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# Upper and lower bounds to atomic and molecular properties. III. Lithium oscillator strengths for various $^2S$-$^2P$ transitions*

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Wave functions, which include interelectron coordinates explicitly, are calculated for the four lowest $^2S$ and four lowest $^2P$ states of Li I. These wave functions are used to calculate oscillator strengths, including upper and lower bounds, for the 16 lines arising from allowed transitions among these four $^2S$ and four $^2P$ states. The results of this study are oscillator strengths for the $1s^2ns\,^2S \to 1s^2mp\,^2P$ Li I transitions for which $n$, $m = 2, 3, 4, 5$ with rigorous upper and lower bounds which in the best case ($1s^22s\,^2S \to 1s^22p\,^2P$) are 3.5%.

## I. INTRODUCTION

Spectroscopic data for atoms and ions fall into a category of fundamental scientific material for which justification of measurement or calculation is scarcely necessary. The measurement of the wavelengths of spectral lines and the subsequent deduction of energy levels is usually not too difficult.[1,2] The study of the strengths (intensities) of spectral lines is, however, a much more formidable problem.[3] On the experimental side, absolute oscillator strengths, or $f$ values, are typically determined with uncertainties of (10–20)% or more.[4] On the theoretical side, Pekeris and co-workers appear to have established some helium $f$ values to 1% or better,[5] and other transitions in the two-electron isoelectronic sequence have been determined to perhaps 5%.[6,7] But results reliable to better than (10–20)% have not been generally accessible in larger systems.[8,9] In addition, the question of the reliability of theoretical predictions has become increasingly acute,[10] and there is a need for procedures which lead to upper and lower bounds for the properties of interest, so that rigorous error limits are attached to the error estimates.

In view of the above, we have calculated $f$ values for various $^2S \to {}^2P$ transitions (by the dipole-length formulation) of Li I. The calculations utilize some of the best wave functions (on an energy criterion) currently available.[11-13] In addition, the procedure of Weinhold[14,15] has been used to calculate upper and lower bounds to the computed $f$ values. The results of this study are oscillator strengths for the $1s^2ns\,^2S \to 1s^2mp\,^2P$ Li I transitions for which $n, m = 2,3,4,5$ with rigorous upper and lower bounds which in the best case ($1s^22s\,^2S \to 1s^22p\,^2P$) are 3.5%.

## II. THEORY

### A. Wave Functions

Weiss[16] has shown that for the resonance transition of lithium, Hartree-Fock wave functions are unreliable and wave functions, including correlation effects, of considerable accuracy must be employed, not only for the ground state, but also for excited states. The procedure adapted here for incorporating correlations into the wave function is the method of Sims and Hagstrom,[13] in which a variational trial function is written as a linear combination of known many-electron functions,

$$\Psi = \sum_k C_k \Phi_k , \tag{1}$$

and the configurations $\Phi_k$ are themselves antisymmetrized projected products of orbitals and interelectronic coordinates. By minimizing the energy with respect to the coefficients $C_k$, one is led to the usual matrix eigenvalue equation for the energy and the coefficients $C_k$. The eigenvalues are always upper bounds to the energy of the corresponding excited (or ground) state.[17] The eigenvalue equation is solved by Jacobi's method[18] after the overlap matrix has been triangulated and the Hamiltonian matrix transformed by the method of Michels, Van Dine, and Elliott.[19]

In Eq. (1), the $\Phi_k$ are

$$\Phi_k = O(L^2) O_{as}\left(\chi_k r_{ij}^{\nu_k} \prod_{s=1}^{3} \phi_{ks}(\vec{r}_s)\right) , \tag{2}$$

where $O(L^2)$ is an idempotent orbital-angular-momentum projection operator[20] and $O_{as}$ is the projection operator that guarantees the antisymmetry of the wave function,

$$O_{as} = (3!)^{-1} \sum_P (-1)^p P , \tag{3}$$

where the summation runs over all the 3! permutations $P$, with $p$ being the parity of the corresponding permutation $P$. For this work, the spin function was taken as

$$\chi_k = \chi = (1/\sqrt{2})(\alpha_1\beta_2 - \beta_1\alpha_2)\alpha_3 ,$$

which has $S = S_k = \frac{1}{2}$. In Eq. (2), $\phi_{ks}(\vec{r}_s)$ refers to the

$s$th basis orbital in the $k$th configuration. The obbital basis consists of Slater-type orbitals (STO's) of the general form

$$\phi(\vec{r})=\{(2\zeta)^{n+1/2}/[(2n)!]^{1/2}\}r^{n-1}e^{-\zeta r}Y_{l,m}, \tag{4}$$

where the set $\{Y_{l,m}\}$ consists of normalized spherical harmonics in the Dirac phase convention.[21] In Eq. (2), the restriction of only one $r_{ij}$ coordinate per term, first proposed by James and Coolidge,[22] has been retained. The basis set consists of $s$ and $p$ STO's and powers of interelectronic coordinates: $r_{ij}^{v}(v=0,1,2)$. Previous calculations[11] have shown that this is an excellent basis set for lithium.

### B. Oscillator strengths

The basic theory of electric-dipole radiation in atomic systems is given by Condon and Shortley,[21] and we follow their terminology closely. Assuming Russell-Saunders (LS) coupling and the nonrelativistic many-electron Hamiltonian (Hartree atomic units)[23]

$$\mathcal{H}=\sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}}, \tag{5}$$

the energy states of an atom are characterized by the set of quantum numbers $\gamma LSM_LM_S$. Here $\gamma$ denotes the electronic configuration, $L$ the total angular momentum, $S$ the total spin, and $M_L$ and $M_S$ are the projections of $L$ and $S$, respectively, on the axis of quantization.[24] For an electric-dipole transition connecting the terms (multiplets) $\gamma LS$ and $\gamma' L'S'$, Condon and Shortley introduced the quantity $S(\gamma LS;\gamma' L'S')$, called the absolute multiplet strength. It is defined in terms of the electric-dipole-moment operator

$$\vec{P}=\sum_{i=1}^{N}\vec{r}_i$$

by[25]

$$S(\gamma LS;\gamma' L'S') = \sum_{M_L,M_S}\sum_{M_{L'},M_{S'}}|\langle\gamma LSM_LM_S|\vec{P}|\gamma' L'S'M_{L'}M_{S'}\rangle|^2. \tag{6}$$

The $f$ value or multiplet oscillator strength is related to $S$ by

$$f(\gamma LS\rightarrow\gamma' L'S')=\frac{2}{3}\,\frac{E(\gamma' L'S')-E(\gamma LS)}{(2L+1)(2S+1)}\,S(\gamma LS;\gamma' L'S'). \tag{7}$$

The familiar electric-dipole selection rules $\Delta S=0$, $\Delta M_S=0$, $\Delta L=\pm1$, and $\Delta M_L=0,\pm1$, hold for the Hamiltonian we use. Moreover, given $\gamma LS$ and $\gamma', L'(=L-1,L,L+1), S'(=S)$, as a consequence of the Wigner-Eckart theorem,[26] every nonvanishing matrix element of the operator $\vec{P}$ can be expressed in terms of a single parameter $\beta(\gamma LS;\gamma' L'S')$ multiplied by expressions involving only $L$, $M_L$, and $M_{L'}$. The parameter is independent of the quantum numbers $M_L$, $M_{L'}$, $M_S$, and $M_{S'}$, the summation indices occurring in Eq. (6). Consequently, the expressions for the multiplet oscillator strength may be written as products of a parameter $\beta(\gamma LS;\gamma' L'S')$ and a single algebraic function of $L$ and $S$ resulting from the summation. Finally, notice that only one nonvanishing matrix element need be evaluated to determine a $\beta(\gamma LS;\gamma' L'S')$, so that instead of computing all the matrix elements occurring in the summations occurring in Eq. (6), a single matrix element suffices to find the multiplet oscillator strength for given $\gamma LS, \gamma' L'S'$.

For the $1s^22s\,{}^2S$-$1s^22p\,{}^2P$ transition, the ${}^2S$ term consists of two states with $L=M_L=0$, $S=\frac{1}{2}$, $M_S=\frac{1}{2},-\frac{1}{2}$. The ${}^2P$ term consists of six states corresponding to $S=\frac{1}{2}$, $M_S=\frac{1}{2}$, $-\frac{1}{2}$, $L'=1$, and $M_{L'}=-1,0,1$. We choose to express $(\gamma LS\rightarrow\gamma' L'S')$ in terms of the matrix element corresponding to the ${}^2S$ state with $M_S=\frac{1}{2}$ and the ${}^2P$ state with $S'=M_{S'}=\frac{1}{2}$, $L'=1$, and $M_{L'}=0$. Then Eq. (6) becomes (unnormalized wave functions), from Goldberg,[27]

$$S(\gamma\,{}^2S;\gamma'\,{}^2P)=3\left|\frac{\int dx_1\ldots dx_n\,\psi_\gamma^*({}^2S,M_S=\frac{1}{2})\vec{P}\psi_{\gamma'}({}^2P,M_{L'}=0,M_{S'}=\frac{1}{2})}{[\langle\psi_\gamma({}^2S,M_S=\frac{1}{2})\,|\,\psi_\gamma({}^2S,M_S=\frac{1}{2})\rangle\langle\psi_{\gamma'}({}^2P,M_{L'}=0,M_{S'}=\frac{1}{2})\,|\,\psi_{\gamma'}({}^2P,M_{L'}=0,M_{S'}=\frac{1}{2})\rangle]}\right|^2, \tag{8}$$

and we need only construct $\psi_\gamma({}^2S,M_S=\frac{1}{2})$ and $\psi_{\gamma'}({}^2P,M_{L'}=0,M_{S'}=\frac{1}{2})$ and evaluate Eq. (8) to compute $S$.

It is generally known[28] that with $\psi_\gamma LSM_LM_S$ as exact eigenfunctions of $H$ [Eq. (5)], the commutation relations of $H$ with $\vec{P}$ (dipole-length operator) lead to two additional relations for $(\gamma LS;\gamma' L'S')$,[8] which arise from the use of the dipole-velocity and dipole-acceleration operators given by

$$\vec{\nabla}=\sum_{i=1}^{N}\vec{\nabla}_i \tag{9}$$

and

$$\vec{A}=\sum_{i=1}^{N}\frac{Ze^2\vec{r}_i}{|\vec{r}_i|^3}, \tag{10}$$

respectively. These three formulas are equivalent when one uses exact eigenfunctions of $H$ [Eq. (5)] or of an independent-electron central-field-model Hamiltonian. However, they disagree whenever the eigenfunctions of a central-field model are improved by including some correlation, even by only the Hartree-Fock (HF) procedure.[29] It has been generally argued[8] that, since the acceleration operator contains terms behaving as $1/r^2$, the dipole-acceleration form is most sensitive to the accuracy of the wave function in the immediate neighborhood of the nucleus, so that oscillator strengths computed with variationally stable approximate wave functions (emphasizing more distant regions) are not reliably given in terms of this operator. Since the dipole-length and dipole-velocity forms should agree as the wave function approaches the exact eigenfunction, some authors have taken the closeness of agreement of $S$ computed with dipole-length and dipole-velocity operators as a measure of the accuracy of their computation of $S$, but there is now abundant evidence that this procedure is not very reliable.[30] In the present work, we compute upper and lower bounds to the operator and use these theoretical bounds as a measure of the accuracy of the $f$ value; we compute values in terms of the dipole-length operator as given by Eq. (8).[31]

To evaluate Eq. (8), we define

$$\begin{aligned} x_0(i) &= Z_i = r_i \cos\theta_i = a r_i Y_{1,0}(i) , \\ x_{+1}(i) &= -\,2^{-1/2}(x_i + i y_i) = a r_i Y_{1,1}(i) , \\ x_{-1}(i) &= 2^{-1/2}(x_i - i y_i) = a r_i Y_{1,-1}(i) , \end{aligned} \tag{11}$$

where $a = (\frac{4}{3}\pi)^{1/2}$ and the $Y_{l,m}$ are the same as in Eq. (4). Let

$$X_0 = \sum_{i=1}^{N} x_0(i), \quad X_{-1} = \sum_i x_{-1}(i), \quad X_1 = \sum_i x_1(i) . \tag{12}$$

Then[32]

$$|\vec{\mathrm{P}}|^2 = |X_0|^2 + |X_{-1}|^2 + |X_1|^2 . \tag{13}$$

Since $x_j(i) = \pm [2,1,j]_0^i$ in terms of unnormalized STO's defined by

$$[n,l,m]_\xi^i = r_i^{n-1} e^{-\xi r_i} Y_{l,m}(i) , \tag{14}$$

we obtain, for $S$,

$$S(\gamma\,{}^2S;\gamma'\,{}^2P) = (\tfrac{4}{3}\pi)3 \sum_{j=-1}^{1} \left| \int dx_1 \ldots dx_n \, \psi_\gamma^*({}^2S, M_S = \tfrac{1}{2}) \sum_{i=1}^{N} [2,1,j]_0^i \psi_{\gamma'}({}^2P, M_{L'} = 0, M_{S'} = \tfrac{1}{2}) \right|^2 \tag{15}$$

$$= 4\pi(|\tilde{W}_{-1}|^2 + |\tilde{W}_0|^2 + |\tilde{W}_{+1}|^2) = 4\pi|\tilde{W}_0|^2 , \tag{16}$$

owing to symmetry. ($j$ must equal 0 or the integral vanishes.) In writing Eq. (15), we have assumed that $\psi_\gamma$ and $\psi_{\gamma'}$ are normalized ($\langle\psi_\gamma|\psi_\gamma\rangle = 1$), and $|\tilde{W}_j|$ is defined by

$$|\tilde{W}_j| = \left| \int dx_1 \ldots dx_n \, \psi_\gamma^*({}^2S, M_S = \tfrac{1}{2}) \times \sum_{i=1}^{N} [2,1,j]_0^i \psi_{\gamma'}({}^2P, M_{L'} = 0, M_{S'} = \tfrac{1}{2}) \right| . \tag{17}$$

To evaluate Eq. (16), we use the fact that the wave functions employed to evaluate Eq. (16) are given by Eq. (1) and are linear combinations of antisymmetrized projected products of orbitals and interelectronic coordinates. Thus

$$|\tilde{W}_j| = \sum_{K,L} C_K C_L |\tilde{W}_j|_{KL} , \tag{18}$$

where

$$|\tilde{W}_j|_{KL} = \left\langle \Phi_K \left| \sum_{i=1}^{N} [2,1,j]_0^i \right| \Phi_L \right\rangle . \tag{19}$$

In Eq. (19), $\Phi_L$ is a linear combination of orbitals and interelectronic coordinates, so that Eq. (19) can be evaluated by expanding the product of $[2,1,j]_0^i$ and the appropriate STO of $\Phi_L$ in terms of STO's by the formulas given in a previous paper.[33]

Then the integrals required to evaluate Eq. (16) are similar in type to those required to calculate overlap matrix elements using these wave functions and can be evaluated as described later.

### C. Upper and lower bounds to oscillator strengths

Weinhold[14] has described a procedure for calculating rigorous upper and lower bounds to dipole strengths. If the exact transition moment is

$$W_{ab} = \langle \Psi_a | W_l | \Psi_b \rangle , \tag{20}$$

where $\Psi_a$ and $\Psi_b$ are the exact wave functions for states $a$ and $b$, respectively, and $W_l$ is some particular Cartesian component of the vector operator $\vec{\mathrm{P}}$, then Weinhold's formula in terms of the estimate

$$\tilde{W}_{ab} = \langle \psi_a | W_l | \psi_b \rangle , \tag{21}$$

where $\psi_a$ and $\psi_b$ are the approximate wave functions for states $a$ and $b$, respectively, is

$$W_{ab} \gtreqless S_{a\pm} S_{b\pm} \tilde{W}_{ab} \pm \epsilon_{a+} S_{b\pm} \Delta_{ab} \pm \epsilon_{b+} [\langle \Psi_a | W_l^2 | \Psi_a \rangle_+ - (S_{a-} \tilde{W}_{ab} - \epsilon_{a+} \Delta_{ab})^2]^{1/2} . \tag{22}$$

Here $S_a \equiv \langle \psi_a | \Psi_a \rangle$, $S_b \equiv \langle \psi_b | \Psi_b \rangle$, i.e., the (positive) overlap integrals of the approximate wave functions $\psi_a, \psi_b$ with the true wave functions $\Psi_a, \Psi_b$, and

$\epsilon_{a+}, \epsilon_{b+}$ are simply

$$\epsilon_{a+} \equiv (1 - S_{a-}^2)^{1/2}, \quad \epsilon_{b+} \equiv (1 - S_{b-}^2)^{1/2} ,$$

and $\Delta_{ab}$ is defined by

$$\Delta_{ab} \equiv (\langle \psi_b | W_l^2 | \psi_b \rangle - \tilde{W}_{ab}^2)^{1/2} . \tag{23}$$

In Weinhold's scheme, $\tilde{W}_{ab}$ and $\langle \psi_b | W_l^2 | \psi_b \rangle$ are computed directly. Without loss of rigor, $S_{a+}, S_{b+}$ may be taken to be 1, and for $\Psi_a, \Psi_b$, the lowest states of their respective symmetries, we can use the "Eckart criterion" to determine $S_{a-}, S_{b-}$; e.g.,

$$S_{a-}^2 = (E_a^* - \langle \psi_a | H | \psi_a \rangle)/(E_a^* - E_a) , \tag{24}$$

where $E_a$ and $E_a^*$ are the ground- and excited-state energy (with the same symmetry as the ground state) of the system with Hamiltonian $H$. The remaining unknown of relation (22) is the upper bound $\langle \Psi_a | W_l^2 | \Psi_a \rangle_+$. Weinhold presents several formulas for its treatment; we take

$$\langle \Psi_a | W_l^2 | \Psi_a \rangle \approx \langle \psi_a | W_l^2 | \psi_a \rangle , \tag{25}$$

where $\psi_a$ is our highly accurate "$S$" wave function. With $|\tilde{W}_j|$'s defined by Eq. (17), we have that

$$S(\gamma\, {}^2S; \gamma'\, {}^2P) = 4\pi |\tilde{W}_0|^2 = 3 \tilde{W}_{ab}^2 , \tag{26}$$

so that

$$|\tilde{W}_0| = (3/4\pi)^{1/2} \tilde{W}_{ab} . \tag{27}$$

Relation (22) holds for $|\tilde{W}_0|$ in place of $\tilde{W}_{ab}$ if we compute $\langle \Psi_a | W_l^2 | \Psi_a \rangle$ by relation (25) and multiply by $3/4\pi$ to account for the difference between $|\tilde{W}_0|$ and $\tilde{W}_{ab}$ given by Eq. (27). Also, the only remaining unknown in the calculation of upper and lower bounds to $|\tilde{W}_0|$ is $\langle \psi_b | W_l^2 | \psi_b \rangle$.

With the aid of[33]

$$\left.\begin{aligned} [2,1,j]_0^{i*}[2,1,j]_0^i &= \sum_{P_a=0}^{1} r_i^2 [(2l_1+1)/(4\pi)]^{1/2} C^{l_1}(1,j;1,j) Y_{l_1,0} \\ &= \sum_{P_a=0}^{1} [(2l_1+1)/(4\pi)]^{1/2} C^{l_1}(1,j;1,j)[3,l_1,0]_0^i \end{aligned}\right\} \quad (l_1 = 2 - 2P_a) , \tag{28}$$

we obtain

$$\langle \psi_0 | (3/4\pi) X_0 X_0 | \psi_b \rangle = \sum_{i=1}^{3} \sum_{P_a=0}^{1} [(2l_1+1)/4\pi]^{1/2} C^{l_1}(1,0;1,0) \langle \psi_b | [3,l_1,0]_0^i | \psi_b \rangle + \sum_{\substack{i,k \\ i\neq k}} \langle \psi_b | [2,1,0]_0^{i*}[2,1,0]_0^k | \psi_b \rangle . \tag{29}$$

Here $C^L(l',m';l,m)$ is the Condon-Shortley coefficient[21] defined by

$$C^L(l',m';l,m) = [4\pi/(2L+1)]^{1/2} \int Y_L^{m'-m}(\theta,\varphi) Y_{l'}^{m'*}(\theta,\varphi) Y_l^m(\theta,\varphi) \sin\theta \, d\theta \, d\varphi .$$

The matrix elements in Eq. (29) are handled similarly to the way $|\tilde{W}_j|$ was treated earlier.

## III. RESULTS

### A. Oscillator strengths

The wave functions employed here for the ${}^2S$ and ${}^2P$ states are the 150-term ${}^2S$ wave functions reported previously[11] and 120-term ${}^2P$ functions, similar to the ones reported previously.[11] The results of the calculations we have done are presented in Table I, where we tabulate $|\tilde{W}_0|$, the absolute multiplet strength $S$, the $f$ values, term energies, the relative term energy $\Delta E = E({}^2P) - E({}^2S)$, and various quantities related to the calculation of upper and lower bounds to $f$. In evaluating $S_{a-}$ and $S_{b-}$, rather than Eq. (24), Weinberger's formula[34] was used,

$$S^2 \geq \frac{E_{n+1} - J_0}{E_{n+1} - E_0} \prod_{v=1}^{n} \frac{E_v - J_0}{E_v - E_0} \frac{J_v - E_0}{J_v - J_0} , \tag{30}$$

where $E_0, E_1, \ldots, E_{n+1}$ are the $n+2$ lowest eigenvalues of $H$ and the $J_i$ are the corresponding Rayleigh-Ritz estimates $\langle \phi_i | H | \phi_i \rangle$. Here the $\phi_i$ are approximations to the exact eigenfunctions and it is assumed that

$$E_0 \leq J_0 \leq E_1 \leq J_1 \leq \ldots \leq E_n \leq J_n \leq E_{n+1} . \tag{31}$$

Overlaps calculated with inequality (30) gave significant improvement over those obtained using the well-known Eckart criterion [Eq. (24)]; in addition, formula (30) is applicable to excited states for which Eckart's formula is no longer valid. To use either Eq. (24) or (30), one must know either the nonrelativistic energies $E$ or their lower bounds. For the Li ground state, the value given by Larsson was used.[35] To obtain the nonrelativistic energy estimate for the other states, we add the experimentally determined relative term energies to the ground-state estimate. The values we used for the estimated exact nonrelativistic en-

TABLE I. Numerical values (in a.u.) for various quantities related to the calculation of $f$ values and upper and lower bounds to $f$ values (see text).

| States | $\lvert\tilde{W}_0\rvert$ | $S$ | $f$ | $E(^2S)$ | $E(^2P)$ | $\Delta E$ (expt)[a, b] |
|---|---|---|---|---|---|---|
| $2\,^2S \rightarrow 2\,^2P$ | 1.146 33 | 33.026 | 0.747 59 | −7.478 023 | −7.410 05 | 0.067 909 |
| $3\,^2S \rightarrow 2\,^2P$ | 0.841 45 | −17.795 | −0.332 53 | −7.354 10 | −7.410 05 | 0.056 06 |
| $4\,^2S \rightarrow 2\,^2P$ | 0.223 86 | −1.2595 | −0.038 47 | −7.318 40 | −7.410 05 | 0.091 63 |
| $5\,^2S \rightarrow 2\,^2P$ | 0.120 15 | −0.362 83 | −0.012 89 | −7.303 40 | −7.410 05 | 0.106 61 |
| $2\,^2S \rightarrow 3\,^2P$ | 0.062 71 | 0.098 842 | 0.004 64 | −7.478 023 | −7.337 00 | 0.140 909 |
| $3^2S \rightarrow 3\,^2P$ | 2.924 15 | +214.90 | 1.213 48 | −7.354 10 | −7.337 00 | 0.016 94 |
| $4\,^2S \rightarrow 3\,^2P$ | 2.074 41 | −108.15 | −0.671 62 | −7.318 40 | −7.337 00 | 0.018 63 |
| $5\,^2S \rightarrow 3\,^2P$ | 0.525 32 | −6.9357 | −0.077 70 | −7.303 40 | −7.337 00 | 0.033 61 |
| $2\,^2S \rightarrow 4\,^2P$ | 0.055 085 | 0.076 26 | 0.004 224 | −7.478 023 | −7.311 74 | 0.166 17 |
| $3\,^2S \rightarrow 4\,^2P$ | 0.009 548 | 0.002 29 | $3.223 \times 10^{-5}$ | −7.354 10 | −7.311 74 | 0.042 20 |
| $4\,^2S \rightarrow 4\,^2P$ | 5.427 03 | +740.228 | 1.6359 | −7.318 40 | −7.311 74 | 0.006 63 |
| $5\,^2S \rightarrow 4^2P$ | 3.803 77 | −363.637 | −1.012 12 | −7.303 40 | −7.311 74 | −0.008 35 |
| $2\,^2S \rightarrow 5\,^2P$ | 0.041 38 | 0.043 03 | 0.002 55 | −7.478 023 | −7.300 14 | 0.177 76 |
| $3\,^2S \rightarrow 5\,^2P$ | 0.052 48 | 0.069 22 | 0.001 24 | −7.354 10 | −7.300 14 | 0.053 80 |
| $4\,^2S \rightarrow 5\,^2P$ | 0.081 69 | −0.178 05 | 0.001 08 | −7.318 40 | −7.300 14 | 0.018 23 |
| $5\,^2S \rightarrow 5\,^2P$ | 8.664 76 | −1886.91 | 2.044 16 | −7.303 40 | −7.300 14 | 0.003 25 |

| States | $\langle\Psi_b\rvert\,(3/4\pi)x_0^2\lvert\Psi_b\rangle$ | $S_{a-}$ | $S_{b-}$ | $\epsilon_{a+}$ | $\epsilon_{b+}$ | $\Delta_{ab}$ |
|---|---|---|---|---|---|---|
| $2\,^2S \rightarrow 2\,^2P$ | 4.0446 | 0.999 873 | 0.999 531 | 0.011 237 | 0.021 659 | 1.652 44 |
| $3\,^2S \rightarrow 2\,^2P$ | 4.0446 | 0.999 220 | 0.999 531 | 0.027 935 | 0.021 659 | 1.826 63 |
| $4\,^2S \rightarrow 2\,^2P$ | 4.0446 | 0.997 081 | 0.999 531 | 0.054 031 | 0.021 659 | 1.998 62 |
| $5\,^2S \rightarrow 2\,^2P$ | 4.0446 | 0.990 153 | 0.999 531 | 0.099 230 | 0.021 659 | 2.007 53 |
| $2\,^2S \rightarrow 3\,^2P$ | 24.2298 | 0.999 873 | 0.998 079 | 0.011 237 | 0.043 825 | 4.921 98 |
| $3\,^2S \rightarrow 3\,^2P$ | 24.2298 | 0.999 220 | 0.998 079 | 0.027 935 | 0.043 825 | 3.959 69 |
| $4\,^2S \rightarrow 3\,^2P$ | 24.2298 | 0.997 081 | 0.998 079 | 0.054 031 | 0.043 825 | 4.463 93 |
| $5\,^2S \rightarrow 3\,^2P$ | 24.2298 | 0.990 153 | 0.998 079 | 0.099 230 | 0.043 825 | 4.894 27 |
| $2\,^2S \rightarrow 4\,^2P$ | 82.0183 | 0.999 873 | 0.995 397 | 0.011 237 | 0.067 841 | 9.056 23 |
| $3\,^2S \rightarrow 4\,^2P$ | 82.0183 | 0.999 220 | 0.995 397 | 0.027 935 | 0.067 841 | 9.056 39 |
| $4\,^2S \rightarrow 4\,^2P$ | 82.0183 | 0.997 081 | 0.995 397 | 0.054 031 | 0.067 841 | 7.250 21 |
| $5\,^2S \rightarrow 4\,^2P$ | 82.0183 | 0.990 153 | 0.995 397 | 0.099 230 | 0.067 841 | 8.218 86 |
| $2\,^2S \rightarrow 5\,^2P$ | 207.645 | 0.999 873 | 0.987 054 | 0.011 237 | 0.113 77 | 14.409 832 |
| $3\,^2S \rightarrow 5\,^2P$ | 207.645 | 0.999 220 | 0.987 054 | 0.027 935 | 0.113 77 | 14.409 796 |
| $4\,^2S \rightarrow 5\,^2P$ | 207.645 | 0.997 081 | 0.987 054 | 0.054 031 | 0.113 77 | 14.409 646 |
| $5\,^2S \rightarrow 5\,^2P$ | 207.645 | 0.990 153 | 0.987 054 | 0.099 230 | 0.113 77 | 11.513 768 |

TABLE I. *(continued)*

| States | $f<$ | $f>$ | $f$ | % Error |
|---|---|---|---|---|
| $2\,^2S\rightarrow 2\,^2P$ | 0.7227 | 0.7720 | 0.7476 | ~3.5% |
| $3\,^2S\rightarrow 2\,^2P$ | −0.2927 | −0.3741 | −0.3325 | ~12% |
| $4\,^2S\rightarrow 2\,^2P$ | −0.0102 | −0.0845 | −0.0385 | ~100% |
| $5\,^2S\rightarrow 2\,^2P$ | −0.0057 | −0.0911 | −0.0129 | >100% |
| $2\,^2S\rightarrow 3\,^2P$ | 0.002 43 | 0.034 44 | 0.004 64 | >100% |
| $3\,^2S\rightarrow 3\,^2P$ | 1.117 28 | 1.307 02 | 1.213 48 | ~7.5% |
| $4\,^2S\rightarrow 3\,^2P$ | −0.519 06 | −0.836 87 | −0.671 62 | ~24% |
| $5\,^2S\rightarrow 3\,^2P$ | −0.040 95 | −0.573 18 | −0.077 70 | >100% |
| $2\,^2S\rightarrow 4\,^2P$ | 0.003 006 | 0.034 248 | 0.004 224 | >100% |
| $3\,^2S\rightarrow 4\,^2P$ | 0 | 0.024 367 | $3.223\times 10^{-5}$ | >100% |
| $4\,^2S\rightarrow 4\,^2P$ | 1.386 56 | 1.880 59 | 1.6359 | 15% |
| $5\,^2S\rightarrow 4\,^2P$ | −0.603 48 | −1.492 67 | −1.012 12 | ~50% |
| $2\,^2S\rightarrow 5\,^2P$ | 0 | 0.061 56 | 0.002 55 | >100% |
| $3\,^2S\rightarrow 5\,^2P$ | 0 | 0.093 32 | 0.001 24 | >100% |
| $4\,^2S\rightarrow 5\,^2P$ | 0 | 0.113 67 | 0.001 08 | >100% |
| $5\,^2S\rightarrow 5\,^2P$ | 1.211 43 | 2.988 98 | 2.044 16 | ~50% |

[a] This is the $\Delta E$ value used in computing $f$ values.

[b] $\Delta E = E(^2P) - E(^2S)$.

ergies are tabulated in Table II along with our computed results.

In Table III we present our direct calculation of the transition moment $\tilde{W}_{ab}$, together with the calculated $f$ value and the calculated error bounds $f\pm$. For comparison we also list the results of previous workers. Note that for the $n\,^2S\rightarrow 2\,^2P$ results, our $f$ values agree most closely with the length results of Ahlenius and Larsson[36] (AL) for the $1s^22s\rightarrow 1s^22p$ transition, and with the velocity results of AL for the other three transitions. If we assume our results to be essentially exact, these results then agree nicely with Crossley's[3] general recommendations concerning the choice between length and velocity formulas for less than exact wave functions. Crossley[3] suggested that for small transition energies, and, in particular, when there is no change in the principal quantum number of the active electron, the length formula is to be preferred, whereas for higher energies, the velocity results are to be preferred.

In examining the $2\,^2S\rightarrow 3\,^2P$ transition, we note that our results tend to confirm previous conjectures[16] that the agreement between length and velocity Hartree-Fock calculations is both fortuitous and wrong, our value of 0.0046 a.u. agreeing more closely with the experimental value of[37] 0.0055 than with the HF results.

Most of our computed $f$ values agree to within (2–4)% of the National Standards Reference Data Service recommended values,[4] the notable exceptions being $2\,^2S\rightarrow 3\,^2P$ ($\approx$18%), $2\,^2S\rightarrow 4\,^2P$ ($\approx$12%), $3\,^2S\rightarrow 4\,^2P$ ($\approx$70%), $2\,^2S\rightarrow 5\,^2P$ ($\approx$24%), and $4\,^2S\rightarrow 5\,^2P$. These are all cases of small transition probabilities, which make them difficult to observe experi-

TABLE II. Exact (nonrelativistic) and computed energies for various Li I $^2S$ and $^2P$ states (in a.u.).

| | Computed | Exact |
|---|---|---|
| $2\,^2S$ | −7.478 023 | −7.478 069 |
| $3\,^2S$ | −7.354 01 | −7.354 10 |
| $4\,^2S$ | −7.318 40 | −7.318 53 |
| $5\,^2S$ | −7.303 40 | −7.303 55 |
| $2\,^2P$ | −7.410 05 | −7.410 16 |
| $3\,^2P$ | −7.337 00 | −7.337 16 |
| $4\,^2P$ | −7.311 74 | −7.311 90 |
| $5\,^2P$ | −7.300 14 | −7.300 30 |
| $6\,^2P$ | −7.293 25 | −7.294 03 |

TABLE III. Calculated transition moments $\tilde{W}_{ab}$ and rigorous error bounds for oscillator strengths in various Li I $^2S\rightarrow{}^2P$ transitions. $F$ values determined by previous workers are included for comparison.

| | | | | | Weiss[a] | | AL[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| Transition | $\tilde{W}_{ab}$ | $f-$ | $f+$ | $f-$ | $(l)$[c] | $(v)$[c] | $(l)$ | $(v)$ | NSRDS[d] |
| $2\,^2S\rightarrow 2\,^2P$ | 1.146 33 | 0.7227 | 0.7720 | 0.7476 | 0.753 | 0.772 | 0.748 | 0.758 | 0.753 |
| $3\,^2S\rightarrow 2\,^2P$ | 0.841 45 | −0.2927 | −0.3741 | −0.3325 | −0.346 | −0.342 | −0.323 | −0.336 | −0.345 |
| $4\,^2S\rightarrow 2\,^2P$ | 0.223 86 | −0.0102 | −0.0845 | −0.0385 | (H.F.)[e] | | −0.045 | −0.039 | −0.038 |
| $5\,^2S\rightarrow 2\,^2P$ | 0.120 15 | −0.0057 | −0.0911 | −0.0129 | | | −0.013 | −0.013 | −0.0126 |
| $2\,^2S\rightarrow 3\,^2P$ | 0.062 71 | | | 0.004 64 | 0.0027<br>(H.F.) | 0.0026 | | | 0.0055 |
| $3\,^2S\rightarrow 3\,^2P$ | 2.924 15 | 1.117 28 | 1.307 02 | 1.213 48 | 1.226<br>(H.F.) | 1.256 | | | 1.23 |
| $4\,^2S\rightarrow 3\,^2P$ | 2.074 41 | −0.519 06 | −0.836 87 | −0.671 62 | | | | | −0.669 |
| $5\,^2S\rightarrow 3\,^2P$ | 0.525 32 | | | −0.077 70 | | | | | −0.0762 |
| $2\,^2S\rightarrow 4\,^2P$ | 0.055 09 | | | 0.004 22 | | | | | 0.0048 |
| $3\,^2S\rightarrow 4\,^2P$ | 0.009 55 | | | $3.223\times10^{-5}$ | | | | | $1.93\times10^{-4}$ |
| $4\,^2S\rightarrow 4\,^2P$ | 5.427 03 | | | 1.6359 | | | | | 1.63 |
| $5\,^2S\rightarrow 4\,^2P$ | 3.803 77 | | | −1.012 12 | | | | | −1.005 |
| $2\,^2S\rightarrow 5\,^2P$ | 0.041 38 | | | 0.002 55 | | | | | 0.0032 |
| $3\,^2S\rightarrow 5\,^2P$ | 0.052 48 | | | 0.001 24 | | | | | |
| $4\,^2S\rightarrow 5\,^2P$ | 0.081 69 | | | 0.001 08 | | | | | $5.81\times10^{-4}$ |
| $5\,^2S\rightarrow 5\,^2P$ | 8.664 76 | | | 2.044 16 | | | | | 2.05 |

[a] Reference 16.

[b] Reference 36.

[c] $l$ = dipole length results. $v$ = dipole velocity.

[d] Reference 4.

[e] Hartree Fock results.

mentally and, on the theoretical side, there presumably is a large cancellation within the integrand of the transition integral which apparently brings one well into the region of inaccuracy of Hartree-Fock and other less accurate wave function calculations than ours.

### B. Error analysis

In most of the transitions that we have calculated $f$ values and bounds for, the term in brackets in Eq. (22) is small enough so that, approximately,

$$W_{ab} \lesseqgtr S_{a\pm}S_{b\pm}\tilde{W}_{ab} \pm \epsilon_{a+}S_{b\pm}\Delta_{ab}\,. \tag{32}$$

$S_{a+}$ and $S_{b+}$ may be rigorously taken to be unity, and for all our calculations $S_{a-}$ and $S_{b-}$ are close to unity so that

$$W_{ab} \approx \lesseqgtr \tilde{W}_{ab} \pm \epsilon_{a+}\Delta_{ab}\,, \tag{33}$$

which provides a useful breakdown of the total error.

Consider, for example, the 150-term Li $^2S$ 120-term Li $^2P$ results for $2\,^2S\rightarrow 2\,^2P$. Here

$$W_{ab} \leqslant \tilde{W}_{ab} + \epsilon_{a+}\Delta_{ab}\,,$$

and $\epsilon_{a+}=0.011237$, which was computed from $S_{a-}=0.999873$ obtained by using Weinberger's Eq. (30). For comparison, the simple Eckart formula, Eq. (24), gave $S_{a-}=-0.99981$ and $\epsilon_{a+}=0.019238$, so using Weinberger's formula, which is a novel feature of the present calculations since we have three very accurate $^2S$ excited states in the present calculations, improves the $\epsilon_{a+}$ calculation by 24%. Then $\Delta_{ab}=1.65244$, so $\epsilon_{a+}\Delta_{ab}=0.0188$ and $W_{ab}\leqslant 1.146+0.019$, so that the transition moment bound is good in an absolute sense. However, the $f$-value upper and lower bounds are 3.5% even for these high-quality wave functions. For the other $2\,^2S\rightarrow m\,^2P$ transitions, $\Delta_{ab}$ does not change much, but $\epsilon$ gets much worse due to the higher $^2S$ roots not being obtained as accurately as the lowest $^2S$ state, and there are fewer interleaving higher roots for Weinberger formula calculations. Also, the transitions become weaker so that the relative error becomes greater, even if the absolute size of the energy error is not much changed.

For the $n\,^2S \rightarrow 3\,^2P$ sequence, there is a strong $3\,^2S \rightarrow 3\,^2P$ transition, but the $3\,^2P$ state is much more diffuse than the $2\,^2P$ state, leading to a larger $\Delta_{ab}$ and bounds of 7.5% in this case. This trend continues for the strong transitions in the $n\,^2S \rightarrow 4\,^2P$ and $n\,^2S \rightarrow 5\,^2P$ sequences, with the bounds for even the strong transitions getting progressively worse.

## IV. DISCUSSION

Wave functions obtained by combined configuration-interaction-Hylleraas-method techniques for the four lowest $^2S$ and four lowest $^2P$ states of Li*I* have been employed in calculating oscillator strengths for the 16 lines arising from allowed transitions among these four $^2S$ and four $^2P$ states. In view of the high quality of these wave functions (on an energy level criterion), the $f$ values obtained are of presumably high quality. Upper and lower bounds[38] are also computed for these $f$ values, which in the best case ($1s^22s\,^2S \rightarrow 1s^22p\,^2P$) are 3.5%.

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[24] Actually the configuration designation is rigorous only for Russell-Saunders (LS) coupling in a central field. We retain the terminology here to conform to standard spectroscopic notation with the understanding that by $1s^22s\,^2S$ and $1s^22p\,^2P$ we mean the lowest terms of those respective symmetries. For a generalization of the multiplet strength form with interacting configurations see, e.g., R. N. Zare, [J. Chem. Phys. 47, 3561 (1967)].

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$\gamma$, $L$, $S$, a computed term separation $\Delta E = E(\gamma' L' S') - E(\gamma L S)$ can be obtained by merely subtracting the two appropriate energy values obtained with the wave functions we use.

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