

## Theoretical lithium $2^2S \rightarrow 2^2P$ and $2^2P \rightarrow 3^2D$ oscillator strengths

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The oscillator strengths for the lithium  $2^2S \rightarrow 2^2P$  and  $2^2P \rightarrow 3^2D$  transitions are calculated to high precision using variational wave functions in Hylleraas coordinates. The calculated oscillator strengths for these transitions are 0.746 957 2(10) and 0.638 570 5(30), respectively. The results resolve disagreements among existing theoretical values and provide definitive predictions. A discrepancy of five standard deviations between the theoretical value and the most accurate measurement of Gaupp *et al.* [Phys. Rev. A **26**, 3351 (1982)] for the  $2^2S \rightarrow 2^2P$  transition remains.

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### I. INTRODUCTION

A long-standing controversy surrounds the oscillator strength for the  $2^2S-2^2P$  resonant transition of lithium. In the case of the  $\text{He}^+ 2p-1s$  transition, where the wave functions are exactly known, theory and experiment agree at the  $\pm 0.075\%$  level [1]. However, for the lithium transition, many calculations yield a value about five standard deviations larger than the  $\pm 0.16\%$  measurement of Gaupp *et al.* [2], but none is sufficiently accurate to be definitive. The results vary over a considerable range (see Table II), and a comparison of the length and velocity forms (when applicable) suggests uncertainties much less than the differences among different calculations. Recent attempts to confirm the experimental value of Gaupp *et al.* have also fallen short of the required accuracy. Carlsson and Sturesson measured the  $2^2P$  lithium lifetime using the delayed coincidence technique [3], from which the oscillator strength can be derived with an uncertainty of 0.74%. Very recently, McAlexander *et al.* [4] extracted a value for the  $2^2P$  lifetime from their photoassociative spectroscopy of ultracold lithium. The uncertainty obtained is 0.59%. For the lithium  $3^2D$  lifetime measurements [5–7], the uncertainty for the most accurate measurement of Schulze-Hagenest *et al.* [5] is 0.9%. The lithium problem is particularly important because of its potential usefulness as a standard of reference for other oscillator strength and lifetime measurements, and as a test of various approximation methods in many-body systems.

The purpose of this Rapid Communication is to report the results of a high precision calculation that establishes a definitive value for the  $2^2S-2^2P$  and  $2^2P-3^2D$  oscillator strengths in the nonrelativistic limit. The calculation is based upon variationally constructed wave functions using multiple basis sets in Hylleraas coordinates [8]. These have been shown previously [8,9] to yield a dramatic improvement in the convergence accuracy of the energies for the  $2^2S$ ,  $2^2P$ , and  $3^2D$  states to a few parts in  $10^{10}$  to  $10^{11}$ . This represents an improvement of three or four orders of magnitude over the best previous calculations, as discussed in Ref. [8].

### II. THEORETICAL FORMULATION

We begin with a discussion of radiative transitions in atoms for the general case of a nucleus of charge  $Ze$  and mass

$M$ . The discussion clarifies and extends earlier derivations [10–12] in order to obtain a generalized equivalence between the length and velocity forms of the transition operator. The proper starting point in the nonrelativistic limit is the minimal coupling Hamiltonian

$$H = \frac{1}{2M} \left[ \mathbf{P}_N - \frac{Ze}{c} \mathbf{A}(\mathbf{R}_N) \right]^2 + \frac{1}{2m} \sum_{i=1}^n \left[ \mathbf{P}_i + \frac{e}{c} \mathbf{A}(\mathbf{R}_i) \right]^2 + V(\mathbf{R}_i, \mathbf{R}_N), \quad (1)$$

where  $\mathbf{A}(\mathbf{r}) = c(2\pi\hbar/\omega\mathcal{V})^{1/2} \hat{\mathbf{e}} e^{i\mathbf{k}\cdot\mathbf{r}}$  is the time-independent part of the vector potential  $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}) e^{-i\omega t} + \text{c.c.}$  for a photon of frequency  $\omega$ , wave vector  $\mathbf{k}$ , and polarization  $\hat{\mathbf{e}} \perp \mathbf{k}$ , normalized to unit photon energy  $\hbar\omega$  in volume  $\mathcal{V}$ .  $\mathbf{R}_i$  and  $\mathbf{R}_N$  are the electronic and nuclear coordinates in an inertial frame. The  $\mathbf{P} \cdot \mathbf{A}$  linear coupling terms from Eq. (1) give the interaction Hamiltonian

$$H_{\text{int}} = -\frac{Ze}{Mc} \mathbf{P}_N \cdot \mathbf{A}(\mathbf{R}_N) + \frac{e}{mc} \sum_{i=1}^n \mathbf{P}_i \cdot \mathbf{A}(\mathbf{R}_i), \quad (2)$$

and from Fermi's golden rule, the decay rate for spontaneous emission from state  $\gamma$  to state  $\gamma'$  is

$$w_{\gamma\gamma'} d\Omega = \frac{2\pi}{\hbar} |\langle \gamma | H_{\text{int}} | \gamma' \rangle|^2 \rho_f, \quad (3)$$

where  $\rho_f = \mathcal{V} \omega^2 d\Omega / (2\pi c)^3 \hbar$  is the number of photon states with polarization  $\hat{\mathbf{e}}$  per unit energy and solid angle in the normalization volume  $\mathcal{V}$ . In the long wavelength and electric dipole approximations, the factor  $e^{i\mathbf{k}\cdot\mathbf{r}}$  in  $\mathbf{A}(\mathbf{r})$  is replaced by unity. After integrating over  $d\Omega$  and summing over polarizations, the decay rate reduces to

$$w_{\gamma\gamma'} = \frac{4}{3} \alpha \omega_{\gamma\gamma'} |\langle \gamma | \mathbf{Q}_p | \gamma' \rangle|^2, \quad (4)$$

where  $\mathbf{Q}_p$  is the dimensionless velocity form of the transition operator

$$\mathbf{Q}_p = -\left( \frac{Z}{Mc} \mathbf{P}_N - \frac{1}{mc} \sum_{i=1}^n \mathbf{P}_i \right). \quad (5)$$

The equivalent length form is

$$\mathbf{Q}_r = -\frac{i}{c} \omega_{\gamma\gamma'} \left( Z\mathbf{R}_N - \sum_{i=1}^n \mathbf{R}_i \right), \quad (6)$$

as follows from the commutator  $[H_0, \mathbf{Q}_r / \hbar \omega_{\gamma\gamma'}] = \mathbf{Q}_p$ , where  $H_0$  is the field-free Hamiltonian.

We now take the center of mass as the coordinate origin and introduce the relative electron coordinates  $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_N$ . Then, with the use of the identities

$$(M + nm)\mathbf{R}_N + m \sum_{i=1}^n \mathbf{r}_i = 0, \quad \mathbf{P}_N + \sum_{i=1}^n \mathbf{p}_i = 0, \quad (7)$$

the transition operators become

$$\mathbf{Q}_p = \frac{Z_p}{mc} \sum_{i=1}^n \mathbf{p}_i, \quad \mathbf{Q}_r = \frac{i\omega_{\gamma\gamma'}}{c} Z_r \sum_{i=1}^n \mathbf{r}_i, \quad (8)$$

with

$$Z_p = \frac{Zm + M}{M}, \quad Z_r = \frac{Zm + M}{nm + M}, \quad (9)$$

and  $H_0$  now contains the  $M^{-1} \sum_{i>j} \mathbf{p}_i \cdot \mathbf{p}_j$  mass polarization term. This must be included explicitly in the calculation of wave functions in order for the identity

$$\langle \gamma | \mathbf{Q}_p | \gamma' \rangle = \langle \gamma | \mathbf{Q}_r | \gamma' \rangle \quad (10)$$

to be satisfied beyond lowest order in  $m/M$ . This represents the generalization of the usual length and velocity forms of the dipole transition operator to the case of finite nuclear mass. The quantities  $-Z_r e$  and  $-Z_p e$  can be thought of as effective radiative charges, with  $Z_r = 1$  for neutral atoms.

Finally, if the oscillator strength for a  $\gamma L \rightarrow \gamma' L'$  transition is defined by

$$f(\gamma \rightarrow \gamma') = \frac{2m\omega_{\gamma\gamma'}}{3\hbar} \left( \frac{Z_r}{Z_p} \right) \left| \left\langle \gamma \left| \sum_{i=1}^n \mathbf{r}_i \right| \gamma' \right\rangle \right|^2 \\ = \frac{2}{3m\hbar\omega_{\gamma\gamma'}} \left( \frac{Z_p}{Z_r} \right) \left| \left\langle \gamma \left| \sum_{i=1}^n \mathbf{p}_i \right| \gamma' \right\rangle \right|^2, \quad (11)$$

then the Thomas-Reiche-Kuhn sum rule  $\sum_{\gamma'} f(\gamma \rightarrow \gamma') = n$  remains valid, independent of  $m/M$ .

### III. CALCULATIONS AND RESULTS

The variational wave functions used here are constructed from multiple basis sets in Hylleraas coordinates, as described in Ref. [8]. The explicit form for the wave functions is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \mathcal{A} \sum_t \sum_{\mu_t} a_{t, \mu_t} \phi_{t, \mu_t}(\alpha_t, \beta_t, \gamma_t) \\ \times (\text{angular function})(\text{spin function}), \quad (12)$$

where

$$\phi_{t, \mu_t}(\alpha_t, \beta_t, \gamma_t) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha_t r_1 - \beta_t r_2 - \gamma_t r_3}, \quad (13)$$

TABLE I. Convergence of lithium  $2^2S-2^2P$  and  $2^2P-3^2D$  oscillator strengths in length and velocity forms for the case of infinite nuclear mass.

No. of terms	$f$ (length)	$f$ (velocity)
$2^2S-2^2P$		
(18, 19)	0.744 774 4	0.773 465 8
(50, 55)	0.747 676 4	0.753 742 4
(120, 130)	0.747 036 8	0.748 054 7
(256, 306)	0.746 957 8	0.747 304 7
(502, 622)	0.746 957 5	0.747 072 1
(918, 1174)	0.746 958 7	0.747 004 8
(1589, 1715)	0.746 957 3	0.746 972 3
Extrapolation	0.746 957 2(10)	0.746 957 1(54)
$2^2P-3^2D$		
(19, 19)	0.636 902 7	0.634 764 7
(55, 57)	0.638 443 5	0.636 647 2
(138, 148)	0.637 675 7	0.638 558 7
(306, 340)	0.638 380 0	0.638 463 4
(622, 586)	0.638 560 3	0.638 576 5
(1174, 1002)	0.638 566 1	0.638 589 6
(1715, 1673)	0.638 568 4	0.638 583 1
Extrapolation	0.638 570 5(30)	0.638 579 3(60)

$\mu_t$  denotes a sextuple of integer powers  $j_1, j_2, j_3, j_{12}, j_{23}$ , and  $j_{31}$ , index  $t$  labels different sets of nonlinear parameters  $\alpha_t, \beta_t$ , and  $\gamma_t$ , and  $\mathcal{A}$  is the three-particle antisymmetrizer. Except for some truncations, all terms are included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega, \quad (14)$$

and the convergence studied as  $\Omega$  is progressively increased. A complete optimization is then performed with respect to all the nonlinear parameters. These techniques yield much improved convergence relative to single basis set calculations. The nonrelativistic energies obtained are  $-7.478\,060\,323\,10(31)$  a.u. for the  $1s^2 2s^2 S$  state,  $-7.410\,156\,521\,8(13)$  a.u. for the  $1s^2 2p^2 P$  state, and  $-7.335\,523\,541\,10(43)$  a.u. for the  $1s^2 3d^2 D$  state, respectively, which are the lowest upper bounds reported so far.

Table I contains the convergence studies of oscillator strengths in both length and velocity forms for the  $2^2S-2^2P$  and  $2^2P-3^2D$  transitions, as  $\Omega$  is progressively increased. The corresponding sizes of the basis sets are denoted by  $(N_1, N_2)$  in the first column, where  $N_1$  and  $N_2$  are the number of terms of the lower and upper states, respectively. The extrapolation to  $\Omega \rightarrow \infty$  is done by taking differences between successive calculations, and by assuming that these differences obey either  $b \exp(-a\Omega)$  or  $b\Omega^{-a}$  for large  $\Omega$ . The least-squares method is used to obtain the best-fit parameters  $a$  and  $b$ . The final extrapolated result is a weighted average of these two single extrapolations. Both the convergence with  $\Omega$  and the agreement between the length and velocity forms indicate an accuracy of about  $\pm 6 \times 10^{-6}$ , with the length form being apparently somewhat more accurate. The actual differences between the length and velocity forms lie within the range spanned by the estimated errors for each.

TABLE II. Comparison of lithium  $2^2S-2^2P$  oscillator strength. The numbers next to the authors' names are dates, i.e., (1973), etc.

Author	Method	Reference	$f$ (length)	$f$ (velocity)
	Theory			
Ahlenius and Larsson (73)	Hylleraas	[13]	0.748	0.758
Sims <i>et al.</i> (76)	CI-Hylleraas	[14]	0.747 59	
Lindgård and Nielsen (77)	Coulomb approx.	[15]	0.741 2	
Cheng <i>et al.</i> (79)	MCDF	[16]	0.765 6	
Fischer (88)	MCHF	[17]	0.747 97	0.748 71
Peach <i>et al.</i> (88)	Opacity project	[18]	0.747 5	
Blundell <i>et al.</i> (89)	MBPT	[19]	0.746 7	0.747 1
Mårtensson-Pendrill and Ynnerman (90)	Coupled-cluster	[20]	0.747 1	
Theodosiou and Curtis (91)	Coulomb approx.	[21]	0.741 45	
Weiss (92)	CI	[22]	0.747 8	0.749 8
Pipin and Bishop (92)	CI-Hylleraas	[23]	0.747 0	
Tong <i>et al.</i> (93)	MCHF	[24]	0.747 2	0.747 0
Chung (93)	FCPC	[25]	0.747 04	0.747 04
Ponomarenko and Shestakov (93)	Green function	[26]	0.754	
Brage and Fischer (94)	MCHF-CCP	[27]	0.747 2	
Barnett <i>et al.</i> (95)	QMC	[28]	0.743 1(6)	
This work ( $M = \infty$ )			0.746 957 2(10)	0.746 957 1(54)
This work (finite $M$ ) <sup>a</sup>			0.746 787 1(10)	0.746 789 2(54)
	Experiment			
Gaupp <i>et al.</i> (82)	Laser excitation	[2]	0.741 6(12)	
Carlsson and Sturesson (89)	Delayed coincidence	[3]	0.743 9(55)	
McAlexander <i>et al.</i> (95)	Photoassociation	[4]	0.750 2(44)	

<sup>a</sup>Result for  $^7\text{Li}$  with  $m/M = 7.820\,814\,7 \times 10^{-5}$ .

Table II lists a comparison of our values with other theoretical calculations, as well as with some experimental measurements, for the  $2^2S-2^2P$  transition. Earlier work on this subject may be found in Ref. [2] and has not been included in this table. Finite nuclear mass effects are accounted for by including the mass polarization term explicitly in the Hamiltonian. The tabulated results show that the length and velocity forms remain in good agreement when Eq. (11) is used for the case of finite nuclear mass. Relativistic corrections are expected to be less than 0.1%.

Although the experimental value of Carlsson and Sturesson is in agreement with the measurement of Gaupp *et al.*, the uncertainty is as large as  $\pm 0.0055$ . The experimental result of McAlexander *et al.* is consistent with the measurement of Carlsson and Sturesson, but lies above the quoted experimental error bar of Gaupp *et al.* Therefore, the more recent measurements tend to support a larger value for  $f$ . Also, with a few exceptions, most of the theoretical calculations are in disagreement with the experimental measurement of Gaupp *et al.*, with a discrepancy of more than four standard deviations. The exceptions include the results from Coulomb approximation calculations of Lindgård and Nielsen as well as Theodosiou and Curtis. A very recent quantum Monte Carlo calculation of Barnett *et al.* seems to support the experimental value of Gaupp *et al.* However, its claimed precision of  $\pm 0.0006$  for  $f$  places it in strong disagreement with the present work. The calculated lifetimes for the  $2^2P$  and  $3^2D$  states, together with the measurements for these states, are listed in Table III. For the  $3^2D$  state, our results are consistent with the theoretical result of Chung and the best measurement of Schulze-Hagenest *et al.*

#### IV. SUMMARY AND CONCLUSIONS

In this paper, the nonrelativistic oscillator strengths for the  $2^2S-2^2P$  and  $2^2P-3^2D$  transitions have been calculated to an accuracy of  $\pm 6 \times 10^{-6}$ . For the  $2^2S-2^2P$  transition, the results resolve disagreements among previous theoretical values, but a significant discrepancy remains with the most

TABLE III. Lithium  $2^2P$  and  $3^2D$  lifetimes.

Author	Lifetime (ns)
$2^2P$	
Experiment	
Gaupp <i>et al.</i> [2]	27.29(4)
Carlsson and Sturesson [3]	27.22(20)
McAlexander <i>et al.</i> [4]	26.99(16)
Theory	
This work ( $M = \infty$ )	27.109 804(36)
This work (finite $M$ )	27.117 301(36)
$3^2D$	
Experiment	
Schulze-Hagenest <i>et al.</i> [5]	14.60(13)
Azencot and Goutte [6]	14.8(1.9)
Heldt and Leuchs [7]	14.5(7)
Theory	
Pipin and Bishop [23]	14.60
Chung [25]	14.58
This work ( $M = \infty$ )	14.583 687(68)
This work (finite $M$ )	14.584 322(68)

accurate experimental measurement of Gaupp *et al.* However, the experiments themselves are not in good agreement with each other, and further work would be desirable to resolve the differences.

*Note added in proof.* After completion of this work, we learned of a new measurement of the  $2^2P$  state lifetime by Volz and Schmoranzler [29]. Their result of  $27.11 \pm 0.06$  ns

is in excellent agreement with theory, and clearly disagrees with the older measurement of Gaupp *et al.*

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