

## Dipole oscillator strengths, with rigorous limits of error, for He and $\text{Li}^+$

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Rigorous upper and lower bounds to dipole oscillator strengths have been calculated for 17 of the low-lying singlet and triplet transitions in He and  $\text{Li}^+$  using accurate Hylleraas-type wave functions of some 135–138 terms. About a third of the calculated  $f$  values can be guaranteed to 1% or better, and in the best case ( $\text{Li}^+ 2^3S - 2^3P$ ) the bounds tighten to about 0.05%, some two orders of magnitude better than corresponding experimental determinations. By comparing with an extensive compilation of experimental results, we find the quality of the rigorous bounds to generally match or exceed that of experimental determinations, and about a dozen experiments can be ruled out entirely. Trends with respect to nuclear charge, spin multiplicity, and principal quantum number are examined, and special emphasis is given throughout to sources of uncertainty in the calculated oscillator strengths which are revealed by the error-bound formulas.

### I. INTRODUCTION

From both theoretical and experimental standpoints, accurate determinations of atomic oscillator strengths ( $f$  values) continue to be of considerable interest. Recent advances in laboratory plasma physics and in satellite astronomy have reemphasized the importance of these fundamental atomic data. In the astrophysical domain, accurate oscillator strengths provide information on the abundance of elements in the spectrum of the solar corona and chromosphere, and aid in the establishment of models for stellar atmospheres where highly excited states of highly ionized atoms may be of particular importance.<sup>1</sup> In the laboratory, oscillator strengths are basic parameters in the study of shock waves, discharges, and electron temperatures in plasmas.<sup>2</sup>

Oscillator strengths are determined experimentally by a variety of techniques of uneven accuracy.<sup>3</sup> The older emission and absorption methods, by which the bulk of the experimental data has been obtained, require a knowledge of the number of radiating or absorbing species, and as such are subject to rather large errors (particularly systematic errors) from inaccurate vapor-pressure data, inadequate spectral resolution or scattered light, and non-Boltzmann population distributions. The newer lifetime measurements, while applicable to fewer spectral lines and generally more difficult to carry out, seem less susceptible to large systematic error. Nevertheless, even in the fruitful applications of the beam-foil techniques,<sup>4</sup> some systematic error may intrude through repopulation of a given level by cascades from higher levels. Thus, in spite of improvements in the experimental methods, there are few experimentally determined  $f$  values appearing certain to within

5%, and an estimated accuracy of 10–20% seems more typical.<sup>5</sup> Of course, *relative* oscillator strengths of much greater precision are readily obtained in the emission and absorption methods, and a few determinations of high *absolute* accuracy would be sufficient to calibrate the experimental methods and place large quantities of such data on a firm absolute basis.

Many theoretical methods have also been developed to calculate oscillator strengths, but the estimated errors (when indeed they were estimated at all) have tended to widely exceed those of experimental studies.<sup>6</sup> Perhaps the most troublesome aspect of such calculations is that the accuracy of the calculated oscillator strength is largely conjectural. Approximate wave functions chosen from an energy-minimization criterion may be wholly inadequate in describing regions of configuration space which are important for the oscillator strength, and one can thus be led to erratic or spurious values.<sup>7</sup>

Traditionally, attempts to judge the accuracy of computed  $f$  values have resorted to three main lines of argument.

1. *Agreement with experiments.* Seen even in its best light, this criterion clearly fails to resolve the accuracy question to within the limits set by the experimental errors themselves. Moreover, in cases where theoretical efforts might provide genuinely new information (as opposed to modest interpolation, extrapolation, or mere reproduction of existing data), this criterion would be unavailable in practice as well as unsatisfactory in principle.

2. *Agreement of "length," "velocity," and "acceleration" forms of  $f$  values.* As is well known, these various forms of the oscillator strength would be equivalent if the true wave functions were employed, but will generally disagree

when computed with approximate wave functions.<sup>8</sup> This furnishes a very useful criterion of *inaccuracy*, in the sense that one is properly alerted to skepticism if these forms disagree widely (though there is still the problem of judging which form might be least error prone). But experience shows that one cannot reliably employ this criterion in the opposite sense, i.e., to conclude that the quality of the calculations is good because the several forms happen to agree. Examples now abound where calculations which provided good agreement between, say, "length" and "velocity" forms were nonetheless shown to be greatly in error, and it is now generally recognized that such fortuitous agreement can occur under rather weak conditions.<sup>9</sup>

3. *Apparent numerical convergence in calculations.* Persuasive evidence of reliability can sometimes be offered when numerical convergence appears to set in as the variation calculations are pressed toward the limit of mathematical completeness. The foremost examples of such extensive calculations are the results of Pekeris and co-workers (based on correlated Hylleraas-type wave functions of hundreds or thousands of terms), which have apparently established  $f$  values for members of the helium isoelectronic series with an estimated accuracy of "1% or better for the large majority of the transitions."<sup>10</sup> Careful studies of the convergence patterns, however, may be impractical even for those few systems where they might be numerically feasible. More frequently, the source or nature of any apparent numerical convergence is completely unknown. The well-known calculations of Taylor and Parr furnish an instructive example in which the apparent "numerical convergence" settled on a spurious limit.<sup>11</sup>

Recently, one of the authors proposed a procedure for calculating rigorous upper and lower bounds to dipole oscillator strengths.<sup>12</sup> The method was illustrated with simple variational trial functions on the hydrogen-molecule ion. In the present work we have used highly correlated wave functions consisting of some 135–138 terms to investigate the transitions of the two-electron atoms He and Li<sup>+</sup>. We have obtained rigorous error bounds of considerably less than 1% (down to about 0.05% in the best case) for several important singlet and triplet transitions of both He and Li<sup>+</sup>, while other transitions are guaranteed to within 5–10%. We are able to give a detailed breakdown of the error sources for each transition, based on the specific quantities which appear in the error-bound formulas.

In Sec. II we review the basic equations for upper and lower bounds to dipole oscillator strengths.

Section III describes the method of calculation, including a description of the wave functions, the determination of overlap, and the handling of important terms within the error-bound formulas. The numerical results are presented in Sec. IV, while Sec. V comprises an error analysis of the calculations, including a detailed discussion of the interdependence of error-bound quantities. Section VI presents some final conclusions.

## II. UPPER AND LOWER BOUNDS

For the electric-dipole transition from state  $\Psi_a$  to state  $\Psi_b$  with respective energies  $E_a$  and  $E_b$ , the oscillator strength  $f_{ab}$  may be expressed in several equivalent forms when employing the true wave functions. We have employed the length formulation in which  $f_{ab}$  is expressed in terms of the usual dipole-moment operator  $\vec{\mu}$  for  $N$  electrons (hartree atomic units,  $\hbar = e = m = 1$ , are used throughout),

$$\vec{\mu} = \sum_{n=1}^N \vec{r}_n$$

in the form

$$f_{ab} = 2(E_b - E_a) |\langle \Psi_a | \mu_x | \Psi_b \rangle|^2, \quad (1)$$

where the incident radiation is taken polarized along the  $z$  axis. We assume the energy levels  $E_a$  and  $E_b$  are known accurately, thus leaving the weight of the calculation entirely upon the transition moment  $w_{ab}$ ,

$$w_{ab} = \langle \Psi_a | \mu_x | \Psi_b \rangle. \quad (2)$$

Such an assumption is exceptionally well justified in the case of two-electron atoms, for which Pekeris and co-workers have calculated highly accurate nonrelativistic eigenvalues.

In terms of approximate wave functions  $\Phi_a$ ,  $\Phi_b$ , the approximate transition moment  $\tilde{w}_{ab}$  is

$$\tilde{w}_{ab} = \langle \Phi_a | \mu_x | \Phi_b \rangle. \quad (3)$$

The following additional quantities are required for the calculation of error bounds: the overlap integrals  $S_a$ ,  $S_b$  between the exact wave functions and their approximate counterparts,

$$S_a \equiv |\langle \Psi_a | \Phi_a \rangle|, \quad S_b \equiv |\langle \Psi_b | \Phi_b \rangle|, \quad (4)$$

the corresponding overlap errors  $\epsilon_a$ ,  $\epsilon_b$ ,

$$\epsilon_a \equiv (1 - S_a^2)^{1/2}, \quad \epsilon_b \equiv (1 - S_b^2)^{1/2}, \quad (5)$$

the "uncertainty"  $\Delta_{ab}$ ,

$$\Delta_{ab}^2 \equiv \langle \Phi_b | \mu_x^2 | \Phi_b \rangle - \tilde{w}_{ab}^2, \quad (6)$$

and the integral  $\langle \Psi_a | \mu_x^2 | \Psi_a \rangle$ . Upper and lower bounds to the transition moment  $w_{ab}$  can then be calculated from the inequalities derived previously,<sup>12</sup>

$$w_{ab} \cong S_{a\pm} S_{b\pm} \tilde{w}_{ab} \pm \epsilon_{a+} S_{b\pm} \Delta_{ab} \pm \epsilon_{b+} [\langle \Psi_a | \mu_{\mp}^2 | \Psi_a \rangle_+ - (S_{a-} \tilde{w}_{ab} - \epsilon_{a+} \Delta_{ab})^2]^{1/2}. \quad (7)$$

The subscript  $\pm$  signs in (7) indicate as usual that the corresponding quantities should be replaced by their upper (+) or lower (-) bounds. A subsidiary restriction assumed in the derivation of (7), that the overlap  $S_a$  be sufficiently near unity to satisfy

$$\epsilon_{a+}/S_{a-} \leq \tilde{w}_{ab}/\Delta_{ab},$$

is easily met by the wave functions considered in this work.

### III. METHOD OF CALCULATION

#### A. Wave functions

The wave functions were obtained by a variational solution to the Schrödinger wave equation,  $\mathcal{H}\Psi = E\Psi$ , where  $\mathcal{H}$  is the nonrelativistic spin-independent Hamiltonian,

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (8)$$

and  $Z$  is the nuclear charge. The trial wave functions were of the form

$$\Phi = \sum_K c_K \chi_K, \quad (9)$$

consisting of linear combinations of Hylleraas-type basis functions containing positive integral powers of  $r_1$ ,  $r_2$ , and the interelectronic distance  $r_{12}$ . The basis functions were specifically of the form

$$\chi_K(1, 2) = (1 \pm P_{12}) r_1^i r_2^j r_{12}^k Y_0^0(1) Y_i^0(2) e^{-\xi r_1 - \eta r_2}, \quad (10)$$

where  $P_{12}$  is the permutation operator,  $Y_l^m$  are the usual ( $m=0$ ) spherical harmonics chosen to give either  $S$  ( $l=0$ ) or  $P$  ( $l=1$ ) symmetry, and the singlet and triplet spin states are associated with the inclusion of the plus or minus sign, respectively. We have ordered the terms of (9) in a conventional manner according to the value of  $\omega = i + j + k$ . Certain terms containing the highest values of  $i$ ,  $j$ , or (especially)  $k$  were thought less likely to be important and were deleted in order to obtain maximum values of  $\omega$  within the computer storage limitations. The restrictions  $j \geq i$  for  $S$ -state singlets and  $j > i$  for  $S$ -state triplets were imposed to ensure the linear independence of the basis set as  $\xi \rightarrow \eta$ . The number of terms in the final wave functions, the resultant

TABLE I. Number of terms, values of  $\omega$ , and restrictions upon indices comprising the final wave functions for states of He and  $\text{Li}^+$ .

States	No. Terms	$\omega$	Restrictions
$^1S$	135	10	$i, j < 9, k < 6$
$^3S$	138	11	$i, j < 9, k < 7$
$^{1,3}P$	137	9	$i, j < 8, k < 5$

values of  $\omega$ , and the restrictions on indices are summarized in Table I.

Although in principle we could have varied the linear as well as the nonlinear parameters to optimize both upper and lower bounds in (7), investigations on smaller wave functions showed small profit from this procedure. The benefits certainly would not be significant for the more complex functions considered here. Instead, the linear coefficients  $c_K$  were obtained in the usual manner from appropriate secular equations, which were solved by an "inverse-power-moment" algorithm for eigenvectors and eigenvalues. The nonlinear parameters  $\xi$ ,  $\eta$  were roughly optimized for the  $^1S$  ground states. For other states, nonlinear parameters interpolated from available literature<sup>13</sup> (based on wave functions of comparable size and constitution) proved nearly optimal, and their adoption resulted in significant savings in computer time. Table II contains the final values of the nonlinear parameters  $\xi$  and  $\eta$  for each state, as well as the energy eigenvalues, the overlap errors  $\epsilon$ , and other expectation values to which we will refer later. The underlined portions of the eigenvalues are those digits which differ from the accurate eigenvalues as calculated by Pekeris and co-workers.<sup>13</sup> The eigenvalues calculated here are seen to be of high quality, especially for states which are lower roots of the secular determinant, and the calculated wave functions are considerably more compact than corresponding Pekeris wave functions of equivalent accuracy.

#### B. Determination of overlap and other error-bound quantities

It is evident from inequalities (7) that overlap between the approximate and true wave functions is an important constraint upon the oscillator-strength bounds. The upper bounds to overlap can be simply set to unity, but the effective use of (7) demands a strenuous effort to achieve the best possible value for the lower bound to overlap. To calculate this lower bound, we have employed Weinberger's formula for overlap,<sup>14</sup> which uses the higher roots  $J_i$  of the secular determinant and can be written in the form

TABLE II. Nonlinear parameters  $\xi$  and  $\eta$ , energy eigenvalues, overlap parameters  $\epsilon$ , and expectation values  $\langle \mu_z^2 \rangle^a$  for states of He and Li<sup>+</sup>.

Atom	State	$\xi$	$\eta$	Energy Eigenvalue <sup>b</sup>	$\epsilon (\times 10^{-3})$	$\langle \mu_z^2 \rangle$	
He	1 <sup>1</sup> S	2.60	2.60	-2.903 724 <u>3662</u>	0.1144	0.752 497 <sup>c</sup>	
	2 <sup>1</sup> S	2.00	0.98	-2.145 973 <u>6783</u>	1.8104	10.684 <sup>d</sup>	
	3 <sup>1</sup> S	2.00	0.62	-2.061 270 <u>2515</u>	6.6819	57.3 <sup>d</sup>	
	2 <sup>3</sup> S	2.00	0.94	-2.175 229 <u>3740</u>	0.1701	7.603 693 <sup>d</sup>	
	2 <sup>1</sup> P	2.00	0.88	-2.123 843 <u>0314</u>	0.7700	18.699 231	
	3 <sup>1</sup> P	2.00	0.56	-2.055 145 <u>6017</u>	4.6924	109.996 120	
	4 <sup>1</sup> P	2.00	0.37	-2.031 065 <u>6469</u>	15.4549	365.264 382	
	2 <sup>3</sup> P	2.00	0.88	-2.133 164 <u>1620</u>	0.5353	15.479 716	
	3 <sup>3</sup> P	2.00	0.56	-2.058 080 <u>5852</u>	3.6879	98.254 214	
	4 <sup>3</sup> P	2.00	0.39	-2.032 321 <u>7663</u>	12.2281	336.417 473	
	Li <sup>+</sup>	1 <sup>1</sup> S	3.90	3.90	-7.279 913 <u>3960</u>	0.0810	0.286 017 <sup>e</sup>
		2 <sup>1</sup> S	3.00	1.71	-5.040 876 <u>4018</u>	0.8932	3.114 444 <sup>e</sup>
2 <sup>3</sup> S		3.00	1.56	-5.110 727 <u>3684</u>	0.0904	2.503 557 <sup>e</sup>	
2 <sup>1</sup> P		3.00	1.65	-4.993 351 <u>0230</u>	0.3751	4.787 617	
3 <sup>1</sup> P		3.00	1.11	-4.720 205 <u>5999</u>	2.2033	27.629 928	
2 <sup>3</sup> P		3.00	1.65	-5.027 715 <u>6590</u>	0.2778	3.968 165	

<sup>a</sup>For S states,  $\langle \mu_z^2 \rangle = \langle \psi_a | \mu_z^2 | \psi_a \rangle$  is taken from the Pekeris calculations (see text).

<sup>b</sup>Those digits which differ from the accurate values are underlined. See d and also

K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).

<sup>c</sup>C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

<sup>d</sup>Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

<sup>e</sup>C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

$$\langle \Psi_k | \Phi_k \rangle^2 \geq \frac{E_{n+1} - J_k}{E_{n+1} - E_k} \prod_{\substack{v=0 \\ (v \neq k)}}^n \frac{E_v - J_k}{E_v - E_k} \frac{J_v - E_k}{J_v - J_k}, \quad (11)$$

where  $n$  is the largest integer for which  $J_n \leq E_{n+1}$ . Any roots of the secular determinant which correspond to states higher than the one of interest will increase the Weinberger bound to overlap, provided these roots still interleave the true eigenvalues. The true eigenvalues  $E_i$  were obtained from highly accurate nonrelativistic calculations,<sup>13</sup> and eigenvalues which appeared certain to less than 12 decimals were arbitrarily rounded downward by one unit in the last secure digit. Overlap calculated with inequality (11) gave significant improvement over those obtained using the well-known Eckart criterion<sup>15</sup>; in addition, formula (11) is applicable to excited states for which Eckart's formula is no longer valid. Table III lists some comparisons of the Eckart and Weinberger formulas for states where both are still valid. The overlap-error parameter

$$\epsilon = (1 - S^2)^{1/2}$$

is convenient for such comparisons, the best overlap values corresponding to the smallest  $\epsilon$  values.

Another important feature of the calculations concerns the integrals  $\langle \Psi_a | \mu_z^2 | \Psi_a \rangle$  and  $\langle \Phi_b | \mu_z^2 | \Phi_b \rangle$  over the operator

$$\mu_z^2 = (z_1 + z_2)^2.$$

We take  $\Psi_a$  to be an S state, and use the full spherical symmetry of the wave function to write

$$\langle \Psi_a | \mu_z^2 | \Psi_a \rangle = \frac{4}{3} \langle \Psi_a | r_1^2 | \Psi_a \rangle - \frac{1}{3} \langle \Psi_a | r_{12}^2 | \Psi_a \rangle. \quad (12)$$

Since (12) involves only ordinary expectation values, little loss of rigor results from the replacement

$$\langle \Psi_a | \mu_z^2 | \Psi_a \rangle \approx \frac{4}{3} \langle \Phi_a | r_1^2 | \Phi_a \rangle - \frac{1}{3} \langle \Phi_a | r_{12}^2 | \Phi_a \rangle, \quad (13)$$

to be calculated in terms of the highly accurate wave function  $\Phi_a$ , or the still more accurate wave functions of Pekeris and co-workers. In the present work, for example, the uncertainty in  $\langle \Psi_a | \mu_z^2 | \Psi_a \rangle$  is probably several orders of magnitude smaller than the uncertainty in the oscillator strength. For a completely rigorous result, an upper bound to  $\langle \Psi_a | \mu_z^2 | \Psi_a \rangle$  might be calculated with the rather weak Rebane-Braun inequality<sup>16</sup>

TABLE III. Comparisons of the overlap parameter  $\epsilon$  for several states of He computed by the Eckart and Weinberger formulas.

He State	$\epsilon (\times 10^{-3})$		% Improvement
	Eckart	Weinberger	
1 <sup>1</sup> S	0.120	0.114	5
2 <sup>1</sup> P	0.890	0.770	13
2 <sup>3</sup> S	0.200	0.170	15
2 <sup>3</sup> P	0.616	0.535	13

$$\langle \Psi_a | \mu_x^2 | \Psi_a \rangle \leq \frac{\frac{1}{2}N}{E_b - E_a}, \quad (14)$$

or generalizations thereof for excited states,<sup>12,17</sup> but this was deemed superfluous in the present application. The error-bound formulas (7) are, in any event, quite insensitive to the value adopted for  $\langle \Psi_a | \mu_x^2 | \Psi_a \rangle$ , and even the use of the weak Rebane-Braun criterion (14) would not significantly detract from the accuracy of the calculated error bounds we report.<sup>18</sup>

The integral  $\langle \Phi_b | \mu_x^2 | \Phi_b \rangle$  over the  $P$ -state approximation cannot be simplified as in (12), due to the lack of spherical symmetry inherent in the  $P$ -state wave functions. Such a simplification was unjustifiably carried out in a previous application of semirigorous bounds for oscillator strengths by Jennings and Wilson.<sup>19</sup> The numerical effect of this replacement is so pronounced that several general conclusions of the Jennings-Wilson study (such as that concerning the relative accuracy of length and velocity forms) must be reopened to consideration. Our final calculated values of  $\langle \Phi_b | \mu_x^2 | \Phi_b \rangle$  and the adopted values for  $\langle \Psi_a | \mu_x^2 | \Psi_a \rangle$  are given in Table II.

#### IV. NUMERICAL RESULTS

We have calculated oscillator strengths with rigorous error bounds for 17 of the low-lying dipole-allowed  $n^1S \rightarrow m^1P$  and  $n^3S \rightarrow m^3P$  transitions in He and  $\text{Li}^+$ . The selected transitions included

$$\begin{aligned} n^1S \rightarrow m^1P: & \quad 1 \leq n \leq 3, \quad 2 \leq m \leq 4 \text{ for He;} \\ & \quad 1 \leq n \leq 2, \quad 2 \leq m \leq 3 \text{ for Li}^+; \\ 2^3S \rightarrow m^3P: & \quad 2 \leq m \leq 4, \text{ for He;} \\ & \quad m = 2 \quad \text{for Li}^+. \end{aligned}$$

These selections were expected to reveal various trends with respect to spin multiplicity, principal quantum number, and nuclear charge which could be of wider general interest.

In Table IV we present our direct estimate of the transition moment  $\tilde{w}_{ab}$ , together with the calculated error bounds for each oscillator strength in the form

$$\text{mean value} \pm \text{error}, \quad \% \text{ error},$$

where

$$\text{mean value} \equiv \frac{1}{2}(f_{ab}^+ + f_{ab}^-),$$

$$\text{error} \equiv \frac{1}{2}(f_{ab}^+ - f_{ab}^-),$$

$$\% \text{ error} \equiv (\text{error}/\text{mean value}) \times 100,$$

and  $f_{ab}^{\pm}$  are the calculated upper and lower bounds. For comparison we also list the values calculated for these same transitions by Pekeris and co-workers.<sup>10</sup> The mean value of the upper and lower bounds essentially coincides with the direct estimate of  $f_{ab}$  calculated from our approximate wave functions, and can be seen from Table IV to agree quite well with the corresponding Pekeris value.

The general quality of the error bounds is quite good. For example, all the  $\text{Li}^+$  transitions con-

TABLE IV. Calculated transition moments  $\tilde{w}_{ab}$  and rigorous error bounds for oscillator strengths  $f_{ab}$  in various He and  $\text{Li}^+$  transitions. The  $f$  values calculated by Pekeris and co-workers are included for comparison

Atom	Transition	$\tilde{w}_{ab}$	$f_{ab}$ (mean) $\pm$ error	% Error	$f_{ab}$ (Pekeris) <sup>a</sup>
He	$1^1S \rightarrow 2^1P$	0.420 742	0.2761 $\pm$ 0.0014	0.51	0.2762
	$1^1S \rightarrow 3^1P$	0.208 064	0.0735 $\pm$ 0.0036	5.0	0.073
	$1^1S \rightarrow 4^1P$	0.130 751	0.0303 $\pm$ 0.0071	23	0.030
	$2^1S \rightarrow 2^1P$	2.916 290	0.3764 $\pm$ 0.0018	0.48	0.3764
	$2^1S \rightarrow 3^1P$	0.911 430	0.151 $\pm$ 0.011	7.4	0.1514
	$2^1S \rightarrow 4^1P$	0.465 629	0.052 $\pm$ 0.018	35	0.049
	$3^1S \rightarrow 2^1P$	1.077 430	-0.1454 $\pm$ 0.0091	6.3	-0.1454
	$3^1S \rightarrow 3^1P$	7.149 288	0.626 $\pm$ 0.011	1.8	0.626
	$3^1S \rightarrow 4^1P$	1.544 448	0.148 $\pm$ 0.045	31	0.144
	$2^3S \rightarrow 2^3P$	2.531 352	0.53909 $\pm$ 0.00047	0.087	0.539 086
	$2^3S \rightarrow 3^3P$	0.524 525	0.0645 $\pm$ 0.0029	4.5	0.064 46
	$2^3S \rightarrow 4^3P$	0.299 929	0.0261 $\pm$ 0.0063	24	0.025 77
	$\text{Li}^+$	$1^1S \rightarrow 2^1P$	0.315 657	0.4566 $\pm$ 0.0010	0.21
$1^1S \rightarrow 3^1P$		0.147 006	0.1106 $\pm$ 0.0023	2.1	0.1106
$2^1S \rightarrow 2^1P$		1.495 471	0.21258 $\pm$ 0.00051	0.24	0.2126
$2^1S \rightarrow 3^1P$		0.632 961	0.2570 $\pm$ 0.0067	2.6	0.257 07
$2^3S \rightarrow 2^3P$		1.361 910	0.30794 $\pm$ 0.00016	0.052	0.307 940

<sup>a</sup>See Ref. 8.

sidered have been bounded to within 3%, and about  $\frac{1}{3}$  of the transitions (both He and Li<sup>+</sup>) can be guaranteed to well within the 1% accuracy estimated overall by Pekeris and co-workers to apply to their results.<sup>10</sup> The most accurately calculated transition is Li<sup>+</sup> 2<sup>3</sup>S - 2<sup>3</sup>P, where the uncertainty has been reduced to about 0.05%, some two orders of magnitude smaller than the estimated errors in the best experimental determinations. The same transition in He can be guaranteed to within 0.1%, again quite suitable for calibration purposes. On the other hand, the (percentage) theoretical uncertainties become much larger—ranging up to 35%—for weak transitions involving high principal quantum number. One can see in a general way from Table IV that the tightness of the error bounds tends to roughly follow the number of significant figures quoted by Pekeris and co-workers, but we emphasize that our rigorous bounds are obtained directly in a single calculation, without recourse to convergence studies, comparisons of length, velocity, and acceleration forms, and so forth.

The availability of rigorous theoretical bounds allows one to considerably sharpen the usual comparisons of theory with experiment. We have assembled a fairly comprehensive list of the various experimental determinations for nine of the transitions treated theoretically, and have compared these measurements—together with their estimated experimental uncertainties, where specified—with our theoretical bounds in Table V.<sup>20</sup> The entries within each transition are in approximate chronological order, and include both lifetime and intensity measurements by various methods. Where the data sources were lifetime measurements in which decay to more than one lower state was possible, we have extracted an experimental oscillator strength by employing theoretical  $f$  values for all but the main transition. This procedure was followed only for lifetimes in which one transition was so clearly dominant that effects of minor uncertainties in the remaining transitions could be ignored, and the experimental lifetime error was therefore

associated fully with the  $f$  value of the dominant transition. In addition, some relative data have been put on an absolute basis by using the theoretical  $f$  value for the He resonance transition as a standard.

The comparison of theoretical and experimental values in Table V shows that the more recent estimates of experimental error have generally been quite realistic. The dozen or so experimental determinations (most of which appeared prior to the calculations of Pekeris and co-workers) which completely fail to overlap the theoretical error bounds are enclosed in square brackets. Figure 1 depicts some recent entries of Table V for the helium resonance transition, 1<sup>1</sup>S - 2<sup>1</sup>P, in a more graphic manner, illustrating the rather substantial improvements in experimental accuracy which have been reported in recent years.

Both Fig. 1 and Table V show that the theoretical error limits generally compare quite reasonably with corresponding experimental error ranges. Even in the worst cases, such as those involving the 4<sup>1</sup>P state in He, the theoretical accuracy does not appear to be significantly lower than that claimed for representative experimental measurements. In making such comparisons, one should recall that experimental error limits are expressed at some arbitrarily chosen level of confidence (for example, one or two standard deviations), and may require estimates of systematic error having some additional subjective element. The theoretical error bounds, by contrast, represent absolute limits outside of which the exact result of nonrelativistic quantum mechanics could never fall. Thus, it is interesting and significant that theoretical methods, in spite of their more stringent definition of "error limits," manage in several cases to achieve an accuracy considerably beyond that accessible to current experimental methods.

## V. ERROR ANALYSIS

The form of the error-bound equations (7) is particularly well suited to analysis of the uncer-

TABLE V. Comparison of experimentally determined  $f$  values and rigorous theoretical bounds for various transitions in He and Li<sup>+</sup>. Experimental values which are ruled out by the theoretical bounds are enclosed in brackets.

	$f$ Value	Accuracy	Reference		$f$ Value	Accuracy	Reference	
He 1 <sup>1</sup> S → 2 <sup>1</sup> P	0.312 ± 0.04	13%	a	He 1 <sup>1</sup> S → 2 <sup>1</sup> P	0.275 ± 0.007	3%	h	
	[0.377 ± 0.035]	[9.3%]	b		0.2761 ± 0.0014	0.51%	this work	
	[0.26 ± 0.012]	[4.6%]	c		He 1 <sup>1</sup> S → 3 <sup>1</sup> P	[0.0898 ± 0.006]	[7%]	a
	0.28 ± 0.02	7%	c			[0.067]		i
	0.26 ± 0.07	27%	d			0.073		j
	0.27 ± 0.02	7%	e			0.080 ± 0.017	21%	k
	0.273 ± 0.011	4.0%	f			[0.0784]		l
0.27 ± 0.01	4%	g	0.0737 ± 0.0044	5.8%	g			

TABLE V (Continued)

	<i>f</i> Value	Accuracy	Reference		<i>f</i> Value	Accuracy	Reference
He 1 <sup>1</sup> S→3 <sup>1</sup> P	0.073		m	He 2 <sup>1</sup> S→4 <sup>1</sup> P	0.0527 ± 0.006	11%	z
	0.0711 ± 0.0040	5.6%	n		0.052 ± 0.018	35%	this work
	0.073 ± 0.005	7%	h	He 3 <sup>1</sup> S→2 <sup>1</sup> P	-0.147 ± 0.008	5%	s
	0.0703 ± 0.004	6%	o		-0.143 ± 0.007	5%	t
	0.0735 ± 0.0036	5.0%	this work		-0.147 ± 0.008	5%	aa
He 1 <sup>1</sup> S→4 <sup>1</sup> P	0.030		j		-0.13 ± 0.01	5%	bb
	[0.050 ± 0.011]	[22%]	k	He 2 <sup>3</sup> S→2 <sup>3</sup> P	-0.1454 ± 0.0091	6.3%	this work
	0.037		l		0.582 ± 0.063	12%	s
	0.032 ± 0.003	11%	g		[~0.53]		cc
	0.0305		m		0.533 ± 0.032	5.9%	t
	0.0303 ± 0.0071	23%	this work		0.502 ± 0.024	4.8%	dd
He 2 <sup>1</sup> S→3 <sup>1</sup> P	0.150 ± 0.002	1%	p		0.54 ± 0.03	5%	ee
	0.155 ± 0.014	9.0%	q		0.583 ± 0.063	11%	aa
	0.15 ± 0.015	10%	r		0.533 ± 0.045	8.5%	ff
	0.153 ± 0.011	7.1%	s		0.539 09 ± 0.000 47	0.087%	this work
	0.164 ± 0.027	17%	t	He 2 <sup>3</sup> S→3 <sup>3</sup> P	[0.054 ± 0.003]	[6%]	p
	0.151 ± 0.002	1%	u		[0.057]		gg
	0.14 ± 0.01	7%	v		[0.053 ± 0.005]	[9%]	q
	0.17 ± 0.02	11%	w		0.057 ± 0.006	10%	r
	0.15 ± 0.01	7%	x		0.0645 ± 0.0029	4.5%	this work
	0.19 ± 0.06	33%	y	Li <sup>+</sup> 2 <sup>3</sup> S→2 <sup>3</sup> P	[0.249 ± 0.013]	[5%]	hh
	0.151 ± 0.011	7.4%	this work		[0.282 ± 0.02]	[7%]	ii
He 2 <sup>1</sup> S→4 <sup>1</sup> P	0.037 ± 0.004	10%	r		[0.41 ± 0.03]	[7%]	jj
	0.057 ± 0.009	16%	s		0.30 ± 0.03	10%	kk
	0.041 ± 0.014	35%	t		0.307 94 ± 0.000 16	0.052%	this work

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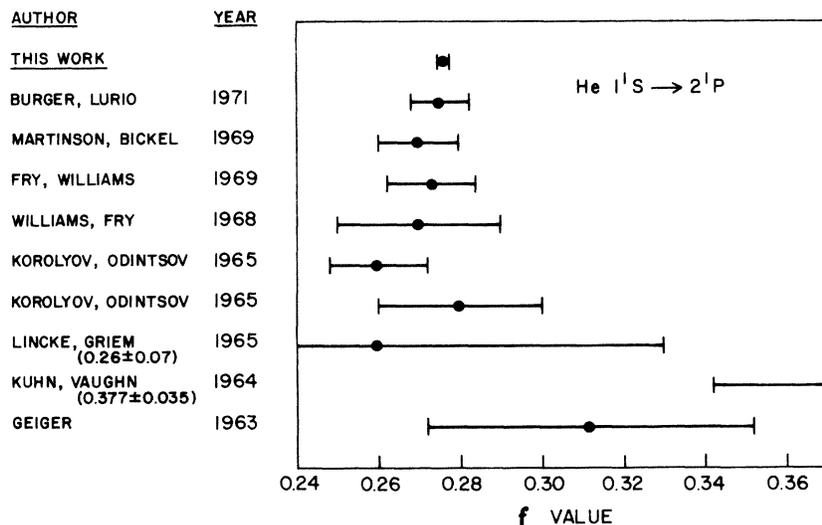


FIG. 1. Comparison of some recent determinations of oscillator strength for the He resonance transition.

tainties entering the calculated  $f$  values, and therefore makes possible a detailed insight into sources of error which could only be inferred indirectly from convergence studies or other means. When the overlap integrals  $S_a$  and  $S_b$  are nearly unity, so that only terms of the order of  $\epsilon_a$  and  $\epsilon_b$  need be included, Eqs. (7) reduce to the simpler form

$$w_{ab} \cong \tilde{w}_{ab} \pm [\epsilon_a (\langle \Phi_b | W^2 | \Phi_b \rangle - \tilde{w}_{ab}^2)^{1/2} + \epsilon_b (\langle \Psi_a | W^2 | \Psi_a \rangle - \tilde{w}_{ab}^2)^{1/2}], \quad (15)$$

where  $W$  is the transition moment operator

$$W = \mu_x = z_1 + z_2. \quad (16)$$

Equation (15) may be further abbreviated as

$$w_{ab} \cong \tilde{w}_{ab} \pm (\epsilon_a \delta_a + \epsilon_b \delta_b), \quad (17)$$

thereby suggesting a very useful breakdown of the total error. We stress that no calculations were carried out with the simplified equation (15), which is introduced only for more qualitative purposes.

The two terms in brackets in Eq. (15) serve to partition the total uncertainty into contributions chiefly attributable to the errors in  $\Phi_a$  and  $\Phi_b$ , respectively:

$$\begin{aligned} \text{"error from } \Phi_a \text{"} &= \epsilon_a \delta_a \\ &= \epsilon_a (\langle \Phi_b | W^2 | \Phi_b \rangle - \tilde{w}_{ab}^2)^{1/2}, \end{aligned} \quad (18a)$$

$$\begin{aligned} \text{"error from } \Phi_b \text{"} &= \epsilon_b \delta_b \\ &= \epsilon_b (\langle \Psi_a | W^2 | \Psi_a \rangle - \tilde{w}_{ab}^2)^{1/2}. \end{aligned} \quad (18b)$$

The three key indicators of error are therefore (i) the  $\epsilon$  factor, which measures the overall qual-

ity of the trial wave function in some global sense; (ii) the average value of  $W^2$ , which can be taken as a measure of diffuseness of the state to which a transition is being made; (iii) the magnitude of the transition moment  $\tilde{w}_{ab}$  itself.

Of these three indicators, the overlap parameter  $\epsilon$  is clearly of dominant importance, for once the trial wave functions are sufficiently accurate to establish the rough magnitude of  $\delta$ , further significant tightening of the bounds can only be effected by successively improving the bound for  $\epsilon$ . However, the *relative* accuracy in a series of transitions will more frequently be sensitive to the factors  $\langle W^2 \rangle$ ,  $\tilde{w}_{ab}$  which enter  $\delta$ .

Examples of the interplay of these factors may be readily found in Table VI, in which we have gathered values of  $\epsilon$ ,  $\tilde{w}_{ab}$ ,  $\langle W^2 \rangle$ , and  $\epsilon\delta$  for each of the various transitions. If we compare the He  $1^1S - 2^1P$  and  $1^1S - 3^1P$  transitions, for example, we can see that the poorer reliability of the latter  $f$  value stems from three distinguishable effects.

(a) The  $3^1P$  state corresponds to a higher root of the secular determinant, so both the eigenvalue and the overlap parameter  $\epsilon$  for this state are considerably poorer than for  $2^1P$ . The effect on overlap becomes progressively more severe with degree of excitation because the true energy levels bunch together more closely, leading to possible "contamination" of the trial function by components from adjoining levels [see Eq. (11)], even if the absolute size of the energy error is not much changed.

(b) The  $3^1P$  is markedly more diffuse than  $2^1P$ , as reflected in the five or sixfold increase in  $\langle W^2 \rangle$ . The calculated  $f$  values will therefore depend on much smaller features of the chosen  $S$

function, e.g., its details at large distances from the nucleus, which are not so well fixed by an energy-minimization criterion.

(c) The transition moment  $\tilde{w}_{ab}$  to  $3^1P$  is smaller by a factor of 2 than that for  $2^1P$ , so that the overall  $\delta$  factor is increased still further beyond that expected from the diffuseness difference discussed above. A stronger value of  $\tilde{w}_{ab}$  therefore tends to diminish the *absolute* size of the error as well as, of course, its relative size as a percentage of the transition moment.

The three effects all work together in the present instance to make the percentage error in the  $1^1S \rightarrow 3^1P$   $f$  value some ten times greater than that for  $1^1S \rightarrow 2^1P$ .

In other cases, these various effects may tend to cancel one another. For example, the error for He  $3^1S \rightarrow 3^1P$  (1.8%) is actually less than that for He  $1^1S \rightarrow 3^1P$  (5.0%), even though the  $\epsilon$  and  $\langle W^2 \rangle$  values are larger by factors of 60 and 80, respectively. These effects are negated, however, by the increased magnitude of  $\tilde{w}_{ab}$  between the two states of equal principal quantum number, which tends to reduce  $\delta$  both in absolute size and (what is much more important here) as a fraction of  $\tilde{w}_{ab}$ .

When applying the general idea that stronger transitions tend to be associated with smaller errors in both an absolute and relative sense, we should note that it is the transition moments, rather than final  $f$  values, which are to be compared. For example, the  $\text{Li}^+$   $1^1S \rightarrow 2^1P$   $f$  value is about twice as large as that of  $\text{Li}^+$   $2^1S \rightarrow 2^1P$ , although the corresponding transition moment is *smaller* by a factor of 5.

If we compare corresponding transitions in He and  $\text{Li}^+$ , we can see that two of the three effects discussed above tend to enhance strongly the accuracy of calculated  $f$  values with increasing nuclear charge  $Z$ . Although the transition moments are somewhat smaller in  $\text{Li}^+$ , the higher value of  $Z$  tends to (i) spread the true energy levels, so that the overlap parameter  $\epsilon$  is improved even if the energy errors are roughly similar, and (ii) strongly contract the wave functions so that  $\langle W^2 \rangle$ , and thus  $\delta$ , are reduced. As a result of these two effects, the oscillator strengths for  $\text{Li}^+$  are calculated with uniformly higher accuracy than those for He, and such an improvement with increasing nuclear charge can probably be expected to hold rather generally.

A similar uniform improvement in accuracy can be seen in the triplet transitions relative to corresponding singlet transitions. This effect is due primarily to the better overlap value, the triplet always corresponding to a lower root of its secular determinant and thereby leading to a more quickly convergent energy value. The triplet states are also somewhat more compact, as reflected in the smaller  $\langle W^2 \rangle$  integrals, but the differences in  $\epsilon$  values (for example, the ten-fold reduction from He  $2^1S$  to  $2^3S$ ) tend to dominate the comparisons.

A most important application of the error breakdown furnished by (17) and (18) is to assist in judging how much attention should be given to each of the trial functions  $\Phi_a$ ,  $\Phi_b$  for any given transition. This point is illustrated in Table VII, which lists values of  $\epsilon_i$  and  $\delta_i$  ( $i = S$  or  $P$ ), and of the percent error contributed by each function

TABLE VI. Numerical values for various parameters which affect the accuracy of the calculated  $f$  values; see text.

Atom	Transition	$f_{ab}$	% Error	$\epsilon_a$ ( $\times 10^{-3}$ )	$\epsilon_b$ ( $\times 10^{-3}$ )	$\langle \psi_a   W^2   \psi_a \rangle$	$\langle \Phi_b   W^2   \Phi_b \rangle$	$\tilde{w}_{ab}$	$\epsilon_a \delta_a$ ( $\times 10^{-3}$ )	$\epsilon_b \delta_b$ ( $\times 10^{-3}$ )	
He	$1^1S \rightarrow 2^1P$	0.2761	0.51	0.11	0.77	0.75	19	0.42	0.49	0.58	
	$1^1S \rightarrow 3^1P$	0.0735	5.0	0.11	4.7	0.75	110	0.21	1.2	4.0	
	$1^1S \rightarrow 4^1P$	0.0303	23	0.11	15	0.75	370	0.13	2.2	13	
	$2^1S \rightarrow 2^1P$	0.3764	0.48	1.8	0.77	11	19	2.9	5.8	1.1	
	$2^1S \rightarrow 3^1P$	0.151	7.4	1.8	4.7	11	110	0.91	19	15	
	$2^1S \rightarrow 4^1P$	0.052	35	1.8	15	11	370	0.47	35	50	
	$3^1S \rightarrow 2^1P$	-0.1454	6.3	6.7	0.77	57	19	1.1	28	5.8	
	$3^1S \rightarrow 3^1P$	0.626	1.8	6.7	4.7	57	110	7.1	51	12	
	$3^1S \rightarrow 4^1P$	0.148	31	6.7	15	57	370	1.5	130	110	
	$2^3S \rightarrow 2^3P$	0.539 09	0.087	0.17	0.54	7.6	15	2.5	0.52	0.59	
	$2^3S \rightarrow 3^3P$	0.0645	4.5	0.17	3.7	7.6	98	0.52	1.7	10	
	$2^3S \rightarrow 4^3P$	0.0261	24	0.17	12	7.6	340	0.30	3.2	34	
	$\text{Li}^+$	$1^1S \rightarrow 2^1P$	0.4566	0.21	0.081	0.38	0.29	4.8	0.32	0.18	0.16
		$1^1S \rightarrow 3^1P$	0.1106	2.1	0.081	2.2	0.29	28	0.15	0.43	1.1
$2^1S \rightarrow 2^1P$		0.212 58	0.24	0.89	0.38	3.1	4.8	1.5	1.4	0.35	
$2^1S \rightarrow 3^1P$		0.2570	2.6	0.89	2.2	3.1	28	0.63	4.7	3.6	
$2^3S \rightarrow 2^3P$		0.307 94	0.052	0.090	0.28	2.5	4.0	1.4	0.13	0.22	

$\Phi_i$  to the total error. In the transition He  $1^1S \rightarrow 3^1P$ , for example, about 77% of the total error can be attributed to the  $P$  function, so there would be little advantage in further refining the  $S$  function.<sup>21</sup> In He  $2^1S \rightarrow 2^1P$ , on the other hand, the  $S$  function is responsible for about 84% of the error, so that any reserve effort should clearly be allocated to its improvement; in particular, the overall accuracy of the calculated  $f$  value might well be improved by substituting a poorer  $2^1P$  representation if the computational capacity thus freed could be transferred to improve the  $2^1S$  function sufficiently. For still other transitions, such as He  $1^1S \rightarrow 2^1P$ , the errors are fairly well "balanced," and an optimum strategy for further improvement would involve simultaneous improvement of both functions. Such considerations could be of practical value in many circumstances, and we note that partial information of this character might be deduced even if the overlap parameter  $\epsilon$  were unavailable (or could only be judged in a qualitative sense). We hope to return to this point in a forthcoming paper.

#### VI. CONCLUSION

We have applied rigorous error-bound formulas to the calculation of dipole oscillator strengths in order (a) to cast light upon the general factors which affect the theoretical errors in such calculations, and (b) to systematically determine various He and Li<sup>+</sup>  $f$  values at a level of accuracy which could be of practical utility. We find that

many of these  $f$  values can be rigorously bracketed with an accuracy which matches or exceeds that currently accessible to experimental methods; for transitions in which this gain in accuracy approaches one or more orders of magnitude, one has a suitable basis for confidently *calibrating* experimental setups and/or identifying sources and magnitudes of systematic error. In this connection, one can note that these two-electron systems would generally be of greater experimental convenience than corresponding one-electron species for which definitive theoretical values are known.

The calculations given here were carried out entirely within the dipole "length" formulation, and have revealed various trends with respect to nuclear charge and to degree of excitation, angular and spin symmetry, and spatial diffuseness of the participating states. It can be expected that calculations in the "velocity" formulation would exhibit somewhat different patterns of dependence on these various factors. We expect in the near future to carry out dipole velocity calculations on these same two-electron species, so as to gain additional insight on the relative error susceptibility of length and velocity calculations for the various classes of transitions, as well as, possibly, to further tighten the error bounds for several of the  $f$  values.

While the error-bound formulas might be applied in a fully rigorous manner to somewhat larger systems, as recently demonstrated by Sims and

TABLE VII. Error parameters and percentage contributions to total error<sup>a</sup> arising from each of the two trial functions  $\Phi_a$ ,  $\Phi_b$ .

	Transition	$\epsilon_a$ ( $\times 10^{-3}$ )	$\delta_a$	% Error $\Phi_a$	$\epsilon_b$ ( $\times 10^{-3}$ )	$\delta_b$	% Error $\Phi_b$
He	$1^1S \rightarrow 2^1P$	0.11	4.3	46	0.77	0.75	54
	$1^1S \rightarrow 3^1P$	0.11	11	23	4.7	0.84	77
	$1^1S \rightarrow 4^1P$	0.11	19	14	15	0.86	86
	$2^1S \rightarrow 2^1P$	1.8	3.2	84	0.77	1.5	16
	$2^1S \rightarrow 3^1P$	1.8	10	56	4.7	3.1	44
	$2^1S \rightarrow 4^1P$	1.8	19	41	15	3.2	59
	$3^1S \rightarrow 2^1P$	6.7	4.2	83	0.77	7.5	17
	$3^1S \rightarrow 3^1P$	6.7	7.9	81	4.7	2.6	19
	$3^1S \rightarrow 4^1P$	6.7	19	54	15	7.4	46
	$2^3S \rightarrow 2^3P$	0.17	3.0	47	0.54	1.1	53
	$2^3S \rightarrow 3^3P$	0.17	9.9	15	3.7	2.7	85
	$2^3S \rightarrow 4^3P$	0.17	18	8	12	2.7	92
Li <sup>+</sup>	$1^1S \rightarrow 2^1P$	0.081	2.2	53	0.38	0.43	47
	$1^1S \rightarrow 3^1P$	0.081	5.3	28	2.2	0.51	72
	$2^1S \rightarrow 2^1P$	0.89	1.6	80	0.38	0.94	20
	$2^1S \rightarrow 3^1P$	0.89	5.2	57	2.2	1.7	43
	$2^3S \rightarrow 2^3P$	0.090	1.5	37	0.28	0.81	63

<sup>a</sup>Percentage error from  $\Phi_a \equiv [\epsilon_a \delta_a / (\epsilon_a \delta_a + \epsilon_b \delta_b)] \times 100$ , etc.; see text.

Whitten on the beryllium atom,<sup>22</sup> it seems likely that their greatest utility would arise in more qualitative applications in which only some portions of the error-bound expressions (such as the factors  $\delta_a$  and  $\delta_b$  of Sec. V) would be evaluated as a guide to the expected errors. The recent resurgence of activity in oscillator-strength calculations for small and medium-size atoms has been characterized by new standards of accuracy and sophistication,<sup>23</sup> to the extent that partial or full employment of the error-bound equations no longer seems completely out of the question. One can expect that, as the computational techniques continue to evolve in the direction of greater accuracy, the need for criteria of reliability which are *internal* to the theoretical calculations themselves (and thus independent of the availability of ex-

perimental comparisons) will be increasingly perceived.

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