[21] C. S. Warke, Phys. Rev. 144, 120 (1966).

[22] F. T. Chan, J. Chem. Phys. 49, 2533 (1968).

[23] J. N. Bardsley, Proc. Phys. Soc. (London) 1, 365 (1968).

[24] G. V. Dubrovsky, V. D. Ob'edkov, and R. K. Janev, Ref. 17, pp. 342–45.

[25] T. F. O'Malley, Phys. Rev. 185, 101 (1969).

[26] J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 621 (1951).

[27] R. S. Berry, Ann. Rev. Phys. Chem. 20, 357 (1969).

[28] See, e.g., J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, J. Chem. Phys. 36, 3332 (1962), and references therein.

[29] W. Kaul, P. Seyfried, and R. Taubert, Z. Naturforsch. 18a, 432 (1963).

[30] P. M. Becker and F. W. Lampe, J. Chem. Phys. 42, 3857 (1965).

[31] M. P. Teter, F. E. Niles, and W. W. Robertson, J. Chem. Phys. 44, 3018 (1966).

[32] W. A. Chupka, M. E. Russell, and K. Refaey, J. Chem. Phys. 48, 1518 (1968).

[33] R. K. Curran, J. Chem. Phys. 38, 2974 (1963).

[34] J. C. Y. Chen and J. L. Peacher, Phys. Rev. 168, 56 (1968).

[35] E. R. Davidson, in *Physical Chemistry III*, edited by H. Eyring, D. Henderson, and W. Jost (Academic, New York, 1969), Chap. 3.

[36] W. Kolos, Intern. J. Quantum Chem. II, 471 (1968).

[37] W. Kolos and L. Wolneiwicz, J. Chem. Phys. 50, 3228 (1969).

[38] W. Kolos and L. Wolneiwicz, J. Chem. Phys. 48, 3672 (1968).

[39] W. Kolos and L. Wolneiwicz, J. Chem. Phys. 45, 509 (1966).

[40] W. Kolos and L. Wolneiwicz, J. Chem. Phys. 43, 2429 (1965).

[41] J. N. Bardsley, Chem. Phys. Letters 1, 229 (1967).

[42] G. H. Dunn and B. Van Zyl, Phys. Rev. 154, 40 (1967).

[43] J. M. Peck, Phys. Rev. 154, 52 (1967).

[44] At 1000 °K, the Boltzmann factor for the seventh vibrational state of H_2^+ is 5×10^{-8}, compared with 5×10^{-2} for the state $v=2$. Hence, if the electronic-coupling crossing-point mechanism introduced by Bates were significant in the DR of $H_2^+ + e$, the mean cross section for the process would have to be at least six orders of magnitude larger than that of the noncrossing vibronic mechanism discussed here. As the results will show, this would imply that the cross section for the Bates mechanism would have to be at least $10^{-12}\,\mathrm{cm}^2$, for states with $v \geq 7$, or that the rate coefficient for DR of H_2^+ in high vibrational states would be of order 4×10^{-6}. This is between one and two orders of magnitude larger than any rate coefficient previously attributed to DR by the Bates mechanism.

[45] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1962), Vol. II, Chap. XIX.

[46] The following misprints in Paper I should be corrected: In the graphs of the transition amplitude integrals $T_1(R)$ (Figs. 2 and 3) multiply the ordinate values by a factor $\frac{1}{16}$.

[47] E. P. Wigner, Phys. Rev. 73, 1002 (1948).

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f Values for Transitions between the Low-Lying *S* and *P* States of the Helium Isoelectronic Sequence up to $Z = 10$*

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f values have been computed for the transitions $m\,{}^1S$-$n\,{}^1P$, $m=1$–5, $n=2$–5 and $m\,{}^3S$-$n\,{}^3P$, $m, n=2$–5 for members of the helium isoelectronic sequence up to $Z=10$. The agreement between the results obtained using the dipole length, and velocity formulas, together with the convergence of the results as an increasing number of terms are included in the expansions of the wave functions, indicate that the values obtained are accurate to within 1% or better for the large majority of the transitions.

Various authors have computed f values for transitions between S and P states of helium and of heliumlike atoms using different types of approximate wave functions.[1-7] The wide variation between the results of the different calculations show the computed f values to be particularly sensitive to the wave function employed. Thus in order to obtain reasonably reliable f values it is necessary to employ wave functions of high accuracy. We have previously[8] obtained accurate wave functions for the states $1\,{}^1S$ and $n\,{}^1S$, $n\,{}^3S$, $n\,{}^1P$, $n\,{}^3P$, $n=2$–5, for members of the helium isoelectronic sequence up to $Z=10$, and have therefore been able to carry out a systematic calculation of the f values for transitions between these states.

The methods used to obtain the wave functions have been described elsewhere,[9-12] and we shall only give a brief outline here. The nonrelativistic Schrödinger wave equation for a two-electron atom with an infinitely heavy nucleus is solved by assuming a solution in the form of a series expansion possessing the appropriate symmetry. Each solution then gives an approximation to the nonrelativistic wave function for one of the states with the given symmetry, while the corresponding eigenvalue E gives an approximation to the energy of this state. To obtain the total energy, the contributions from the relativistic effects and a correction for the finite mass of the nucleus have to be added. The nonrelativistic wave function obtained is, however, accurate enough for computing the f values. The dependence of the wave function on the angular coordinates of the two electrons is determined by considerations of symmetry. Thus it remains to determine the dependence on the three variables r_1, r_2, and r_3, the distances of the two electrons from the nucleus and the interelectronic distance, respectively. In view of the fact that these three variables have to satisfy the triangle condition $|r_1-r_2|\leq r_3 \leq r_1+r_2$, it is found convenient to work in terms of the perimetric coordinates[9] u, v, and w, which are linear combinations of r_1, r_2, and r_3 so chosen as to all range from zero to infinity. For the ground state,[9,10] the wave function was taken to be of the form

$$\psi = e^{-\epsilon(r_1+r_2)}F(u, v, w) ,$$

where $\epsilon=(-E)^{1/2}$. For the other S states, an expansion

$$\psi=(1\pm P_{12})\, e^{-\xi r_1 - Z r_2} S(u, v, w)$$

was taken, while for the P states, the form

$$\psi=(1\pm P_{12})\, e^{-\xi r_1 - Z r_2}\, r_1 \cos\theta_1 P(u, v, w)$$

was assumed, where θ_1 is the polar angle of electron one, and P_{12} signifies interchange of electrons 1 and 2. Here, $F(u, v, w)$ and $S(u, v, w)$ are triple series of Laguerre polynomials of u, v, and w, while $P(u, v, w)$ is a triple series in simple powers of these variables. The parameter ξ remains to be specified. For the excited S states, the calculations were carried out with two different choices for ξ. In method C,[11] ξ is given the value $(-2E-Z^2)^{1/2}$, so that the wave function has the correct asymptotic behavior as one or another of the electrons goes to infinity. In method D,[12] ξ is chosen so as to optimize the energy E. In the case of the P states, wave functions were obtained by method D only, except for a few early calculations for helium.

In the computations, truncated expansions were used, and we included all terms in the series for which the sum of the powers of u, v, and w are less than some given number Ω. In the case of the ground state, expansions containing up to 1078 terms, corresponding to $\Omega=21$, were used. For the other S states, type-C expansions containing up to 364 terms ($\Omega=11$) and type-D expansions containing up to 220 terms ($\Omega=9$) were used, in general, although for some of the low-lying S states, the expansions could only be carried out up to a smaller number of terms due to loss of accuracy. The type-D expansions used for the P states were carried up to 364 terms.

Before computing the f values, each wave function expansion was converted from the perimetric coordinates to the variables r_1, r_2, and r_3. Each f value was computed in the dipole approximation using the "length," "velocity," and "acceleration" formulas[13]

$$f_{\text{len}} = 2(E_p - E_s)\left|\int \psi_p^* (z_1+z_2)\psi_s \, d\tau\right|^2 ,$$

$$f_{\text{vel}} = \left(\frac{2}{E_p-E_s}\right)\left|\int \psi_p^* \left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)\psi_s \, d\tau\right|^2 ,$$

$$f_{\text{acc}} = \left(\frac{2}{(E_p-E_s)^3}\right)\left|Z\int \psi_p^* \left(\frac{z_1}{r_1^3}+\frac{z_2}{r_2^3}\right)\psi_s \, d\tau\right|^2 ,$$

where ψ_s and ψ_p are the S- and P-state wave functions, respectively, E_s and E_p are the nonrelativistic 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 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 comes, respectively, from the region at large distances, at medium distances, and at small distances from the nucleus, 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. Each of these three formulas was evaluated using S- and P-state wave functions belonging to the same value of Ω. The convergence of the results as Ω is increased, together with the measure of agreement between the values obtained using the different formulas, give an idea of the accuracy which has been achieved.

Some typical results which are obtained for the f values are listed in Tables I–IV. In Table I, we list the results for transitions from the ground state to the 2^1P and 5^1P states in helium, C V, and Ne IX (values for the 1^1S-5^1P transition in helium could not be computed using the expansions of or-

TABLE I. *f* values for transitions from the ground state; comparison of results obtained using the length (*l*), velocity (*v*) and acceleration (*a*) formulas.

		He		C v		Ne IX	
		$1\,^1S$-$2\,^1P$	$1\,^1S$-$5\,^1P$	$1\,^1S$-$2\,^1P$	$1\,^1S$-$5\,^1P$	$1\,^1S$-$2\,^1P$	$1\,^1S$-$5\,^1P$
order 220	*l*	0.276 10	0.015 01	0.647 064	0.026 16	0.722 624	0.027 18
	v	0.276 16	0.014 96	0.647 067	0.026 17	0.722 625	0.027 18
	a	0.276 04	0.014 58	0.647 047	0.026 09	0.722 613	0.027 14
order 364	*l*	0.276 15		0.647 067	0.026 17	0.722 625	0.027 18
	v	0.276 16		0.647 067	0.026 18	0.722 625	0.027 19
	a	0.276 13		0.647 062	0.026 15	0.722 622	0.027 17

der 364, due to loss of accuracy in this case). The convergence of the results is excellent, as is also the agreement between the values obtained from the three different formulas. For transitions between two excited states, we found that the acceleration formula gave results which converged far more slowly, if they converged at all, than the results obtained using the length and velocity formulas. This effect was particularly pronounced in the case of transitions between two states possessing the

TABLE II. Convergence of *f* values for transitions between close-lying states. The results obtained using *S*-state wave functions of types *C* and *D* are listed.

		$2\,^1S$-$2\,^1P$		$5\,^1S$-$5\,^1P$		$2\,^3S$-$2\,^3P$		$5\,^3S$-$5\,^3P$	
		C	*D*	*C*	*D*	*C*	*D*	*C*	*D*
						He			
order 56	*l*	0.375 082	0.375 810	1.023 42	1.025 76	0.539 105 9	0.539 088 3	1.515 2	1.515 2
	v	0.375 697	0.377 290	1.036 49	1.100 58	0.539 545 6	0.539 555 8	1.565 4	1.625 3
order 120	*l*	0.376 124	0.376 371	1.058 20	1.070 07	0.539 087 7	0.539 086 9	1.540 7	1.540 6
	v	0.376 152	0.376 498	1.052 11	1.093 50	0.539 125 3	0.539 126 0	1.542 3	1.546 6
order 220	*l*	0.376 354		1.066 80	1.079 65	0.539 086 1		1.532 8	1.533 0
	v	0.376 358		1.066 66	1.087 50	0.539 086 6		1.534 6	1.534 9
order 364	*l*	0.376 413				0.539 086 1			
	v	0.376 414				0.539 086 2			
						Li II			
order 56	*l*	0.212 214	0.212 447	0.623 9	0.624 7	0.307 940 8	0.307 939 9	0.893 70	0.894 74
	v	0.212 363	0.212 748	0.613 4	0.634 7	0.307 924 4	0.307 925 9	0.903 65	0.919 17
order 120	*l*	0.212 503	0.212 565	0.628 3	0.633 5	0.307 940 1	0.307 940 2	0.892 63	0.892 71
	v	0.212 514	0.212 589	0.625 2	0.638 4	0.307 940 3	0.307 940 4	0.894 29	0.894 74
order 220	*l*	0.212 558		0.630 7	0.635 0	0.307 940 2		0.890 06	0.890 06
	v	0.212 560		0.630 2	0.636 4	0.307 940 3		0.890 43	0.890 46
order 364	*l*			0.633 1				0.889 70	
	v			0.632 9				0.889 73	
						C v			
order 56	*l*	0.092 998	0.093 035	0.285 66	0.285 74	0.131 381 1	0.131 381 1	0.385 17	0.385 27
	v	0.093 005	0.093 058	0.275 52	0.279 78	0.131 362 4	0.131 362 5	0.385 91	0.387 98
order 120	*l*	0.093 044		0.284 97	0.286 00	0.131 381 1		0.383 76	0.383 77
	v	0.093 045		0.284 26	0.286 61	0.131 381 0		0.384 73	0.384 75
order 220	*l*	0.093 052		0.285 29	0.286 04			0.383 33	0.383 33
	v	0.093 052		0.285 04	0.286 06			0.383 39	0.383 39
order 364	*l*			0.285 72				0.383 29	
	v			0.285 74				0.383 30	

TABLE III. Convergence of f values for transitions between excited singlet states. The results obtained using S-state wave functions of types C and D are listed.

		$2\,^1S$-$5\,^1P$		$3\,^1S$-$4\,^1P$		$3\,^1S$-$5\,^1P$		$5\,^1S$-$2\,^1P$	
		C	D	C	D	C	D	C	D
					He				
order 56	l	0.023 19	0.023 30	0.147 60	0.116 75	0.047 20	0.055 32	0.009 514	0.009 772
	v	0.022 91	0.022 88	0.148 69	0.146 04	0.048 81	0.052 49	0.008 495	0.008 780
order 120	l	0.020 27	0.022 74	0.145 64	0.136 12	0.044 24	0.055 82	0.009 516	0.009 667
	v	0.022 06	0.022 24	0.144 63	0.143 94	0.049 43	0.050 39	0.009 330	0.009 532
order 220	l	0.020 75		0.144 40	0.141 74	0.048 43	0.053 39	0.009 520	0.009 620
	v	0.022 19		0.144 31	0.143 96	0.050 28	0.050 34	0.009 532	0.009 628
order 364	l			0.144 09				0.009 577	
	v			0.144 07				0.009 606	
					Li II				
order 56	l	0.031 78	0.032 53	0.269 500	0.248 384	0.072 81	0.086 58	0.007 199	0.007 262
	v	0.032 33	0.032 39	0.267 073	0.267 115	0.078 86	0.081 65	0.006 755	0.006 831
order 120	l	0.030 35	0.031 76	0.265 901	0.261 263	0.074 94	0.084 04	0.007 167	0.007 217
	v	0.031 48	0.031 57	0.265 278	0.265 240	0.079 21	0.079 68	0.007 111	0.007 171
order 220	l	0.030 96		0.265 237	0.264 153	0.078 73	0.081 62	0.007 168	0.007 200
	v	0.031 51		0.265 176	0.265 102	0.079 71	0.079 74	0.007 181	0.007 208
order 364	l			0.265 130		0.079 64		0.007 188	
	v			0.265 135		0.079 76		0.007 201	
					C V				
order 56	l	0.037 76	0.038 29	0.381 778	0.372 923	0.098 24	0.107 60	0.005 326	0.005 333
	v	0.038 34	0.038 37	0.379 876	0.380 460	0.102 95	0.104 15	0.005 169	0.005 179
order 120	l	0.037 30		0.379 491	0.377 993	0.100 82	0.105 07	0.005 288	0.005 296
	v	0.037 78		0.379 329	0.379 411	0.102 72	0.102 87	0.005 275	0.005 285
order 220	l	0.037 59		0.379 271		0.102 57		0.005 284	0.005 290
	v	0.037 74		0.379 257		0.102 90		0.005 290	0.005 295
order 364	l			0.379 250		0.102 87		0.005 289	
	v			0.379 251		0.102 90		0.005 294	

same principal quantum number (n^1S-n^1P or n^3S-n^3P), where the energy difference is very small. Some typical results for transitions of this type are given in Table II. It will be seen that in the case of the triplet transitions, the results obtained from the length formula converge much more rapidly than those obtained using the velocity formula. For the singlet case, however, the two sets of results converge about equally well. This result is of particular interest, as it has been previously assumed[14,15] that the length formula is always to be preferred for transitions between states with a small energy difference. Some typical results for transitions of the type m^1S-n^1P and m^3S-$n\,^3P$ (m not equal to n) are listed in Tables III and IV, respectively. It will be noted that, whereas for the singlet transitions of this type, the velocity results are almost invariably superior, for the triplet transitions sometimes the length and sometimes the velocity results converge better. Thus, in general, the triplet transitions quite often favor the length formula, whereas for the singlet transitions, the velocity formula almost invariably gives at least as good and often a better result.

Tables II–IV include the results obtained using S-state wave functions of types C and D. As we have pointed out elsewhere,[8] the results obtained for the energy E converge more rapidly if type-D wave functions are employed than is the case if type-C wave functions are used. On the other hand, the final results are generally more or less the same, due to the availability of type-C expansions containing a larger number of terms. Similarly, it is found that the f values obtained using the largest S-state expansions available of types C and D are usually almost equal to one another, despite

TABLE IV. Convergence of *f* values for transitions between excited triplet states. The results obtained using *S*-state wave functions of types *C* and *D* are listed.

		$2\,^3S$–$5\,^3P$		$3\,^3S$–$4\,^3P$		$3\,^3S$–$5\,^3P$		$5\,^3S$–$2\,^3P$	
		C	*D*	*C*	*D*	*C*	*D*	*C*	*D*
						He			
order 56	*l*	0.011 779	0.011 799	0.046 03	0.046 47	0.022 84	0.021 29	0.011 419	0.011 754
	v	0.010 845	0.010 856	0.046 21	0.046 18	0.020 07	0.019 99	0.010 778	0.011 086
order 120	*l*	0.012 185	0.012 331	0.049 72	0.049 46	0.022 20	0.022 87	0.011 333	0.011 356
	v	0.011 978	0.011 985	0.049 26	0.049 28	0.022 08	0.022 09	0.011 285	0.011 320
order 220	*l*	0.012 375		0.050 04	0.049 98	0.022 67	0.022 99	0.011 311	0.011 311
	v	0.012 351		0.049 99	0.049 99	0.022 67	0.022 67	0.011 334	0.011 337
order 364	*l*	0.012 463		0.050 08		0.022 88		0.011 322	
	v	0.012 468		0.050 07		0.022 88		0.011 343	
						Li II			
order 56	*l*	0.025 375	0.025 450	0.185 394	0.184 804	0.060 678	0.061 331	0.008 049	0.008 127
	v	0.024 647	0.024 657	0.184 248	0.184 323	0.059 916	0.059 940	0.007 898	0.007 967
order 120	*l*	0.025 452	0.025 551	0.186 766	0.186 589	0.060 838	0.061 648	0.008 062	0.008 067
	v	0.025 338	0.025 342	0.186 462	0.186 478	0.060 959	0.060 962	0.008 052	0.008 057
order 220	*l*	0.025 553		0.186 851	0.186 824	0.061 321	0.061 519	0.008 052	0.008 052
	v	0.025 556		0.186 830	0.186 832	0.061 364	0.061 363	0.008 061	0.008 061
order 364	*l*			0.186 859		0.061 414		0.008 055	
	v			0.186 860		0.061 418		0.008 062	
						C V			
order 56	*l*	0.035 37	0.035 42	0.340 62	0.340 15	0.094 66	0.095 61	0.005 425	0.005 434
	v	0.035 02	0.035 03	0.339 78	0.339 83	0.094 81	0.094 83	0.005 391	0.005 398
order 120	*l*	0.035 36		0.340 69	0.340 63	0.094 97	0.095 36	0.005 420	0.005 420
	v	0.035 33		0.340 64	0.340 64	0.095 04	0.095 04	0.005 420	0.005 420
order 220	*l*			0.340 69		0.095 18		0.005 417	0.005 417
	v			0.340 70		0.095 20		0.005 421	0.005 421
order 364	*l*							0.005 419	
	v							0.005 421	

the more rapid convergence of the results obtained with the type-*D* wave functions. There are, however, some cases where the type-*C* results converge to one or two more significant digits than the corresponding values for type *D*. In view of the excellent agreement between the results obtained with the two different types of *S*-state wave functions, the *f* values for ions with $Z > 6$ were calculated with the type-*C* functions only. We have not, therefore, included results for values of $Z > 6$ in Tables II–IV. The results for these higher values of *Z* are completely satisfactory. Indeed, it is found that, in general, as the atomic number increases, the results obtained using a given formula converge more rapidly, and also the results obtained by evaluating the three alternative formulas agree more closely with one another. The considerable improvement in the results as one goes from helium to Li II is particularly noticeable. Another general feature of the results is that the *f* values obtained for a given triplet transition converge more rapidly than those for the corresponding

TABLE V. *f* values for transitions in helium.

	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$1\,^1S$	0.276 2[a]	0.073[a]	0.030	0.015
$2\,^1S$	0.376 4[a]	0.151 4	0.049	0.02
$3\,^1S$	0.145 4	0.626	0.144	0.05
$4\,^1S$	0.025 8	0.306	0.85	0.15
$5\,^1S$	0.009 6	0.055	0.47	1.1
	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$
$2\,^3S$	0.539 086	0.064 46	0.025 77	0.0125
$3\,^3S$	0.208 54	0.890 9	0.050 1	0.023
$4\,^3S$	0.031 7	0.435 7	1.215 3	0.044
$5\,^3S$	0.011 3	0.068	0.67	1.53

[a] See Ref. 16.

TABLE VI. *f* values for transitions in Li II.

	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$1\,^1S$	0.456 6	0.110 6	0.043 7	0.0217
$2\,^1S$	0.212 6	0.257 07	0.073	0.031
$3\,^1S$	0.094 7	0.362 4	0.265 1	0.080
$4\,^1S$	0.018 8	0.205	0.500	0.285
$5\,^1S$	0.007 2	0.041 3	0.322	0.63
	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$
$2\,^3S$	0.307 940	0.187 1	0.057 5	0.026
$3\,^3S$	0.117 10	0.512 8	0.186 86	0.0614
$4\,^3S$	0.021 47	0.255 0	0.703 6	0.1962
$5\,^3S$	0.008 06	0.048 0	0.400	0.890

TABLE VIII. *f* values for transitions in B IV.

	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$1\,^1S$	0.608 91	0.135 4	0.052 0	0.025 5
$2\,^1S$	0.114 36	0.333 71	0.087 1	0.037
$3\,^1S$	0.068 54	0.198 1	0.357 09	0.098 7
$4\,^1S$	0.014 43	0.152 0	0.275	0.391 7
$5\,^1S$	0.005 65	0.032 6	0.242	0.35
	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$
$2\,^3S$	0.162 6	0.291 2	0.079	0.033 7
$3\,^3S$	0.075 438	0.271 71	0.310 29	0.089 10
$4\,^3S$	0.015 22	0.170 14	0.373 9	0.339 02
$5\,^3S$	0.005 87	0.035 3	0.271 7	0.473 6

singlet case. This is again similar to the behavior of the energy E and of the expectation values of various operators, where for both S and P states the triplet values converge more rapidly.[8]

Our final results for the f values are given in Tables V–XIII. They are based on the computations with the S-state wave functions of type C. (The final results obtained with the aid of type-C and type-D wave functions almost invariably agreed with one another to the number of figures to which they had both converged, the maximum discrepancy being two in the last digit.) The values listed are estimated to be accurate to within an error of not more than one, or occasionally two, in the last digit quoted. The number of digits which we give in these tables was determined in each case in order to satisfy two requirements. First, that to the number of digits quoted, the length and velocity formulas gave results agreeing with one another to within one or two in the last place. Secondly, that for each of these two formulas, the results obtained with the aid of the largest expansions employed agree to within one or occasionally two in the last digit quoted with the "extrapolated" value; i.e., with the value which we estimate would have been obtained if expansions containing an infinite number of terms had been used. Satisfaction of this second requirement is, we feel, particularly important, since the measure of the agreement between the results obtained by evaluating two different formulas using the same wave functions is not a sufficiently reliable guide to the accuracy of the final result. This point is well illustrated by the convergence of the results given in Tables II–IV. As an example, we may consider the $2\,^1S$-$2\,^1P$ transition in helium, shown in Table II. Using type-C wave functions for the $2\,^1S$ state, for order 120, the length and velocity formulas give 0.376 124 and 0.376 152, respectively, from which one might be tempted to conclude that the final result is 0.376 14, with an error of not more than ± 0.000 02. However, using the corresponding expansions of order 220, we obtain 0.376 354 and 0.376 358, respectively, from the two formulas, which by the same reasoning would lead to an estimate of $0.376\,356 \pm 0.000\,002$ for the final result. Again, the results for order 364 are 0.376 413 and 0.376 414, which would give $0.376\,414 \pm 0.000\,001$. However, consideration of the results for the different orders indicates that one could confidently quote a result of 0.3764, but that the next digit cannot be given with certainty. We have therefore

TABLE VII. *f* values for transitions in Be III.

	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$1\,^1S$	0.551 55	0.126 9	0.049 2	0.024 3
$2\,^1S$	0.148 54	0.305 9	0.082	0.035
$3\,^1S$	0.077 37	0.256 0	0.323 22	0.092 0
$4\,^1S$	0.015 95	0.169 9	0.355	0.352
$5\,^1S$	0.006 2	0.035 7	0.269	0.45
	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$
$2\,^3S$	0.213 14	0.252 6	0.072	0.030 9
$3\,^3S$	0.088 705	0.355 70	0.264 09	0.079 31
$4\,^3S$	0.017 33	0.197 44	0.488 9	0.285 2
$5\,^3S$	0.006 62	0.039 6	0.313 2	0.619 0

TABLE IX. *f* values for transitions in C V.

	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$1\,^1S$	0.647 07	0.140 5	0.053 5	0.026 2
$2\,^1S$	0.093 05	0.351 68	0.090 1	0.038
$3\,^1S$	0.063 16	0.161 55	0.379 25	0.102 9
$4\,^1S$	0.013 47	0.141 1	0.224 7	0.417 9
$5\,^1S$	0.005 29	0.030 7	0.226	0.29
	$2\,^3P$	$3\,^3P$	$4\,^3P$	$5\,^3P$
$2\,^3S$	0.131 4	0.316 5	0.083 7	0.035 4
$3\,^3S$	0.067 84	0.219 68	0.340 7	0.095
$4\,^3S$	0.013 96	0.154 37	0.302 4	0.374 56
$5\,^3S$	0.005 42	0.032 7	0.247 7	0.383 3

TABLE X. *f* values for transitions in N VI.

	$2\,{}^1P$	$3\,{}^1P$	$4\,{}^1P$	$5\,{}^1P$
$1\,{}^1S$	0.674 20	0.143 8	0.054 5	0.026 6
$2\,{}^1S$	0.078 47	0.364 23	0.092 1	0.038
$3\,{}^1S$	0.059 53	0.136 41	0.394 87	0.105 7
$4\,{}^1S$	0.012 80	0.133 7	0.189 9	0.436 4
$5\,{}^1S$	0.005 05	0.029 3	0.214 7	0.24
	$2\,{}^3P$	$3\,{}^3P$	$4\,{}^3P$	$5\,{}^3P$
$2\,{}^3S$	0.110 2	0.334 2	0.086 8	0.036 5
$3\,{}^3S$	0.062 950	0.184 32	0.362 13	0.099 37
$4\,{}^3S$	0.013 13	0.144 13	0.253 9	0.399 69
$5\,{}^3S$	0.005 12	0.030 9	0.232 0	0.321 8

TABLE XII. *f* values for transitions in F VIII.

	$2\,{}^1P$	$3\,{}^1P$	$4\,{}^1P$	$5\,{}^1P$
$1\,{}^1S$	0.710 13	0.147 9	0.055 6	0.027 0
$2\,{}^1S$	0.059 78	0.380 60	0.094 7	0.039 2
$3\,{}^1S$	0.054 94	0.104 02	0.415 43	0.109 4
$4\,{}^1S$	0.011 94	0.124 55	0.144 9	0.460 9
$5\,{}^1S$	0.004 72	0.027 6	0.200 8	0.18
	$2\,{}^3P$	$3\,{}^3P$	$4\,{}^3P$	$5\,{}^3P$
$2\,{}^3S$	0.083 27	0.357 5	0.090 8	0.037 9
$3\,{}^3S$	0.057 036	0.139 40	0.390 31	0.104 67
$4\,{}^3S$	0.012 104	0.131 66	0.192 1	0.432 79
$5\,{}^3S$	0.004 742	0.028 7	0.212 8	0.243 6

preferred to quote the result in such a case as 0.3764. It should be added that in cases where the acceleration results had also converged to the number of figures quoted in the tables, the value obtained was found to agree with the length and velocity results to within one or two in the last digit.

The most accurate previous calculations of *f* values for the helium isoelectronic sequence are those of Weiss,[6] who used basis functions similar to those employed in the current work, but only included up to 54 terms in the expansions of the wave functions, and of Sanders and Scherr,[7] who used a perturbation expansion in powers of Z^{-1}. The results of the three calculations for helium, C V, and Ne IX are compared in Table XIV. Our results quoted in this table are those which were obtained from the largest expansions employed, and are estimated to have converged to within the number of digits quoted in each case. The results of the three calculation are in excellent agreement.

Extensive calculations of *f* values for helium have also been made by Green *et al.*[3] In Table XV, we compare the results of the two calculations for the singlet transitions. (A comparison of the results for the triplet transitions would show similar features.) We felt a detailed comparison of the two sets of results to be worthwhile, as it illustrates the relative accuracy of the wave functions employed. One can see quite clearly that Green *et al.* obtain results superior to those of the current work for transitions between two highly excited states. In other cases, the results of the current work are better. This difference reflects the comparative accuracy of the wave functions. The wave functions of Green *et al.* are based on a configuration interaction scheme, and are therefore particularly suited to describe the higher excited states, where the interaction between the electrons is relatively unimportant. Our wave functions, on the other hand, are derived using a correlated basis, and hence are best suited to describe the low-lying states, where correlation effects are known to be important. Thus, for the case of helium, the calculations of Green *et al.* and the present work may be regarded as being complementary to one another.

To summarize, we have carried out a systematic calculation of the *f* values for transitions between low-lying *S* and *P* states for members of the helium isoelectronic sequence up to $Z = 10$. We have also made an estimate of the accuracy of the values obtained. In the large majority of cases, an accuracy of 1% or better has been achieved.

TABLE XI. *f* values for transitions in O VII.

	$2\,{}^1P$	$3\,{}^1P$	$4\,{}^1P$	$5\,{}^1P$
$1\,{}^1S$	0.694 45	0.146 1	0.055 2	0.026 9
$2\,{}^1S$	0.067 86	0.373 49	0.093 6	0.038 8
$3\,{}^1S$	0.056 91	0.118 03	0.406 48	0.107 8
$4\,{}^1S$	0.012 31	0.128 5	0.164 4	0.450 2
$5\,{}^1S$	0.004 86	0.028 4	0.206 7	0.21
	$2\,{}^3P$	$3\,{}^3P$	$4\,{}^3P$	$5\,{}^3P$
$2\,{}^3S$	0.094 85	0.347 4	0.089 1	0.037 3
$3\,{}^3S$	0.059 542	0.158 75	0.378 04	0.102 39
$4\,{}^3S$	0.012 54	0.136 96	0.218 7	0.418 37
$5\,{}^3S$	0.004 903	0.029 7	0.221 0	0.277 3

TABLE XIII. *f* values for transitions in Ne IX.

	$2\,{}^1P$	$3\,{}^1P$	$4\,{}^1P$	$5\,{}^1P$
$1\,{}^1S$	0.722 63	0.149 2	0.056 0	0.027 2
$2\,{}^1S$	0.053 430	0.386 24	0.095 6	0.039 6
$3\,{}^1S$	0.053 390	0.092 98	0.422 55	0.110 7
$4\,{}^1S$	0.011 65	0.121 47	0.129 5	0.469 4
$5\,{}^1S$	0.004 61	0.027 1	0.196 1	0.165
	$2\,{}^3P$	$3\,{}^3P$	$4\,{}^3P$	$5\,{}^3P$
$2\,{}^3S$	0.074 20	0.365 5	0.092 1	0.038 3
$3\,{}^3S$	0.055 116	0.124 25	0.400 05	0.106 46
$4\,{}^3S$	0.011 764	0.127 59	0.171 3	0.444 25
$5\,{}^3S$	0.004 617	0.028 0	0.206 5	0.217 17

TABLE XIV. Comparison of the results of the present work with those of Weiss (Ref. 6) and of Sanders and Scherr (Ref. 7).

			$1\,^1S-2\,^1P$	$1\,^1S-3\,^1P$	$2\,^1S-2\,^1P$	$2\,^1S-3\,^1P$	$2\,^3S-2\,^3P$	$2\,^3S-3\,^3P$
He:	Weiss	*l*	0.2759	0.0734	0.3764	0.1478	0.5391	0.0641
		v	0.2761	0.0730	0.3774	0.1506	0.5401	0.0634
	Sanders and Scherr	*l*	0.276 113				0.540 553	
		v	0.276 182				0.543 145	
		a	0.276 012				0.549 327	
	Present work	*l*	0.2761	0.074	0.3764	0.1514	0.539 086 1	0.064 461
		v	0.276 165	0.073 436	0.3764	0.1514	0.539 086	0.064 46
		a	0.2761	0.0734				
C v:	Weiss	*l*	0.6470	0.1406	0.0930	0.3495	0.1314	0.3163
		v	0.6470	0.1404	0.0932	0.3524	0.1315	0.3163
	Sanders and Scherr	*l*	0.647 051				0.131 381	
		v	0.647 068				0.131 383	
		a	0.647 038				0.131 063	
	Present work	*l*	0.647 07	0.1405	0.093 05	0.351 68	0.131 381	0.3165
		v	0.647 067	0.140 478	0.093 05	0.351 68	0.1314	0.316 48
		a	0.6471	0.1405				
Ne IX:	Weiss	*l*	0.7226	0.1492	0.0534	0.3841	0.0742	0.3651
		v	0.7226	0.1492	0.0535	0.3869	0.0742	0.3656
	Sanders and Scherr	*l*	0.722 617				0.074 198	
		v	0.722 625				0.074 199	
		a	0.722 606				0.073 863	
	Present work	*l*	0.722 62	0.1492	0.053 430	0.386 24	0.074 198	0.365 50
		v	0.722 625	0.149 160	0.053 430	0.386 24	0.074 20	0.3655
		a	0.7226	0.149 16				

TABLE XV. Comparison of the results of the present work with those of Green *et al.* (Ref. 3) for singlet transitions in helium.

			$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
$1\,^1S$	Green *et al.*	*l*	0.275 37	0.072 92	0.029 57	0.014 81
		v	0.275 86	0.072 96	0.029 60	0.014 87
		a	0.269 08	0.070 47	0.028 35	0.014 19
	Present work	*l*	0.2761	0.074	0.030	0.015
		v	0.276 165	0.073 436	0.0299	0.015
		a	0.2761	0.0734	0.030	0.015
$2\,^1S$	Green *et al.*	*l*	0.3773	0.1513	0.0493	0.0224
		v	0.3950	0.1540	0.0506	0.0231
	Present work	*l*	0.3764	0.1514	0.049	0.02
		v	0.3764	0.1514	0.0492	0.022
$3\,^1S$	Green *et al.*	*l*	0.1457	0.6279	0.1429	0.0499
		v	0.1446	0.6448	0.1433	0.0506
	Present work	*l*	0.1453	0.626	0.144	0.05
		v	0.1454	0.626	0.144	0.05
$4\,^1S$	Green *et al.*	*l*	0.0260	0.3081	0.8603	0.1455
		v	0.0256	0.3092	0.8754	0.1445
	Present work	*l*	0.0259	0.306	0.85	0.15
		v	0.0258	0.306	0.85	0.15
$5\,^1S$	Green *et al.*	*l*	0.009 67	0.0554	0.4767	1.0869
		v	0.009 51	0.0556	0.4780	1.0901
	Present work	*l*	0.0095	0.056	0.47	1.07
		v	0.0096	0.055	0.47	1.1

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

[2] B. Schiff and C. L. Pekeris, Phys. Rev. 134, A638 (1964).

[3] L. C. Green, N. C. Johnson, and E. K. Kolchin, Astrophys. J. 144, 369 (1966).

[4] A. Dalgarno and E. M. Parkinson, Proc. Roy. Soc. (London) A301, 253 (1967).

[5] M. Cohen and P. S. Kelly, Can. J. Phys. 45, 2079 (1967).

[6] A.W. Weiss, J. Res. Natl. Bur. Stds. 71A, 163 (1967).

[7] F. C. Sanders and C. W. Scherr, Phys. Rev. 181, 84 (1969).

[8] Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A 4, 516 (1971).

[9] C. L. Pekeris, Phys. Rev. 112, 1649 (1958).

[10] C. L. Pekeris, Phys. Rev. 126, 1470 (1962).

[11] C. L. Pekeris, Phys. Rev. 127, 509 (1962).

[12] B. Schiff, H. Lifson, C. L. Pekeris, and P. Rabinowitz, Phys. Rev. 140, A1104 (1965).

[13] S. Chandrasekhar, Astrophys. J. 102, 223 (1945).

[14] P. Jennings and E. B. Wilson, J. Chem. Phys. 47, 2130 (1967).

[15] R. J. S. Crossley, Advan. Atomic Molecular Phys. 5, 237 (1969).

[16] For a recent experimental verifications of the f values for the 1^1S-2^1P and 1^1S-3^1P transitions in helium, as well as the isotope shift of the 2^1S–2^1P line, see J. M. Burger and A. Lurio, Phys. Rev. A3, 64 (1971); 3, 76 (1971).

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Structure of Heavy Atoms: Three-Body Potentials*

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A discussion of the problem of the construction of a configuration-space Hamiltonian describing a many-electron atom with relativistic effects included is given. It appears that the total three-body energy in such an atom must be small if the problem of the construction of this Hamiltonian is to be simply solvable. To that end, a relativistic three-body potential is constructed for a three-electron system. It has novel terms which arise from a pathology of the two-body Hamiltonian previously noted. It is shown that a speculative generalization to the many-electron system results in a total three-body energy which may be many rydbergs but which is still a small perturbation on the total result.

I. INTRODUCTION

A fundamental problem of atomic physics is the question of just what configuration-space Hamiltonian (CSH) should be used as a starting point for the calculation of properties of a heavy atom. The advent of large digital computers has made this more than just an academic problem since it is now possible to do Hartree-Fock calculations in such systems provided the original CSH is not too complicated.[1] If we accept the belief that the fundamental description of a many-electron system is the field-theoretic one of quantum electrodynamics (QED), the problem becomes one of the extraction of a CSH from a Fock-space formulation. This is a problem which is not unique to atomic physics; it exists for any elementary-particle problem. However, it may well be solvable for QED where the coupling constant is small. It is clearly beyond our present skills in strong-interaction physics.

In either problem, the Hamiltonian formulation may not be the most useful one. Alternative approaches such as a many-particle generalization of the Bethe-Salpeter equation may, in the end, prove to be the more fruitful configuration-space formulation. However, this method yields a many-time equation for which numerical techniques are still in their infancy. By contrast, operating single-time (Hamiltonian) numerical approximation methods already exist. For this reason we shall concentrate upon the Hamiltonian approach here. The construction of the CSH will not be accomplished here. In this first paper we shall only take the first steps of the delineation of the total problem and a small step towards its solution. In the process we construct the three-body potential. This has been done before nonrelativistically[2,3]; however, when relativistic effects are introduced, novel potentials are encountered. The problem we start with is QED in the presence of an infinitely heavy point charge $+Ze$ where $Z \gg 1$ such that $Z\alpha$ is approximately unity. The parameters of the problem are then $Z\alpha$, α, and $N\alpha$, where $\alpha \simeq \frac{1}{137}$ is the fine-structure constant and N is the number of electrons