results for the series boron through fluorine.[6,7]

From the results reported here and in previous papers[4-7] we may tentatively conclude that the SEHF functions give much more reliable Fermi contact terms for atoms with open *s* shells than for those having open *p* shells; energy reductions are very small in both cases. Additional calculations will be needed to check the validity of these statements.

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Properties of the Lithium Sequence

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It is shown that in a perturbation description based upon a zero-order single-particle Hamiltonian, the diagonal and off-diagonal matrix elements of a single-particle operator for an N-particle system are essentially just linear combinations of matrix elements for two-particle systems. A similar statement applies to a restricted class of two-particle operators. The theory is applied to the calculation of the leading terms in the relativistic and mass-polarization corrections for the lithium sequence and to the calculation of the $2s-2p$ and $3s-3p$ dipole transition probabilities of the lithium sequence. Comparison of the transition probabilities with experimental data and with the results of refined variational calculations shows that high accuracy can be obtained.

1. INTRODUCTION

Suppose that $\Phi^{(0)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \equiv \Phi^{(0)}(N)$ is an approximate representation of the eigenfunction $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ of an N-electron atomic system, $\vec{r}_i$ being the position vector of the ith electron measured from the nucleus. Suppose further that $\Phi^{(0)}$ is the eigenfunction of a single-particle Hamiltonian $H_0(N)$, where

$$H_0(N) = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + V_i\right), \tag{1}$$

Z being the nuclear charge. The expression $\Phi^{(0)}(N)$ satisfies the eigenvalue equation

$$H_0(N)\Phi^{(0)}(N) = E^{(0)}(N)\Phi^{(0)}(N) \tag{2}$$

and can be constructed from the orthonormal set of single-particle states ϕ_n that are solutions of

$$H_0(1)\phi_n = \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r} + V\right)\phi_n = \epsilon_n\phi_n. \tag{3}$$

The first-order correction, $\Phi^{(1)}(N)$, to $\Phi^{(0)}(N)$ is the solution of the first-order perturbed equation

$$[H_0(N)-E^{(0)}(N)]\Phi^{(1)}(N)+\Big(\sum_{i<j}^{N}\frac{1}{|\vec{r}_i-\vec{r}_j|}-\sum_{i=1}^{N}V_i\Big)\Phi^{(0)}(N)=E^{(1)}(N)\Phi^{(0)}(N). \tag{4}$$

Chisholm and Dalgarno[1] have pointed out that the N-particle solution $\Phi^{(1)}(N)$ of (4) can be written in terms of the two-particle solutions $\Phi^{(1)}(2)$ of

$$[H_0(2)-E^{(0)}(2)]\Phi^{(1)}(2)+[\,|\vec{r}_1-\vec{r}_2|^{-1}-V(r_1)-V(r_2)]\Phi^{(0)}(2)=E^{(1)}(2)\Phi^{(0)}(2). \tag{5}$$

This statement is contained implicitly in much recent work on correlation. It appears to have been noted first by Bacher and Goudsmit.[2] Chisholm and Dalgarno[1] have also written out the explicit form of the solution of (4). In L-S coupling,

$$\Phi^{(1)}(\Gamma SL|N)=A\sum_{\Gamma_1S_1L_1}\sum_{\Gamma_2S_2L_2}(\Gamma_1S_1L_1,\,\Gamma_2S_2L_2|\}\Gamma SL)[\Phi^{(0)}(\Gamma_1S_1L_1|N-2),\,\Phi^{(1)}(\Gamma_2S_2L_2|2)], \tag{6}$$

where $[\Phi^{(0)}(\Gamma_1S_1L_1|N-2),\,\Phi^{(1)}(\Gamma_2S_2L_2|2)]$

is a vector-coupled product of normalized antisymmetric $(N-2)$-particle eigenfunctions $\Phi^{(0)}(\Gamma_1S_1L_1|N-2)$ and normalized antisymmetric two-particle eigenfunctions $\Phi^{(1)}(\Gamma_2S_2L_2|2)$, the factor $(\Gamma_1S_1L_1,\,\Gamma_2S_2L_2|\}\Gamma SL)$ is a two-particle fractional parentage coefficient, and A is the antisymmetrizing operator. All the two-particle fractional parentage coefficients necessary to construct first-order wave functions corresponding to the zero-order configuration $1s^a2s^b2p^q$ have been tabulated.[3]

It follows from (6) that diagonal and off-diagonal matrix elements of any single-particle operator for an N-particle system can be calculated to second order from a knowledge of the first-order two-particle wave functions $\Phi^{(1)}(2)$ and that to first order the matrix elements for an N-particle system are essentially just linear combinations of the matrix elements for the two-particle systems. A similar statement holds for a restricted class of two-particle operators.

In order to avoid algebraic complexity, we present the detailed development for the three-particle systems described in zero order by the configurations $1s^2ns\,{}^2S$ and $1s^2mp\,{}^2P^\circ$.

2. THEORY

Define the single-particle operator

$$Q_1(N)=\sum_{i=1}^{N}q(i), \tag{7}$$

and the two-particle operator

$$Q_2(N)=\sum_{i=j}^{N}q(ij). \tag{8}$$

To first order,

$$\langle\Psi_i(N)|Q_\alpha(N)|\Psi_f(N)\rangle=\langle i|Q_\alpha{}^{(0)}(N)|f\rangle+\langle i|Q_\alpha{}^{(1)}(N)|f\rangle, \tag{9}$$

where $\langle i|Q_\alpha{}^{(0)}(N)|f\rangle=\langle\Phi_i{}^{(0)}(N)|Q_\alpha(N)|\Phi_f{}^{(0)}(N)\rangle$ (10)

and $\langle i|Q_\alpha{}^{(1)}|f\rangle=\langle\Phi_i{}^{(0)}(N)|Q_\alpha(N)|\Phi_f{}^{(1)}(N)\rangle+\langle\Phi_i{}^{(1)}(N)|Q_\alpha(N)|\Phi_f{}^{(0)}(N)\rangle.$ (11)

For the $1s^2ns\,{}^2S$ configuration,[1]

$$\Phi^{(0)}(1s^2ns\,{}^2S)=3^{-1/2}[\Phi^{(0)}(1s^2\,{}^1S),\,\Phi^{(0)}(ns\,{}^2S)]-6^{-1/2}[\Phi^{(0)}(1sns\,{}^1S),\,\Phi^{(0)}(1s\,{}^2S)]-2^{-1/2}[\Phi^{(0)}(1sns\,{}^3S),\,\Phi^{(0)}(1s\,{}^2S)], \tag{12}$$

and

$$\Phi^{(1)}(1s^2ns\,{}^2S)=A\{3^{-1/2}[\Phi^{(1)}(1s^2\,{}^1S),\,\Phi^{(0)}(ns\,{}^2S)]-6^{-1/2}[\Phi^{(1)}(1sns\,{}^1S),\,\Phi^{(0)}(1s\,{}^2S)]-2^{-1/2}[\Phi^{(1)}(1sns\,{}^3S),\,\Phi^{(0)}(1s\,{}^2S)]\}. \tag{13}$$

For the $1s^2mp\,{}^2P^\circ$ configuration,[4]

$$\Phi^{(0)}(1s^2mp\,{}^2P^\circ)$$

$$= 3^{-1/2}[\Phi^{(0)}(1s^2\,{}^1S),\Phi^{(0)}(mp\,{}^2P^\circ)] - 6^{-1/2}[\Phi^{(0)}(1smp\,{}^1P^\circ),\Phi^{(0)}(1s\,{}^2S)] - 2^{-1/2}[\Phi^{(0)}(1smp\,{}^3P^\circ),\Phi^{(0)}(1s\,{}^2S)] \quad (14)$$

and $\Phi^{(1)}(1s^2mp\,{}^2P^\circ)$

$$= A\{3^{-1/2}[\Phi^{(1)}(1s^2\,{}^1S),\Phi^{(0)}(mp\,{}^2P^\circ)] - 6^{-1/2}[\Phi^{(1)}(1smp\,{}^1P^\circ),\Phi^{(0)}(1s\,{}^2S)]$$

$$- 2^{-1/2}[\Phi^{(1)}(1smp\,{}^3P^\circ),\Phi^{(0)}(1s\,{}^2S)]\}. \quad (15)$$

It follows by direct substitution that

$$\langle 1s^2ns\,{}^2S|Q_1{}^{(0)}(3)|1s^2ns\,{}^2S\rangle$$

$$= \tfrac{1}{2}[\langle 1s^2\,{}^1S|Q_1{}^{(0)}(2)|1s^2\,{}^1S\rangle + \tfrac{1}{2}\langle 1sns\,{}^1S|Q_1{}^{(0)}(2)|1sns\,{}^1S\rangle + \tfrac{3}{2}\langle 1sns\,{}^3S|Q_1{}^{(0)}(2)|1sns\,{}^3S\rangle] \quad (16)$$

and that $\langle 1s^2ns\,{}^2S|Q_1{}^{(1)}(3)|1s^2ns\,{}^2S\rangle$

$$= [\langle 1s^2\,{}^1S|Q_1{}^{(1)}(2)|1s^2\,{}^1S\rangle + \tfrac{1}{2}\langle 1sns\,{}^1S|Q_1{}^{(1)}(2)|1sns\,{}^1S\rangle + \tfrac{3}{2}\langle 1sns\,{}^3S|Q_1{}^{(1)}(2)|1sns\,{}^3S\rangle]. \quad (17)$$

The zero-order contribution (16) can, of course, be written more simply as a sum of $Q_1{}^{(0)}(1)$. We express it in the form (16) to elucidate the structure of the first-order contribution (17), which reduces the three-particle expectation value to a sum of two-particle expectation values.

A similar analysis of the off-diagonal matrix element $\langle\Psi_i(3)|Q_1(3)|\Psi_f(3)\rangle$ yields the zero-order contribution

$$\langle 1s^2ns\,{}^2S|Q_1{}^{(0)}(3)|1s^2mp\,{}^2P^\circ\rangle = \tfrac{1}{2}\langle 1sns\,{}^1S|Q_1{}^{(0)}(2)|1smp\,{}^1P^\circ\rangle + \tfrac{3}{2}\langle 1sns\,{}^3S|Q_1{}^{(0)}(2)|1smp\,{}^3P^\circ\rangle \quad (18)$$

and the first-order contribution

$$\langle 1s^2ns\,{}^2S|Q_1{}^{(1)}(3)|1s^2mp\,{}^2P^\circ\rangle = \tfrac{1}{2}\langle 1sns\,{}^1S|Q_1{}^{(1)}(2)|1smp\,{}^1P^\circ\rangle + \tfrac{3}{2}\langle 1sns\,{}^3S|Q_1{}^{(1)}(2)|1smp\,{}^3P^\circ\rangle, \quad (19)$$

the structure being identical to that of the diagonal matrix element.

The two-particle matrix elements $\langle i|Q_1{}^{(1)}(2)|f\rangle$ are conveniently calculated by the use of an interchange theorem,[5] which avoids the necessity of determining the first-order two-particle wave functions $\Phi^{(1)}(2)$. Thus (17) and (19) show that the diagonal and off-diagonal matrix elements of a single-particle operator for an N-particle system can be calculated to first order from the solutions of single-particle equations.

The same interchange theorem allows the calculation of the matrix elements of a single-particle operator for an N-particle system to be carried out to second order from a knowledge of the first-order two-particle wave functions $\Phi^{(1)}(2)$, but there is no simple relationship between the second-order two-particle matrix elements.

For a two-particle operator (8), the structure is usually more complicated. If $\chi^{(1)}(\vec{r}_1,\vec{r}_2|\Gamma SL)$, is the spatial part of $\Phi^{(1)}(\vec{r}_1,\vec{r}_2|\Gamma SL)$, satisfying the first-order two-particle equation

$$[H_0(2) - E^{(0)}(2|\Gamma SL)]\chi^{(1)}(\vec{r}_1,\vec{r}_2|\Gamma SL) + [|\vec{r}_1-\vec{r}_2|^{-1} - V(r_1) - V(r_2)]\chi^{(0)}(\vec{r}_1,\ {}_2|\Gamma SL)$$

$$= E^{(1)}(2|\Gamma SL)\chi^{(0)}(\vec{r}_1,\vec{r}_2|\Gamma SL), \quad (20)$$

where $\chi^{(0)}(\vec{r}_1,\vec{r}_2|1s^2\,{}^1S) = \phi_{1s}(r_1)\phi_{1s}(r_2)$ (21)

and $\chi^{(0)}(\vec{r}_1,\vec{r}_2|1s2s\,{}^{1,3}S) = 2^{-1/2}[\phi_{1s}(r_1)\phi_{2s}(r_2) \pm \phi_{1s}(r_2)\phi_{2s}(r_1)]$, (22)

then $\langle 1s^2ns|Q_2{}^{(1)}(3)|1s^2ns\rangle$

$$\begin{aligned}
&= \langle 1s^2\,{}^1S|Q_2{}^{(1)}(2)|1s^2\,{}^1S\rangle + \tfrac{1}{2}\langle 1sns\,{}^1S|Q_2{}^{(1)}(2)|1sns\,{}^1S\rangle + \tfrac{3}{2}\langle 1sns\,{}^3S|Q_2{}^{(1)}(2)|1sns\,{}^3S\rangle\\
&\quad + 2\langle\chi^{(0)}(\vec{r}_1,\vec{r}_2|1s^2\,{}^1S)\phi_{2s}(\vec{r}_3)|q(13)|\chi^{(1)}(\vec{r}_1,\vec{r}_2|1s^2\,{}^1S)\phi_{2s}(\vec{r}_3)\rangle\\
&\quad + \langle\chi^{(0)}(\vec{r}_1,\vec{r}_2|1sns\,{}^1S)\phi_{1s}(\vec{r}_3)|q(13)|\chi^{(1)}(\vec{r}_1,\vec{r}_2|1sns\,{}^1S)\phi_{1s}(\vec{r}_3)\rangle\\
&\quad + 3\langle\chi^{(0)}(\vec{r}_1,\vec{r}_2|1sns\,{}^3S)\phi_{1s}(\vec{r}_3)|q(13)|\chi^{(1)}(\vec{r}_1,\vec{r}_2|1sns\,{}^3S)\phi_{1s}(\vec{r}_3)\rangle\\
&\quad - \sqrt{2}[\langle\chi^{(0)}(\vec{r}_1,\vec{r}_2|1s^2\,{}^1S)\phi_{ns}(\vec{r}_3)|q(13)|\chi^{(1)}(\vec{r}_1,\vec{r}_2|1sns\,{}^1S)\phi_{1s}(\vec{r}_3)\rangle\\
&\quad + \langle\chi^{(0)}(\vec{r}_1,\vec{r}_2|1sns\,{}^1S)\phi_{1s}(\vec{r}_3)|q(13)|\chi^{(1)}(\vec{r}_1,\vec{r}_2|1s^2\,{}^1S)\phi_{ns}(\vec{r}_3)\rangle]. \qquad (23)
\end{aligned}$$

The additional cross terms that arise because of the exclusion principle are comparable in complexity to those occurring in the evaluation of the second-order two-particle eigenvalues. However, if $q(ij) = q(ji)$ is of odd parity in each of its variables $\vec{r}_i$ and $\vec{r}_j$, the additional terms are identically zero, and

$$\begin{aligned}&\langle 1s^2ns\ {}^2S|Q_2{}^{(1)}(3)|1s^2ns\ {}^2S\rangle\\ &\quad=\langle 1s^2\ {}^1S|Q_2{}^{(1)}(2)|1s^2\ {}^1S\rangle+\tfrac{1}{2}\langle 1sns\ {}^1S|Q_2{}^{(1)}(2)|1sns\ {}^1S\rangle+\tfrac{3}{2}\langle 1sns\ {}^3S|Q_2{}^{(1)}(2)|1sns\ {}^3S\rangle .\end{aligned}\tag{24}$$

The first-order diagonal matrix element of a two-particle operator for the three-particle system is then a linear combination of the diagonal matrix elements for the two-particle system, just as for the single-particle operators as shown in (17). The odd-parity condition is satisfied by operators such as $\vec{r}_i\cdot\vec{r}_j$, $\cos(\hat{r}_i\cdot\hat{r}_j)$, and $\nabla_i\cdot\nabla_j$.

Unlike the matrix elements of single-particle operators, the structure of the zero-order matrix element of the two-particle operators is identical to that of the first-order matrix elements. Thus

$$\begin{aligned}&\langle 1s^2ns\ {}^2S|Q_2{}^{(0)}(3)|1s^2ns\ {}^2S\rangle\\ &\quad=\langle 1s^2\ {}^1S|Q_2{}^{(0)}(2)|1s^2\ {}^1S\rangle+\tfrac{1}{2}\langle 1sns\ {}^1S|Q_2{}^{(0)}(2)|1sns\ {}^1S\rangle+\tfrac{3}{2}\langle 1sns\ {}^3S|Q_2{}^{(0)}(2)|1sns\ {}^3S\rangle .\end{aligned}\tag{25}$$

3. APPLICATIONS

In order to demonstrate the utility of the theory, we consider some properties of the lithium sequence for the case in which $V(\vec{r}_i)$ is taken to be zero.

Relativistic Corrections

The relativistic corrections to the $1s^22s\ {}^2S$ eigenvalues of the lithium isoelectronic sequence are to $O(\alpha^2)$ and in units of α^2 rydberg, α being the fine-structure constant.[6]

$$E_1{}'=-\tfrac{1}{4}\langle\psi|\sum_{i=1}^{3}\nabla_i^4|\psi\rangle,\quad E_1{}''=\pi Z\langle\psi|\sum_{i=1}^{3}\delta(\vec{r}_i)|\psi\rangle,\quad E_1{}'''=2\pi\langle\psi|\sum_{i=1}^{3}\delta(\vec{r}_i-\vec{r}_j|\psi\rangle,$$

and $$E_3{}'=\langle\psi|\sum_{i=j}^{3}\frac{1}{|\vec{r}_i-\vec{r}_j|}[\nabla_i\cdot\nabla_j+\vec{n}\cdot(\vec{n}\cdot\nabla_i)\nabla_j]|\psi\rangle,$$

where $\vec{n}=(\vec{r}_i-\vec{r}_j)/|\vec{r}_i-\vec{r}_j|$.

From the helium calculations for the $1s^2\ {}^1S$,[7] $1s2s\ {}^1S$, and $1s2s\ {}^3S$[8] states, we obtain immediately from (16) and (17) that to first order in Z^{-1},

$$E_1{}'=-\frac{173}{64}Z^4+\left(\frac{9940}{729}\ln 2-\frac{19\,880}{729}\ln 3+\frac{140\,075}{4374}\right)\frac{Z^3}{4}$$

and $$E_1{}''=\frac{17}{8}Z^4-\left(\frac{9940}{729}\ln 2-\frac{19\,980}{729}\ln 3+\frac{76\,225}{2187}\right)\frac{Z^3}{8}.$$

To the order of $Z^3\alpha^2$, it follows from (25) that $E_1{}'''=-\frac{89}{324}Z^3$, $E_3{}'=0$.

These results have been obtained previously[9] by a direct application of an interchange theorem to the three-particle system. The procedure used here is much less laborious.

Isotope Shift

Greater interest attaches to the first-order matrix element of a two-particle operator, since its evaluation cannot be greatly simplified by the use of any interchange theorems. We consider the matrix element $\langle\psi|\sum_{i\neq j}\nabla_i\cdot\nabla_j|\psi\rangle$, which describes the specific mass or mass-polarization effect. For the $1s^22s\ {}^2S$ state, the zero-order contribution vanishes. Using[10]

$$\langle 1s^2\ {}^1S|(\nabla_1\cdot\nabla_2)^{(1)}|1s^2\ {}^1S\rangle = 0.133\,293Z\ \text{Ry}$$

and estimating from the data of Pekeris[11] that

$$\langle 1s2s\ {}^1S|(\nabla_1\cdot\nabla_2)^{(1)}|1s2s\ {}^1S\rangle = 0.012\,201Z\ \text{Ry}$$

and $\langle 1s2s\ {}^3S|(\nabla_1\cdot\nabla_2)^{(1)}|1s2s\ {}^3S\rangle = 0.010\,126Z$ Ry, we obtain from (24)

$$\langle 1s^2 2s\ {}^2S | \sum_{i\neq j} \nabla_i \cdot \nabla_j)^{(1)} | 1s^2 2s\ {}^2S\rangle = 0.154\ 586 Z\ \text{Ry}.$$

The mass-polarization effect has been evaluated for several members of the lithium sequence by Prasad and Stewart,[12] using the 45-parameter variational representation of Weiss.[13] Analyzing their results as a power series in Z^{-1}, we obtain

$$\langle 1s^2 2s\ {}^2S | (\sum_{i=j} \nabla_i \cdot \nabla_j)^{(1)} | 1s^2 2s\ {}^2S\rangle = 0.153 Z\ \text{Ry}$$

in harmony with our prediction.

Transition Probabilities

The probability of the electric-dipole transition $1s^2 ms\ {}^2S - 1s^2 np\ {}^2P^\circ$ can be determined from the matrix element of the operator

$$Q_1(3) = \sum_{i=j}^{3} r_i \cos\theta_i .$$

The two-particle matrix elements $\langle 1s2s\ {}^{1,3}S | Q_1(2) | 1s2p\ {}^{1,3}P^\circ\rangle$ have been calculated exactly to first order in Z^{-1}. They are given by [14, 15]

$$\langle 1s2s\ {}^1S | Q_1(2) | 1s2p\ {}^1P^\circ\rangle = -(3/Z) - (3.0479/Z^2) + O(Z^{-3}),$$

and $$\langle 1s2s\ {}^3S | Q_1(2) | 1s2p\ {}^3P^\circ\rangle = -(3/Z) - (2.2772/Z^2) + O(Z^{-3}).$$

Following the same procedures,[5] we obtain

$$\langle 1s3s\ {}^1S | Q_1(2) | 1s3p\ {}^1P^\circ\rangle = -(3\sqrt{6}/Z) - (3.0654\sqrt{6}/Z^2) + O(Z^{-3})$$

and $$\langle 1s3s\ {}^3S | Q_1(2) | 1s3p\ {}^3P^\circ\rangle = -(3\sqrt{6}/Z) - (2.5839\sqrt{6}/Z^2) + O(Z^{-3}).$$

It may be noted incidentally that in the Hartree-Fock approximation,[16]

$$\langle 1s3s\ {}^1S | Q_1(2) | 1s3p\ {}^1P^\circ\rangle = -(3\sqrt{6}/Z) - (3.0819\sqrt{6}/Z^2) + O(Z^{-3}),$$

$$\langle 1s3s\ {}^3S | Q_1(2) | 1s3p\ {}^3P^\circ\rangle = -(3\sqrt{6}/Z) - (2.5896\sqrt{6}/Z^2) + O(Z^{-3}).$$

The Hartree-Fock expansions differ only slightly from the exact expansions (at least to first order in Z^{-1}), in harmony with the suggestion that in the absence of zero-order degeneracies the Hartree-Fock approximation is satisfactory for dipole transitions in which the active electron does not undergo a change in its principal quantum number.[14]

Before we proceed to the calculation of the lithium transition probabilities, it is instructive to examine the accuracy of the predicted helium transition probabilities. This is conveniently carried out in terms of the oscillator strengths

$$f(i-f) = 2(E_f - E_i) | \langle i | Q_1 | f\rangle |^2,$$

where E_i and E_f are the eigenenergies of the initial and final states and all quantities are measured in atomic units. In the screening approximation,[17]

$$f(1s2s\ {}^1S - 1s2p\ {}^1P^\circ) = (E_f - E_i) 18/(Z - 1.016)^2, \tag{26}$$

$$f(1s2s\ {}^3S - 1s2p\ {}^3P^\circ) = (E_f - E_i) 18/(Z - 0.759)^2, \tag{27}$$

$$f(1s3s\ {}^1S - 1s3p\ {}^1P^\circ) = (E_f - E_i) 108/(Z - 1.022)^2, \tag{28}$$

$$f(1s3s\ {}^3S - 1s3p\ {}^3P^\circ) = (E_f - E_i) 108/(Z - 0.861)^2 . \tag{29}$$

A comparison with the accurate variational calculations of Weiss[18] is presented in Table I for the singlet and triplet $2s - 2p$ transitions. Even for neutral helium, the error is less than 10%; and for the ionized systems, it is negligible. The comparison confirms the accuracy of the complicated calculations carried out by Weiss.

TABLE I. Oscillator strengths for the ($1s2s\ ^{1,3}S - 1s2p\ ^{1,3}P^\circ$) transitions. The transition energies were taken from Weiss (Ref. 18).

	Singlet		Triplet	
Z	Weiss[18]	Eq. (26)	Weiss[18]	Eq. (27)
2	0.376	0.411	0.539	0.492
3	0.213	0.217	0.308	0.298
4	0.149	0.150	0.213	0.209
5	0.114	0.115	0.163	0.161
6	0.0930	0.0932	0.131	0.130
7	0.0785	0.0786	0.110	0.110
8	0.0679	0.0679	0.0948	0.0945
9	0.0598	0.0598	0.0833	0.0830
10	0.0534	0.0534	0.0742	0.0740

TABLE II. Oscillator strengths for the ($1s3s^{1,3}S - 1s3p^{1,3}P^0$) transitions. The transition energies were taken from Wiese *et al.* (Ref. 19).

Z	Weiss (c.f. Ref. 19)	Eq. (28)	Weiss (c. f. Ref. 19)	Eq. (29)
2	0.629	0.692	0.896	0.884
3	0.362	0.374	0.509	0.510

Wiese *et al.*[19] have reported accurate values of the singlet and triplet $3s$ - $3p$ transitions for helium and ionized lithium; a comparison is presented in Table II. The accuracy of (28) and (29) is again high, and it is clear that the two formulas will provide accurate values of the oscillator strengths for more highly ionized systems, when data on the transition energies become available.

By use of computed values of the coefficients of the series expansions of the $1s2s\ ^{1,3}S$ and $1s2p\ ^{1,3}P$ eigenenergies,[20] the two leading terms in the series expansion of the oscillator strength can be derived. Thus from

$$E(1s2p\ ^1P^\circ)-E(1s2s\ ^1S)=0.028\,045Z-0.042\,547$$

and $$E(1s2p\ ^3P^\circ)-E(1s2s\ ^3S)=0.037\,799Z-0.025\,588$$

we obtain $f(1s2s\ ^1S-1s2p\ ^1P^\circ)=(0.505/Z)\,(1+0.515/Z)$

and $f(1s2s\ ^3S-1s2p\ ^3P^\circ)=(0.680/Z)\,(1+0.841/Z)$.

To $O(Z^{-1})$, these are equivalent to the expressions

$$f(1s2s\ ^1S-1s2p\ ^1P^0)=0.505/(Z-0.515),$$

$$f(1s2s\ ^3S-1s2p\ ^3P^0)=0.680/(Z-0.841).$$

These simple formulas are asymptotically exact. Even for neutral helium the error does not exceed 11%.

Returning to the lithium sequence, we determine immediately from (18) and (19) that to first order in Z^{-1}

$$\langle 1s^22s\ ^2S|Q_1(3)|1s^22p\ ^2P^\circ\rangle=-(3/Z)-(4.9398/Z^2)+O(Z^{-3}),$$

$$\langle 1s^23s\ ^2S|Q_1(3)|1s^22p\ ^2P^\circ\rangle=-(3\sqrt{6}/Z)-(5.4087\sqrt{6}/Z^2)+O(Z^{-3}).$$

The comparable expressions in the Hartree-Fock approximation are

$$\langle 1s^22s\ ^2S|Q_1(3)|1s^22p\ ^2P^0\rangle=-(3/Z)-(5.0961/Z^2)+0(Z^{-3}),^5$$

$$\langle 1s^23s\ ^2S|Q_1(3)|1s^23p\ ^2P^0\rangle=-(3\sqrt{6}/Z)-(5.4192\sqrt{6}/Z^2)+0(Z^{-3}),$$

differing only slightly from the exact expansions. In the screening approximation, the oscillator strengths are given by

$$f(1s^22s^2S-1s^22p\ ^2P^\circ)=(E_f-E_i)18/(Z-1.647)^2, \tag{30}$$

$$f(1s^23s\ ^2S-1s^23p^2P^\circ)=(E_f-E_i)108/(Z-1.803)^2. \tag{31}$$

A comparison of (30) with the results of refined 45-parameter variational calculations[21] is presented in Table III. Table III also includes a comparison of the transition probabilities derived from Weiss[21]

TABLE III. Oscillator strengths f and transition probabilities A sec^{-1} for the $1s^22s\ ^2S - 1s^22p\ ^2P^\circ$ transitions. The transition energies were taken from Weiss (Ref. 21).

	Oscillator strengths		Transition probabilities (10^8 sec^{-1})		
Z	Weiss[21]	Eq. (30)	Weiss[21]	Eq. (30)	Experiment[22]
3	0.753	0.668	0.372	0.330	...
4	0.505	0.473	1.15	1.08	...
5	0.366	0.353	1.91	1.84	...
6	0.286	0.279	2.65	2.59	2.97±0.11
7	0.234	0.230	3.38	3.34	3.34±0.12
8	0.196	0.196	4.08	4.09	3.94±0.14
9	...	0.170	...	4.85	4.48±0.16
10	...	0.151	...	5.64	5.55±0.19

TABLE IV. Transition probabilities of the $1s^23s\ ^2S - 1s^23p\ ^2P^0$ transition in 10^7 sec^{-1}.

Z	Hartree-Fock[21]	Eq. (31)
3	0.377	0.393
4	1.28	1.28
5	2.22	2.22
6	3.18	3.17
7	4.13	4.13_5
8	5.10	5.11
9	6.04	6.11

and from (30) with experimental measurements.[22] As is to be expected from the investigation of the helium-sequence oscillator strengths, the accuracy of (30) is high. In the worst case, neutral lithium, the error is about 12%. The energy of the $1s^22s\,^2S-1s^22p\,^2P^\circ$ transition is given by[4]

$$E(1s^22p\,^2P^\circ)-E(1s^22s\,^2S)=0.070\,721Z-0.119\,022+O(Z^{-1}).$$

Thus, $f(1s^22s\,^2S-1s^22p\,^2P^\circ)=(1.273/Z)(1+1.610/Z)$,

or equivalently to $O(Z^{-1})$,

$$f\,(1s^22s\,^2S-1s^22p^2P^\circ)=1.273/(Z-1.610). \tag{32}$$

Expression (32) overestimates by about 20% for neutral lithium but by less than 3% for $Z=5$.

The most accurate values of the oscillator strengths for the $1s^23s\ ^2S - 1s^23p\ ^2P^0$ transition are those calculated by Weiss[21] in the Hartree-Fock approximation. The difference between the exact and the Hartree-Fock expansions is small, and we can directly compare (31) with Weiss's results. The comparison is presented in Table IV in the form of transition probabilities. The accuracy of (31) is again very high.

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