial wave function $\chi_{\epsilon_n}(r_2)$ for the continuum p electron satisfies the equation

$$\begin{gathered}\frac{d^2}{dr^2}\chi_{\epsilon n}(r)+\left(k_n^2-V_{nn}(r)-\frac{2}{r^2}\right)\chi_{\epsilon n}(r)=0,\\ V_{nn}(\mathbf{r}_2)=\int u_n^*(\mathbf{r}_1)2\left(\frac{1}{r_{12}}-\frac{z}{r_2}\right)u_n(\mathbf{r}_1)d^3\mathbf{r}_1.\end{gathered} \quad (16)$$

Writing the potential $V_{nn}(r)$ in the form

$$V_{nn}(r)=2Z_n(r)/r,$$

where $Z_n(r)$ is the effective charge seen by the continuum electron at radial distance r_1, we find

$$Z_1(r)=1+(1+2r)e^{-4r},\quad Z_2(r)=1+(1+\tfrac{3}{2}r+r^2+r^3)e^{-2r}$$

for a bound $1s$ and $2s$ electron, respectively. With ψ the symmetrized form of Eq. (15) and E the energy in Eq. (14), we normalize $\chi(r_2)$ so that

$$\int \psi_E{}^*\psi_{E'}\, d^3r_1 d^3r_2=\delta(E-E'). \quad (17)$$

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[15] J. P. Vinti, Phys. Rev. 42, 632 (1932).

Because of the δ-function normalization, we shall obtain the differential oscillator strength

$$\frac{df}{dE}=\tfrac{2}{3}(E_1-E_0)\sum_{m=-1,0,1}|\langle 0|M|n\rangle|^2, \tag{18}$$

with the matrix elements

$$\langle n|M^*|0\rangle=\int\psi^*M^*\phi d^3r_1d^3r_2.$$

The summation is over the magnetic quantum number m of the excited p electron in a continuum state.

We shall consider only the momentum matrix elements

$$M_{n0}^*=\frac{1}{E-E_0}\left\langle n\left|\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right|0\right\rangle. \tag{19}$$

In evaluating M_{n0}^* we use for the ground-state wave function $\phi(\mathbf{r}_1,\mathbf{r}_2)$, the 18-parameter wave function of Chandrasekhar and Herzberg.[2,9] After performing angular integrations and integration over one of the radial variables, the momentum matrix elements are reduced to the form

$$M_{n0}^*=\frac{A_n}{E-E_0}\int_0^\infty\chi_{\epsilon_n}(r)F_n(r)dr, \tag{20}$$

where

$$F_1(r)=\sum_{m=1}^{1}L_mr_me^{-\frac{1}{2}kr}+\sum_{m=1}^{2}S_mr^me^{-(z+k)r},$$

and $A_1=32N\pi/\sqrt{3}$ for transitions to $(1s,\epsilon p)\,{}^1P$ states. Here N is the normalization constant of the ground-state wave function. The expressions for the coefficients L_m and S_m as functions of the nuclear charge z and the variational parameters of the ground-state wave function are given elsewhere.[16]

Similarly, the matrix element for the transition to $(2s,\epsilon p)\,{}^1P$ state can be written as

$$M_{n0}^*=\frac{8N\pi}{E-E_0}\left(\frac{2}{3}\right)^{\frac{1}{2}}\int_0^\infty\chi_{\epsilon_2}(r)F_2(r)dr. \tag{21}$$

The function $F_2(r)$ can be obtained from $F_1(r)$ by applying the operator $(1+\partial/\partial Z)$ to $F_1(r)$ and setting Z equal to unity after the differentiation has been performed. The numerical values of the coefficients L_m and S_m in the overlap functions $F_1(r)$ and $F_2(r)$ can be found in reference 16.

The radial differential equations (16) were integrated numerically, using the formula for two-fold integration.[17] The normalization constant of the wave function was determined by joining the numerical solution to the W.K.B. wave function at the maximum or minimum, in the region where the W.K.B. solution is valid. At zero energy, $\chi_{\epsilon_n}(r)$ is a linear combination of the Bessel and Neumann functions outside the Hartree potential and is given by

$$\chi_{\epsilon_n}(r)=(2r)^{\frac{1}{2}}[J_3[(8r)^{\frac{1}{2}}]\cos\delta-N_3[(8r)^{\frac{1}{2}}]\sin\delta]. \tag{22}$$

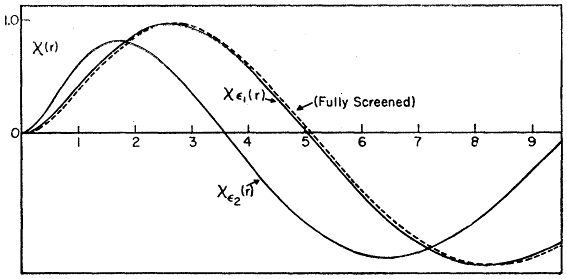

FIG. 1. The zero-energy wave functions of the p electron moving in the field of effective charges $Z_1(r)$ and $Z_2(r)$.

The phase shift δ was determined from the location of the zeros of the numerical solution and the normalization constant obtained by joining the numerical solution outside the Hartree potential to (22). The f values for transitions to the $(1s,\epsilon p)$ and $(2s,\epsilon p)\,{}^1P$ states were calculated on the Cornell Burroughs 220 computer and the results are tabulated in Table II.

In Fig. 1 we illustrate the zero energy wave functions of the p electron moving in the fields of charges $Z_1(r)$ and $Z_2(r)$ along with the hydrogenic wave function with charge $Z-1$. The phase shift is quite small when the bound electron is in the $1s$ state. Incidentally, this shows that the use of Hartree wave functions at very low energies would not yield f values for transitions to $(1s,\epsilon p)\,{}^1P$ states substantially different from those obtained from the assumption of full screening.

The f values of the spectral head for transitions to $(1s,\epsilon p)\,{}^1P$ states turns out to be too large compared to Huang's value[18] and most of the increase in the f value, thus, arises from the improvement in the ground-state wave function. However, the recent calculations of the contribution of the free-free transitions to the absorption coefficient of the negative hydrogen ion indicates that the exchange and polarization reduces this contribution by 50%. Therefore, our f values for low excitation energies for transitions to $(1s,\epsilon p)\,{}^1P$ states may be about 10% higher than the actual values.

(v) For the remaining doubly excited states in which at least one of the electrons is in the continuum, ω is not bounded, and it is quite possible that they make large contributions to the sum rules $\sum_n\omega_{n0}f_{n0}$ and $\sum_n\omega_{n0}^2f_{n0}$, so we must consider them more carefully.

However, most probably the important contributions, if any, will come from those states in which one electron remains in an s state; so we first consider transitions to $(ms,\epsilon p)$ and $(\epsilon's,\epsilon p)\,{}^1P$ states.

For the states in which the p electron has high

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[17] D. R. Hartree, *Numerical Analysis* (Clarendon Press, Oxford, 1952), p. 126.

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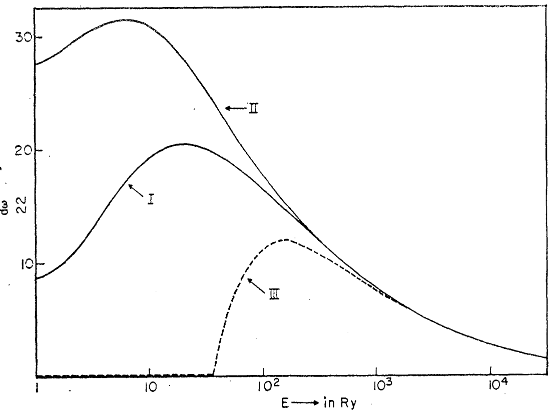

FIG. 2. The weight functions $\omega^3 df/d\omega$ derived from the f values for transitions to $(1s,\epsilon p)$, $(2s,\epsilon p)$, and $(ms,\epsilon p)\ {}^1P$ states $(m>2)$. The $(2s,\epsilon p)\ {}^1P$-state weight function is multiplied by 22.047 and the weight function of $(ms,\epsilon p)\ {}^1P$ states is multiplied by 34.036 to have the same asymptotic values at high energies.

excitation energy, the sum of the f values for transitions to $(ms,\epsilon p)$ $(m>2)$ and $(\epsilon' s,\epsilon p)\ {}^1P$ states is given by

$$8.45E^{-7/2}(1-2\pi/E^{\frac{1}{2}}+\cdots), \tag{23}$$

which is roughly 3% of the corresponding f value for transition to $(1s,\epsilon p)\ {}^1P$ states. Most of the contribution to (23) comes from s states of low excitation energy, for when the s electron has high excitation energy, the f values vary with the s electron energy as $E^{-9/2}$. This, then, suggests that the contribution to the f sum of transitions to $(ms,\epsilon p)$ $(m>2)$, $(\epsilon' s,\epsilon p)$, $(\epsilon' s,np)\ {}^1P$ states may be about 4 to 5 percent. In Fig. 2 we exhibit the shape of the weight functions $\omega^3 df/d\omega$ derived from the f values for transitions to $(1s,\epsilon p)$ and $(2s,\epsilon p)\ {}^1P$ states (Table II) and from (23). The weight functions have been normalized to give the same asymptotic value at high energies.

III. ASYMPTOTIC OSCILLATOR STRENGTHS

In the calculation of $\ln k_0$, high energies are important; therefore, the Born series for the oscillator strengths is of interest. The coefficient of the term of relative order $1/k$ in the asymptotic form of the oscillator strengths for transition to $(1s,\epsilon p)\ {}^1P$ states is $-\pi$, when the p electron is described by a hydrogenic wave function with charge $Z=1$ (full screening). However, the real coefficient is -2π, as though the p-electron wave function were a hydrogen eigenfunction with charge $Z=2$ (unscreened). For this reason, the Hartree potential was used since it yields the correct value of the coefficient of the term of relative order $1/k$.

At low energies, however, the Hartree wave function for the p electron does not differ very much from the hydrogenic wave function with charge $Z=1$ (Fig. 1), if the bound electron is in the $1s$ state. Therefore, the main error at low energies in K.S. was due to the neglect of the electron exchange and polarization, rather than the Hartree potential.

Kabir and Salpeter have given a method to determine the asymptotic form of the transition matrix elements when the excited electron may be described by the Born approximation. We shall make use of the K.S. method to determine the high-frequency behavior of the matrix elements calculated with various Hylleraas-type wave functions for the ground state and compare them with the matrix elements calculated directly. We shall also calculate the next term of the asymptotic series and also obtain the first two terms of the total contribution of all the excited states.

We consider a wave function which asymptotically represents one bound-state hydrogenic $(Z=2)$ electron with wave function u_n plus one free electron of momentum k. In Born approximation the potential $V(r_1,r_2)=2(1/r_{12}-Z/r_1)$ is treated as a perturbation. Up to first order in this perturbation, the Born approximation wave function in momentum space is then found to be

$$\psi(\mathbf{p}_1,\mathbf{p}_2)=u_n(\mathbf{p}_1)\delta(\mathbf{p}_2-\mathbf{k})+\left(\sum_m+\int d\epsilon\right)u_m(\mathbf{p}_1)V_{mn}(\mathbf{p}_2-\mathbf{k})/(p_2{}^2-k_m{}^2),$$

where $k_m{}^2=2(E-E_m)$ and

$$V_{mn}=\int d^3r_1\, u_m{}^*(\mathbf{r}_1)2\left(\frac{1}{r_{12}}-\frac{Z}{r_2}\right)u_n(\mathbf{r}_1). \tag{24}$$

The diagonal term of the series represents the contribution of the static potential of the nucleus and the bound electron. The off-diagonal terms of this series represent the nonstatic effects of the bound electron and are termed the "polarization" effects. When we evaluate the second term of the Born expansion of matrix elements, it will become evident that the polarization contributes only to relative order $1/k^2$.

If one assumes that only those intermediate states contribute in which the bound electron is in a state of low excitation energy, then $k_m{}^2$ can be replaced by k^2. We can now sum over the intermediate states and the expression for $\psi(p_1,p_2)$ simplifies to

$$\psi(\mathbf{p}_1,\mathbf{p}_2)=u_n(\mathbf{p}_1)\delta(\mathbf{p}_2-\mathbf{k})+\frac{1}{\pi^2(p_2{}^2-k^2)|\mathbf{p}_2-\mathbf{k}|^2}\times[Zu_n(\mathbf{p}_1)-u_n(\mathbf{p}_1+\mathbf{p}_2-\mathbf{k})]. \tag{25}$$

We require the matrix element D_j of the operator $(\mathbf{p}_1+\mathbf{p}_2)$ between the symmetrized form $\psi(\mathbf{p}_1,\mathbf{p}_2)$ of Eq. (25) and the ground-state momentum space wave function $\phi(\mathbf{p}_1,\mathbf{p}_2)$. Using Eq. (25) and with the normalization factor $(4\pi k)^{\frac{1}{2}}$ for ψ, we have

$$D_j\equiv D_{0j}+D_{1j};$$

$$D_{0j}=(8\pi k)^{\frac{1}{2}}\int d^3p_1\, u_n{}^*(\mathbf{p}_1)(\mathbf{p}_1+\mathbf{k})\phi(\mathbf{p}_1,\mathbf{k}),$$

and

$$D_{1j}=\frac{(8\pi k)^{\frac{1}{2}}}{\pi^2}\int\frac{d^3p_1d^3p_2}{(p_2^2-k^2)|\mathbf{p}_2-\mathbf{k}|^2}$$
$$\times[Zu_n^*(\mathbf{p}_1)-u_n^*(\mathbf{p}_1+\mathbf{p}_2-\mathbf{k})](\mathbf{p}_1+\mathbf{p}_2)_j\phi(\mathbf{p}_1,\mathbf{p}_2). \quad (26)$$

The lowest order Born approximation is contained in D_{0j}. For its evaluation we can use a simplified form of the ground-state wave function $\phi(p,k)$, which satisfies the equation

$$(E_0-\tfrac{1}{2}p_1^2-\tfrac{1}{2}k^2)\phi(\mathbf{p}_1,\mathbf{k})=\frac{1}{2\pi^2}\int d^3q[-Z\phi(\mathbf{p}_1+\mathbf{q},\,\mathbf{k})$$
$$-Z\phi(\mathbf{p}_1,\,\mathbf{k}+\mathbf{q})+\phi(\mathbf{p}_1+\mathbf{q},\,\mathbf{k}-\mathbf{q}]/\mathbf{q}^2. \quad (27)$$

When either of its arguments greatly exceeds the Bohr momentum, $\phi(p,k)$ falls off rapidly (with negative fourth power of this argument). Thus for large k, the main contributions to the right-hand side of Eq. (27) comes from the second term, from regions of the integrand for which $|\mathbf{q}+\mathbf{k}|$ is of the order of the Bohr momentum. Omitting the other two terms and replacing $1/q^2$ by $1/k^2$ in the integrand, one finds

$$\phi(\mathbf{p}_1,\mathbf{k})\sim\frac{Z}{\pi^2k^4}\int d^3r\,\phi(\mathbf{r},0)e^{-i\mathbf{p}_1\cdot r}. \quad (28)$$

Substituting this expression, whose error is only of relative order $1/k^2$, into Eq. (26) gives

$$8Zk_jk^{-7/2}\int d^3r\,u_n^*(\mathbf{r})\phi(\mathbf{r},0). \quad (29)$$

The integral in Eq. (29) can be evaluated quite accurately when n stands for the 1s state and D_{0j} contributes $287.2E^{-7/2}$ to df/dE. The sum over all n can be evaluated even more simply by means of a sum rule and gives

$$\sum_n\frac{df}{dE}=\frac{512}{3}\langle\delta(\mathbf{r}_1)\rangle_{00}E^{-7/2}\equiv CE^{-7/2}. \quad (30)$$

Using the 39-parameter ground-state wave function one finds $C=309.09$. For high excitation energies the doubly excited states thus contribute only about 7% to df/dE.

The error in Eq. (29) for D_{0j} is only of relative order $1/k^2$, but D_{1j} contains a term of relative order $1/k$ which we now calculate. Let I be the first of the two terms, for D_{1j} in Eq. (25). This integral can be transformed into the contour integral

$$I=\frac{z8\pi k}{\pi}\int d^3p_1\,u_n^*(\mathbf{p}_1)\int_0^{\pi}d\theta\,\sin\theta\,\cos\theta\oint_C dp_2$$
$$\times\frac{p_2^3\phi(\mathbf{p}_1,\mathbf{p}_2)}{(p_2^2-k^2)(p_2-ke^{i\theta})(p_2-ke^{-i\theta})}, \quad (31)$$

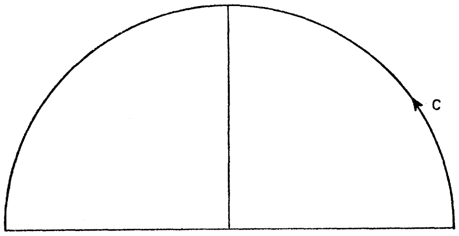

FIG. 3. Contour C.

where the contour is shown in Fig. 3. One finds that only the pole at $p_2=ke^{i\theta}$ contributes to order D_{0j}/k. Approximating $\phi(\mathbf{p}_1,\mathbf{p}_2)$ as in Eq. (28), one finds

$$I=-8\pi Zk^{-7/2}\int d^3ru_n^*(\mathbf{r})\phi(\mathbf{r},0). \quad (32)$$

One can show that the second term of D_{1j} contributes only terms of order D_{0j}/k^2.

One can also evaluate the first two terms in the Born expansion for the momentum space wave function in which the continuum electron is considered to move in the Hartree potential. The first term is identical with the first term in Eq. (25) and leads again to D_{0j}. The contribution to D_j of the second term can be evaluated easily and, to order D_{0j}/k, is found to be identical with Eq. (32). This shows that our use of the Hartree approximation contributes only errors of relative order $1/k^2$ to df/dE for high excitation energies.

When the bound electron is in 1s state, the asymptotic oscillator strengths are given by the expression,

$$\frac{df}{dE}=287.6E^{-7/2}\left(1-\frac{2\pi}{E^{\frac{1}{2}}}+\frac{G(E)}{E}+\cdots\right), \quad (33)$$

where $G(E)$ is a slowly varying function of energy. For $E\geq 1000$ ry it is quite adequate to use the asymptotic form obtained empirically from the f value at $E=1000$ ry. The asymptotic form is found to be

$$\frac{df}{dE}=287.6E^{-7/2}\left(1-\frac{2\pi}{E^{\frac{1}{2}}}+\frac{23.77}{E}+\cdots\right). \quad (34)$$

The exchange amplitude, which has also been omitted, contributes to the Born approximation to relative order $1/k^2$, and is thus unimportant at high energies. However, at low energies the electron exchange is very important and may alter the oscillator strengths substantially.

In Fig. 4 we illustrate the values of the weight function obtained from the momentum matrix elements (20), from the one-, two-, and three-term asymptotic forms, from the f values given by Kabir and Salpeter. It is easy to see that Kabir and Salpeter did not have the correct coefficient of the second term of the asymptotic form.

Finally, we compare in Table III the coefficients of

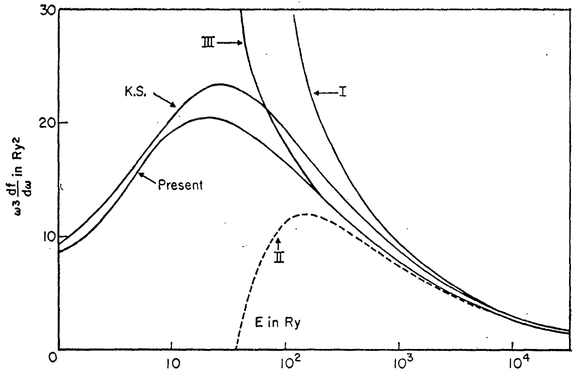

FIG. 4. The weight functions $\omega^3 df/d\omega$ for transitions to $(1s,\epsilon p)\,{}^1P$ states obtained from the momentum matrix elements, from the one-, two-, and three-term asymptotic forms, and from the f values given by Kabir and Salpeter.

the asymptotic oscillator strengths derived from D_{0j} with those obtained directly from the momentum matrix elements (20), for the various ground-state wave functions. It is evident that the coefficient derived from D_{0j} would be more accurate since it is obtained by iterating the wave equation satisfied by the ground wave function in momentum space. The two methods should yield identical results for the exact ground-state wave function. It is seen from Table III that the values of the asymptotic coefficients obtained from the two methods get closer and closer as the number of parameters increases.

IV. CALCULATION OF k_0 AND SUMMARY OF THE RESULTS

Recently Pekeris[4] has given a method of inferring the order of magnitude of $\ln k_0$. We outline his method below. Let $S(k)$ and $P(k)$ be defined by

$$S(k)=\sum_n(E_n-E_0)^k f_{n0};\quad P(k)=d\ln S(k)/dk. \tag{35}$$

Then $\ln k_0$ is equal to $P(2)$. Now the various $S(k)$ are known from the sum rules:

$$S(-1)=\tfrac{1}{3}\langle(\mathbf{r}_1+\mathbf{r}_2)^2\rangle_{00}, \tag{36}$$

$$S(0)=Z, \tag{37}$$

$$S(1)=\tfrac{4}{3}E_0+\langle\mathbf{p}_1\cdot\mathbf{p}_2\rangle_{00}, \tag{38}$$

$$S(2)=(16z\pi/3)\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}. \tag{39}$$

It is also known from the work of Kabir and Salpeter[6] that $S(2.5)=\infty$. By fitting a polynomial for $1/S(k)$ at the points $k=1$, 0, 1, 2, and 2.5 and evaluating the derivative of the polynomial at $k=2$, Pekeris[4] obtained the value 4.5 for $\ln k_0$.

We shall now describe the calculation of the sum rules $S(-1)$, $S(0)$, $S(1)$, and $S(2)$ and the sum $S'(2)$ using the oscillator strengths discussed in Secs. II and III. The evaluation of the contribution of transitions to the discrete states is straightforward so we shall now discuss the calculation of the integrals over the f values for transitions to the $(s,\epsilon p)\,{}^1P$ states. These contributions may be classified into three groups.

TABLE III. Values of the asymptotic coefficients.

Wave function	1s state Momentum matrix elements	1s state K.S. method	2s state Momentum matrix elements	2s state K.S. method
1-parameter	181.8	255.4		
3-parameter	271.1	280.0		
6-parameter[a]	290.9	288.3	15.47	14.08
10-parameter[b]	284.2	286.3		
14-parameter[c]	285.2	286.7		
18-parameter[c]	287.599	287.157	13.04455	13.2399
10-parameter[d]		286.68		
39-parameter[d]		287.199		

[a] See reference 10. [b] See reference 19. [c] See reference 2. [d] See reference 9.

(i) The integrals over the f values for transitions to $(1s,\epsilon p)\,{}^1P$ states are evaluated numerically from $E=0$ to 1000 ry. For $E>1000$ ry, the asymptotic formula (34) is used, and integrations performed analytically.

(ii) For transitions to $(2s,\epsilon p)\,{}^1P$ states, the integrals over the energy interval $E=0$ to 631 ry are evaluated numerically. For $E\geq 631$ ry the asymptotic form is found by using the f value at $E=631$ ry obtained from the machine calculation and is given by

$$\frac{df}{dE}=13.045E^{-7/2}\left(1-\frac{2\pi}{E^{\frac{1}{2}}}+\frac{18.9}{E}\right). \tag{40}$$

(iii) As already discussed in Sec. II, the contribution to the f sum of the transitions to states $(ms,\epsilon p)$ $(m>2)$ and $(\epsilon' s,\epsilon p)$ may perhaps amount to 4 or 5% of those from $(1s,\epsilon p)\,{}^1P$ states, and may, in fact, be proportional to them in the whole energy range. However, we have pointed out in the last section that the f values for transitions to $(1s,\epsilon p)\,{}^1P$ states are probably 10% higher than their actual values for low excitation energies. In order to compensate for this overestimate, the f values for transitions to $(ms,\epsilon p)$ $(m>2)$ and $(\epsilon' s,\epsilon p)$ states are taken to be zero from $E=0$ to $E=4\pi^2$; from $E=4\pi^2$ ry to infinity the asymptotic form (23) is used.

The results of integrations along with the contribution of the discrete states are displayed in Table IV. The sums $S(-1)$, $S(0)$, $S(1)$, and $S(2)$ calculated here differ by a few percent from their more accurate values obtained from the sum rules. The ratio of $S'(2)$ and $S(2)$ yields

$$\ln(k_0/\mathrm{ry})=4.436, \tag{41}$$

We shall now use a slight modification of the Pekeris method to obtain a much more accurate value of the average excitation energy. Let $E(k)$ be the difference between the value of $S(k)$ obtained from the sum rule and that evaluated by using the approximate f values; then the error in $S'(2)$ is given by $E'(2)$. We also know that $E(3.5)=\infty$ since the error in f_{n0} varies as $E^{-9/2}$ with the energy of the electron for high excitation

TABLE IV. Various contributions to the sums $S(k)$ and $S'(k)$.

Sum	$(1s,\epsilon p)$	$(2s,\epsilon p)$	$(1s,np)$	$(2s,np)$	$(ms,\epsilon p)$ $(m>2)$ $(\epsilon' s,\epsilon p)$	Total	Exact value
$n(-1)$	0.53985	0.00384	0.27188	0.00130	0.00000	0.81687	0.75249756
$S(0)$	1.5771	0.0282	0.4421	0.0060	0.0001	2.0535	2
$S(1)$	6.8522	0.3180	0.7194	0.0277	0.0060	7.9233	8.1674502
$S(2)$	109.445	5.578	1.176	0.1284	1.4130	117.740	121.3354
$S'(2)$	487.687	24.897	0.5802	0.1934	9.261	522.618	

energies. By fitting polynomial for $E(k)$ at $k=-1$, 0, 1, 2, and 3.5 and evaluating the derivative of this polynomial at $k=2$, we get

$$E'(2)=9.913. \tag{42}$$

Adding $E'(2)$ to $S'(2)$ and dividing by the value of $S(2)$ obtained from the sum rule, we get

$$\ln(k_0/\text{ry})=4.389+\delta', \tag{43}$$

which differs very little from the value obtained by Kabir and Salpeter. The value of $\ln k_0$ obtained by Pekeris[4] differs from (43) roughly by 2%. It would then appear most likely[19] that the error in $E'(2)$ is not more than 10% and that δ' almost certainly lies between ± 0.01. Dalgarno and Stewart[14] obtain a value 4.37 for $\ln k_0$ with a probable error of ± 0.03.

There remains to be discussed the contributions of relative order α^4 ry; for the one electron ion, the major contribution comes from the relativistic corrections to the Lamb shift and is of relative order $Z^3\alpha^4$. This correction has already been calculated by several authors[20,21] and is given by

$$E_{L,1}'=8\pi Z^2\alpha^4\frac{z^3}{\pi}\left(1+\frac{11}{128}-\frac{1}{2}\ln 2+\frac{5}{192}\right)\text{ ry}. \tag{44}$$

For the helium ion $E_{L,1}'$ has the value 0.061 cm^{-1}. There are also corrections of relative order $Z^2\alpha^4$ arising from the fourth-order radiative corrections but they are expected to be much smaller than the corrections of relative order $Z^3\alpha^4$.

For the two-electron atom, there are a large number of corrections of relative order α^4 ry (i.e., $Z^3\alpha^4$, $Z^2\alpha^4\ln\alpha$, $Z^2\alpha^4$, $Z\alpha^4\ln\alpha$, and $Z\alpha^4$), but the leading terms again will be of relative order $Z^3\alpha^4$. These terms arise from the relativistic corrections to the Lamb shift terms $E_{L,2}$ and can be estimated quite easily if one assumes that the electrons move independently of each other in a field $V(r)$. On the basis of such a picture one would expect these corrections to be given by

$$E_{L,2}'=8\pi Z^2\alpha^4\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle\left(1+\frac{11}{128}-\frac{1}{2}\ln 2+\frac{5}{192}\right), \tag{45}$$

where the expectation value of the operator $[\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)]$ is to be evaluated with the Hartree wave function for the ground state. For the ground state of helium $E_{L,2}'$ has the value 0.086 cm^{-1}. Thus the corrections of relative order $Z^3\alpha^4$ contribute to the ionization energy, the amount

$$\eta=E_{L,1}'-E_{L,2}'=0.025\text{ cm}^{-1}. \tag{46}$$

Since we have neglected a large number of corrections of order $Z^2\alpha^4\ln\alpha$, $Z^2\alpha^4$, etc., the uncertainty in the value of the corrections η of order α^4 ry is probably ± 0.01 cm^{-1} using the estimate (46) for η, and putting $\delta'=\pm 0.01$ in Eq. (43), I_{th} becomes

$$I_{\text{th}}=(198\,310.665\pm 0.043)\text{ cm}^{-1}. \tag{47}$$

This is in excellent agreement with the experimental value, Eq. (1).

The major part of the uncertainty in the theoretical vulue of the ionization energy is due to the uncertainty in the experimental value of Rydberg's constant (109 722.267±0.012 cm^{-1}). For an exact value of the Rydberg constant, the error in I_{th} would only be ± 0.02 cm^{-1}, appreciably less than the Sucher term of -0.069 cm^{-1}. However, the present uncertainty in the experimental value in Eq. (1) is about twice the Sucher term and a significant comparison of Sucher term with experiment must await a further refinement in the experimental determination of Rydberg constant and the ionization energy.

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