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Variational Calculations for Quartet States of Three-Electron Atomic Systems*

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The conventional Rayleigh-Ritz variational method in which one uses pure Slater-type orbitals and correlated factors $r_{\mu\nu}^2$ in the basis functions has been applied to obtain the eigenvalues of the five lowest lying states with symmetries ${}^4P^0$, ${}^4P^e$, and ${}^4S^e$ for three-electron atomic systems. To find the absolute minimum which is attainable for each eigenvalue, the nonlinear parameters (exponential parameters) have been varied freely in submatrices up to order 30 with 20 noncorrelated and 10 correlated basis functions. This variation has been carried through separately to find the five lowest eigenvalues of each symmetry in Li and for only the lowest one in He$^-$. For the other members of the isoelectronic sequence up to $Z=10$, the absolute minima of the three lowest lying eigenvalues are found approximately by using the correlated subset of order 30 with common fixed exponential parameters for each symmetry and by freely varying the scale parameter. The lowest ${}^4P^0$ state is found to be bound in He$^-$ with a binding energy ≥ 0.033 eV. No sign of binding is indicated for the lowest ${}^4S^e$ state, but the lowest ${}^4P^e$ state is also found to be bound by ≥ 0.20 eV. The results for Li indicate as certain that the transitions ${}^4S^e(1)$-${}^4P^0(1)$ and ${}^4P^e(1)$-${}^4P^0(1)$ are responsible for the two observed multiplets present at 2934 and 3714 Å, respectively in the optical spectrum. These lines cannot be classified in the normal singly excited spectrum of the atom or ion. The results for Li are compared in detail with those obtained by recent electron-impact experiments and by other theoretical calculations.

I. INTRODUCTION

The main purposes of the present work are an effort to identify more exactly the energy levels responsible for some lines present in the optical spectrum of Li$^+$ which cannot be assigned to the normal singly-excited spectrum of that atom or ion,[1] and the determination of electron binding energies in He$^-$.

It is clear that levels with lifetimes sufficiently long to produce the observed narrow lines must be considered. All levels subject to auto-ionization via the Coulomb interaction into the adjacent continua can be excluded. Obviously, all quartet states with symmetries ${}^4S^e$, ${}^4P^o$, ${}^4P^e$, ${}^4D^o$ and ${}^4D^e$, which do not couple to adjacent continua via the Coulomb interaction, can be considered as possible levels involved in the transitions.

The unassigned multiplets[1] are as follows: at 3714.2 Å (3.34 eV), at 2934.2 Å (4.22 eV) and at 2337.0 Å (5.31 eV). The first two have been previously observed by Shüler[2] and Werner,[3] and the last one has also been observed by Werner.[3] Herzberg and Moore[1] give eight, four, and three observed fine-structure components associated, respectively, with these multiplets; but they point out that two components of the first line are not completely resolved. Similar uncertainties are probably connected with the observation of the number of components in the two other multiplets. In addition to these multiplets, the assignments of two single-component lines at 4607.34 Å (2.69 eV) and at 8517.37 Å (1.45 eV) also remain unsettled[1–5] in the spectrum of Li$^+$. A previous set of assignments for some of these lines has been made by Garcia and Mack.[6]

In addition to help in making spectroscopic assignments for these unidentified lines in the Li$^+$ spectrum, this investigation will give information on the accuracy of estimated thresholds of the observed peaks in the electron-impact excitation function for states in Li which are metastable with respect to auto-ionization.[7]

II. VARIATIONAL PROCEDURE

In the present investigation we have restricted our consideration to quartet states with the specific symmetries ${}^4S^e$, ${}^4P^o$, and ${}^4P^e$ associated with the doubly-excited configurations $1s2sns$, $n\geq 3$ ($n=2$ is excluded according to the Pauli exclusion principle); $1snsn'p$, $n,n'\geq 2$; and $1s2pnp$, $n\geq 2$ ($n=2$ is allowed because only $m\neq m'$ enters), respectively. The quartet states with the symmetries ${}^4D^e$ and ${}^4D^o$ associated with the configurations $1s2snd$, $n\geq 3$; $1s2pnp$, $n\geq 2$; and $1s2pnd$, $n\geq 3$ are very important as possible levels for the unidentified lines, and a similar investigation of these states will be carried out in the near future.

The lowest ${}^4P^o$ state with the three fine-structure components $J=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ is the only one which is metastable with respect to both auto-ionization and radiative decay; therefore this state is very important as a lower level of the principal transitions. The component ${}^4P^o{}_{5/2}$ has a longer lifetime than the other two because it is coupled to the adjacent continuum state $(1s^2kf)^2F^o{}_{5/2}$ only through the spin-spin interaction. The other two fine-structure components are connected to continuum

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[1] G. Herzberg and H. R. Moore, Can. J. Phys. **37**, 1293 (1959).

[2] H. Shüler, Ann. Physik **76**, 292 (1925).

[3] S. Werner, Nature (London) **118**, 154 (1926).

[4] G. W. Series and K. Willis, Proc. Phys. Soc. **71**, 274 (1958).

[5] Y. G. Toresson and B. Edlen, Arkiv Fysik **23**, 117 (1963).

[6] J. D. Garcia and J. E. Mack, Phys. Rev. **138**, A987 (1965).

[7] P. Feldman and R. Novick, Phys. Rev. (to be published).

states by spin-orbit and spin-spin interactions[7] via intermediate states such as ${}^2P_{1/2,3/2}$ associated with the same configuration, $1s2s2p$. The other quartet states are metastable with respect to auto-ionization in a similar way, but they will all cascade by radiative decay to the lowest ${}^4P^o$ level.

As a starting point we can make it clear that the standard variation method can be applied to all these quartet states. First, we note that states of the three-electron Hamiltonian which lie lower than the lowest ${}^4P^o$ states are all singly-excited doublets with $S=\frac{1}{2}$. Obviously, the eigenfunctions for the quartet states with $S=\frac{3}{2}$ are automatically orthogonal to the discrete $(1s^2nL)^2L$ and continuum $(1s^2kL)^2L$ states. The selection rule $\Delta S=0$ in the pure LS-coupling approximation, as already mentioned, makes all the quartet states metastable with respect to auto-ionization in the sense that no radiationless transitions to the adjacent continuum states $(1s^2kL)^2L$ can take place. The quartet continuum states $(1s2skL)^4L$ and $(1s2pkL)^4L$ all lie above the energy states of interest in this investigation.

Secondly, the eigenfunctions of the ${}^4P^e$ states are orthogonal to those of the ${}^4P^o$ states because of their different parities, and ${}^4S^e$ eigenfunctions are orthogonal to those of both types of P states because of their different L values. Furthermore, within each symmetry, when the matrix is diagonalized the trial functions belonging to higher eigenvalues of the energy matrix are automatically orthogonal to those belonging to all the lower eigenvalues. According to the Hylleraas-Undheim theorem, we know that all eigenvalues obtained by the variational procedure are always rigorous upper bounds to the exact values.

The trial function which has the correct L and parity for the state of interest can be approximated as a linear combination of Slater determinants ψ_i:

$$\Psi=\textstyle\sum_i c_i\psi_i, \tag{1}$$

where the coefficients c_i are taken as those which minimize the total energy. The total energy of the state then is (for real wave functions)

$$E=\frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\sum_{i,j} c_ic_jH_{ij}\Big/\sum_{i,j} c_ic_jN_{ij}. \tag{2}$$

Here $H_{ij}=\langle\psi_i|\mathcal{H}|\psi_j\rangle$, $N_{ij}=\langle\psi_i|\psi_j\rangle$, and $\mathcal{H}$ is the nonrelativistic spin-independent Schrödinger Hamiltonian for infinite nuclear mass:

$$\mathcal{H}=-\sum_{\mu=1}^{3}\left\{\nabla_\mu^2+\frac{1}{r_\mu}\right\}+\frac{1}{Z}\sum_{\mu>\nu}\frac{1}{r_{\mu\nu}}, \tag{3}$$

with $a_0/2Z$ as the unit of length and Z^2 Ry as the unit of energy.

The condition for making the energy an extremum leads to a system of linear homogeneous equations in the c_i's, the solution for which is given by the well known secular equation

$$|H_{ij}-\tfrac{1}{4}EN_{ij}|=0. \tag{4}$$

The solution of (4) for the energy eigenvalues E is equivalent to the diagonalization of the energy matrix derived from a nonorthogonal basis set.

III. BASIS FUNCTIONS

In the present investigation we have used products of Slater-type, one-electron orbitals $e^{-ar/2}r^nY_{lm}(\theta,\phi)$ as basis functions for our noncorrelated trial functions and similar terms with the additional correlation factor $r_{\mu\nu}^2=r_\mu^2+r_\nu^2-2r_\mu r_\nu\cos\Theta_{\mu\nu}$ for our correlated trial functions. We limited the basis to include only correlated terms of this form in view of the complexity encountered in handling correlated factors of the general form $r_{12}^dr_{13}^er_{23}^f$ where d, e, $f\geq1$.

For the quartet states with $S=\frac{3}{2}$, the Slater determinants may be written as

$$\psi_i=\frac{1}{\sqrt{6}}\sum_P(-1)^PP\phi_i(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\times r_{23}^t\chi_{1/2}(1)\chi_{1/2}(2)\chi_{1/2}(3), \tag{5}$$

where P is the permutation operator to allow for the antisymmetry in the space coordinates and where $\chi_{1/2}$ is the Pauli spinor with $m_s=\frac{1}{2}$. Here $t=0$ gives noncorrelated terms and $t=2$ gives correlated terms of our basis set of trial functions.

The basic product of Slater-type orbitals may be written

$$\phi_i(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=e^{-1/2\eta(a_ir_1+b_ir_2+c_ir_3)}r_1^mr_2^nr_3^qF_p(\hat{r}_1,\hat{r}_2,\hat{r}_3) \tag{6}$$

with a_i, b_i, and c_i as nonlinear parameters to be varied simultaneously, η as the scale parameter, and m, n, and q as fixed powers of the electron-nucleus distances. The angular function F_p is constructed such that it is an eigenfunction of L^2, L_z, and parity for the state under consideration. Since the eigenvalues are degenerate with respect to all possible M values of L_z, we have used $M=0$ for all the quartet states. The specific forms of $F_p(\hat{r}_1,\hat{r}_2,\hat{r}_3)$ which have been used are

$$\begin{array}{rl} 1 & \text{for } {}^4S^e, \\ \cos\theta_3 & \text{for } {}^4P^o, \\ \sin\theta_2\sin\theta_3\sin(\phi_2-\phi_3) & \text{for } {}^4P^e. \end{array} \tag{7}$$

When using the correlated factors $r_{\mu\nu}^2$ in the basis, all the matrix elements can be evaluated by using the conventional spherical polar coordinates as integration variables for each of the electrons.

IV. RESULTS AND DISCUSSION

The basis functions are all linearly independent, and the choice of N of them leads to an $(N\times N)$-dimensional energy matrix, which when diagonalized gives rigorous upper bounds to the N lowest lying eigenvalues

TABLE I. Variational estimates of the lowest $^4P^o$ eigenvalue of He^- ($Z=2$) in units of Z^2 Ry. The lower values are the positions in electron volts above the He ground state. The 20th order subset includes 15 noncorrelated and 5 correlated basis functions.

Atom and state	Dimensions of submatrices (20×20)	 (30×30)	"Exact" value of the $(1s2s)^3S$ limit[a]
He^- ($Z=2$), $(1s2s2p)^4P^o$	−1.087834	−1.088230 (19.785 eV)	−1.087615 (19.818 eV)

[a] C. Pekeris, Phys. Rev. **115**, 1216 (1959).

of $\mathcal{H}$. More exactly, we solve the secular Eq. (4). By varying the nonlinear parameters a_i, b_i, and c_i to separately minimize each of the eigenvalues of each symmetry, and also by varying the scale parameter to satisfy the virial theorem, we can in principle obtain the lowest upper bound to each eigenvalue which is compatible with the assumed trial function. Such a complete simultaneous variation of all the parameters would be prohibitive. We found that the most effective procedure, especially for the lower roots, was to keep the same exponential parameter for each electron coordinate throughout the basis set and then make a simultaneous variation of a, b, and c. Optimization of the scale parameter for each subset of the basis set was also found to be very helpful in minimizing the lower roots. The selection of basis functions, i.e., the selection of m, n, and q, was for the most part made arbitrarily, and subsets of the basis up to order 30 were considered practical for the numerical computations.

A. He^- ($Z=2$)

In the present investigation we made a search for possible bound states of He^- by concentrating on lowering the lowest root belonging to each symmetry. The lowest $^4P^o$ state turns out to be bound with an electron affinity $E_A \geq 0.033$ eV. The results are listed in Table I. Weiss (see Ref. f in Table V) finds this state bound with the greater upper bound $E_A \geq 0.069$ eV. This increase by a factor of two in the affinity arises from a lowering of the total energy by 6 parts in 10^4. We have used the same type of correlated functions for obtaining variationally the eigenvalues of the two-electron $(1s2s)^3S^e$ state of He and Li^+, and the results obtained seem to be good in comparison with the Pekeris "exact" values. The results are listed in Table II. Although other correlated terms such as $r_{\mu\nu}$ or $r_{\mu\nu}^3$ might further lower the energy, it appears that the $(1s2s2p)^4P^o$ state of He^- is very loosely bound. The $J=\frac{5}{2}$ component of this state is metastable with respect to auto-ionization with a lifetime of about 10^{-3} sec.[8] It is reasonable to assume that the true binding energy lies in the range 0.069 eV$<E_A<$0.1 eV.

A serious analytic error has crept into the previous calculation[9] of the matrix elements for the kinetic energy component of the Hamiltonian (i.e., $M_{p'p}$ on p. 821 of Ref. 9), and this error changes the total energy considerably. The previous result $E_A \geq 0.075$ eV, obtained by a four-dimensional subset of the same basis as is listed in Table I of the paper,[9] is erroneous. In reality, the use of this subset together with the same exponential parameters gives a negative electron affinity. One has to use much larger subsets to have any chance of obtaining a bound state. An erratum is submitted for publication to Proc. Phys. Soc. (London).

The state of He^- which appears most abundantly in double electron captures by He^+ is apparently this $^4P^o$ state, even though it is very weakly bound. This weak binding is clearly demonstrated experimentally by the decay of the ion in an electric field,[10] and the state is metastable against both auto-ionization (via the Coulomb interaction) and radiative decay. On the other hand, the results for the lowest $^4S^e$ state show no sign of binding as the parameters in the trial function are varied. It appears that no state of that symmetry can be bound in He^-.

The results obtained for the lowest $^4P^e$ state of He^- indicate that this state is also bound with respect to the $^3P^o$ state of He and with a larger binding energy than in the $^4P^o$ state. We find $E_A \geq 0.20$ eV, i.e., a calculated affinity approximately six times larger. This state is also metastable against auto-ionization; i.e., no radiationless transition to the adjacent continuum state can take place via the Coulomb interaction. It

TABLE II. Variational estimates of the lowest eigenvalue $^3S^e$ of two-electron atoms He and Li^+ in units of Z^2 Ry.

Atom and state	Noncorrelated trial function (20th order subset)	Correlated trial function (30th order subset)
He ($Z=2$), $(1s2s)^3S^e$	−1.087132	−1.087579 ("exact"[a] −1.087615)
Li^+ ($Z=3$), $(1s2s)^3S^e$	−1.135417	−1.135679 ("exact"[b] −1.135717)

[a] C. Pekeris, Phys. Rev. **115**, 1216 (1959).
[b] C. Pekeris, Phys. Rev. **126**, 143 (1962).

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[8] J. L. Pietenpol, Phys. Rev. Letters **7**, 64 (1961).

[9] E. Holøien and J. Midtdal, Proc. Phys. Soc. (London) **A68**, 815 (1955).

[10] A. C. Riviere and D. R. Sweetman, Phys. Rev. Letters **5**, 560 (1960).

TABLE III. Variational estimates of the lowest eigenvalue ${}^4P^e$ of He$^-$ ($Z=2$) in units of Z^2 Ry. The lower values are the positions in electron volts above the He ground state. The subsets of dimensions 21 and 25 include 20 noncorrelated, and 1 and 5 correlated basis functions, respectively.

Atom and state	Dimensions of submatrices (21×21)	 (25×25)	 (30×30)	"Exact" value of the $(1s2p)^3P$ limit[a]
He$^-$ ($Z=2$), $(1s2p2p)^4P^e$	−1.068741	−1.06943	−1.070329 (20.758 eV)	−1.066582 (20.962 eV)

[a] C. Pekeris, Phys. Rev. **137**, A1672 (1965).

may auto-ionize directly via the spin-spin interaction and indirectly through spin-orbit coupling to the ${}^2D^e$ and ${}^2S^e$ states, so the auto-ionization lifetime should be of the same order as for the ${}^4P^o$ state. This state may be produced by the capture of two $2p$ electrons by the He$^+$($1s$) ion, and then may radiate to the metastable ${}^4P^o$ state (with a lifetime of approximately 10^{-8} to 10^{-7} sec). This transition should give rise to a relatively strong He line (~1 eV) far outside the visible region in the infrared, and indeed the analogous line in Li has been observed (see below). The observed He$^-$ beams probably contain ions in both the ${}^4P^o$ and ${}^4P^e$ states, although we do not know the relative magnitudes of their production cross sections.[11,12] The estimate of the mean affinity (0.08 eV) made by Demkov and Drukarev,[13] based upon observed electric field dissociation results,[10] lies between our two computed values.

The results of our variational computations on the $(1s2p^2)^4P^e$ state are condensed in Table III. The two bound levels are plotted in the form of an energy-level diagram for He$^-$ in Fig. 1.

B. Li ($Z=3$)

We have made a thorough variation of the parameters in the case of Li to depress the lowest roots of each symmetry as much as possible, i.e., to locate the lowest absolute minima for the trial function used. We have limited our attention to the five lowest roots. The best values of the roots (upper bounds to the true eigenvalues) are given in Table IV, and for completeness the best noncorrelated values are also given. It is obvious that the upper roots (4 and 5) give rough approximations compared to the three lower ones. Included in the table is a comparison of the effects of the angular correlation on the various levels. It is interesting to note the relatively large angular correlation effect for the ${}^4P^o(2)$ and ${}^4P^o(3)$ states, which both can be associated with the configurations $1s2s3p$ and $1s3s2p$, or more exactly with linear combinations of them. In the unperturbed problem the states $1s2s3p$ and $1s3s2p$ are nearly degenerate, and their interaction will lead to a (+, −) classification of the excited ${}^4P^o$ states which is similar to that introduced by Cooper, Fano, and Prats[14] for the ${}^1P^o$ and ${}^3P^o$ compound states of two-

TABLE IV. Variational estimates of the five lowest-lying eigenvalues of the quartet states of Li with symmetry ${}^4P^o$, ${}^4P^e$ and ${}^4S^e$ in units of Z^2 Ry.

Atom and states	Configuration assignments	Noncorrelated trial function	Angular correlation energy	Correlated trial function	Excitation energy in eV
Li ($Z=3$)					
${}^4P^o(1)$	$(1s2s2p)$	−1.1911	0.0013	−1.19242	57.47
${}^4P^o(2)$	$(1s,23sp+)$	−1.1516	0.0093	−1.16088	61.33
${}^4P^o(3)$	$(1s,23sp-)$	−1.1435	0.0057	−1.14917	62.77
${}^4P^o(4)$	$(1s,24sp+)$	−1.1392	0.0005	−1.13966	63.93
${}^4P^o(5)$	$(1s,24sp-)$	−1.1371	0.0004	−1.13747	64.20
${}^4S^e(1)$	$(1s2s3s)$	−1.1566	0.0014	−1.15801	61.69
${}^4S^e(2)$	$(1s2s4s)$	−1.1454	0.0004	−1.14583	63.18
${}^4S^e(3)$	$(1s2s5s)$	−1.1412	0.0003	−1.14145	63.73
${}^4S^e(4)$	$(1s2s6s)$	−1.1390	0.0002	−1.13922	63.99
${}^4S^e(5)$	$(1s2s7s)$	−1.1371	0.0002	−1.13726	64.33
${}^4P^e(1)$	$(1s2p2p)$	−1.1638	0.0020	−1.16576	60.74
${}^4P^e(2)$	$(1s2p3p)$	−1.1317	0.0003	−1.13197	64.88
${}^4P^e(3)$	$(1s2p4p)$	−1.1242	0.0004	−1.12460	65.78
${}^4P^e(4)$	$(1s2p5p)$	−1.1211	0.0003	−1.12139	66.17
${}^4P^e(5)$	$(1s2p6p)$	−1.1195	0.0002	−1.11967	66.38

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[11] J. W. Hiby, Ann. Physik (Leipzig) 34, 473 (1939); R. Dopel, *ibid.* **76**, 1 (1925).

[12] V. M. Dukelski, V. V. Afrosimov, and N. V. Federenko, Zh. Eksperim. i Teor. Fiz. **30**, 792 (1956) [English transl.: Soviet Phys.—JETP **3**, 764 (1956)]; P. M. Windham, P. J. Joseph, and J. A. Weinman, Phys. Rev. **109**, 1193 (1958); S. K. Allison, Rev. Mod. Phys. **30**, 1137 (1958).

[13] Y. N. Demkov and G. F. Drukarev, Zh. Eksperim. i Teor. Fiz. **47**, 918 (1964) [English transl.: Soviet Phys.—JETP **20**, 614 (1965)].

[14] J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Letters **10**, 518 (1963); P. L. Altick and E. N. Moore, *ibid.* **15**, 100 (1965).

TABLE V. Comparison of some of the calculated eigenvalues with available experimental data and results obtained by theoretical calculations. The positions are given in electron volts above the Li ground state.

Lithium state	This paper	Expert.[a]	Theor.[b]	Theor.[c]	Theor.[d]	Theor.[e]	Theor.[f]
$^4P^o(1)$	57.47	57.3±0.3	57.99	57.68	57.52	55.47	57.44
$^4P^e(1)$	60.74	59.9±0.3				59.67	60.76
$^4P^o(2)$	61.33					61.75	
$^4S^e(1)$	61.69	61.9±0.3				61.11	61.65
$^4P^o(3)$	62.77					63.17	
$^4S^e(2)$	63.18	63.2±0.3					
$^4P^e(2)$	64.88						64.81

[a] P. Feldman and R. Novick, Ref. 7 (observed thresholds of the Li excitation function).
[b] Ta-You Wu and S. T. Shen, Chinese J. Phys. **5**, 150 (1944).
[c] S. Manson, to be published (15-parameter Hartree-Fock).
[d] F. Minn, to be published (15-parameter configuration interaction trial function).
[e] J. D. Garcia and J. E. Mack, Ref. 6, (screening parameter evaluation).
[f] A. W. Weiss (private communication). These are obtained by the method of superposition of configurations similar to that described in A. W. Weiss, Phys. Rev. **122**, 1826 (1961) and are rigorous upper bounds. Dr. Weiss has also calculated the positions of the lowest-lying $^4D^e$ and $^4D^o$ states to be 62.73 and 65.08 eV, respectively, above the ground state of Li.

electron atoms. The + and − concept, i.e.,

$$|1s,\,2n\pm\rangle = 1/\sqrt{2}\{|1s,2snp\rangle \pm |1s,2pns\rangle\},$$

can be introduced to classify the pair states, especially the lowest lying ones. Of course, for the two-electron system this classification is more natural because the $2s$ and $2p$ one-electron levels are degenerate; in the three-electron system this is not the case because the third electron ($1s$) will cause departures from a Coulomb field at small radii. In these states with the quartet symmetry involving electrons which have parallel spins, the plus level of each pair presumably lies below the minus level, as is predicted for the triplet two-electron states. The lowest root associated with the $1s2s2p$ configuration belongs to the + classification. The plus levels converge as a Rydberg series to the $(1s2s)^3S$ limit, whereas the upper minus levels tend to converge to the $(1s2p)^3P$ limit. For large n values this classification becomes meaningless, since the near degeneracy of the unperturbed levels disappears. For the levels considered in this investigation, it is reasonable to use these designations for the $^4P^o$ states, as we have done in Table IV. The quartet levels of Li are plotted in the form of an energy-level diagram in Fig. 2, and a comparison of the calculated positions with experiments and other theoretical results is made in Table V. It is surprising to notice that the lowest $^4P^o$ prediction obtained by the screening variation procedure is so far off. The agreement of the other calculated states with data available for comparison is fairly good. Note that the previously obtained result of 56.0 eV [15] for the $^4P^o(1)$ state is erroneous because of the mentioned analytic error in the calculation of Ref. 9.

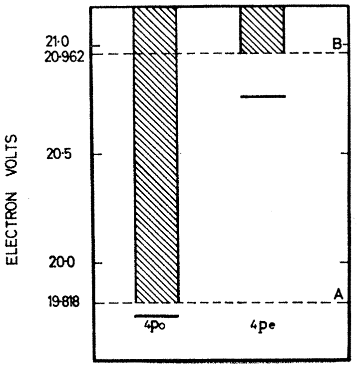

FIG. 1. Energy diagram of the calculated bound levels in He⁻. The energies are given in electron volts above the ground state of He. *A* is the $^3S^e$ limit of He (19.818 eV); *B* is the $^3P^o$ limit of He (20.962 eV).

C. Be^{+} ··· up to Ne^{7+} ($Z=4, \cdots, 10$)

Dmitriev *et al.*[16] have recently reported evidence for the production of the metastable state $(1s2s2p)^4P^o{}_{5/2}$ in N^{4+} and O^{5+}. The evidence, however, concerns only the observation of lifetimes of the order of 10^{-8} sec for the states, and no estimate of energy thresholds has been made. For comparison with possible future observations of highly excited spectroscopic lines, we have carried through the above variational calculation for all members of the isoelectronic sequence up to and including Ne^{7+} ($Z=10$). We have restricted our attention

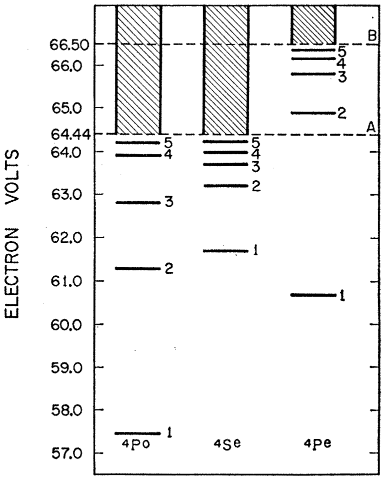

FIG. 2. Energy diagram of the five lowest-lying levels of each symmetry in Li. The energies are given in electron volts above the ground state of Li. *A* is the $^3S^e$ limit of Li$^+$ (64.44 eV); *B* is the $^3P^o$ limit of Li$^+$ (66.50 eV).

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[15] E. Holøien, Proc. Phys. Soc. (London) **83**, 537 (1964).

[16] I. S. Dmitriev, L. I. Vinogradova, V. S. Nikolaev, and B. M. Popov, JETP Pis'ma v Redaktsily **3**, 35 (1966) [English transl.: JETP Letters **3**, 20 (1966)].

TABLE VI. Variational estimates of the three lowest eigenvalues of each symmetry of all members of the isoelectronic sequence up to Ne in units of Z^2 Ry. Correlated trial function of the order 30 includes 20 noncorrelated and 10 correlated terms.

States \ Ions	$Z=4$ Be^{+}	$Z=5$ B^{2+}	$Z=6$ C^{3+}	$Z=7$ N^{4+}	$Z=8$ O^{5+}	$Z=9$ F^{6+}	$Z=10$ Ne^{7+}
${}^4P^o(1)$	-1.25785	-1.30104	-1.33135	-1.35373	-1.37090	-1.38448	-1.39549
${}^4P^o(2)$	-1.19482	-1.22427	-1.24497	-1.26028	-1.27205	-1.28137	-1.28893
${}^4P^o(3)$	-1.18196	-1.21362	-1.23617	-1.25277	-1.26548	-1.27552	-1.28366
${}^4P^e(1)$	-1.23360	-1.27974	-1.31262	-1.33709	-1.35597	-1.37096	-1.38315
${}^4P^e(2)$	-1.17790	-1.20952	-1.23203	-1.24882	-1.26178	-1.27208	-1.28045
${}^4P^e(3)$	-1.15571	-1.18442	-1.20402	-1.21834	-1.22930	-1.23796	-1.24497
${}^4S^e(1)$	-1.20221	-1.23095	-1.25098	-1.26570	-1.27696	-1.28585	-1.29304
${}^4S^e(2)$	-1.18240	-1.20979	-1.23201	-1.24871	-1.26156	-1.27175	-1.28002
${}^4S^e(3)$	-1.17646	-1.20464	-1.22148	-1.23367	-1.24297	-1.25030	-1.25623

to the three lowest eigenvalues by using the 30-dimensional subset and the same nonlinear parameters as in the case of Li. Note that the scale parameter has been freely varied for each ion. In this way the results for the lowest eigenvalue should probably be fairly good, but not quite so good for the other two. The results are given in Table VI.

V. ASSIGNMENTS OF OBSERVED Li LINES

Table VII gives the energy differences for all possible transitions between the five lowest-lying states connecting the symmetries ${}^4S^e \leftrightarrow {}^4P^o$ and ${}^4P^e \leftrightarrow {}^4P^o$, respectively. Note that transitions between the ${}^4S^e$ and ${}^4P^e$ states (no parity change) are not allowed via dipole radiation. The energy differences in electron volts are calculated from the best eigenvalues (correlated trial functions) given in Table IV.

According to our best values, we have the transitions

$$(1s2s3s)^4S^e{}_{3/2} - (1s2s2p)^4P^o{}_{5/2,3/2,1/2} = 4.22 \text{ eV},$$

$$(1s2p^2)^4P^e{}_{5/2,3/2,1/2} - (1s2s2p)^4P^o{}_{5/2,3/2,1/2} = 3.27 \text{ eV}.$$

As can be seen, the first transition agrees exactly with the line at 2934 Å having three (or four) observed fine-structure components. The number of observed components then is consistent with the number of possible transitions between the fine-structure levels with the symmetries ${}^4S^e$ and ${}^4P^o$. The second transition agrees to a lesser degree with the line at 3714 Å (the difference is 0.07 eV) with six (or eight) observed fine-structure components. The Weiss value (Table V) for this transition energy is within 0.02 eV of the observed line. This large number of resolved components is also consistent with the number (seven) of possible transitions between the fine-structure levels of the ${}^4P^e$ and ${}^4P^o$ states.

TABLE VII. All possible transitions between states ${}^4P^o$ and ${}^4S^e$, ${}^4P^o$ and ${}^4P^e$ with energy differences in electron volts.

	${}^4P^o(1)$	${}^4P^o(2)$	${}^4P^o(3)$	${}^4P^o(4)$	${}^4P^o(5)$
${}^4S^e(1)$	$+4.22$	$+0.36$	-1.08	-2.24	-2.51
${}^4S^e(2)$	$+5.71$	$+1.85$	$+0.41$	-0.75	-1.02
${}^4S^e(3)$	$+6.26$	$+2.40$	$+0.96$	-0.20	-0.47
${}^4S^e(4)$	$+6.52$	$+2.66$	$+1.22$	$+0.06$	-0.21
${}^4S^e(5)$	$+6.76$	$+2.90$	$+1.46$	$+0.30$	$+0.03$
${}^4P^e(1)$	$+3.27$	-0.57	-2.03	-3.19	-3.16
${}^4P^e(2)$	$+7.41$	$+3.55$	$+2.11$	$+0.95$	$+0.68$
${}^4P^e(3)$	$+8.31$	$+4.45$	$+3.01$	$+1.85$	$+1.59$
${}^4P^e(4)$	$+8.70$	$+4.84$	$+3.40$	$+2.24$	$+1.97$
${}^4P^e(5)$	$+8.91$	$+5.05$	$+3.61$	$+2.45$	$+2.18$

As can be seen from Table VII, we cannot on the basis of the present work make any certain assignment of the line at 2337 Å (5.31 eV) with three fine-structure components. However, on the basis of the work by Weiss this line can definitely be assigned to the $(1s2s3d)^4D^e$-$(1s2s2p)^4P^o$ transition. Using his values quoted in Table V gives the transition energy 5.29 eV, in excellent agreement with the observed line.

We can give only a very tentative pair of possible assignments to the two lines at 4607 Å (2.69 eV) and at 8517 Å (1.45 eV), both lines having only a single observed component. The fact that these lines are observed to have only one component is not particularly significant because the difficulty of separating the components in the observations increases for transitions to higher levels. If one uses Weiss's value for the ${}^4D^e(1)$ state and ours for the ${}^4P^o(2)$ state, one finds an energy difference of 1.40 eV. This is our best guess for the assignment of the 8517 Å line. The 4607 Å line could arise from the transition ${}^4D^e(2)$-${}^4P^o(2)$, but this assignment cannot be made definite until reliable calculations are available for the higher ${}^4D^e$ levels. From Table VII it can be seen that some of the higher ${}^4S^e$-${}^4P^o$ transition energies are fairly close to that of the 4607 Å (2.69 eV) line, but the transition probabilities for these would most likely be too low.[6]

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