1995

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

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(Received 25 August 1995)

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.

PACS number(s): 31.20.Di, 32.70.Cs

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 Sturresson 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

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

(1)

where $\mathbf{A}(\mathbf{r}) = (2\pi\hbar/\omega \mathcal{F})^{1/2} \mathbf{e} e^{-\mathbf{r}}$ 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 $\mathbf{e}$. $\mathcal{F}$, normalized to unit photon energy $\hbar \omega$ in volume $\mathcal{F}$. $\mathbf{R}_n$ and $\mathbf{R}_i$ 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

$$H_{\text{int}} = -\frac{Ze}{Mc} P_n' \mathbf{A}(\mathbf{R}_n) + \frac{e}{mc} \sum_{i=1}^{n} P_i \cdot \mathbf{A}(\mathbf{R}_i),$$

(2)

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

$$w_{\gamma'\gamma} d\Omega = \frac{2\pi}{\hbar} \left| \langle \gamma | H_{\text{int}} | \gamma' \rangle \right|^2 \rho_f,$$

(3)

where $\rho_f = \mathcal{F} \omega^2 d\Omega/(2\pi c)^3 \hbar$ is the number of photon states with polarization $\mathbf{e}$ per unit energy and solid angle in the normalization volume $\mathcal{F}$. 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

$$w_{\gamma'\gamma} = \frac{3}{2} \alpha \omega_{\gamma'\gamma} \left| \langle \gamma | Q_p | \gamma' \rangle \right|^2,$$

(4)

where $Q_p$ is the dimensionless velocity form of the transition operator

$$Q_p = -\left( \frac{Z}{Mc} P_n - \frac{1}{mc} \sum_{i=1}^{n} P_i \right).$$

(5)

The equivalent length form is
LITHIUM

THEORETICAL LITHIUM $^2S_1\rightarrow^2P^0$ AND $^2P^0\rightarrow^2D^0$ 

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

(6)

as follows from the commutator $[H_0, \mathbf{Q}_r/\hbar \omega_{\gamma'}] = \mathbf{Q}_p$, 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

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

(7)

the transition operators become

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

(8)

with

\[ Z_p = \frac{Z m + M}{M}, \quad Z_r = \frac{Z m + M}{nm + M}, \]

(9)

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

\[ \langle \gamma | \mathbf{Q}_p | \gamma' \rangle = \langle \gamma | \mathbf{Q}_r | \gamma' \rangle \]

(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 $-Z \epsilon$ and $-Z \mu \epsilon$ can be thought of as effective radiative charges, with $Z = 1$ for neutral atoms.

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

\[ f(\gamma \rightarrow \gamma') = \frac{2m \omega_{\gamma'} \left( Z_N \right)}{3\hbar} \left( \sum_{i=1}^{n} \mathbf{r}_i \right) \left( \gamma | \sum_{i=1}^{n} \mathbf{r}_i | \gamma' \right)^2, \]

(11)

then the Thomas-Reiche-Kuhn sum rule $\Sigma_{\gamma'} f(\gamma \rightarrow \gamma') = n$ 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 function is

\[ \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \mathcal{A} \sum_{\mu} \sum_{\alpha, \beta, \gamma} a_{\mu} \phi_{\mu, \alpha, \beta, \gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \times (\text{angular function})(\text{spin function}), \]

(12)

where

\[ \phi_{\mu, \alpha, \beta, \gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = f_{\mu, \alpha, \beta, \gamma}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) e^{-\alpha r_1 - \beta r_2 - \gamma r_3}, \]

(13)

\[ \mu \text{ is a sextuple of integer powers } j_1, j_2, j_3, j_{12}, j_{13}, j_{23}, \text{ and } j_{123}, \text{ index } i \text{ labels different sets of nonlinear parameters } \alpha_i, \beta_i, \text{ and } \gamma_i, \text{ and } \mathcal{A} \text{ is the three-particle antisymmetrizer. Except for some truncations, all terms are included such that} \]

\[ j_1 + j_2 + j_3 + j_{12} + j_{13} + j_{23} + j_{123} \ll \Omega, \]

(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 $1s^22s^2S$ state, $-7.410 156 521 8(13)$ a.u. for the $1s^22p^2P$ state, and $-7.335 523 541 10(43)$ a.u. for the $1s^22d^2D$ 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 $^2S\rightarrow^2P$ and $^2P\rightarrow^2D$ transitions, as $\Omega$ is progressively increased. The corresponding size 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 $\Omega = \infty$ 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>
<thead>
<tr>
<th>No. of terms</th>
<th>$f$ (length)</th>
<th>$f$ (velocity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2S\rightarrow^2P$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(18, 19)</td>
<td>0.744 774 4</td>
<td>0.773 465 8</td>
</tr>
<tr>
<td>(50, 55)</td>
<td>0.747 676 4</td>
<td>0.753 742 4</td>
</tr>
<tr>
<td>(120, 130)</td>
<td>0.747 036 8</td>
<td>0.748 054 7</td>
</tr>
<tr>
<td>(256, 306)</td>
<td>0.746 957 8</td>
<td>0.747 304 7</td>
</tr>
<tr>
<td>(502, 622)</td>
<td>0.746 957 5</td>
<td>0.747 072 1</td>
</tr>
<tr>
<td>(918, 1174)</td>
<td>0.746 957 3</td>
<td>0.746 004 8</td>
</tr>
<tr>
<td>(1589, 1715)</td>
<td>0.746 957 3</td>
<td>0.746 972 3</td>
</tr>
<tr>
<td>Extrapolation</td>
<td>0.746 957 2(10)</td>
<td>0.746 957 1(54)</td>
</tr>
<tr>
<td>$^2P\rightarrow^2D$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(19, 19)</td>
<td>0.636 902 7</td>
<td>0.634 764 7</td>
</tr>
<tr>
<td>(55, 57)</td>
<td>0.638 443 5</td>
<td>0.636 647 2</td>
</tr>
<tr>
<td>(138, 148)</td>
<td>0.637 675 7</td>
<td>0.638 558 7</td>
</tr>
<tr>
<td>(306, 340)</td>
<td>0.638 380 0</td>
<td>0.638 463 4</td>
</tr>
<tr>
<td>(622, 586)</td>
<td>0.638 560 3</td>
<td>0.638 576 5</td>
</tr>
<tr>
<td>(1174, 1002)</td>
<td>0.638 566 1</td>
<td>0.638 589 6</td>
</tr>
<tr>
<td>(1715, 1673)</td>
<td>0.638 568 4</td>
<td>0.638 583 1</td>
</tr>
<tr>
<td>Extrapolation</td>
<td>0.638 570 5(30)</td>
<td>0.638 579 3(60)</td>
</tr>
</tbody>
</table>
TABLE II. Comparison of lithium 22S-22P oscillator strength. The numbers next to the authors' names are dates, i.e., (1973), etc.

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

*Result for 7Li with m/M = 7.820 814 7 × 10^-3.*

Table II lists a comparison of our values with other theoretical calculations, as well as with some experimental measurements, for the 22S-22P 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 ±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 ±0.0006 for f places it in strong disagreement with the present work. The calculated lifetimes for the 22P and 32D states, together with the measurements for these states, are listed in Table III. For the 32D 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 22S-22P and 22P-32D transitions have been calculated to an accuracy of ±6 × 10^-6. For the 22S-22P transition, the results resolve disagreements among previous theoretical values, but a significant discrepancy remains with the most
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 Schmoranzer [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.

ACKNOWLEDGMENT

Research support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.