Radiative Corrections to the Ground-State Energy of the Helium Atom*

P. K. KABIR† AND E. E. SALPETER
Laboratory of Nuclear Studies, Cornell University, Ithaca, New York

(Received August 5, 1957)

The radiative corrections of relative order $Z^2\alpha^3$ (absolute order $Z^4\alpha^3$ ry), corresponding to the Lamb shift terms arising from the nuclear Coulomb potential, and some of the $Z\alpha^3$ corrections, arising from radiative interactions between the electrons, are calculated for the ground-state energy of the helium atom. The $Z^2\alpha^3$ corrections are all calculated, but of the $Z\alpha^3$ corrections, which are expected to be much smaller, we retain only those containing $\ln\alpha$ as a factor—these may be estimated rather easily—and neglect the rest, regarding unity as being small compared to $\ln\alpha$.

The $Z^2\alpha^3$ corrections require the calculation of an "average excitation energy" similar to the one defined by Bethe for the hydrogen atom. It is found that virtual transitions to states $(1s)\times$(continuous p)^1P are the most important, and these are calculated using the momentum matrix-elements obtained by Huang, who used a six-parameter Hylleraas wave function for the ground state, and a product wave function with $Z=2$ for the s-electron and $Z=1$ for the p-electron (full screening), for the excited states. Transitions to states other than $(1s)$(continuous p)^1P are also considered, and the value of the "average excitation energy" for helium is found to be 80.5 ± 10 ry, where the limits represent an estimate of the probable error of the result. The radiative correction to the ionization potential, which will be the difference of the corrections for the two-electron atom and the ion, is found to be -1.26 ± 0.2 cm^{-1}, where the error includes an estimation of the $Z\alpha^3$ terms which are not calculated.

The corresponding radiative corrections are calculated, less accurately, also for Li^+, and the results generalized for helium-like ions of higher Z by an extrapolation formula.

I.

RECENT improvement[1] in the determination of the first ionization potential of helium has renewed interest in the theoretical calculation of the ground-state energy of the helium atom. Several investigators[2–5] have extended Hylleraas'[6] variational calculation of the nonrelativistic eigenvalue to the point that Kinoshita's[5] value,

$$I_{NR}=198\,316.97\ \text{cm}^{-1}, \tag{1}$$

obtained with a wave function of 39 parameters, is probably within about 0.3 cm^{-1} of the true eigenvalue.

The relativistic corrections, of relative order $Z^2\alpha^2$ and $Z\alpha^2$ have all been calculated[7,8] and evaluated with the 39-parameter wave function,[5] as also the "mass-polarization," which is a correction of the same numerical order of magnitude. The sum of the relativistic and mass-polarization corrections calculated by Kinoshita[5] is

$$\Delta I_R=(-5.36\pm0.2)\ \text{cm}^{-1}. \tag{2}$$

Comparing (1) and (2) with the experimental value[1]

$$I_{\text{exp}}=(198\,310.5\pm1)\ \text{cm}^{-1}, \tag{3}$$

and remembering that the variational eigenvalue (1) is a strict lower bound to the "nonrelativistic ionization potential," we see that $\Delta I_R(2)$ is not large enough to bring the theoretical ionization potential down to the experimental value (3). Therefore, we must invoke the radiative corrections arising from quantum electrodynamics to avoid disagreement between theory and experiment. These have been estimated by Günther[9] as -1.6 cm^{-1} and by Håkansson[10] as between -0.7 cm^{-1} and -1.7 cm^{-1}, respectively. While the sign and order of magnitude are in the direction of improved agreement, the uncertainty in these numbers is quite large and we see that a more detailed examination of these higher order corrections is warranted, particularly in view of the planned refinement of the experimental determination (3).

All the corrections of relative order $Z^2\alpha^3$ (absolute order $Z^4\alpha^3$ ry) and some of the $Z\alpha^3$ corrections are calculated in Sec. II. For the one-electron ion that remains when a two-electron atom is ionized, the radiative correction to the ground-state energy of relative order $Z^2\alpha^3$ is just the (lowest-order) Lamb shift, which has been calculated by many authors[11,12]

$$E_{L,1}=\frac{8}{3}Z\alpha^3\frac{Z^3}{\pi}\left[2\ln\frac{1}{Z\alpha}-\ln\frac{K_0}{Z^2\,\text{ry}}+\frac{19}{30}\right]\text{ry}, \tag{4}$$

where $K_0=19.77\,Z^2$ ry is the "average excitation energy" for a $1S$ state as defined by Bethe,[11] and evaluated by Håkansson[10] and Harriman.[13] There are no terms of relative order $Z\alpha^3$.

For the two-electron atom, the only radiative corrections of relative order $Z^2\alpha^3$ are also Lamb shift terms arising from the nuclear potential, described by the Feynman diagrams in Figs. 1(a) and 1(b), giving for

* Supported in part by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission.

† Now at the Institute for Advanced Study, Princeton, New Jersey.

[1] G. Herzberg and R. Zbinden (unpublished). See reference 2, footnote 12.

[2] S. Chandrasekhar and G. Herzberg, Phys. Rev. **98**, 1050 (1955).

[3] H. M. Schwartz, Phys. Rev. **103**, 110 (1956).

[4] E. Hylleraas and J. Midtal, Phys. Rev. **103**, 829 (1956).

[5] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[6] E. Hylleraas, Z. Physik **54**, 347 (1929).

[7] G. Breit, Phys. Rev. **34**, 553 (1929); **36**, 383 (1930); **39**, 616 (1932).

[8] H. Eriksson, Z. Physik **109**, 762 (1938); V. Berestetskii and L. Landau, J. Exptl. Theoret. Phys. U.S.S.R., **19**, 637 (1949); J. Sucher and H. M. Foley, Phys. Rev. **95**, 966 (1954).

[9] M. Günther, Physica **15**, 675 (1949).

[10] H. Håkansson, Arkiv Fysik **1**, 555 (1950).

[11] H. A. Bethe, Phys. Rev. **72**, 339 (1947).

[12] Bethe, Brown, and Stehn, Phys. Rev. **77**, 370 (1950).

[13] J. M. Harriman, Phys. Rev. **101**, 594 (1956).

the total correction of relative order $Z^2\alpha^3$

$$E_{L,2}=-\frac{8}{3}Z\alpha^3\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}\left[2\ln\frac{1}{\alpha}-\ln\frac{k_0}{\mathrm{ry}}+\frac{19}{30}\right]\mathrm{ry}, \quad (5)$$

where $\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}$ is the expectation value, in (Hartree) atomic units, of the operator $[\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)]$ for the ground state of the helium atom. The average excitation energy k_0 is defined in a manner analogous to that for one-electron atoms,[11] and may be written in the form

$$\ln k_0=\int\omega_{n0}^2\ln\omega_{n0}df_{n0}\Big/\int\omega_{n0}^2df_{n0},\ \omega_{n0}\equiv E_n-E_0, \quad (6)$$

where the integrals are to be interpreted in the Stieltjes sense and extend over all states n to which dipole transitions are possible from the ground state, and f_{n0} is the nonrelativistic oscillator strength (without retardation) for transitions from the ground state to the state n. The calculation of k_0 is described in Sec. III.

For the two-electron atom, there are, in addition, a large number of terms which contribute to order $Z\alpha^3$. These arise from radiative interactions between the two electrons, and a complete treatment of these terms would require the use of a fully relativistic treatment for two electrons in an external field. Now, for high Z, these corrections will be small compared to the $Z^2\alpha^3$ corrections and even for low Z, these corrections which, in a simple approximation, are proportional to the expectation value of the operator $\delta(\mathbf{r}_{12})$, are numerically not very important because $\langle\delta(\mathbf{r}_{12})\rangle_{00}$ is many times smaller than $\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}$, the factor appearing in the $Z^2\alpha^3$ corrections. For He,

$$\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}=34.0\langle\delta(\mathbf{r}_{12})\rangle_{00},$$

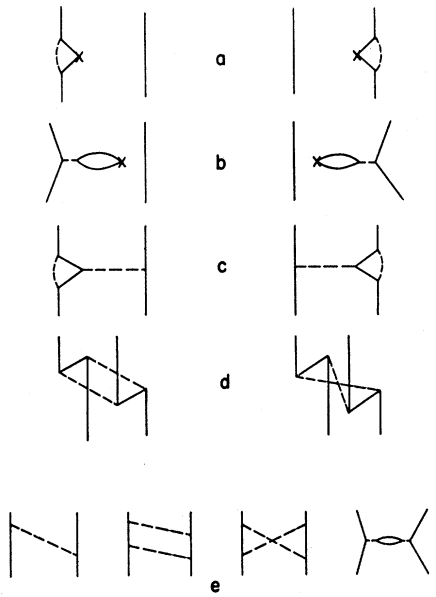

FIG. 1. Feynman diagrams for helium atom Lamb shift.

while for Li^+,

$$\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}=25.2\langle\delta(\mathbf{r}_{12})\rangle_{00}.$$

Moreover, since the $Z\alpha^3$ corrections which contain $\ln\alpha$ may be calculated rather easily, we retain only these, regarding unity as being small compared to $\ln\alpha$. The sum of the $Z\alpha^3\ln\alpha$ corrections will be shown to be

$$E_{L,2}'=-\frac{28}{3}\alpha^3\langle\delta(\mathbf{r}_{12})\rangle_{00}\ln\frac{1}{\alpha}\,\mathrm{ry}. \quad (7)$$

The radiative correction to the ionization potential of a two-electron atom is then

$$\Delta I_L=E_{L,1}-E_{L,2}-E_{L,2}',$$

and the results are summarized in Sec. IV.

In Sec. V, we discuss the radiative corrections to the ionization potentials of helium-like ions of higher Z, on the basis of a calculation for Li^+ and an extrapolation formula.

II.

The Lamb shift for a one-electron atom is so well known that we need only quote the result (4).

For the two-electron atom also, the major contribution is from virtual photons of "low" momentum, and this is calculated by the method of Bethe.[11] Using this for photon momenta $0<k<\lambda$, where $\lambda\sim\alpha m$ so that retardation may be neglected, we obtain the nonrelativistic contribution to the self-energy correction for the electrons (in natural units $\hbar=c=1$),

$$W_{S,NR}=\frac{e^2}{4\pi^2m^2}\sum_n\sum_{e\perp k}\int\frac{d^3k}{k^2}\frac{|p_{e,n0}^{(1)}|^2+|p_{e,n0}^{(2)}|^2}{E_n-E_0-k}\times(E_n-E_0) \quad (8)$$

$$=\frac{2e^2}{3\pi m^2}\sum_n[|\mathbf{p}_{n0}^{(1)}|^2+|\mathbf{p}_{n0}^{(2)}|^2]\times(E_n-E_0)\ln\frac{\lambda}{E_n-E_0},$$

where we have neglected (E_n-E_0) in comparison with λ in the numerator of the logarithmic term.

We consider next processes in which one electron emits the photon and the other absorbs it. A large part of this effect has already been included in the relativistic corrections, Eq. (2), by virtue of the Breit operator; this operator is exactly the part obtained by neglecting (E_n-E_0) compared with k in the energy denominators of the exact expression. Subtracting this off, we obtain as a further correction[14] similar to (8),

$$W_{B,NR}=\frac{e^2}{2\pi^2m^2}\sum_n\sum_{e\perp k}\int\frac{d^3k}{k^2}\times\frac{\langle0|p_e^{(1)}e^{i\mathbf{k}\cdot\mathbf{r}_1}|n\rangle\langle n|p_e^{(2)}e^{-i\mathbf{k}\cdot\mathbf{r}_2}|0\rangle}{E_n-E_0+k}(E_n-E_0). \quad (9)$$

[14] E. E. Salpeter, Phys. Rev. 87, 328 (1952).

If we explicitly calculate (8) and (9), it is seen that (9) exactly cancels the part of (8) which arises from the interelectron interaction if we replace the exponential factors in (9) by unity. However, this cancellation occurs only when retardation is neglected in (9), and there will be a finite difference for "high" photon momenta. If we combine (8) and (9) together, we obtain

$$W_{NR}=\frac{2e^2}{3\pi m^2}\sum_n|\langle 0|\,\mathbf{p}_1+\mathbf{p}_2|n\rangle|^2 \times(E_n-E_0)\ln\frac{\lambda}{|E_n-E_0|}. \quad (10)$$

Apart from the slowly varying logarithmic factor, the sum over n can be expressed in closed form. It is therefore convenient to write

$$\sum|\langle 0|\,\mathbf{p}_1+\mathbf{p}_2|n\rangle|^2(E_n-E_0)\ln\frac{\lambda}{|E_n-E_0|} =\{\sum|\langle 0|\,\mathbf{p}_1+\mathbf{p}_2|n\rangle|^2(E_n-E_0)\}\ln\frac{\lambda}{k_0}, \quad (11)$$

this being the definition of k_0, which is easily seen to be equivalent to (6) since

$$f_{n0}=\tfrac{2}{3}|\langle n|\,\mathbf{p}_1+\mathbf{p}_2|0\rangle|^2/(E_n-E_0). \quad (12)$$

Then we may write

$$W_{NR}=\frac{e^2}{3\pi m^2}\langle(\nabla_1^2+\nabla_2^2+2\boldsymbol{\nabla}_1\cdot\boldsymbol{\nabla}_2)V\rangle_{00}\ln\frac{\lambda}{k_0}, \quad (13)$$

since

$$\sum_n|\langle 0|\,\mathbf{p}_1+\mathbf{p}_2|n\rangle|^2(E_n-E_0)=\tfrac{1}{2}\langle(\nabla_1^2+\nabla_2^2+2\boldsymbol{\nabla}_1\cdot\boldsymbol{\nabla}_2)V\rangle_{00},$$

where V is the potential in the helium atom, including the Coulomb interaction between the electrons:

$$V=-\frac{Ze^2}{r_1}-\frac{Ze^2}{r_2}+\frac{e^2}{r_{12}},$$
$$\nabla_j^2V=4\pi e^2[Z\delta(\mathbf{r}_j)-\delta(\mathbf{r}_{12})],\quad \boldsymbol{\nabla}_1\cdot\boldsymbol{\nabla}_2V=4\pi e^2\delta(\mathbf{r}_{12}). \quad (14)$$

Thus

$$W_{NR}=\frac{4\alpha^2Z}{3m^2}\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}\ln\frac{\lambda}{k_0}. \quad (13')$$

We now consider contributions from high photon momenta $k>\lambda$. In this region the electron, after emitting an energetic virtual photon, is practically free in the intermediate state, so it is permissible to treat it by Born approximation. This is essentially a scattering approximation, and the results on the radiative correction to electron scattering[15] may be used. These refer to the scattering by a static potential, described by the Feynman graphs (a) in Fig. 1. If we include the vacuum polarization, represented by the diagram in (b), we obtain for the contribution to the Lamb shift, due to the nuclear potential,

$$W_{Z,R}=\frac{e^2}{3\pi m^2}\left(\ln\frac{m}{2\lambda}+\frac{5}{6}-\frac{1}{5}\right)\langle(\nabla_1^2+\nabla_2^2)V_0\rangle_{00} \quad (15)$$

from photons of momentum greater than λ, where V_0 is the nuclear potential only. Added to (13′), this yields, for the $Z^2\alpha^3$ corrections to the ground-state energy

$$W_{L,2}=\frac{4Z\alpha^2}{3m^2}\left(\ln\frac{m}{2k_0}+\frac{19}{30}\right)\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}, \quad (16)$$

which is identical with (5), when written in atomic units. The $Z\alpha^3\ln\alpha$ correction arising from a similar process, described by the Feynman diagrams [Fig. 1(c)], is similarly found to be

$$W_{1,R}=-\frac{8\alpha^2}{3m^2}\ln\frac{m}{2\lambda}\langle\delta(\mathbf{r}_{12})\rangle_{00}, \quad (17)$$

which is exactly what we would have obtained by including the interelectron interaction in the potential in (15). The low-momentum contributions to this term were exactly cancelled by the correction (9) to the Breit interaction. In the self-energy terms which lead to (16) it can be shown that[16] retardation may be neglected for all values of the photon momentum k and the value of λ does not appear in (16). Retardation can be similarly neglected in the terms which lead to (17). In the terms leading to (9), however, an actual exchange of momentum k occurs between the two electrons and a retardation factor is present explicitly. This retardation factor decreases the contribution of these terms severely if k is large compared with αm, the Bohr momentum. In keeping with our scheme of neglecting unity compared with $\ln\alpha$ in terms of order $Z\alpha^3$, we put $\lambda=\alpha m$, retain (9) without any retardation correction (since $k<\lambda$) and omit the high-frequency terms ($k>\lambda$), which correspond to (9), completely.

Finally, we must consider the processes involving the exchange of two transverse photons between the electrons. These contribute corrections of order $Z\alpha^3$ but a nonrelativistic calculation reveals no terms containing $\ln\alpha$. However, we do obtain a term containing $\ln\alpha$ if we consider processes involving negative energy states, and these can be estimated quite easily by ordinary perturbation theory.[14] These processes are described by the Feynman graphs in Figs. 1(d), in which the time-ordering is significant, and if the photon momenta are taken as $\mathbf{k}$, $\mathbf{q}-\mathbf{k}$, contributions to order $Z\alpha^3\ln\alpha$ come only from values of $q<\alpha m$, $\alpha m<k<m$. Then the contribution

[15] Z. Koba and S. Tomonaga, Progr. Theoret. Phys. Japan **3**, 290 (1948); R. P. Feynman, Phys. Rev. **76**, 769 (1949); J. Schwinger, Phys. Rev. **76**, 790 (1949).

[16] H. A. Bethe and E. E. Salpeter, *Encyclopaedia of Physics* (Springer Verlag, Berlin, 1957), Vol. 35, p. 186.

to the level-shift is found to be

$$W_T=-\frac{2\alpha^2}{m^2}\ln\left(\frac{m}{\alpha m}\right)\langle\delta(\mathbf{r}_{12})\rangle_{00}, \tag{18}$$

and if we add the $Z\alpha^3$ corrections (17) and (18), we obtain

$$W_{L,2}'=-(14/3)\alpha^2\ln(1/\alpha)\langle\delta(\mathbf{r}_{12})\rangle_{00}, \tag{19}$$

which, written in atomic units, is (7).

III.

The calculation of the average excitation energy k_0, defined in (6), requires a knowledge of the oscillator strengths for transitions to all states which may be reached by dipole transitions from the ground state $1\,^1S_0$. These must all be ^1P states, and may be classified in two groups:

(a) Those states which give rise to lines of the He atomic spectrum, in which one electron remains in the lowest ($1s$) state while the other electron is excited to a higher p state. This may be either (i) one of the higher discrete states, in which case the configuration of the excited state is $(1s)(np)\,^1P$, or (ii) one of the continuum states, in which case the excited state configuration is $(1s)$(continuous p)$\,^1P$.

(b) In addition, there are the states in which both electrons are excited to higher levels. By the Laporte rule, the only such states that combine with the ground state $^1S_0$ are the singlet configurations arising from $(ms)(np)$, $(mp)(nd)$, $(md)(nf)$, etc. There are then different subgroups arising from the various possibilities that (i) both m and n are discrete levels, or (ii) one is a discrete level, and the other belongs to the continuous range, or (iii) both belong to the continuous range.

Since exact eigenfunctions of the helium energy levels are not known for any of the states, we are obliged to make use of oscillator-strengths derived from matrix-elements calculated with approximate wave functions. The calculation for the $(1s)$(continuous p)$\,^1P$ states, which are responsible for by far the largest contributions to the integrals in (6), will be considered in detail, but for the others we either make use of previous calculations or give rough estimates. We now discuss the contributions of the various groups of states.

(i) The oscillator strengths for transitions to the discrete states of the "principal series" have been calculated previously for $n=2$, by Wheeler,[17] who used a six-parameter wave function for the ground state, and for $n=3$ to 7 by Vinti,[18] using a two-parameter wave function. We have used these numerical results and for $n=8$ to ∞ the asymptotic form $f_{n0}=C/n^3$. From requirements of continuity it follows[19] that the constant C equals $2df/dE$ evaluated at the series limit. Our results (next section) with a six-parameter ground-state function give $C=1.958$; using a two-parameter function, Vinti obtaining $C=2.09$. Summing over all the discrete states, we obtain the two sums

$$\sum_{n=2}^{\infty}\omega_{n0}^2 f_{n0}=1.19\ \text{ry}^2,$$
$$\sum_{n=2}^{\infty}\omega_{n0}^2\ln(\omega_{n0}/\text{ry})f_{n0}=0.59\ \text{ry}^2, \tag{20}$$

the contribution of $n=8$ to ∞ to these two sums being only 0.062 ry^2 and 0.037 ry^2, respectively. About half the contribution to these sums comes from $n=2$. The error of the two sums in (20) is probably of the order of ± 0.2 ry^2.

(ii) Oscillator-strengths for transitions to $(1s)$(continuous p)$\,^1P$ states have been calculated by Wheeler[17] and by Huang,[20] using a Hylleraas six-parameter wave function[6] for the ground state and a product wave function of hydrogen eigenfunctions with charge Z for the $1s$-electron and with charge $(Z-1)$ (full screening) for the p-electron, for the excited state. Since this must also be a singlet state, we must use the appropriate symmetric combination

$$\psi_{\epsilon,m}=[u_0(1)v_{\epsilon,m}(2)+u_0(2)v_{\epsilon,m}(1)]/\sqrt{2} \tag{21}$$

for the evaluation of matrix-elements, where

$$u_0=\pi^{-\frac{1}{2}}Z^{\frac{3}{2}}e^{-Zr_1},\quad \epsilon_0=-\tfrac{1}{2}Z^2, \tag{22}$$

and

$$v_{\epsilon,m}=\left[\frac{3}{16\pi^3}\frac{(e^{2\pi(Z-1)/k}-1)}{(1+|m|)(Z-1)[k^2+(Z-1)^2]}\right]^{\frac{1}{2}}\times e^{\pi(Z-1)/k}P_1^m(\cos\theta)e^{im\varphi}R_\epsilon(r), \tag{23}$$

where

$$-2iR_\epsilon=r\int_{-ik}^{ik}e^{xr}(x+ik)^{1+i(Z-1)/k}(x-ik)^{1-i(Z-1)/k}dx,$$

and where we use (Hartree) atomic units throughout, unless otherwise specified, $k=(2\epsilon)^{\frac{1}{2}}$. The normalization of v is $\int v_\epsilon^* v_{\epsilon'}d\tau=\delta(\epsilon-\epsilon')$.

While Wheeler calculated only the dipole matrix-element, Huang considered the equivalent forms

$$M_{0n}=\frac{1}{E_n-E_0}\left\langle n\left|\frac{\partial}{\partial x_1}+\frac{\partial}{\partial x_2}\right|0\right\rangle=\langle n|x_1+x_2|0\rangle, \tag{24}$$

which lead to identical results when exact eigenfunctions are employed, but may here differ from each other (and from the correct value). According to Chandrasekhar,[21] the values derived from the momentum operator are more reliable. Huang found that, while the

[17] J. A. Wheeler, Phys. Rev. **43**, 258 (1933).
[18] J. P. Vinti, Phys. Rev. **42**, 632 (1932).
[19] J. Hargreaves, Proc. Cambridge Phil. Soc. **25**, 91 (1928).
[20] S. S. Huang, Astrophys. J. **108**, 354 (1948).
[21] S. Chandrasekhar, Astrophys. J. **102**, 223 (1945).

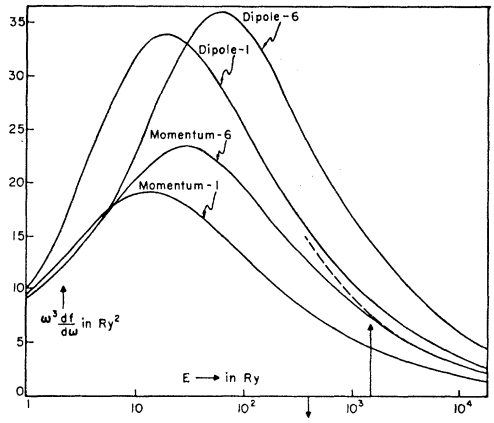

FIG. 2. The weight function $\omega^3(df/d\omega)$ plotted against the energy E of the excited electron. The four graphs correspond to momentum and dipole matrix elements obtained with the one- and six-parameter wave functions.

dipole and momentum matrix-elements gave almost identical results over the range of frequencies in which the oscillator-strength is appreciable, at high frequencies the f-values derived from the two matrix elements, while small and showing the same general dependence on energy, differ considerably,[22] the values obtained from the dipole moment being appreciably higher. Since high excitation energies are weighted quite heavily in the calculation of the mean excitation energy k_0, this leads to quite different values of k_0 in the two cases. In Fig. 2, we exhibit the values of $\omega^3(df/d\omega)=\omega^2(df/d\ln\omega)$ for the two matrix-elements in the two cases when a six-parameter and a one-parameter function are used to describe the ground state.

Tabulated below in Table I are the contributions to the integrals $\int\omega^2 df$ and $\int\omega^2\ln\omega df$ calculated with the different oscillator strengths. As a check, we also give the values of $(8\pi/3)\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}$ for the corresponding wave functions, since we have the sum rule

$$\int\omega_{n0}^2 df_{n0}=\tfrac{4}{3}\pi Z\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}. \tag{25}$$

It is seen that the oscillator-strengths derived from the momentum matrix element give quite good agreement with the sum rule, provided there are no large contributions from states other than $(1s)$(continuous p) ^1P, whereas the dipole matrix elements violate (25) rather badly.

The reason for the differences between the two f-values at high frequencies is not hard to find. The wave function v of the excited electron in (21) may always be written as

$$v=v_0+\frac{1}{\epsilon-H_0}Vv, \tag{26}$$

where v_0 is a plane wave solution of $(\epsilon-H_0)v=0$, and V is the potential seen by this electron. For high excitation energies, the second term is negligible compared to the first, so the matrix element M_{n0} (24) takes the form

$$\int d\tau_1 d\tau_2[u_0^*(\mathbf{r}_1)e^{-i\mathbf{k}\cdot\mathbf{r}_2}+u_0^*(\mathbf{r}_2)e^{-i\mathbf{k}\cdot\mathbf{r}_1}]\Omega\phi(\mathbf{r}_1,\mathbf{r}_2)$$

where $\phi(\mathbf{r}_1,\mathbf{r}_2)$ is the ground-state wave function and Ω is taken as (x_1+x_2) or $[1/(E_n-E_0)](\partial/\partial x_1+\partial/\partial x_2)$ according as the dipole matrix element or the momentum matrix element is desired. In either case, we see that the Fourier transform with respect to one of the arguments of the ground-state wave function is involved; if the ground state is described by a variational wave function which yields a good value for the energy operator, we may be confident that it will furnish a good description of the actual wave function for those Fourier components which contribute strongly to the energy operator, but there is no guarantee whatever that it will yield accurate values for the Fourier components to which the Hamiltonian is relatively insensitive, in particular for the very high momentum components which contribute little to the ground state. However, by writing the Schrödinger equation satisfied by the ground-state wave function in momentum space, we have a means of determining the asymptotic form of the transition matrix element, when the excited electron may be described by Born approximation, without explicitly requiring a knowledge of the high-momentum behavior of the ground-state wave function. For, written in momentum space, the momentum matrix element is

$$D_j=\int d^3p_1 d^3p_2\psi^*(\mathbf{p}_1,\mathbf{p}_2)(\mathbf{p}_1+\mathbf{p}_2)_j\phi(\mathbf{p}_1,\mathbf{p}_2),$$

where ψ is given by (21), in which we take[23] $v=(4\pi k)^{\frac{1}{2}}\times\delta(\mathbf{p}-\mathbf{k})$, $k=(2\epsilon)^{\frac{1}{2}}$, so that

$$D_j=(8\pi k)^{\frac{1}{2}}\int d^3p_1 u_0^*(\mathbf{p}_1)(\mathbf{p}_1+\mathbf{k})_j\phi(\mathbf{p}_1,\mathbf{k}),$$

TABLE I. The two integrals involving the weight functions. All quantities are in units of ry².

Ground-state wave function	$\frac{8\pi}{3}\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}$	$\int\omega^2 df$		$\int\omega^2\ln\frac{\omega}{\text{ry}}df$	
		Dipole	Momentum	Dipole	Momentum
1-parameter	102.51	165.24	93.25	719.12	383.32
6-parameter	121.76	188.21	122.41	954.28	542.85

[22] There is a misprint in Huang's paper. Equation (25) on p. 358 of reference 20 should read

$$M_d^2=\gamma_1 I_d^2,\quad M_m^2=(4/E)\gamma_1 I_m^2,\quad M_a^2=(16/E^2)\gamma_1 I_a^2,$$

instead of

$$M_d^2=\gamma_1 I_d^2,\quad M_m^2=\gamma_1 I_m^2,\quad M_a^2=\gamma_1 I_a^2.$$

The results in his Table II are, however, correct.

[23] The factor under the square root sign makes the normalization $\int v_\epsilon v_{\epsilon'}d\tau=\delta(\epsilon-\epsilon')$, which is the normalization employed in (23).

where the ground-state wave function ϕ satisfies the equation

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

Now the ground-state wave function falls off rapidly when either of its arguments greatly exceeds the Bohr momentum. Therefore, if k is much larger than the Bohr momentum, the contribution to D_j of the second term on the right-hand side, which is essentially from values of $\mathbf{q}\sim\mathbf{k}$, will be much larger than those of the other two. This term contributes exactly

$$(8\pi k)^{\frac{1}{2}}Zk_j\pi^{-2}\int\int d^3sd^3pu_0^*(\mathbf{p})(k^2+p^2-2E_0)^{-1}$$
$$\times|\mathbf{k}-\mathbf{s}|^{-2}\phi(\mathbf{p},\mathbf{s}),$$

and the leading term in powers of $1/k$ is

$$D_{0j}=(8)^{\frac{1}{2}}\pi^{-\frac{3}{2}}Zk_jk^{-7/2}\int\int d^3sd^3pu_0^*(\mathbf{p})\phi(\mathbf{p},\mathbf{s})$$

which in coordinate space has the simple form

$$D_{0j}=8Zk_jk^{-7/2}\int d^3ru_0^*(\mathbf{r})\phi(\mathbf{r},0).$$

This can be calculated quite easily with even the most accurate known wave function and leads to an asymptotic form for the oscillator-strength which is found to be not nearly as sensitive to the details of the ground-state wave function as that obtained directly from the matrix elements. In Table II, we give the coefficients for the asymptotic behavior of the oscillator-strength

$$df/d\epsilon=C\epsilon^{-7/2}, \tag{27}$$

where ϵ is measured in rydbergs, together with the corresponding coefficients obtained directly from the asymptotic forms of the matrix elements. It is evident that the correct asymptotic coefficient must lie close to the value derived directly from the momentum matrix element and it would appear that a value of $C=286(\text{ry})^{\frac{5}{2}}$ could not be far wrong. An asymptotic curve with this value of C is indicated by the dotted line in Fig. 2.

Huang's momentum matrix element, which we have used in our calculations, appears to be reliable both at low excitations, where it agrees with the dipole result and may therefore be trusted, and also at very high energies, where it agrees with the correct asymptotic value, and also gives good agreement with the sum rule (25). However, we see from Fig. 2 that it is exactly the intermediate region, where the reliability of the result is not so well established, that is of greatest importance for our integrals (6). The agreement between the dipole matrix elements and the momentum matrix elements at low excitations indicates that the assumption of full screening is a fairly good one for these states, whereas the asymptotic behavior obviously depends only on the first term in (26) and is independent of the choice of distorting potential. But it may be questioned whether the assumption of full screening is a valid one in the intermediate range. However, lacking a more certain guide to the intermediate region, we retain the f-values obtained from the momentum matrix-element with the wave function (21) as the best representation of the oscillator-strength over the whole range. In order to obtain an estimate of the possible limits on $\ln k_0$, we make modifications in the f-values in the intermediate range, holding $\int\omega^2df$ constant at the value prescribed by the sum rule (25) since this is known very accurately. These modifications are shown in Fig. 3, and the values of $\ln k_0$ obtained thereby are given in Sec. IV.

TABLE II. Values of the coefficient C in Eq. (27) in $(\text{ry})^{5/2}$.

Wave function	Matrix element: Dipole	Momentum	New method
1-parameter	360.1	181.8	255.4
6-parameter	591.4	290.9	288.3
10-parameter:			
Chandrasekhar			286.4
Kinoshita			285.7

(iii) We finally consider transitions to doubly excited states. Vinti[18] has discussed the oscillator strengths for transitions to the discrete doubly excited states, explicitly calculating the first few and estimating the rest. Using his results, we estimate the contribution of all discrete doubly excited states to $\int\omega^2df$ and $\int\omega^2\ln(\omega/\text{ry})df$ to be about 0.39 ry^2 and 0.62 ry^2, respectively.

(iv) For the doubly excited states in which at least one electron is in the continuum, ω is not bounded. Therefore, even though their f-sum is small, as shown by Vinti, it is possible that they may make large contributions. We therefore proceed as follows. Green *et al.*[24] have expanded the six-parameter helium ground-state wave function in a series of central field functions representing various configurations. From the coefficients of the higher terms in these series one can estimate that the f-values for transitions to $(2p)(nd)$, etc. should be less than 10^{-3} times those for $(1s)(np)$. We therefore restrict ourselves only to doubly excited sp-states. For transitions to these states we should get a reasonable order of magnitude estimate by using the simple hydrogenic wave function with $Z'=Z-\frac{5}{16}$ for the ground state (the overlap integral between this function and the much more complicated six-parameter function, for instance, is as large as 0.993). In this case the matrix element to a doubly excited state $(ns)(mp)$ is simply the product of an overlap integral Φ_n (between the $1s$ hydrogenic function for $Z'=Z-\frac{5}{16}$ and the

[24] L. C. Green *et al.*, Phys. Rev. **85**, 65 (1952).

TABLE III. Various contributions to the two integrals involving the weight function (in units of 121.28 ry²).

Range	$\int \omega^2 df$	$\int \omega^2 \ln\frac{\omega}{\text{ry}} df$
Discrete single excitation	0.0098	0.0048
Discrete double excitation	0.0032	0.0051
$(1s)$(continuous p) ^1P		
ϵ[a]=0−10 ry	0.1981	0.3478
ϵ=10−400 ry	0.5743	2.3470
ϵ=400 ry− ∞	0.2370	1.7812
Sum	1.0224	4.4859

[a] ϵ is the energy of the p-electron. For ϵ>400 ry, the asymptotic form of Huang's formula was used, and the integration performed analytically.

ns-function for $Z'=Z$) and a one-electron dipole matrix element M_{0m}. We find (for $Z=2$) that $\Phi_1^2=0.98$, $\Phi_2^2=0.01$, $\Phi_3^2=0.002$, and therefore that the sum of Φ_n^2 for all s-states in the continuum is considerably less than 0.01. For states in which the s-electron is in the continuum with high excitation energy, one can show that the oscillator strength decreases more rapidly with increasing excitation energy than for the $(1s)$(continuous p)-states. We finally consider states in which the s-electron is in a low excited state and the p-electron in the continuum. These states will contribute of the order of 1% to the integrals $\int \omega^2 df$ and $\int \omega^2 \ln(\omega/\text{ry}) df$, but it can be shown that (at least for the product type ground-state wave function) $df/d\omega$ arising from these states has almost the same shape as that arising from $(1s)$(continuous p). Thus the contributions of these states to the ratio of the two integrals, which occurs in the definition of the mean excitation energy k_0, is much smaller. To summarize, we expect the error introduced into our value of k_0, due to the neglect of doubly excited states[25] to be of the order of one percent or less.

IV.

The contributions of the states other than (ii) have already been given. The contributions of the states (ii) were calculated on the Cornell IBM 650 computer using Huang's formulas, and the integrals evaluated by Simpson's rule.

In Table III, we show the contributions of different states to the desired integrals, calculated with the momentum matrix element, in units of the sum-rule value $\frac{4}{3}\pi Z\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}=121.28$ ry² calculated with Kinoshita's 39-parameter wave function.

As discussed already in the previous section, the contributions of the other states, while amounting perhaps to as much as two or three percent of those from the $(1s)$(continuous p) ^1P states, are proportional to them and consequently have a much smaller effect on the value of $\ln k_0$. The ratio of the two integrals in Table III thus yields

$$\ln(k_0/\text{ry})=4.39, \quad k_0=80.5 \text{ ry},$$

which is nearly equal to the "mean excitation energy" for He^+: $19.77Z^2$ ry$=79.08$ ry. The main uncertainty, however, arises from the question of the reliability of the oscillator strengths for transitions to $(1s)$(continuous p) ^1P states with intermediate excitation energies. In order to determine the effect of this uncertainty, we recalculate the value of $\ln k_0$ in the two cases where the f-values in the intermediate range are altered so as to yield the curves marked A and B in Fig. 3, respectively. These curves are so adjusted as to give the same area as the original curve, since this is determined by the sum rule (25).

The values of $\log(k_0/\text{ry})$ thus obtained are

Modification	$\ln(k_0/\text{ry})$
A	4.3
B	5.0

The curves A and B represent rather extreme distortions of the original curve and it is unlikely that the value of $\ln k_0$ lies outside the limits given by them. We therefore write

$$\ln(k_0/\text{ry})=4.39+\delta, \tag{28}$$

where δ most probably lies between ± 0.2 and almost certainly between -0.2 and $+0.6$. Substituting this value in (5), we obtain for He

$$E_{L,2}=(5.009-0.823\delta\pm 0.005) \text{ cm}^{-1},$$

where the error corresponds to a probable uncertainty of 0.1% in the value of $\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle_{00}$, calculated with the 39-parameter wave function. Now, for $Z=2$,

$$E_{L,1}=3.535 \text{ cm}^{-1}$$

and

$$E_{L,2}'=-(0.210+0.043\eta\pm 0.002) \text{ cm}^{-1},$$

allowing an error of 1% in $\langle\delta(\mathbf{r}_{12})\rangle_{00}$ evaluated with the 39-parameter function, where we have rewritten (7) as

$$E_{L,2}'=-(28/3)\alpha^3\langle\delta(\mathbf{r}_{12})\rangle_{00}[\ln(1/\alpha)+\eta] \text{ ry}.$$

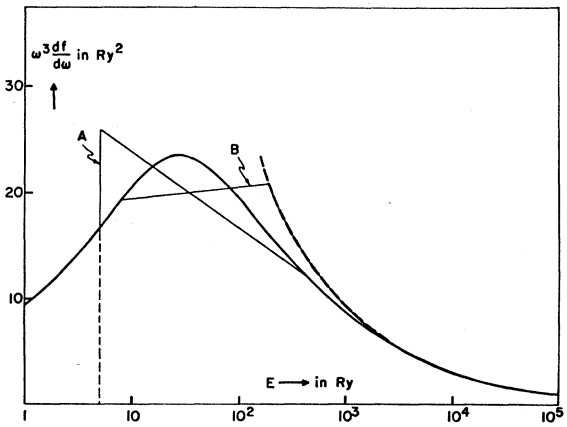

FIG. 3. The heavy curve is the "Momentum-6" curve of Fig. 2. The thin curves are two arbitrary modifications. The dotted curve is the asymptotic form of the weight factor.

[25] For a more detailed discussion, see P. K. Kabir, Ph.D. thesis, Cornell University, 1957 (unpublished).

The term η is included to take account of the $Z^3\alpha^3$ ry corrections which we have not calculated. Thus, the radiative correction to the ionization potential of the helium atom, to order α^3 ry, is found to be

$$\Delta I_L = E_{L,1} - E_{L,2} - E_{L,2}' = (-1.264 + 0.823\delta + 0.043\eta \pm 0.007)\ \text{cm}^{-1}, \quad (29)$$

where δ is estimated to be of the order of ± 0.2, and η is a number of the order of unity. If we add (29) to (1) and (2), we obtain a value for the theoretical ionization potential

$$I_{\text{th}} = 198\,310.35\ \text{cm}^{-1}$$

which is in excellent agreement with the experimental result (3). However, the quoted experimental error is almost as large as the total electrodynamic correction; consequently a *significant* comparison of our calculation with experiment must await a refinement of the experimental determination, in which case also a more accurate evaluation of $\ln k_0$ will probably be necessary. Principally, this would require the development of an improved treatment for the $(1s)$(continuous p) ^1P states with intermediate excitation energies.

V.

In order to estimate the corresponding radiative corrections for helium-like ions of higher Z, the value of $\ln k_0$ was calculated, less accurately, for Li^+. A six-parameter wave function was constructed for the ground state, and oscillator-strengths for transitions to $(1s)$-(continuous p) ^1P states were calculated with the same approximations used in the case of helium. Transitions to discrete states of the principal series were estimated using two-parameter wave functions to describe both ground and excited states. No other states were considered. The value of k_0 thus obtained was $k_{0,\text{Li}^+} = 191.6$ ry which, within the accuracy of our calculation, is the same as the "average excitation energy" for the one-electron ion Li^{++}. Since in the case of helium also, we found the "average excitation energy" to be very nearly the same as that of ionized helium, we may conclude that the average excitation energy for helium-like ions of higher Z will all be very close to $K_0 = 19.77Z^2$ ry, since the effect of screening will become less important as Z increases. For the energy correction, we also require the probabilities of finding an electron at the nucleus and at the position of the other electron, respectively. Using the results for Li^+ and O^{6+} obtained by Kinoshita *et al.*[26] with the 10-parameter wave functions of Chandrasekhar and Herzberg,[2] we construct the extrapolation formulas

$$\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2) \rangle_{00} = \frac{2Z^3}{\pi}\left[1 - \frac{0.653}{Z} + \frac{0.138}{Z^2}\right],$$

$$\langle \delta(\mathbf{r}_{12}) \rangle_{00} = \frac{Z^3}{8\pi}\left[1 - \frac{1.877}{Z} + \frac{1.189}{Z^2}\right]$$

and if we adopt the value of $19.77Z^2$ ry for the mean excitation energy k_0 for all Z, we obtain

$$\Delta I_L = \frac{8Z^4\alpha^3}{3\pi}\left[-7.490 + 2\ln Z + \frac{1}{Z}(11.93 - 2.61\ln Z) - \frac{1}{Z^2}(6.12 - 0.55\ln Z)\right] \text{ry},$$

leading to values of ΔI_L as shown below, in cm^{-1}, together with the corresponding "observed Lamb shifts" [27] for Li^+ and O^{6+}.

Z	3	4	5	6	7	8
$-\Delta I_L$	8.2	27.5	66	134	236	385
$-(\Delta I_L)_{\text{obs}}$	6.6±25					565±600

These values lead to improved agreement in each instance, but since the experimental errors are larger than the radiative correction in each case, a meaningful comparison of these results with experiment is not yet possible.

ACKNOWLEDGMENTS

We are grateful to T. Kinoshita and J. Sucher for helpful discussions. One of us (P. Kabir) would like to thank the Ford Foundation for the grant of a fellowship.

[26] T. Kinoshita *et al.* (private communication).
[27] J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).