

$V/2$ at low E/p_{300} values is equal to $kT/e=0.0258$ eV. Then the amount that each curve was shifted equals $\log f(R)$, and the final composite curve is a plot of $\log(D/\mu)$ vs $\log(E/p_{300})$. How well the curves can be

superimposed is a good test of the assumptions that have been made. Figures 2 and 3 show the two empirical ratio vs β_0 curves developed in this way for each tube from the data for helium at 300°K.

L-Shell Fluorescence Yields of Pt, Tl, and Pb†

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Partial *L*-shell fluorescence yields for three heavy elements have been measured using an x-ray coincidence counting method. Vacancies in the *K* shell of the atom are produced either by *K*-electron capture or internal conversion of a nuclear gamma ray in the *K* shell. The coincidence rate between the *K* and *L* x rays observed after the creation of the *K* vacancy determines the partial fluorescence yield, ω_{KL} . This quantity is defined as the fluorescence yield of those vacancies in the *L* shell created by K_{α_1} and K_{α_2} x-ray emission. In some cases, it was also possible to determine the partial fluorescence yield, ω_{LL} of the *L* shell following *L*-electron capture. The results obtained are in reasonable agreement with previous measurements. The relationship between ω_{KL} , ω_{LL} , and the fluorescence yields of individual *L* subshells is discussed.

I. INTRODUCTION

AN atom with a vacancy in one of its inner shells may emit either an x ray or an Auger electron^{1,2} which results from the transition of an electron in a higher shell to the vacancy. The fluorescence yield of the shell or subshell is defined as the ratio of the number of characteristic x rays emitted in transitions to this shell or subshell to the number of vacancies created in the shell or subshell

$$\omega = N_x / N_v. \quad (1)$$

There are a number of methods which have been employed to measure ω . The most direct way of determining ω for a given shell is to place a sample in an x-ray beam with a quantum energy sufficiently high to ionize the shell in question. The intensity of the fluorescence x rays emitted by the sample is then compared to the attenuation of the incident beam by the sample. The ratio of these quantities is proportional to the fluorescence yield. Lay³ has made systematic measurements of a large number of *K*- and *L*-shell fluorescence yields using photographic films to make the intensity measurements. Stephenson⁴ and Küstner and Arends⁵ employed a variation of Lay's method by using ionization chambers rather than photographic plates to determine the beam intensities. Kinsey⁶ has computed a number of *L*-shell yields by comparing the widths of

the x-ray absorption edges with those of the emission lines. The width of the absorption line is proportional to the total width of the level and the width of the emission line depends only on the radiative part of the matrix element. The ratio of the two widths is therefore proportional to the fluorescence yield. A large number of other experiments have also been performed, using a radioactive decay process (either electron capture or internal conversion) to create the vacancies in the atomic shells. Since this is the method employed in the present work, appropriate references will be made when individual cases are discussed.

II. EXPERIMENTAL METHODS

In the present experiments, a coincidence counting method previously used by Schmied and Fink⁷ and Jopson *et al.*⁸ is employed. A vacancy is created in the *K* shell of the atom either by *K* capture or internal conversion. About 80% of these vacancies are filled by the emission of K_{α} x rays in which electrons from the L_{II} and L_{III} subshells make transitions to the *K* shell. Vacancies in the L_{II} and L_{III} subshells are therefore created and these, in turn, give rise to *L* x rays or *L* Auger electrons. The coincidence rate between *L* and *K* x rays is given by

$$N_C = N_K a (E_L A_L \Omega_L) \omega_{KL}, \quad (2)$$

where N_K is the number of *K* x rays observed in the *K* counter, a is the fraction of these corresponding to K_{α} transitions, $(E_L A_L \Omega_L)$ is the factor defining the effi-

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¹ P. Auger, *Ann. Phys. (New York)* **6**, 183 (1926).

² E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, New York, 1952).

³ H. Lay, *Z. Physik* **91**, 533 (1934).

⁴ R. J. Stephenson, *Phys. Rev.* **51**, 637 (1937).

⁵ H. Küstner and E. Arends, *Ann. Physik* **22**, 443 (1935).

⁶ B. B. Kinsey, *Can. J. Research* **A26**, 404 (1948).

⁷ H. Schmied and R. Fink, *Phys. Rev.* **107**, 1062 (1957).

⁸ R. C. Jopson, H. Mark, C. D. Swift, and J. H. Zenger, *Phys. Rev.* **124**, 157 (1961).

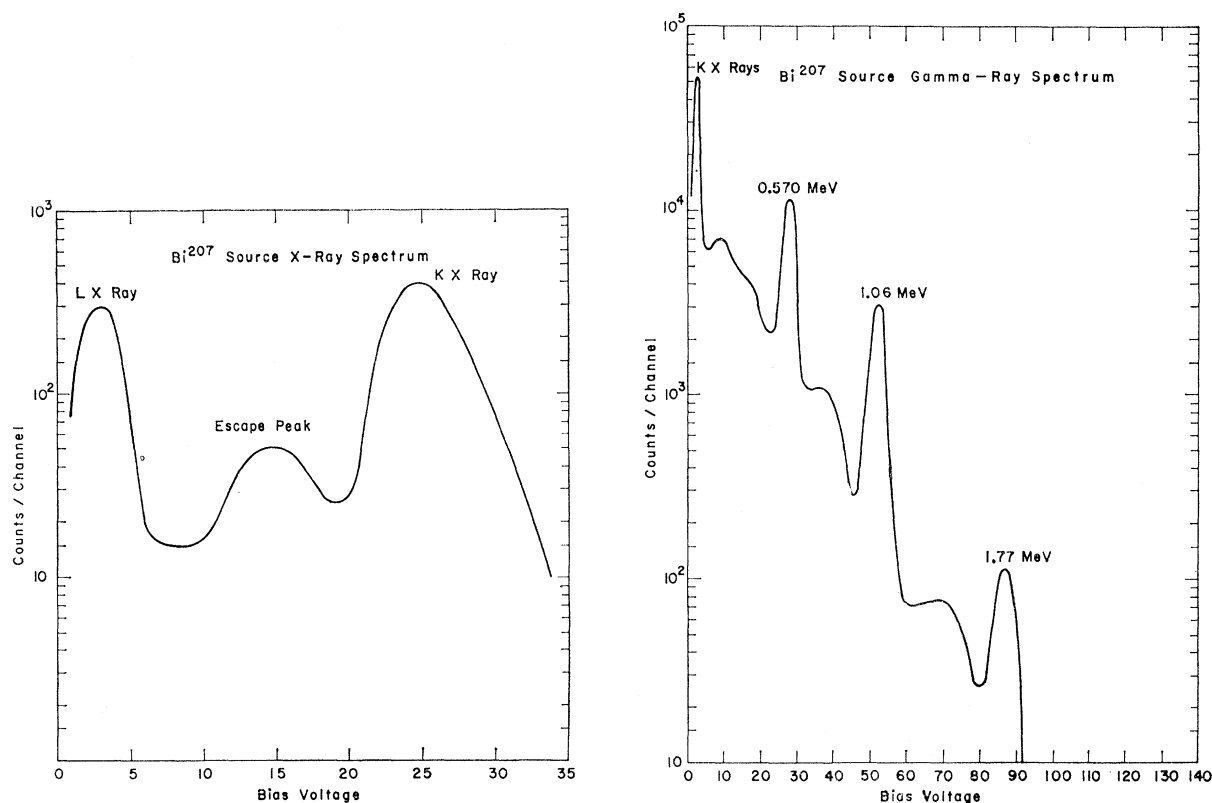


FIG. 1. The left panel shows the pulse-height spectrum observed in the x-ray counter (60-mil NaI crystal) from a Bi^{207} source. The right panel shows the high-energy gamma-ray spectrum emitted by the same source. The low intensity of the gamma rays relative to the x rays makes it possible to measure ω_{KL} since false coincidences due to internal conversion of the gamma rays are negligible.

ciency, window transmission, and geometry of the L x-ray counter, and ω_{KL} is the desired fluorescence yield. This equation is applicable no matter how the K -shell vacancies were created.

The L -shell fluorescence yield measured in any experiment depends on how the L shell was ionized. The reason for this is that the three subshells $L_I(s_{1/2})$, $L_{II}(p_{1/2})$, and $L_{III}(p_{3/2})$ have different fluorescence yields. Therefore, if the three shells are ionized in different proportions, different fluorescence yields will be measured. In the present experiment, vacancies are created only in the L_{II} and L_{III} subshells since the $\Delta l = 1$ selection rule forbids transitions from the L_I to the K shell. The fluorescence yield defined in Eq. (2) is thus a linear combination of $\omega_{L_{II}}$ and $\omega_{L_{III}}$, the partial yields of the L_{II} and L_{III} subshells. The coefficients are determined approximately by the electron populations in the subshells

$$\omega_{KL} = 0.35\omega_{L_{II}} + 0.65\omega_{L_{III}}. \quad (3)$$

In some cases, it is possible to measure a different partial L -shell fluorescence yield. If an unstable isotope undergoes L capture to an excited level which decays to the ground state of the daughter nucleus by gamma-ray emission, then the coincidence rate between the number of gamma rays observed in the gamma counter N_γ and

the L x rays is

$$N_C = N_\gamma (E_L A_L \Omega_L) \omega_{LL}. \quad (4)$$

The fluorescence yield ω_{LL} is the partial L -shell yield following L capture. In the case of allowed and first-forbidden transitions,

$$\omega_{LL} \approx \nu_{L_I}, \quad (5)$$

since the electrons in the L_I shell have the highest probability of being captured by the nucleus.⁹ The fluorescence yield ν_{L_I} is not the same as the partial fluorescence yield of the L_I subshell defined in Eq. (1). The fluorescence yield ν_{L_I} is defined as the ratio of all L -shell x rays emitted to the number of vacancies in the L_I subshell, not only those which are caused by transitions to the L_I subshell. The reason for this definition will be discussed in the final section. The error made in the assumption that ω_{LL} and ν_{L_I} are equal should not exceed 15%.

The methods used to perform these experiments have been described in reference 8. NaI(Tl) crystal scintillation counters were used to detect both the L and the K x rays. A typical pulse-height spectrum obtained with these counters is shown in Fig. 1. (The spectrum

⁹ B. Robinson and R. W. Fink, Revs. Modern Phys. 32, 117 (1960).

in the left panel shows the L and K x rays from a Bi^{207} source.) Since each of the isotopes discussed in this work presented slightly different problems, they will be discussed individually in the next section. The sources used for the experiments were made by placing a drop of active solution on a 2-mil Mylar sheet and evaporating the liquid. The source was then covered with another 2-mil Mylar sheet and sealed. Care must be taken to make the sources as thin as possible so that the self-absorption of L x rays in the source does not affect the results. The source strengths used in these experiments were of the order of $10 \mu\text{C}$. The sources were placed approximately 6 cm from each of the counters. The real coincidence counting rates observed under these circumstances were of the order of two or three per minute. The random and background counting rates were about 5% of the real rates.

III. EXPERIMENTAL RESULTS

A. Au^{195} (Measurement of ω_{LL} in Pt)

Au^{195} decays by electron capture to Pt^{195} . The process can occur either to the ground state of the daughter nucleus or to two excited levels at 99 keV and 130 keV.¹⁰ The 130-keV level, in turn, decays to the Pt^{195} ground state directly or by cascade through the 99-keV level. Since both levels have very short lifetimes, it is not possible to determine the partial fluorescence yield ω_{KL} of Pt using Eq. (2). There are several ways in which coincidences between K and L x rays can occur other than the creation of L vacancies by K_α x-ray emission. For example, L x rays from L capture can be in coincidence with K x rays from the internal conversion of either the 130- or the 99-keV levels, or K x rays from K capture can be in coincidence with the corresponding L -conversion x rays. Finally, L x rays from the internal conversion of the 30-keV cascade transition can be in coincidence with K x rays from the conversion of the 99-keV level. The only fluorescence yield of Pt which can be measured is the partial yield ω_{LL} defined in Eq. (5). Even this quantity cannot be determined without a small ambiguity; however, it will be shown that the error introduced by this source of false signals is small.

The coincidence rate between L x rays and 130-keV gamma rays emitted by the source is

$$N_C = N_{130\gamma} C_L (E_{LA} \Omega_L) \omega_{LL} + N_{130\gamma} C_K n_{KL} (E_{LA} \Omega_L) \omega_{KL}, \quad (6)$$

where $N_{130\gamma}$ is the observed counting rate for the 130-keV gamma rays, C_L is the probability of L capture to the 130-keV level, C_K is the probability of K capture to that level, and n_{KL} is the number of L -shell vacancies created per vacancy in the K shell. The fluorescence yields ω_{KL} and ω_{LL} , as well as the factor $(E_{LA} \Omega_L)$, have already been defined.

Equation (6) contains some unknown quantities which must be evaluated before a solution for ω_{LL} can be obtained. To do this, some of factors in Eq. (6) will be redefined as follows: The probabilities of electron capture to the various shells, C_K, C_L, C_M, C_N , etc., obey the condition

$$C_K + C_L + C_M + C_N + \dots = 1. \quad (7)$$

The ratio

$$m = C_L / (C_L + C_M + C_N + \dots) \quad (8)$$

defines the ratio of L -shell captures to the sum of captures from the L, M, N , and higher shells. Combining Eqs. (7) and (8) gives

$$C_L = (1 - C_K) m. \quad (9)$$

The ratio m is quite accurately determined only by the electron densities of the various atomic shells at the nucleus. This is true because the factor depending on the energy of the electron capture process is near unity for those shells with an electron binding energy small compared to the total decay energy. The partial fluorescence yield ω_{KL} usually differs from ω_{LL} only by 10 to 20% and it is therefore convenient to define

$$\eta \omega_{LL} = \omega_{KL}, \quad (10)$$

where η is a factor close to unity.

Equation (6) can now be solved using definitions (9) and (10)

$$\omega_{LL} = \frac{N_C(130\gamma \text{ to } L \text{ x-ray})}{N_{130\gamma} (E_{LA} \Omega_L)} \frac{1}{m + C_K(n_{KL}\eta - m)}. \quad (11)$$

The probability of K capture to the 130-keV level C_K is determined by measuring the coincidence rate between the 130-keV gamma rays and the K x rays emitted by the source

$$N_C(K \text{ x rays to } 130\text{-keV } \gamma \text{ rays}) = N_{130\gamma} C_K \omega_K (E_{KA} \Omega_K). \quad (12)$$

If ω_K , the K -shell fluorescence yield, is taken as 0.95, the measured value of C_K is 0.18. (This result is not very sensitive to the precise value of ω_K , which in this region of the periodic table is very close to one.) The best value of m from the data given in "Nuclear Spectroscopy Tables"¹¹ is 0.79, n_{KL} for Pt is 0.81, and η is approximately 1.20. (All these numbers have been computed from data given in references 9 and 10.) The second term in the denominator of Eq. (11) is of the order of 0.03. Therefore, even though some of the quantities in this factor are not directly measured, inaccuracies which exist are small and will not strongly affect the computed value of ω_{LL} . The best value of ω_{LL} for Pt obtained from this measurement is 0.32 ± 0.02 .

¹⁰ J. M. Hollander and G. T. Seaborg, *Revs. Modern Phys.* **30**, 585 (1958).

¹¹ A. H. Wapstra, G. J. Nijgh, and R. van Lieshout, *Nuclear Spectroscopy Tables* (North-Holland Publishing Company, Amsterdam, 1959).

B. Hg^{203} (Measurement of ω_{KL} in Tl)

Hg^{203} decays to an excited level in Tl^{203} at 279 keV by electron emission.¹⁰ The mean life is 47 days. The 279-keV level then decays directly to the ground state of Tl^{203} by gamma-ray emission or by internal conversion (conversion coefficient $\alpha_T=0.2$), the partial fluorescence yield ω_{KL} is determined by Eq. (2) from the L -to- K x-ray coincidence rate. The principal trouble with this isotope is that the β -decay electrons are in coincidence with the observed L and/or K x rays since the lifetime of the 279-keV level is very short (about 10^{-10} sec). Great care must therefore be taken to make certain that no pulses appear in the respective windows in either crystal which were caused by the decay electrons. Since the maximum electron energy is quite low, it is not difficult to accomplish this either by placing the source in a strong magnetic field or by absorbing the electrons with suitable Be windows. Both of these methods were employed in the experiment and good agreement was found between them. Background rates were measured by determining the coincidence rates between the L x-ray peak and various portions of the continuous spectrum. A background estimated in this manner was subtracted from the measured K -to- L x-ray coincidence rate to give the true coincidence rate, N_C . The best value of the partial fluorescence yield obtained for this case is $\omega_{KL}=0.38\pm0.02$.

C. Bi^{207} (Measurement of ω_{KL} and ω_{LL} in Pb)

Bi^{207} decays by electron capture to excited levels in Pb^{207} at 2341 and 1634 keV.¹⁰ Eight percent of the decays go to the upper level and the remaining 92% go to the 1634-keV level. The mean life of the electron capture process is 8 yr. The three most prominent gamma rays visible in the spectrum are shown in the right panel, Fig. 1. The 1.77-MeV line is the cascade transition between the 2341- and 570-keV level, the 1.06-MeV line is the cascade transition between the 1634- and the 570-keV level, and the 570-keV line is the ground-state transition from that level. A peak corresponding to the K x rays is also observed. The low-energy spectrum showing the L and K x rays observed with the thin crystal is displayed in the left half of the figure.

In spite of the complex level scheme of Pb^{207} , it is possible to get an accurate measurement of ω_{KL} . The most important point is that the 1634-keV level is an isomeric state with a mean life of the order of 80 sec. Thus, none of the L x rays (or K x rays) arising from the internal conversion of the lower lines will be in coincidence with K x rays (or L x rays) following the electron capture process. The high-energy level at 2341 keV is not an isomeric level and therefore false coincidences of the type described above can occur. Fortunately, this decay branch is relatively weak and, in addition, the internal conversion coefficients of the

TABLE I. Experimental results.

Element and atomic number	Isotope used for experiment	ω_{KL}	ω_{LL}	Previous measurements	
				ω_{KL}	ω_{LL}
Pb (82)	Bi^{207}	0.44 ± 0.02	0.36 ± 0.02	0.53 ^a 0.33 ^b 0.46 ^c	0.49 ^a 0.37 ^b 0.43 ^c
Tl (81)	Hg^{203}	0.38 ± 0.02	...	0.33 ^d	...
Pt (78)	Au^{195}	...	0.30 ± 0.02	...	0.35 ± 0.08^e

^a J. Burde and S. G. Cohen, Phys. Rev. **104**, 1085 (1956).

^b J. Tousset and A. Moussa, J. phys. radium **19**, 39 (1958).

^c K. Risch, Z. Physik **150**, 87 (1958).

^d See reference 6.

^e See reference 9.

various levels are sufficiently small so that this effect is negligible.

The value of ω_{KL} is computed from Eq. (2) after small corrections for background effects are made. The result is $\omega_{KL}=0.44\pm0.02$.

In addition to the measurement of ω_{KL} discussed above, ω_{LL} can also be determined. The coincidence rate between L x rays and the 1.8-MeV gamma rays resulting from cascade transitions between the 2341- and 570-keV levels is used for this measurement. The high energy of the gamma ray makes it necessary to replace the K x-ray counter with a large (2 in. \times 2 in.) NaI crystal. The value of ω_{LL} is then computed according to Eq. (4). The result of this measurement is $\omega_{LL}=0.36\pm0.02$.

IV. DISCUSSION OF RESULTS

Table I shows the measured values of ω_{KL} and ω_{LL} for the elements studied. The estimated standard error is also shown. This error includes the standard deviation due to counting statistics (approximately 5%) and also an estimated error in the measurement of the counting geometry and the absorption of the low-energy x rays in the source, the air, and the counter window. Comparison with a number of previous measurements is also shown in Table I. Care must be taken that the comparisons are made with the proper values listed in the literature. The value of ω_{KL} can be computed using listed values of the subshell yields ω_{LII} and ω_{LIII} and Eq. (3). In the case of ω_{LL} , the situation is more complex since this quantity depends on all three subshell yields, ω_{LI} , ω_{LII} , ω_{LIII} and the Coster-Kronig¹¹ transition probabilities between the L_I and L_{II} and L_I and L_{III} subshells. Following the notation in reference 11:

$$\omega_{LL} \approx \nu_{LI} \approx \omega_{LI} + f_{L_I L_{II}} \omega_{L_{II}} + f_{L_I L_{III}} \omega_{L_{III}}, \quad (13)$$

where $f_{L_I L_{II}}$ and $f_{L_I L_{III}}$ are the appropriate Coster-Kronig transition probabilities.

Very complete comparisons are possible in the case of lead ($Z=82$). The values of ω_{KL} shown in Table I have been computed from the three most recent measurements of ω_{LII} and ω_{LIII} obtained from the analysis of Auger electron spectra following internal conversion. A similar comparison for the value of ω_{LL} has also been

made using Eq. (13). The best over-all agreement between the present results and previous measurements seems to be obtained if the results of Risch (see reference c of Table I) are used. It should also be pointed out that the previous results quoted in Table I are obtained by a completely different method than the present measurement and are the result of averaging a number of observations for elements with atomic number 81 (Tl^{208}) and 83 (Bi^{212}). The value of ω_{KL} obtained for thallium ($Z=81$) in the present work is considerably lower than the value quoted for lead ($Z=82$). Kinsey⁶ gives values of ω_{LII} and ω_{LIII} from which the number for ω_{KL} ($Z=81$) given in Table I is calculated using Eq. (3). This number is smaller than the one measured in the present experiment by about 15%. The cause

for the disagreement may be that the L_{III} shell yield given by Kinsey is too small. Recent measurements⁹ of this number give somewhat larger values in this region of atomic numbers. The measurement of ω_{LL} for $Z=78$ is compared with an L_I subshell yield measured by Roos and quoted in reference 9. (It is assumed that this yield is ν_{L_I} rather than ω_{L_I} as quoted in reference 9. This assumption is reasonable since ω_{L_I} should be only about one third as large due to the effect of Coster-Kronig transitions.) The agreement between these two numbers is only fair and may be accidental because of the large experimental error quoted for the previous measurement.

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Two-Electron Atoms. I. Perturbation Study of the Ground State

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A variational perturbation method used by Hylleraas has been extended to include 70-term basis sets as approximations to the first-order wave function of the two-electron atomic species. An upper limit of -0.15766625^+ a.u. has been found for the second-order perturbation energy coefficient. It is estimated that this value is converged to at least two units in the seventh decimal place. A value of the third-order perturbation energy coefficient of 0.00869868 a.u. is calculated from the same variational first-order wave function. A number of expectation values to first-order for certain operators [e.g., $\delta(\mathbf{r}_1)$, $\delta(\mathbf{r}_{12})$, p_1^4 , r_1^n , $\cos\theta_{12}$, etc.] are computed, and compared, where possible, to known values. A variety of basis sets is studied, including a set that contains negative powers of the metric variables ("Kinoshita" type) and one that contains only positive powers ("Hylleraas" type). A scheme is proposed that uses first and higher order expectation values for the analysis and characterization of approximate wave functions. This scheme, which is not restricted to two electrons, also opens the possibility of a nonenergetic variational procedure for obtaining wave functions.

I. INTRODUCTION

AN upper limit for the second-order perturbation energy coefficient, ϵ_2 , of the two-electron atomic species is found here which is the deepest so far reported. It is estimated that the value of¹

$$\epsilon_2 = -0.15766625^+ \text{ a.u.} \quad (1)$$

is converged to at least two units in the seventh decimal place. The method employed is due to Hylleraas,² and is admirably adapted to retaining the full numerical accuracy available with an electronic computer. First-order approximations to other properties of interest are also found, and in Sec. IV a proposal is made for the application of perturbation theory results to the analysis and characterization of approximate wave functions.

Conventional Schrödinger perturbation theory presents an atomic wave function as an expansion in powers of the nuclear charge Z :

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

where the sum to a particular n is called the n th order wave function. This expansion leads to what might be called a perturbation expansion for the expectation value of an operator. Thus, the expansion through first order of the expectation value of an operator is given in obvious notation by

$$\langle \Omega \rangle_0 + Z^{-1} \langle \Omega \rangle_1 = \int d\tau \psi_0^* \Omega \psi_0 + 2Z^{-1} \int d\tau \psi_1^* \Omega \psi_0. \quad (3)$$

Recently a fund of information on such perturbation expansion terms of various expectation values averaged over the ground states of the first few members of the two-electron isoelectronic sequence has become avail-

¹ Atomic units (of length, the Bohr radius; of energy, $2Rhc$) are used throughout.

² E. Hylleraas, *Z. Physik* **65**, 209 (1930).