f Values for Transitions between the 1^1S, 2^1S, and 2^3S, and the 2^1P, 2^3P, 3^1P, and 3^3P States in Helium*

B. SCHIFF AND C. L. PEKERIS
Department of Applied Mathematics, Weizmann Institute of Science, Rehovoth, Israel
(Received 16 December 1963)

The S- and P-state helium wave functions recently obtained by the authors have been used to make an accurate calculation of the f values for transitions between the 1^1S, 2^1S, and 2^3S states and the 2^1P, 2^3P, 3^1P, and 3^3P states in this atom. The accuracy of the results has been estimated by evaluating the dipole length, velocity, and acceleration forms of the matrix element for the transition, and by the inclusion of differing numbers of terms in the expansions of the wave functions. Wave functions containing up to 220 terms have been used, and the least accurate f value is estimated to be correct to within ± 0.0002, an accuracy sufficient for all practical applications.

A KNOWLEDGE of the f values for transitions from a discrete S state to discrete and continuum P states in two-electron atoms is important in determining the value of the average excitation energy k_0[1] occurring in the expression for the Lamb shift of the corresponding level. Since no accurate wave functions are available for the continuum, it has only been possible to evaluate k_0 approximately, and the various sum rules[2] which the f values must satisfy have therefore been used to improve the result of the computation. Salpeter and Zaidi[3] have used the sum rules directly to compute a correction to their result for k_0. Other authors[2,4,5] have used these rules to modify their calculated f values for transitions to the continuum and those obtained by Huang[6] and by Stewart and Wilkinson[7] before using them to compute k_0. As the sum rules involve a summation over the discrete states as well as an integration over the continuum, it will be seen that a knowledge of the dominant f values for the discrete states can to a certain extent be used to compensate for the relatively poor accuracy of the f values for transitions to the continuum.

The widely differing f values previously obtained for transitions to the low-lying discrete P states in helium, as summarized and tabulated by Dalgarno and Lynn[2] and by Dalgarno and Kingston[4], show how sensitive the computed values are to the particular type of approximation adopted for the wave functions. We have therefore utilized the recent availability of highly accurate S-state[8–10] and P-state[11] wave functions for the low-lying states of helium to make an accurate calculation of the f values for transitions between 1^1S, 2^1S, and 2^3S states and the 2^1P, 2^3P, 3^1P, and 3^3P states in this atom. We have also been able to form an estimate of the accuracy of our computations by the use of differing numbers of terms in the expansion of the wave functions, and by evaluating Chandrasekhar's[12] three alternative, but equivalent, expressions for the matrix elements involved.

For the S-state wave functions, we used those previously obtained.[8–10] In the case of the ground state, we used the functions which had been obtained by "method A,"[8] and for the 2^1S and 2^3S states the functions obtained by "method C".[10] We have introduced modifications to our previous method[11] for calculating P-state wave functions, leading to an improved rate of convergence for the energy eigenvalue. The improvement results from relaxing the condition that the wave function should have the correct asymptotic behavior at infinity, thus permitting a better representation of the function to be obtained over the rest of space.

The two methods will be described in detail elsewhere. In view of the close analogy between our original method and Pekeris's "method C" for calculating S-state wave functions, we shall refer to the P-state wave functions obtained by means of the original and the improved methods as "C" and "D" functions, respectively.

We have calculated f values for all of the transitions using the P-state D-type functions, and the results are given in Tables I–VI. For the purposes of comparison, we also computed the 1^1S–2^1P and the 1^1S–3^1P f values using the P-state C-type wave functions and the results are given in Tables VII and VIII. The results are given for P-state wave functions containing 56, 120, and 220 terms in the expansion, corresponding to the inclusion

* Research supported by the U. S. Air Force Office of Scientific Research through the European Office of OAR under Grant AF EOAR 63-69.

[1] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957).
[2] A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **A70**, 802 (1957).
[3] E. E. Salpeter and M. H. Zaidi, Phys. Rev. **125**, 248 (1962).
[4] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **72**, 1053 (1958).
[5] A. Dalgarno and A. L. Stewart, Proc. Phys. Soc. (London) **76**, 49 (1960).
[6] S. Huang, Astrophys. J. **108**, 354 (1948).
[7] A. L. Stewart and W. J. Wilkinson, Proc. Phys. Soc. (London) **75**, 796 (1960).
[8] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[9] C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).
[10] C. L. Pekeris, Phys. Rev. **127**, 509 (1962).
[11] C. L. Pekeris, B. Schiff, and H. Lifson, Phys. Rev. **126**, 1057 (1962).
[12] S. Chandrasekhar, Astrophys. J. **102**, 223 (1945).

of all terms for which the sum ω of the exponents of r_1, r_2 and r_{12} (the interelectron distance) are less than or equal to 5, 7, and 9, respectively.[11] In each case, the S-state wave function with the same value of ω was used, except in the case of the 2^1S state, where the $\omega=6$ function (containing 84 terms) was used instead of the $\omega=5$ function due to the nonavailability of the latter. In the cases where the f values for wave functions containing 56, 120, and 220 terms in the expansion showed signs of converging well, an extrapolation was made to estimate the f value which would be obtained using wave functions with an infinite number of terms. The extrapolation formula used was

$$f_{\text{extrapolated}}=f_1+\frac{(f_1-f_0)(f_2-f_1)}{2f_1-f_0-f_2},$$

where f_0, f_1 and f_2 are the values at order 56, 120, and 220, respectively. The results are included in the tables.

Following Chandrasekhar,[12] we have computed each f value using the dipole "length," "velocity," and "acceleration" formulas

$$f_{\text{length}} = 2(E_n-E_0)\left|\int \psi_n^*(z_1+z_2)\psi_0 d\tau\right|^2,$$

$$f_{\text{velocity}} = \frac{2}{(E_n-E_0)}\left|\int \psi_n^*\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)\psi_0 d\tau\right|^2,$$

$$f_{\text{acceleration}} = \frac{2}{(E_n-E_0)^3}\left|Z\int \psi_n^*\left(\frac{z_1}{r_1^3}+\frac{z_2}{r_2^3}\right)\psi_0 d\tau\right|^2,$$

where ψ_n and ψ_0 are the P-state and S-state wave functions, respectively, E_n and E_0 are the energies of the respective states in atomic units, Z is the atomic number, and lengths are given in atomic units. The integration is over the whole of the two-electron space. The three expressions would give identical results if they could be evaluated using the exact eigenfunctions of the

TABLE I. f value for the transition He $1\,^1S(A)-2\,^1P(D)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.274 955	0.276 016	0.273 246
120	0.275 897	0.276 150	0.275 576
220	0.276 102	0.276 163	0.276 036
Extrapolated	0.276 159	0.276 164	0.276 149

TABLE II. f value for the transition He $1\,^1S(A)-3\,^1P(D)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.073 668	0.073 151	0.071 301
120	0.073 727	0.073 407	0.072 722
220	0.073 604	0.073 434	0.073 193
Extrapolated		0.073 437	0.073 427

TABLE III. f value for the transition He $2\,^1S(C)-2\,^1P(D)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.375 813	0.376 396	0.604 537
120	0.376 124	0.376 152	0.398 661
220	0.376 354	0.376 358	0.381 452

TABLE IV. f value for the transition He $2\,^1S(C)-3\,^1P(D)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.152 266	0.150 949	0.135 394
120	0.151 189	0.151 428	0.147 145
220	0.151 372	0.151 391	0.150 279

TABLE V. f value for the transition He $2\,^3S(C)-2\,^3P(D)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.539 106	0.539 546	0.570 732
120	0.539 088	0.539 125	0.531 291
220	0.539 086	0.539 087	0.537 977
Extrapolated	0.539 086	0.539 083	

TABLE VI. f value for the transition He $2\,^3S(C)-3\,^3P(D)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.064 037	0.063 644	0.043 829
120	0.064 427	0.064 416	0.062 389
220	0.064 459	0.064 463	0.064 790
Extrapolated	0.064 461	0.064 466	

TABLE VII. f value for the transition He $1\,^1S(A)-2\,^1P(C)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.274 330	0.274 611	0.266 032
120	0.275 787	0.275 788	0.271 569
220	0.276 080	0.276 065	0.274 007
Extrapolated	0.276 154	0.276 150	

TABLE VIII. f value for the transition He $1\,^1S(A)-3\,^1P(C)$.

No. of terms in expansion	$f$length	$f$velocity	$f$acceleration
56	0.072 924	0.072 027	0.068 282
120	0.073 389	0.072 727	0.069 823
220	0.073 492	0.073 136	0.071 222
Extrapolated	0.073 521		

nonrelativistic Hamiltonian. However, since the latter are not known, we have to use our approximate wave functions, which will give a different result in each case. In the three formulas, the main contribution to the integral comes from the region at large distances, at medium distances, and at small distances from the nucleus, respectively, and the relative accuracy of the different results will depend on how closely our wave functions approximate to the true eigenfunctions in each of the three regions of space.

It will be seen that, on the whole, the length and velocity formulas give equally good convergence. This is to be expected, as the S wave functions are biased to give the correct behavior at infinity, whereas the D-type P-state wave functions are determined using solely the energy criterion and may therefore be expected to give a more accurate representation of the function in the middle range. It will be noted that in the case of the 1^1S–2^1P and 1^1S–3^1P transitions, the velocity formula gives a slightly better convergence when the D-type P-state wave function is used, but if the C-type function, which is biased to give the correct behavior at infinity, is used, the length formula gives a better result. The use of the acceleration formula leads to results which converge rather poorly, particularly in the case of the 2^1S–2^1P and the 2^3S–2^3P transitions. The reason for this is partly that the functions used are not such good representations of the true wave function in the region near the origin. There is, however, another reason why this formula should give inaccurate results. If the energy difference E_n–E_0 is small, the acceleration formula has a very small denominator, e.g., of the order 10^{-4} to 10^{-5} for the two transitions mentioned. The numerator must therefore also be small, and will be computed as the small difference of larger quantities, with corresponding loss of accuracy.

TABLE IX. Estimated f values and error bounds.

Transition	f value
1^1S-2^1P	0.27616 ±0.00001
1^1S-3^1P	0.0734 ±0.0001
2^1S-2^1P	0.3764 ±0.0002
2^1S-3^1P	0.1514 ±0.0002
2^3S-2^3P	0.539086±0.000005
2^3S-3^3P	0.06446 ±0.00001

TABLE X. Comparison of calculations of f values for transitions from the 2^1S and 2^3S states of helium.

Author	Formula	2^1S–2^1P	2^1S–3^1P	2^3S–2^3P	2^3S–3^3P
Trefftz *et al.* (See Ref. 13.) (Hartree-Fock)	length	0.370	0.156	0.568	0.057
	velocity	0.358	0.158	0.600	0.050
Present work (220)	length	0.3764	0.1514	0.5391	0.0645
	velocity	0.3764	0.1514	0.5391	0.0645
	acceleration	0.3815	0.1503	0.5380	0.0648

Our results are summarized in Table IX, which contains our estimates of the f values and of their probable accuracies. In view of the smallness of the energy difference E_n–E_0 in the case of the 2^1S and 2^3S states, the results of the acceleration formula have been ignored when making a final estimate of the f values, but they have been taken into account in the case of the transitions involving the 1^1S state, where the energy difference is larger by an order of magnitude. Trefftz *et al.*[13] have also computed f values for transitions from the 2^1S and 2^3S states using both the dipole length and velocity formulas, and their results are compared with those of our calculations in Table X. The closeness of agreement between our results obtained using the dipole length and velocity formulas in comparison with the agreement between the results using the corresponding formulas obtained by Trefftz *et al.* lends support to the belief that our results are accurate to within the bounds given in Table IX. However, one cannot completely exclude the possibility that the two formulas give results which are in error by the same amount. The results for the transitions from the ground state are for this reason more firmly based in view of the good agreement also obtained using the acceleration formula.

The majority of the computations were carried out on the electronic computer WEIZAC, and the authors are indebted to Miss Yael Kempinski for assistance in programming.

[13] E. Trefftz, A. Schluter, K. H. Dettmar, and K. Jörgens, Z. Astrophys. 44, 1 (1957).