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# 1/Z expansion study of the $(1s)^2 2s\ ^2S$ and $(1s)^2 2p\ ^2P$ states of the lithium isoelectronic sequence*

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A 1/Z expansion method is used to calculate the eigenvalues and eigenfunctions for the $(1s)^2 2s\ ^2S$ and $(1s)^2 2p\ ^2P$ states of the lithium isoelectronic sequence. The dipole-length and dipole-velocity forms of the oscillator strengths for the $2s$-$2p$ resonance transitions are compared with the results of direct variational calculations for individual values of the nuclear charge $Z$. It is explicitly demonstrated that the length formulation of the dipole matrix element is more accurate than the velocity formulation for the $2s$-$2p$ transitions.

## I. INTRODUCTION

Recent measurements from rocket-borne instrumentation of the sun have established the presence of a large number of spectral lines both in the extreme ultraviolet and the soft-x-ray region[1] which can be attributed to ions of the lithium isoelectronic sequence. Some atomic calculations using configuration-interaction methods have been carried out for a few members of the sequence.[2,3] Procedures can be developed with which the calculations can be performed as a function of the nuclear charge $Z$ and in this paper we use an expansion in powers of $Z^{-1}$ to calculate the eigenfunctions and eigenvalues for the $(1s)^2 2s\ ^2S$ and $(1s)^2 2p\ ^2P$ states of the entire lithium isoelectronic sequence. We calculate also the oscillator strengths of the $1s^2 2s$-$1s^2 2p$ transitions.

## II. THEORY

The Schrödinger equation for the lithium sequence is

$$(H - E_n)|\psi_n\rangle = 0 . \qquad (1)$$

The Hamiltonian $H$ is given by

$$H = H_0 + Z^{-1} V , \qquad (2)$$

where $H_0$ is the hydrogenic Hamiltonian

$$H_0 = \sum_{i=1}^{3} \left( -\frac{1}{2}\nabla_i^2 - \frac{1}{r_i} \right),$$

$V$ is the electronic repulsion term

$$V = \sum_{i<j}^{3} \frac{1}{|\vec{r}_i - \vec{r}_j|} , \qquad (3)$$

$\vec{r}_i$ is the position vector of the $i$th electron measured in units of $Z^{-1}a_0$, and energy is measured in units of $Z^2$ a.u.

If we expand the eigenfunction $\psi_n$ and eigenvalue $E_n$ according to

$$|\psi_n\rangle = \sum_{s=0}^{\infty} Z^{-s} |\psi_n^{(s)}\rangle , \quad E_n = \sum_{s=0}^{\infty} Z^{-s} E_n^{(s)} , \qquad (4)$$

Eq. (1) reduces to the set of equations

$$(H_0 - E_n^{(0)})|\psi_n^{(0)}\rangle = 0 , \qquad (5)$$

$$(H_0 - E_n^{(0)})|\psi_n^{(s)}\rangle + (V - E_n^{(1)})|\psi_n^{(s-1)}\rangle - \sum_{r=2}^{s} E_n^{(r)} |\psi_n^{(s-r)}\rangle = 0 . \qquad (6)$$

The set is equivalent to the variational statement that

$$\delta J_n^{(s)} = 0 , \qquad (7)$$

where the functional $J_n^{(s)}$ is given by

$$J_n^{(s)} = \langle \psi_n^{(s)} | H_0 - E_n^{(0)} | \psi_n^{(s)} \rangle + 2 \langle \psi_n^{(s)} | V - E_n^{(1)} | \psi_n^{(s-1)} \rangle - 2 \sum_{r=2}^{2s-1} E_n^{(r)} \sum_{q=s-r}^{r} \langle \psi_n^{(q)} | \psi_n^{(2s-r-q)} \rangle . \qquad (8)$$

Following Dalgarno and Drake[4] we introduce a basis set $\Phi_k$, one of which, $\Phi_0$, is $\psi_n^{(0)}$. Without loss of generality we require that

$$\langle \Phi_k | H_0 | \Phi_{k'} \rangle = \epsilon_k \delta_{kk'} , \quad k, k' = 1, 2, \ldots, N$$
$$\langle \Phi_k | \Phi_{k'} \rangle = \delta_{kk'} . \qquad (9)$$

Then $\epsilon_0 = E_n^{(0)}$. The trial form

$$|\psi_n^{(s)}\rangle = \sum_{k=1}^{N} a_k^{(s)} |\Phi_k\rangle \qquad (10)$$

leads, when substituted into (7) and (8), to the result

$$\langle \psi_n^{(s)} | = \sum_{k\neq 0}^{N} \frac{\langle \psi_n^{(s-1)} | V | \Phi_k \rangle \langle \Phi_k |}{\epsilon_0 - \epsilon_k} - \sum_{k\neq 0}^{N} \sum_{p=1}^{s} \frac{E_n^{(p)} \langle \psi_n^{(s-p)} | \Phi_k \rangle \langle \Phi_k |}{\epsilon_0 - \epsilon_k} , \qquad (11)$$

$$E_n^{(s)} = \langle \psi_n^{(s-1)} | V | \psi_n^{(0)} \rangle - \sum_{p=1}^{s-1} E_n^{(p)} \langle \psi_n^{(s-p)} | \psi_n^{(0)} \rangle . \qquad (12)$$

After the initial diagonalization of the basis set $\Phi_k$ with respect to $H_0$ has been performed, the recurrence relationships (11) and (12) may be rapidly evaluated. Provided the expansions converge, the results are identical to those given by diagonalizations of $\Phi_k$ with respect to $H_0 + Z^{-1}V$ for each value of $Z$.

The oscillator strength for a dipole transition from an initial state $\psi_n$ to a final state $\psi_{n'}$ is given in the length formulation by

$$f_L = \tfrac{2}{3}(E_{n'} - E_n) \left| \langle \psi_n | \sum_{i=1}^{3} \vec{r}_i | \psi_{n'} \rangle \right|^2 , \qquad (13)$$

and in the velocity formulation by

$$f_V = \tfrac{2}{3}(E_{n'} - E_n)^{-1} \left| \langle \psi_n | \sum_{i=1}^{3} \vec{\nabla}_i | \psi_{n'} \rangle \right|^2 . \qquad (14)$$

Using (4), we may generate expansions of oscillator strengths in powers of $Z^{-1}$. If the eigenfunctions are exact, the coefficients in the length and velocity forms are identical.

## III. CALCULATIONS AND RESULTS

In the method of configuration interaction, the form for each configuration in the wave function expansion may be expressed as[3]

$$\begin{aligned} | \Phi_{pqK,\lambda} \rangle &= (\chi_p \chi_q)\chi_K \\ &= (6D_\lambda)^{-1/2} \sum_{\mu} [\, | \chi_{p\lambda}^{\mu} \alpha(1) \bar{\chi}_{q\lambda}^{\mu} \beta(2) \chi_K \alpha(3) | \\ &\qquad - | \bar{\chi}_{p\lambda}^{\mu} \beta(1) \chi_{q\lambda}^{\mu} \alpha(2) \chi_K \alpha(3) | \,] \end{aligned} \qquad (15a)$$

and

$$\begin{aligned} | \Phi_{pqK,\lambda} \rangle &= (\chi_p \chi_q)^3 S \chi_K \\ &= \tfrac{1}{3}(2D_\lambda)^{-1/2} \sum_{\mu} [\, 2 | \bar{\chi}_{p\lambda}^{\mu} \alpha(1) \chi_{q\lambda}^{\mu} \alpha(2) \chi_K \beta(3) | \\ &\qquad - | \bar{\chi}_{p\lambda}^{\mu} \alpha(1) \chi_{q\lambda}^{\mu} \beta(2) \chi_K \alpha(3) | \\ &\qquad - | \bar{\chi}_{p\lambda}^{\mu} \beta(1) \chi_{q\lambda}^{\mu} \alpha(2) \chi_K \alpha(3) | \,] . \end{aligned} \qquad (15b)$$

Each single electron $\chi$ function is a Slater-type orbital that is normalized but not orthogonal:

$$\chi_{p\lambda}^{\mu}(\zeta) = \frac{(2\zeta)^{p+1/2}}{[(2p)!]^{1/2}} r^{p-1} e^{-\zeta r} Y_{\lambda,\mu}(\theta, \phi) . \qquad (16)$$

The $\alpha$ and $\beta$ spin functions represent the two components of spin and the sum over the azimuthal quantum index $\mu$ ensures that the electron pair forming the $K$ shell core will be of either $^1S$ (15a) or $^3S$ (15b) symmetry. The orbital angular momentum index $\lambda$ specifies the spin-orbital symmetry while $D_\lambda$ designates the degeneracy. The bar over the spin-orbital connotes complex conjugation, with the phase of the spherical harmonic chosen such that $\bar{Y}_{\lambda,\mu} = Y_{\lambda,-\mu}$.

Since the $1/Z$ expansion method converges more rapidly for the higher values of the nuclear charge, the Weiss wave functions[2, 3] for the highest published $Z$ values (O VI with $Z = 8$) were selected to generate the basis sets. After the addition of the necessary hydrogenic configurations in the $^2S$ and $^2P$ wave functions, the variational wave functions were found to give values of $E^{(2)}(1s^2 2s\, ^2S) = -0.39783$ a.u. and $E^{(2)}(1s^2 2p\, ^2P) = -0.51122$ a.u. for the second-order perturbed energies. The more accu-

TABLE I. Added configurations and screening parameters to the Weiss ($1s\,^2 2s\,^2S$) and ($1s\,^2 2p\,^2P$) configuration interaction wave functions ($Z = 8$).

| $(1s)^2 2s\,^2S$ | | $(1s)^2 2p\,^2P$ | |
|---|---|---|---|
| | | $\zeta$ | |
| $\zeta 1s_1 = 8.38$ | $\zeta 3s_5 = 2.40$ | $\zeta 1s_2 = 6.49$ | $\zeta 2p_5 = 6.20$ |
| $\zeta 2s_2 = 3.27$ | $\zeta 2s_6 = 3.27$ | $\zeta 1s_3 = 8.81$ | $\zeta 3p_1 = 2.29$ |
| $\zeta 1s_3 = 6.74$ | $\zeta 3s_7 = 2.19$ | $\zeta 2s_3 = 5.62$ | $\zeta 3d_1 = 5.93$ |
| $\zeta 1s_4 = 10.08$ | | $\zeta 2p_4 = 4.21$ | $\zeta 4f_1 = 1.62$ |
| | | $\zeta 3p_4 = 3.75$ | $\zeta 3d_2 = 2.33$ |
| | | $\zeta 4p_4 = 2.99$ | |
| | | Configuration | |
| $(1s2s)3s_7$ | $(1s_1 3s_5)1s_3$ | $(1s)^2 3p_1$ | $(1s_3 3p_4)\,^1P1s_2$ |
| $(1s1s')3s_7$ | $(2s_6 2s_2)1s_3$ | $(1s1s')3p_1$ | $(2s2p_4)\,^1P1s_2$ |
| $(1s2s')3s_7$ | $(1s_1 2s_2)\,^3S1s_3$ | $(1s2s)3p_1$ | $(2s_3 3p_4)\,^1P1s_2$ |
| $(1s3s')3s_7$ | $(1s_1 1s_4)\,^3S1s_3$ | $(1s2p_4)\,^1P3d_1$ | $(1s_3 2p_4)\,^3P1s_2$ |
| $(1s_1 2s_2)1s_3$ | $(1s_1 3s_5)\,^3S1s_3$ | $(1s2p_4)\,^3P3d_1$ | $(1s_3 3p_4)\,^3P1s_2$ |
| $(1s_1 1s_4)1s_3$ | $(2s_6 2s_2)\,^3S1s_3$ | $(1s3d_2)\,^1D4f_1$ | $(1s2p_5)\,^3P1s_2$ |
| | | $(1s3d_2)\,^3D4f_1$ | $(2s2p_4)\,^3P1s_2$ |
| | | $(1s_3 2p_4)\,^1P1s_2$ | $(2s_3 2p_4)\,^3P1s_2$ |
| | | | $(2s_3 3p_4)\,^3P1s_2$ |
| | | | $(2s_3 4p_4)\,^3P1s_2$ |

TABLE II. Eigenvalues and second-order energies of O VI in a.u.

| | $1s^2 2s\,^2S$ | $1s^2 2p\,^2P$ |
|---|---|---|
| | $E^{(2)}$ | |
| Weiss | −0.3978 | −0.5112 |
| This paper | −0.4049 | −0.5173 |
| Exact | −0.4082 | −0.5286 |
| | $E$ | |
| Weiss | −64.226 61 | −63.783 14 |
| This paper | | |
| variational | −64.226 72 | −63:785 90 |
| $Z$ expansion | −64.226 72 | −63.785 90 |
| Exact | −64.229 17[a] | −63.789 71[b] |

[a] Reference 2.

[b] Reference 3.

TABLE III. Energy expansion coefficients $E_n^{(s)}$ a.u.

| order $s$ | $(1s)^2 2s\ {}^2S$ | $(1s)^2 2p\ {}^2P$ |
|---|---|---|
| 0 | −1.125 000 00(0) | −1.125 000 00(0) |
| 1 | 1.022 805 22(0) | 1.093 526 14(0) |
| 2 | −4.048 677 85(−1) | −5.172 543 17(−1) |
| 3 | −4.572 466 85(−2) | −1.459 101 30(−1) |
| 4 | 8.339 444 47(−2) | 9.481 784 55(−2) |
| 5 | 1.140 469 40(−1) | −1.525 309 51(−1) |
| 6 | −3.746 788 13(−1) | 3.478 861 76(−1) |
| 7 | −7.531 849 24(−1) | 3.823 832 72(0) |
| 8 | 9.575 483 56(−1) | 4.251 682 97(0) |

rate results of Horak *et al.*[5] give $E^{(2)}(1s^2 2s\,{}^2S) = -0.40816$ a.u. and $E^{(2)}(1s^2 2p\,{}^2P) = -0.52858$ a.u.

We attempted to improve the Weiss variational wave functions by selectively increasing the number of configurations. The second-order energy of a three-electron system may be given in terms of second-order energies of two-electron systems[6]:

$$E^{(2)}(1s^2 2s) = E^{(2)}(1s^2\,{}^1S) + \tfrac{1}{2}E^{(2)}(1s2s\,{}^1S) + \tfrac{3}{2}E^{(2)}(1s2s\,{}^3S) + \zeta(2s)\,,$$

$$E^{(2)}(1s^2 2p) = E^{(2)}(1s^2\,{}^1S) + \tfrac{1}{2}E^{(2)}(1s2p\,{}^1P) + \tfrac{3}{2}E^{(2)}(1s2p\,{}^3P) + \zeta(2p)\,,$$

where the $\zeta(nl)$'s are a sum of single-electron integrals. These forms suggest the addition of configurations of a ${}^3S$ core nature for the ${}^2S$ wave function and the inclusion of configurations with both ${}^1P$ and ${}^3P$ core symmetry for the ${}^2P$ wave function.

In view of the small expansion coefficients obtained by Weiss[3] for certain configurations, the $(5g)^2 2p''$, $(3p)^2 2p'''$, $(3d3d')2p'''$, and $(5d3d')\,{}^3S2p'''$ were removed from the ${}^2P$ wave function. In all, 12 configurations involving seven new optimized screening parameters (obtained in the standard variational minimization of total energy) were added to make a 58 term ${}^2S$ wave function. Similarly, 18 new configurations with 11 optimized screening parameters were added to make a 60-term ${}^2P$ wave function. The values for the additional screening parameters and the list of new configurations are shown in Table I. The form of the configurations for cores of symmetry other than ${}^1S$ and ${}^3S$ follows from using simple angular momentum coupling techniques to generalize Eq. (15). Table II contains a comparison between the variational energies and second order energies obtained from Weiss's original wave functions with the values calculated here.

TABLE IV. 1/$Z$ expansion eigenvalues in a.u. for the lithium isoelectronic sequence.

| $Z$ | $-E[(1s)^2 2s\ {}^2S]$ | $-E[(1s)^2 2p\ {}^2P]$ |
|---|---|---|
| 5 | 23.421 45 | 23.199 63 |
| 6 | 34.773 16 | 34.477 77 |
| 7 | 48.374 92 | 48.006 56 |
| 8 | 64.226 72 | 63.785 90 |
| 9 | 82.328 58 | 81.815 65 |
| 10 | 102.680 48 | 102.095 71 |
| 11 | 125.282 42 | 124.626 01 |
| 12 | 150.134 39 | 149.406 50 |
| 13 | 177.236 39 | 176.437 12 |
| 14 | 206.588 41 | 205.717 87 |

TABLE V. Length $f_L$ and velocity $f_V$ expansion coefficients.

| $s$ | $f_L^{(s)}$ | $f_V^{(s)}$ |
|---|---|---|
| 0 | 0 | 0 |
| 1 | 1.273 0(0) | 1.262 7(0) |
| 2 | 2.172 2(0) | 2.395 0(0) |
| 3 | 2.892 4(0) | 1.966 1(0) |
| 4 | 1.897 8(0) | 5.012 8(0) |
| 5 | −7.673 0(0) | −6.305 5(0) |
| 6 | −4.095 1(1) | −1.368 4(2) |
| 7 | −8.711 8(1) | −3.582 1(2) |
| 8 | 1.534 1(2) | 3.498 0(2) |
| 9 | 1.558 5(3) | 4.043 9(3) |
| 10 | 3.623 4(3) | 9.369 7(3) |

Our enlarged basis sets substantially reduce the discrepancy between the second order energies derived from the 45-term trial functions and the exact values of Horak *et al.*[5] and will necessarily lead to more precise eigenvalues at large $Z$. Table II shows that in the case of the ${}^2S$ state, the eigenvalue for O VI is a small improvement over the original variational computation and that in the ${}^2P$ case it is a considerable improvement over the 45-term calculation. Our predicted wavelength for the ${}^2S$-${}^2P$ spectral line is 1033.6 Å compared to the experimental value 1033.8 Å.[11]

Using the basis sets derived from the new variational wave functions, perturbed wave functions and eigenenergies for the entire lithium isoelectronic sequence were generated from expressions (11) and (12). Table II shows the excellent agreement between the eigenenergies derived variation-

TABLE VI. Oscillator strengths for the $1s^2 2s\ {}^2S$-$1s^2 2p\ {}^2P$ resonance transition of O VI.

| | $f_L$ | $f_V$ |
|---|---|---|
| Weiss | 0.1960 | 0.2010 |
| This paper | | |
| variational | 0.1988 | 0.1995 |
| $Z$ expansion | 0.1988 | 0.1995 |

TABLE VII. Nonrelativistic $1/Z$ expansion oscillator strengths for the $(1s)^2 2s\ ^2S-(1s)^2 2p\ ^2P$ transition of the lithium isoelectronic sequence. (Relativistic effects are less than 5% for all $Z \leq 14$).

| | $f_L$ | | $f_V$ | |
|---|---|---|---|---|
| $Z$ | Weiss (Ref. 3) | $Z$ exp | Weiss (Ref. 3) | $Z$ exp |
| 5 | 0.3664 | 0.3630 | 0.3760 | 0.3607 |
| 6 | 0.2857 | 0.2855 | 0.2915 | 0.2857 |
| 7 | 0.2339 | 0.2346 | 0.2393 | 0.2353 |
| 8 | 0.1960 | 0.1988 | 0.2010 | 0.1995 |
| 9 | | 0.1723 | | 0.1729 |
| 10 | | 0.1520 | | 0.1525 |
| 11 | | 0.1359 | | 0.1363 |
| 12 | | 0.1229 | | 0.1232 |
| 13 | | 0.1121 | | 0.1123 |
| 14 | | 0.1031 | | 0.1032 |

ally for O VI with those obtained from the $1/Z$ expansion theory. The energy expansion coefficients for the $(1s)^2 2s\,^2S$ and $(1s)^2 2p\,^2P$ states of the lithium sequence are given through eighth order in Table III. Table IV lists the $1/Z$ expansion eigenvalues for the lithium isoelectronic sequence from B III to Si XII.

The dipole length and dipole velocity expansion coefficients for the $2s$-$2p$ resonance transition of the lithium sequence,

$$f_L = \sum_{s=0} Z^{-s} f_L^{(s)} ,$$

$$f_V = \sum_{s=0} Z^{-s} f_V^{(s)}$$

are listed in Table V. The correct value of the leading term in each series is the hydrogenic value 1.273.[7] It is reproduced exactly by the length expansion but the velocity expansion underestimates. For high $Z$, then, there is a clear preference for the values derived from the length formulation. At low $Z$ some cancellation of error occurs in the velocity form; the correct value of the second order coefficient is[7] 2.026 compared to the value 2.172 computed for $f_L^{(2)}$ and 2.395 for $f_V^{(2)}$. Most of the error in $f_L^{(2)}$ and $f_V^{(1)}$ arises in the eigenvalues and not in the matrix elements, which implies that greater accuracy could be obtained by using experimental energy differences.

Although all the Hamiltonians responsible for generating particular forms of the transition matrix elements can be derived from one another by classical infinitesimal transformations,[8] Starace[9] has argued recently that in any calculation involving diagonalization of an approximate nonlocal Hamiltonian, the length formula is the appropriate expression and the $Z$-dependent method does demonstrate in our case its superiority. That it should be in situations where the levels are closely spaced was demonstrated in an elementary way by Dalgarno and Lewis.[10]

Table VI displays the excellent agreement between the oscillator strengths derived variationally for O VI with those obtained from the $1/Z$ expansion theory. Table VII is a collection of values of $f_L$ and $f_V$ for B III to Si XII. They differ little from, but are more securely founded than, the values recommended by Wiese *et al.*[11,12]

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[1] L. Heroux, M. Cohen, and M. Malinovsky, Solar Physics 23, 369 (1972).

[2] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[3] A. W. Weiss, Astrophys. J. 138, 1262 (1963).

[4] A. Dalgarno and G. W. F. Drake, Chem. Phys. Lett. 3, 349 (1969).

[5] Z. J. Horak, M. N. Lewis, A. Dalgarno, and P. Blanchard, Phys. Rev. 185, 21 (1969).

[6] C. D. H. Chisholm, A. Dalgarno, and F. R. Innes, Phys. Rev. 167, 60 (1968).

[7] A. Dalgarno and E. M. Parkinson, Phys. Rev. 176, 73 (1968).

[8] Aage E. Hansen, Theoret. Chim. Acta 16, 217 (1970).

[9] Anthony F. Starace, Phys. Rev. A 3, 1242 (1971).

[10] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. Lond. A 69, 285 (1956).

[11] W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities* (U. S. GPO, Washington, D. C., 1966), Vol. I.

[12] W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities* (U. S. GPO, Washington, D. C., 1969), Vol. II.