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HIGH PRECISION VARIATIONAL CALCULATIONS FOR THE
$2^3S-2^3P$ AND $2^1S-2^1P$ TRANSITIONS OF Li$^+$. 

by

Chiranjit Deka

Submitted to the
Faculty of Graduate Studies and Research
through the Department of Physics
in partial fulfillment
of the requirements for the Degree of
Master of Science at
the University of Windsor

Windsor, Ontario, Canada
1989
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Abstract

High precision variational calculations using double basis sets in Hylleraas co-ordinates are done for $2^3S$, $2^3P$, $1^1S$ and $2^1P$ states of Li$^+$. The final energies calculated include the non-relativistic energy, the first order relativistic corrections of order $\alpha^2$ and the QED corrections of order $\alpha^3$. Accuracies of the order of 1 part in $10^{13}$ or better in the non-relativistic energies are obtained. The variational wave functions generated in these calculations allow the relativistic and QED corrections to be calculated to accuracies of better than 1 ppm. Theoretical values for the $2^3S$-$2^3P$ and $1^1S$-$2^1P$ transition frequencies are calculated and compared with existing experimental results obtained by Laser Spectroscopic methods. This enables accurate values for higher order relativistic and QED corrections to be extracted from the experimental data.

In addition, results obtained for the non-relativistic energies of $1^1S$, $n^1S$, $n^3S$, $n^1P$, $n^3P$ states ($n=3, 4$ for $n^1S$ states and $n=3, 4, 5$ for the rest) by using the same technique, are presented to facilitate further works on these states in future.
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Chapter 1

Introduction.

Two-electron atoms and ions are of fundamental importance because they are the simplest atomic systems which display the complexities of a many-body problem. Although exact analytic solutions to the Schroedinger equation are not possible, accurate approximation methods are available which allow high precision comparison between theory and experiment. Until recently, interest was focussed primarily on neutral helium because only in this case were accurate measurements of transition frequencies available. However new improved measurements for the $1s2s^3S - 1s2p^3P$ transition in Li$^+$ $^1,2s$ call for a similar improvement in theory.

A primary result of this work is that higher order relativistic and quantum electrodynamic corrections can be extracted from the experimental data and compared with theoretical estimates. The total energy of an atomic state can be written in the form

$$E = E_{nr} + E_{rel} + E_{QED}$$

where $E_{nr}$ is the nonrelativistic energy, $E_{rel}$ represents the relativistic corrections of $\mathcal{O}(\alpha^2)$ and $E_{QED}$ represents the sum of all QED effects of $\mathcal{O}(\alpha^3)$ and higher relative to $E_{nr}$. The contribution from $E_{QED}$ can be extracted from the experimental data only to the extent that $E_{nr}$ and $E_{rel}$ are known to sufficient precision. Experimental values for $E_{QED}$ are of considerable interest as a test of theoretical methods for estimating this term. A rigorous theory of radiative effects such as the Lamb-shift in many-electron atoms is not well developed, and direct calculations are difficult.
The basic problem to be solved to find $E_{nr}$ and $E_{rel}$ in (1.1) is the two-electron nonrelativistic Schrödinger equation

$$H \Psi(\vec{r}_1, \vec{r}_2) = E_{nr} \Psi(\vec{r}_1, \vec{r}_2) \quad (1.2)$$

where,

$$H = \frac{\hbar^2}{2m} \left( \frac{Z_1 e^2}{r_1} + \frac{Z_2 e^2}{r_2} + \frac{e^2}{r_{12}} \right). \quad (1.3)$$

It is the $\frac{e^2}{r_{12}}$ electron-electron repulsion term which prevents exact analytic solutions. The most accurate approximate solutions have been obtained by the Hylleraas variational method $4_{3.32-35}$ in which $\Psi(\vec{r}_1, \vec{r}_2)$ is expanded in a finite basis set of functions of the form

$$a_{ijk} r_1^{i} r_2^{j} r_{12}^{k} e^{-\alpha r_1 - \beta r_2} \times \text{(angular functions)} \quad (1.4)$$

where $r_{12} = |\vec{r}_1 - \vec{r}_2|$. The $a_{ijk}$ are linear variational parameters determined by making the functional

$$L = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.5)$$

an extremum.

The above basis set is complete $49$ so that convergence to the correct answer is assured as the basis set is enlarged. The non-linear parameters $\alpha$ and $\beta$ in (1.4) can also be adjusted to minimize the energy. An important feature of (1.5) is that it always yields an upper bound to the exact eigenvalue.

Some of the most successful pioneering efforts in applying the above variational techniques to the two-electron system were made in the early sixties by Schwartz$^4$ and Pekeris et al.$^{5-8}$. Schwartz$^4$ used a trial function of the Hylleraas
type but the non-linear parameters in the variational wave functions were not optimized individually; two fixed values for the non-linear parameters, \( \kappa = 4.62 \) and \( \sigma = .92 \), were used for all the calculations. For their early calculations, Pekeris et al.\(^3\)\(^5\)\(^\text{-11}\) expanded the wave function in a triple series of Laguerre polynomials of the perimetric coordinates which are linear combinations of \( r_1, r_2 \) and \( r \). In the calculations for the ground state and the \( 2^3S \) of neutral helium\(^5\) these coordinates were first defined as

\[
u = \epsilon(r_2 + r - r_1), \quad v = \epsilon(r_1 + r - r_2), \text{and} \quad w = 2\epsilon(r_1 + r_2 - r),
\]

where \( \epsilon = \sqrt{E} \), \( E \) being the energy eigenvalue. In terms of these coordinates the wave function was taken in the form

\[
\Psi = (1 \pm P_{12})e^{-\frac{1}{2}(u+v+w)}F(u,v,w), \tag{1.6}
\]

where \( P_{12} \) is the exchange operator. Here the expansion \( F \) was taken as

\[
F = \sum_{i,j,k} a_{ijk}L_i(u)L_j(v)L_k(w). \tag{1.7}
\]

The above form amounts to setting both non-linear parameters \( \alpha \) and \( \beta \) in (1.4) equal to \( \sqrt{E} \). The accuracy achieved in the calculated non-relativistic energies was of the order of 1 part in \( 10^9 \) (or \( 0.001 \) cm\(^{-1}\)). Including mass-polarization and relativistic corrections they obtained a value for the ionization energy of 198312.0258 cm\(^{-1}\) from a 1078 term wave function for the \( 1^1S \) state. With a Lamb shift correction of \(-1.339 \) cm\(^{-1}\)\(^\text{12,13}\), this leads to a theoretical value for the ionization energy of 198310.687 cm\(^{-1}\), compared with Herzberg's existing experimental value of 198310.8 ± 0.15 cm\(^{-1}\)\(^\text{14}\). For the \( 2^3S \) state, on the other hand, with 715 terms in the basis set they obtained an energy value of \(-2.17522937822 \) a.u. with an estimated error of the order of 1 in the last figure. With mass polarization, relativistic and Lamb shift corrections the total ionization energy in this case was calculated to be 38454.66 cm\(^{-1}\) as against Herzberg's experimental value of
38454.73 ±0.05 cm⁻¹. The above agreements were a great improvement over any previous work. When Herzberg¹⁵ completed his spectroscopic determination of the ionization energy, achieving an accuracy of ± 0.15 cm⁻¹, the best theoretical results available were due to Kinoshita¹⁶ obtained variationally from a 39-term solution, for which the uncertainty was estimated to be ± 0.5 cm⁻¹.

In 1962 more results were forthcoming from Pekeris et al. for 1S and 2³S of helium and also 1S of H⁺. In the case of helium, it was probably the first time that an almost complete merging of the upper and lower bounds for 2³S energy was achieved⁷; for a 715 term calculation the gap was 0.0006 cm⁻¹ whereas the existing experimental error in the 2³S term value itself was 0.05 cm⁻¹. A 1078 term calculation gave the ionization energy for this state to be 38454.827375 cm⁻¹ including a relativistic correction of 1.922013 cm⁻¹ and a mass polarization correction of -0.2238810 cm⁻¹. The accuracy of the above result allowed for a meaningful inclusion of the Lamb shift correction for comparison with experimental results. With Suh and Zaidi's⁵⁵ value for Lamb shift of -0.109±0.009 cm⁻¹, the final ionization energy for the 2³S came out to 38454.718±0.009 cm⁻¹, as against Herzberg's experimental value of 38454.73±0.05 cm⁻¹. Similarly, for the 2¹S state the ionization energy calculated was 32033.214±0.014 cm⁻¹ as against the existing experimental value of 32033.26±0.03 cm⁻¹, also due to Herzberg.

In the same year⁵ the theoretical values of ionization energies of 1¹S and 2³S states of Li⁺ were calculated to be 610087.449±0.005 cm⁻¹(from 444 term calculations) and 134045.2612±0.0001 cm⁻¹(from 308 terms) respectively. With a Lamb shift of -7.83 cm⁻¹⁹ the theoretical ionization energy for 1¹S was 610079.61 cm⁻¹ as against the existing experimental value of 610079. ± 5[±3] cm⁻¹¹⁷. For the 2³S state with a Lamb shift of -1.14 cm⁻¹ the total ionization energy was 134044.12 cm⁻¹ as against
an experimental value of $134044.19 \pm 0.10 \text{ cm}^{-1}$\textsuperscript{17}.

Although the above variational energies are accurate to one part in $10^9$ to $10^{10}$ which is more than two orders of magnitude better than experimental accuracy available at that time, the accuracy of the corresponding variational wave functions were definitely not as precise. As a matter of fact even an expected average accuracy of 1 part in $10^4$ to $10^5$ was not assured for particular regions in space\textsuperscript{18}. In order to improve the convergence of the energy eigenvalues, and hence to obtain better wave functions, various non-conventional terms were tried in the trial functions. For example, variational calculations for the ground state of the two electron system were carried out\textsuperscript{18} with a wave function containing terms like $\ln(r_1 + r_2)$, $[\ln(r_1 + r_2)]^2$ and $(r_1^2 + r_2^2)^{1/2}$. It is obvious that if the logarithmic terms do indeed appear in the true wave functions, their inclusion in the variational wave function should accelerate convergence of the non-relativistic energies as the size of the basis set is increased. The trial function used in the above calculations\textsuperscript{18} was of the form,

$$\Psi(s,u,t) = \phi(ks, ku, kt)$$

where $\phi = e^{-t/2} P(s, t, u, (s^2 + t^2)^{1/2}, \ln s)$

with,

$$P = \sum_{n, t, m, i, j} C(n, t, m, i, j) s^n t^l u^m (s^2 + t^2)^{1/2} (\ln s)^j$$  \hspace{1cm} (1.8)

for the symmetrical case. (For the anti-symmetrical case odd powers of $t$ are used).

In (1.8) the variables $n, l, m, i, j$ are all positive integers and $k$ is a scaling parameter. The coordinates are defined as $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r$. The constraints used in determining the size of the basis set are $i = 0$ or 1 and $n + l + m + j \leq w$, $n + w \geq 1$ and $n + l + m + i \geq 2j$, where $w$ is a positive integer. With this scheme, solving for determinants up to order 246 containing all terms with $\ln s$ and $(\ln s)^2$, energies were
calculated for $Z = 1$ to 10. The values obtained thus were found to be better than those found earlier without the non-conventional terms. For example, for Li$^+$ the 246 term solution was $-7.2799134126660$ a.u. which was also stable to the 10th figure after the decimal point. However, the above representation did not give any appreciably better results for $2^1S$ and $2^3S$ states, indicating that logarithmic terms are significant mainly for the $1^1S$ state where both electrons are close to the nucleus.

In 1971 Accad, Pekeris and Schiff$^3$ calculated non-relativistic energies as well as mass-polarization and relativistic corrections for the excited S and P states ($n=2$ to 5, both singlet and triplet) of the helium isoelectronic sequence up to $Z=10$. These calculations were accurate to about 1 part in $10^{10}$ and were the most accurate results available for many years for Li$^+$ and helium. The method used in these calculations was basically the same as that employed for helium in earlier works$^5$-$^{11}$. Thus the wave functions were taken in the form of (1.6), and for the S states the expansion $F$ was again taken in the form of (1.7), while, for the P states it was expanded as

$$F = \sum_{i,j,k} c_{ijk} u^i v^j w^k [r_1 \cos \theta_1], \quad (1.9)$$

where $\theta_1$ is the polar angle of the electron-1.

The non-linear parameter $\alpha$ was optimized for all calculations involving the P states and a definite improvement in the rate of convergence was observed. The parameter $\beta$ was given the fixed value $Z$, the atomic number of the atom concerned. For the S state calculations, however, accuracy of the results was found to deteriorate appreciably when the calculations were done by varying $\alpha$. The loss of accuracy was most serious for the lowest-lying states of a given ion. Also, the accuracy deteriorated for a given state when the atomic number was increased.
Therefore, for these states the calculations were done also by taking $\alpha = (-2E - Z^2)^{1/2}$ and $\beta = Z$, as was done in some of the earlier works$^8$. These values were chosen because they give the correct asymptotic behaviour as one or the other electron goes to infinity. Although the rate of convergence decreased, the loss of accuracy was found to be less severe in these calculations. Again, for the particular case of $2^1S$ states both the parameters were made equal to $\sqrt{E}$. This, however, was found to yield poor results for the higher excited states due to the inadequacy of using the same value for the screening constants.

In 1972, using two-electron wave functions of the Hylleraas type, more variational calculations were carried out by Hambro$^{19}$ to obtain high precision values for the fine structure of the $2^3P$ state by including also the second-order corrections due to the Breit operators and the mass-polarisation operator. The non-relativistic trial function chosen for $2^3P$ state was of the form

$$\Psi_o = \sum_{l,m,n} C_{lmn} \frac{1 - P_{12}}{4\pi \sqrt{2}} r_1 r_2 r_{12} \exp[(-\kappa_1 \sigma_1 - \kappa_2 \tau_2)/2]$$

(1.10)

which is the same as that used by Schwartz$^4$ to calculate the expectation value of the spin-dependent Breit-Pauli operators which represent the non-relativistic corrections due to the relativistic effects in the two-electron systems. With $\omega = 10$ and 286 terms in the expansion (1.10) the results were accurate to 1 part in $10^4$.

Since the energy levels are given by a power series expansion in $\alpha^2$ of the form

$$E_j - E_o = \alpha^2 \langle O|H_2|O \rangle + \alpha^4 \langle O|H_2[1/(E_o - H_o)H_2]|O \rangle_j$$

$$+ \alpha^4 \langle O|H_4|O \rangle_j + O(\alpha^6) + \ldots$$

(1.11)

and $\alpha^2$ is of the order of $10^{-4}$, to obtain the final results to an accuracy of order of 1 ppm an accuracy of 1% for the second order integrals would have been sufficient to
match the accuracy to which the first order integrals (expectation values of $H_2$) could be calculated at that time$^4$; and for this purpose the terms $\mathcal{O}(\alpha^5)$ and smaller could well be neglected. $H_4$ represents operators of intrinsic order $\alpha^4$ not contained in the Breit-interaction. In 1965 Kim$^{20}$ did some work on the analytical forms for spin-dependent part of the operators $H_4$. This was followed by a more complete analysis, starting from the Bethe-Salpeter equation, by Douglas$^{21}$. The expectation values of the spin-dependent part of $H_4$ were subsequently evaluated to 1% by Daley$^{22}$. The spin-independent part of $H_4$, however, is still not known.

Concerning the trial function, in the above calculations$^{19}$ the screening parameters were not optimized because of the complexity of the problem, and Schwartz's values $\kappa=4.62$ and $\sigma=0.29$ were used for all the calculations.

Further results on the helium $^3P_{j=0,1,2}$ fine structure were reported with an accuracy of ~1 ppm by Daley et al.$^{23}$.

As more and more highly accurate results became available in the experimental measurements of the spectra of the two-electron ions, it became imperative that the theoretical calculations also be more accurate than ever. Following their earlier calculations on $S$ and $P$ states of the helium isoelectronic sequence, Pekeris et al.$^{24}$ calculated the correction to the $n^3P_1$ levels due to the singlet–triplet mixing which was not included before, using the wave functions described in Ref(3). With wave function expansions containing up to 364 terms for He and Li$^+$ and up to 120 terms for the other ions with up to $Z=10$ satisfactory convergence was obtained. On adding the corrections to the theoretical values already available for the fine structure splitting of the $2^3P$ levels$^3$, the agreement with experimental results improved as was also confirmed independently by Ermolaev and Jones$^{25}$. 
In 1978 Lewis and Serafin026 also calculated second order contributions to the fine structure of the 23P levels of Helium from all all intermediate states. It was shown that given the precision of existing experiments27,28 which determined the larger intervals \( \nu_{01} \) to an accuracy of 1.2 ppm, the fine structure constant can be determined to better than 1 ppm if the theoretical splitting is accurate to 1 ppm or better, which entails computations of the order of \( \alpha^6mc^2 \). In an earlier work, Hambro19,29,30 calculated the second order corrections to the Breit and mass polarization operators but still \( \alpha \) could be determined to 3 ppm only. The variational technique followed by Lewis and Serafin0 was the same as in Hambro's work which means that no new optimization of the non-linear parameters was done.

The final theoretical results up to order \( \alpha^6mc^2 \) were much more accurate for \( \nu_{01} \) than for \( \nu_{12} \). The theoretical value for \( \nu_{01} \) is 29616.904 ± 0.042 MHz (1.44 ppm) as against the experimental value of 29616.864 ± 0.036 (1.2 ppm). On the other hand the theoretical value of 2291.283 ± 0.081 MHz (35 ppm) for \( \nu_{12} \) did not match the accuracy of the corresponding experimental value 2291.196 ± 0.005 MHz (2.2 ppm). The value of \( \nu_{01} \) was used to extract a fine structure constant value of \( \alpha = 1/[137.03608(±0.00003)] \) (0.94 ppm) which was better than any other previous measurement.

As more experimental results on the spectra of helium-like ions became available giving accurate information on the energy of a variety of states, both singly and doubly excited, a generalized formalism for calculating a wide class of two-electron matrix elements in Hylleraas coordinates was called for. This problem was solved by Drake who developed a general technique for the reduction of a wide class of two-electron matrix elements in Hylleraas coordinates to finite sums of radial integrals31. This was a major step forward in the field of variational
calculations for two-electron systems since it facilitated calculations for states of arbitrary angular momentum.

A brief review of the above technique, which has been discussed in great detail by Drake and Actonick elsewhere, is given in Appendix-II.

Using the above technique, extensive calculations with correlated variational wave functions have already been done for a wide range of excited states of helium, including 2\(^1\)S, 2\(^3\)S, 2\(^1\)P, 2\(^3\)P, n\(^1\)D, n\(^3\)D (n=3 to 8), and also for the 1\(^1\)S state for both helium and H\(^+\). Incorporating the new double-basis set procedure involving multiple non-linear parameters in the above calculations, Drake has shown that accuracies of the order of 1 part in 10\(^{14}\) in the non-relativistic energies can be achieved with basis sets of moderate size without numerical problems. This accuracy represents three more significant figures than any previous results. Drake and Makowski could achieve the accuracy of the 560 term calculation of Schiff \textit{et al.} with only 240 terms in the basis set; these are also substantially more accurate than those of Kono and Hattori for basis sets of comparable size.

The primary objective of the present work is to obtain high-precision variational calculations for the 2\(^3\)S – 2\(^3\)P transition frequencies of Li\(^+\). The non-relativistic energy eigenvalues of 1\(^1\)S, n\(^1\)S, n\(^3\)S, n\(^1\)P, n\(^3\)P (n=2 to 5) states of Li\(^+\) are calculated by the variational method using double basis sets in Hylleraas co-ordinates. Corrections due to the mass-polarization, relativistic and QED effects are calculated for the 2\(^1\)S, 2\(^3\)S, 2\(^1\)P and 2\(^3\)P states. Finally, the theoretical results for the 2\(^3\)S – 2\(^3\)P transition frequencies are compared with high precision experimental results obtained by Laser-spectroscopic methods. This allows well-defined values for residual higher order relativistic and QED corrections, which are not included in the theory, to be extracted from the experimental data.
Chapter 2

General Theory of Variational Calculations With Two-Electron Systems

In this chapter the construction of the two-electron variational trial function and its application to the variational calculation of the non-relativistic energies is discussed. This is followed by a description of the relativistic and the QED corrections which contribute to the total energy of any state in a two-electron system.

2.0 The Variational Wave Function

One of the most important objectives of the variational calculations is the construction of a trial function which has the correct form to represent the actual physical system as closely as possible. The purpose of these calculations is to determine theoretically the total energies of various atomic states to such a degree of accuracy that meaningful comparison with high precision experimental results can be made and useful information extracted from the latter. However, the accuracy of the relativistic corrections of the order $\alpha^2$ calculated by the perturbation method is limited by the accuracy of the wave functions used. For example, if a variational calculation gives a non-relativistic energy with $N$ significant figures (accuracy of 1 part in $10^N$), then the corresponding wave function, when used to calculate the expectation value of any given operator in the first order, gives a result which is accurate to only 1 part in $10^{N/2}$. This is because the non-relativistic energy is stationary with respect to first order variations in the wave function whereas the expectation values of the correction operators are not, as can be seen in the following.
Let the trial function be written in the form

\[ \Psi_{tr} = \Psi_n + \sum_{i \neq n} a_i \Psi_i \]  

(2.1)

where \( \Psi_n \) is the exact wave function of the system and the summation on the right hand side of (2.1) represents the error in the trial wave function. The non-relativistic energy is given by

\[ E_{nr} = \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} = \frac{E_n}{1 + \sum_{i \neq n} a_i^2} + \frac{\Sigma a_i^2}{1 + \sum_{i \neq n} a_i^2} \]  

(2.2)

Thus, if the uncertainty in the wave function, the measure of which is given by the order of magnitudes of the coefficients \( a_i \)'s in (2.1), is, say \( 10^{-7} \), then the non-relativistic energy can still be obtained with an accuracy of the order of 1 part in \( 10^{14} \). But, when the same wave function is used to calculate the expectation value of an operator in the first order, one gets

\[ \langle \Psi_{tr} | A | \Psi_{tr} \rangle = \langle \Psi_n | A | \Psi_n \rangle + 2 \sum_{i \neq n} \langle \Psi_n | A | \Psi_i \rangle a_i \sum_{i \neq j} \langle \Psi_i | A | \Psi_j \rangle a_i a_j. \]  

(2.3)

This has an accuracy of the order of 1 part in \( 10^7 \) only. Therefore, to obtain high precision values of the total energies which includes the relativistic corrections (to the order of \( \alpha^2 \)) and the QED corrections (to the order of \( \alpha^3 \)), a properly optimized variational wave function should be as close to the exact wave function as possible.

An indication of the accuracy of the generated wave functions is given by the degree of convergence of the non-relativistic variational energy eigenvalues as the size of the basis set is increased progressively. Now, it is imperative that for good
convergence the trial function chosen for the variational calculation have the correct
form to truly represent the actual physical system. In their calculations, Schiff et al.\textsuperscript{11} used the non-relativistic two electron wave function of the Hylleraas
type of the form
\[
\psi(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{ijk} a_{ijk} \hat{r}_i^1 \hat{r}_j^2 \hat{r}_k^{12} \exp(-\alpha r_1 - \beta r_2) \mathcal{J}_{l_1l_2L}(\hat{r}_1, \hat{r}_2) \tag{2.4}
\]
where \(P_{12}\) is the exchange operator and \(r_{12} = |\hat{r}_1 - \hat{r}_2|\), (or equivalently in terms of
powers of \(s = r_1 + r_2\), \(t = r_1 - r_2\), and \(u = r_{12}\)). \(\mathcal{J}_{l_1l_2L}(\hat{r}_1, \hat{r}_2)\) is the vector
coupled product of solid spherical harmonics \(r_1^{l_1}Y_{l_1}^m(\hat{r}_1) \) and \(r_2^{l_2}Y_{l_2}^m(\hat{r}_2)\) to form a
state of total angular momentum \(L\). In their works, Hambra\textsuperscript{19} and Lewis and
Serafino\textsuperscript{26} also used similar wave functions, but their variational energies were
optimized for the linear coefficients only. The non-linear parameters were the same
as used earlier by Schwartz\textsuperscript{4}. Pekeris et al. varied only one non-linear parameter
in their calculations for \(S\) and \(P\) states of the helium isoelectronic sequence\textsuperscript{9} to find
the energy minima. In these variational calculations using trial functions which
have the form of equation (2.4), the convergence of the calculation is studied by
including all terms such that \(i+j+k \leq N\), where \(N\) is an integer, and then
progressively increasing \(N\).

The problem with the above approach is that the number of terms generated,
being equal to \((N+1)(N+2)(N+3)/6\), increases rapidly with \(N\). For example, the
largest calculation in Ref (3) has \(N=11\) which gives 364 terms. The resulting
energies for the \(2^1S\) states of \(Li^+\) are accurate to 1 part in 10\textsuperscript{10}. For the \(2^1S\) and
\(2^3S\) states only 220 terms could be included before numerical problems set in. A
substantial improvement in accuracy would require much larger basis sets. But if
the expansion contains too many terms numerical cancellation problems tend to
make the generated wave functions and the eigenvalues unstable. The loss of
accuracy is most serious in their work for the lowest lying states of any given ion. Also the accuracy deteriorates for a given state as the nuclear charge is increased.

Most of the above problems can be avoided and excellent convergence achieved when use is made of the double-basis set wave function of Drake\textsuperscript{34–36} of the form

$$\Psi(\hat{r}_1, \hat{r}_2) = \sum_{ijk} (1 \pm P_{12}) \left[ a_{ijk}^{(1)} \varphi_{ijk}(\alpha_1, \beta_1) + a_{ijk}^{(2)} \varphi_{ijk}(\alpha_2, \beta_2) \right]$$

(2.5)

where \( \varphi_{ijk}(\alpha, \beta, \ell) = \gamma_{12}^{i, j, k} \exp(-\alpha \hat{r}_1 - \beta \hat{r}_2) \beta_{12}^M \iota_{12} L(\hat{r}_1, \hat{r}_2) \).

Here each combination of \( i, j, k \) is included twice with different non-linear parameters \( \alpha_1, \beta_1 \) and \( \alpha_2, \beta_2 \). A complete optimization of the energy with respect to all four non-linear parameters leads to well-defined and numerically stable values for the parameters, with the two sets in general being well separated from each other. It has been found that for the first set, the optimum values of \( \alpha_1 \) and \( \beta_1 \) are close to their screened hydrogenic values \( \alpha_1 \approx Z \) (unscreened hydrogenic 1s state) and \( \beta_1 \approx Z-1 \) \( \frac{1}{n} \) (screened hydrogenic \( n\ell \) electron) in atomic units. These terms describe the asymptotic behaviour of the wave function. The second set of parameters \( \alpha_2, \beta_2 \) are usually much larger and increase with the size of the basis set. These terms describe the complex inner correlation effects. The complete optimization thus divides the basis set into two sectors with different distance scales.

It was further found that for 1sn\( \ell \) states, it is essential to include a third block in the basis set with non-linear parameter the same as in the first block but \( \ell_1 = 1 \) and \( \ell_2 = \ell - 1 \), where \( \ell \) is the orbital angular momentum of the second electron in the configuration 1sn\( \ell \). The size of this block is usually quite small. For example in
the present work for the $1snp$ states only thirty-five terms for this block was found to be sufficient.

2.1 Non-Relativistic Hamiltonian For Two-Electron System

Due to the near-screened hydrogenic nature of the excited states of $\text{Li}^+$, we can write the nonrelativistic Hamiltonian for infinite nuclear mass in the form

$$
\mathbf{H} = \mathbf{H}_0(r_1, Z) + \mathbf{H}_0(r_2, Z-1) + \left( \frac{1}{r_1} - \frac{1}{r_2} \right)
$$

with $\mathbf{H}_0(r_1, Z) = -\frac{1}{2} \mathbf{V}_1^2 - \frac{Z}{r_1}$ and $\mathbf{H}_0(r_2, Z-1) = -\frac{1}{2} \mathbf{V}_2^2 - \frac{Z-1}{r_2}$.

The eigenvectors of $\mathbf{H}_0(r_1, Z) + \mathbf{H}_0(r_2, Z-1)$ are

$$
\Psi_0(1s, n\ell) = \psi_0(1s, Z) \psi_0(n\ell, Z-1), \text{with eigenvalues}
$$

$$
E_{\text{sh}} = \left[-\frac{1}{2} - \left( \frac{Z-1}{Z} \right)^2 (1/2n^2) \right] Z^2 \text{ in a.u.}
$$

It is numerically advantageous to include $\Psi_0(1s, n\ell)$ in the basis set and to cancel algebraically the screened hydrogenic contribution $E_{\text{sh}}$ to the matrix elements so that the variational principle applied to $\mathbf{H} - E_{\text{sh}}$ yields directly the correction to $E_{\text{sh}}$. Thus the basis set now is written as

$$
\Psi(i_1, i_2) = a_0 \Psi_0(1s, n\ell) + \sum_{i, j, k} (1 \pm P_{12}) [a^{(1)}_{i, j, k} \phi_{i, j, k}(\alpha_1, \beta_1) + a^{(2)}_{i, j, k} \phi_{i, j, k}(\alpha_2, \beta_2) + (1 - \delta_{i_2, 0}) a^{(3)}_{i, j, k} \phi_{i, j, k}(\alpha_1, \beta_1)]
$$

where

$$
i + j + k \leq N1 \text{ for block-1}
$$

$$
i + j + k \leq N2 \text{ for block-2}
$$

$$
i + j + k \leq N3 \text{ for block-3}
$$

The term corresponding to $i=j=k=0$ in the first summation is omitted because it is nearly the same as the $\Psi_0(1s, n\ell)$ when $\alpha_1$ and $\beta_1$ are close to the screened hydrogenic values.
2.2 Optimization Of The Non-Relativistic Energy

With the trial function $|\Psi>$ and Hamiltonian $H$, the variational energy is given by Schrödinger's variational principle

$$ E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{2.7} $$

which is an upper bound to the exact eigenvalue. The energy is first optimized with respect to the linear coefficients $a_{ijk}$'s which is equivalent to diagonalizing the Hamiltonian matrix.

Next, the energy is optimized with respect to each nonlinear parameter. Complete optimization of the $\alpha$'s and $\beta$'s can be efficiently accomplished by calculating the derivatives

$$ \frac{\partial E}{\partial \alpha_t} = -2 \langle \Psi | H - E | r_1 \psi(\mathbf{r}_1, \mathbf{r}_2; \alpha) \pm r_2 \psi(\mathbf{r}_2, \mathbf{r}_1; \alpha) \rangle $$

$$ \frac{\partial E}{\partial \beta_t} = -2 \langle \Psi | H - E | r_2 \psi(\mathbf{r}_1, \mathbf{r}_2; \beta) \pm r_1 \psi(\mathbf{r}_2, \mathbf{r}_1; \beta) \rangle \tag{2.8} $$

$$ t = 1, 2 $$

where $\psi(\mathbf{r}_1, \mathbf{r}_2; \alpha) = \sum_{i,j,k} a_{ijk}^{(t)} \varphi_{ijk}(\mathbf{r}_1, \mathbf{r}_2; \beta)$, and we have assumed the normalization condition $\langle \Psi | \Psi \rangle = 1$.

Once the first derivatives are known, the second derivatives are estimated by changing the $\alpha_t$'s and $\beta_t$'s in the direction of lower energy and taking differences. The method of Newton is applied to locate the zeroes of the first derivatives. Since the initial $\alpha$'s and $\beta$'s for the relatively large basis sets are already close to the minimum the procedure converges in just a few iterations.

The implicit dependence of the $a_{ijk}$ on $\alpha_t$ does not contribute to the derivatives if the former are already optimized as can be seen by the following
argument. The total derivatives of the energy are

$$\frac{dE}{d\alpha_t} = \sum_{i,j,k,t'} \left( \frac{\partial E}{\partial a_{i,j,k}^{t'}} \right) \frac{\partial a_{i,j,k}^{t'}}{\partial \alpha_t} + \frac{\partial E}{\partial \alpha_t}$$

(2.9)

where the first term expresses the implicit dependence of the linear coefficients $a_{i,j,k}^{t'}$ etc. on $\alpha_t$ which contributes, in general, to a change in $E$. But since the linear coefficients are already optimized, $\frac{\partial E}{\partial a_{i,j,k}^{t'}} = 0$ for all $t'$ and this contribution vanishes so that $\frac{dE}{d\alpha_t} = \frac{\partial E}{\partial \alpha_t}$.

To locate the zeroes of the first derivatives we proceed as follows. In the first iteration, small preset changes are given to the parameters in the direction of $\frac{\partial E}{\partial \alpha_i}$. Let $(x_{i0}, D_{i0})$ and $(x_{i1}, D_{i1})$ be the parameter values and the corresponding first derivatives $\frac{\partial E}{\partial x_i}$ from the first two iterations. If we plot these on a graph, linear extrapolation gives the value of $x_i$ for which the derivative will be zero. Let us call this value $x_{i2}$ which is given by

$$x_{i2} = \frac{D_{i0} x_{i1} - D_{i1} x_{i0}}{D_{i0} - D_{i1}}$$

(2.10)

so that the step size now will be

$$\Delta x_i = x_{i2} - x_{i1} = \left[ \frac{x_{i1} - x_{i0}}{D_{i0} - D_{i1}} \right] D_{i1}.$$  

(2.11)

The above process is carried out for all the non-linear parameters and is repeated until the derivatives as well as the changes in the successive values of the energy, which is given by

$$E(x_j, x_{j'}, \ldots, x_n) = E(X_j, X_{j'}, \ldots, X_n) + \sum_{i=1}^n \Delta x_i \left. \frac{\partial E}{\partial x_i} \right|_{\hat{x}}$$

(2.12)

are sufficiently small. For the present work a value of the the order of $10^{-15}$ or less for the first derivatives and $10^{-16}$ for the change in energy was considered sufficient.
2.3 Correction Due to Finite Nuclear Mass

In calculating the non-relativistic energies, the nucleus so far has been considered to be infinitely heavy. However in reality we cannot ignore the fact that the nucleus has only a finite mass, which means that in treating the present problem we must consider the motion of a three particle system instead of just the two electrons moving around a fixed center of force. With proper choice of co-ordinates, however, the final results can still be expressed in terms of the two-electron system but with a modified hamiltonian to take into account the effect of the nuclear motion.

If \( \mathbf{r}_N, \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are the position vectors of the nucleus and the two electrons respectively in an inertial co-ordinate system, then the complete Schroedinger equation is

\[
H\Psi = E\Psi
\]

with

\[
H = -\frac{\hbar^2}{2M} \nabla_N^2 - \frac{\hbar^2}{2m}\left(\nabla_i^2 + \nabla_N^2\right) - e^2 \left(\frac{Z}{r_{1N}} + \frac{Z}{r_{2N}} - \frac{1}{r_{12}}\right)
\]

(2.13)

where \( r_{1N} = |\mathbf{r}_1 - \mathbf{r}_N| \) and \( r_{2N} = |\mathbf{r}_2 - \mathbf{r}_N| \). \( M \) and \( m \) are the nuclear and electronic mass respectively.

Defining the center of mass vector

\[
\mathbf{R} = \frac{1}{M+2m} \left[ M\mathbf{r}_N + m(\mathbf{r}_1 + \mathbf{r}_2) \right]
\]

(2.14)

and the relative coordinates

\[
\mathbf{\xi}_i = \mathbf{r}_i - \mathbf{R}, \quad (i = 1, 2)
\]

(2.14')

we have the following transformation relations

\[
\mathbf{\hat{v}}_i = \mathbf{\hat{v}}_i' + \frac{m}{M+2m} \mathbf{\hat{v}}_{\text{cm}}, \quad (i=1,2)
\]

\[
\mathbf{\hat{v}}_N = -\frac{2}{\mathbf{\hat{r}}_i} + \frac{M}{M+2m} \mathbf{\hat{v}}_{\text{cm}}.
\]

(2.15)

Therefore we can now write
\[ \hat{\Psi}^2 = \left( \frac{m}{M + 2m} \right)^2 \hat{\Psi}^2_{cm} + \hat{\Psi}^\prime_1^2 + \frac{m}{M + 2m} \left( \hat{\Psi}_{cm} \cdot \hat{\Psi}^\prime_1 \hat{\Psi} \right) \tag{2.16} \]

and
\[ \hat{\Psi}^2 = \left( \frac{M}{M + 2m} \right)^2 \hat{\Psi}^2_{cm} - \frac{M}{M + 2m} \sum_{k \neq k'} \left( \hat{\Psi}_{cm} \cdot \hat{\Psi}^\prime_k \hat{\Psi}^\prime_{k'} + \hat{\Psi}^\prime_1 \cdot \hat{\Psi} \hat{\Psi}_{cm} \right) + \sum_{i \neq k} \hat{\Psi}^\prime_i \cdot \hat{\Psi}^\prime_1. \tag{2.16'} \]

Substituting (2.16) and (2.16') in (2.13) we then have
\[ H = -\frac{\hbar^2}{2(M+2m)} \hat{\Psi}^2_{cm} + \frac{1}{2(M+2m)} \sum_{i \neq k} \hat{\Psi}^\prime i \cdot \hat{\Psi}^\prime k + V(s_1, s_2, \ldots) \tag{2.17} \]

where \( V = -e^2 (Z/s_1 + Z/s_2 - 1/|\mathbf{s}_1 - \mathbf{s}_2|) \).

Thus the Schroedinger equation for the two–electron system in the c.m. frame can be written as
\[ [-\frac{\hbar^2}{2\mu} (\hat{\Psi}^2_1 + \hat{\Psi}^2_2) - \frac{\hbar^2}{M} \hat{\Psi}^\prime_1 \cdot \hat{\Psi}^\prime_2 + V(s_1, s_2, \ldots)] \Psi = E \Psi. \tag{2.18} \]

Finally, defining scaled distances \( \rho_i = Z \mathbf{s}_i / a_\mu \), where \( a_\mu \) is the reduced mass Bohr radius given by \( a_\mu = \mu / \mu \), \( (a_0 = \hbar^2 / me^2) \), and expressing the energy as \( \mathcal{E} = E / (Z^2 e^2 / a_\mu) \), equation (2.18) can be rewritten as
\[ [-\frac{1}{2} (\hat{\Psi}^2_1 + \hat{\Psi}^2_2) - \frac{\mu}{M} \rho_1 \cdot \hat{\rho}_2 - \frac{1}{\rho_1} - \frac{1}{\rho_2} + \frac{Z^{-1}}{\rho_{12}}] \Psi = \mathcal{E} \Psi. \tag{2.19} \]

The effect of finite nuclear mass is thus described in terms of the mass–polarization operator \( H_{mp} = \frac{\mu}{M} \hat{\rho}_1 \cdot \hat{\rho}_2 \). So, if we solve the non–relativistic equation in the c.m. frame, the correction necessary due to the mass–polarization in the first order perturbation is given by
\[ (\frac{\mu}{M}) \Delta \mathcal{E} = -\frac{\mu}{M} \langle \hat{\Psi}_\rho_1 \cdot \hat{\Psi}_\rho_2 | \Psi \rangle \]

or,
\[ \Delta E = -\frac{\mu^2}{M m} \langle \hat{\Psi}_\rho_1 \cdot \hat{\Psi}_\rho_2 | \Psi \rangle e^{-2/a_0}, \text{ in a.u.} \]

In the second order the correction is,
\[ (\frac{\mu}{M})^2 \delta^2(\mathcal{E}) = \langle \frac{\mu}{M} \rangle \sum_i <\Psi_n | \hat{\Psi}_\rho_1 \cdot \hat{\Psi}_\rho_2 | \Psi_i > - \langle \Psi_i | \hat{\Psi}_\rho_1 \cdot \hat{\Psi}_\rho_2 | \Psi_n > \delta_n - \delta_i. \]
The higher order terms could be calculated directly, but it is simpler just to include the mass-polarization terms in the Hamiltonian from the outset and to extract the higher order dependence on $\frac{\mu}{M}$ by differencing. Thus the energy for finite nuclear mass case is

$$\tilde{\mathcal{E}}_M = \tilde{\mathcal{E}}_\infty + (\frac{\mu}{M})\Delta \tilde{\mathcal{E}}^{(1)} + (\frac{\mu}{M})^2 \Delta \tilde{\mathcal{E}}^{(2)} + \ldots$$

The effect of the mass-polarization correction is particularly large for the P-states. The reason for this can be easily seen if we consider a wave function of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \pm \psi_{1p}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2).$$

The energy shift is then given by

$$\Delta E = -\frac{\mu^2}{M\hbar^2} \left[ \langle \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \mid \hat{\mathbf{V}}_{\rho_1} \cdot \hat{\mathbf{V}}_{\rho_2} \mid \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \rangle 
+ \langle \psi_{1p}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \mid \hat{\mathbf{V}}_{\rho_1} \cdot \hat{\mathbf{V}}_{\rho_2} \mid \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \rangle 
\pm 2 \langle \psi_{1s}(\mathbf{r}_1)\psi_{1p}(\mathbf{r}_2) \mid \hat{\mathbf{V}}_{\rho_1} \cdot \hat{\mathbf{V}}_{\rho_2} \mid \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2) \rangle \right]. \quad (2.20)$$

Now $\hat{V}_{\rho_1}$ and $\hat{V}_{\rho_2}$ transform like tensors of rank 1. Therefore for 1snp states the last term in (2.20) is non-vanishing although the other two are zero due to the triangular rule for addition of angular momenta. For 1sns states, on the other hand, all the above terms are zero due to the triangular rule. The same is also true for all configurations 1snl when $\ell \neq 1$. The only contribution in these cases can therefore come from terms like $\psi_{np}(r_1)\psi_{n'p'}(r_2)$ induced by powers of $r$ in the variational wave function. The presence of such terms can be seen by writing $r^2 = r_1^2 + r_2^2 - 2r_1r_2\cos \theta$, where $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and using the spherical harmonic addition theorem $\cos \theta = \frac{4\pi}{3} \sum \frac{m}{m} Y^m_J (\theta_1 \varphi_1) Y^{-m}_J (\theta_2 \varphi_2)$, $\theta$ being the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. $(\theta_1 \varphi_1)$ and $(\theta_2 \varphi_2)$ are the spherical polar angles of the electron 1 and 2 respectively.
2.4 Relativistic corrections

In the relativistic theory, the system of two interacting electrons is described by the Breit equation given by

\[ \left( -i \mathbf{e} \cdot \mathbf{A}_1 \cdot \mathbf{v}_1 + \mathbf{B}_1 mc^2 \right) \mathbf{I}_1 - \left( i \mathbf{e} \cdot \mathbf{A}_2 \cdot \mathbf{v}_2 + \mathbf{B}_2 mc^2 \right) \mathbf{I}_2 \]

\[ \left( \frac{e^2}{\mathbf{r}_1} - \frac{e^2}{\mathbf{r}_2} + \frac{e^2}{\mathbf{r}_{12}} \right) \mathbf{I}_1 \mathbf{I}_2 + \mathcal{H}_B(1,2) \psi_{(1,2)} = E \psi_{(1,2)}. \]  

(2.21)

where \( \psi_{(1,2)} \) is a 16-component spinor composed of the direct product of the 4-dimensional Dirac spinors. The 'Dirac' matrices here are 4×4 matrices given by

\[ \mathbf{\alpha}_1 = \begin{bmatrix} \sigma_1 & 0 \\ 0 & \sigma_1 \end{bmatrix}, \quad \beta_1 = \begin{bmatrix} \mathbf{1}_1 & 0 \\ 0 & -\mathbf{1}_1 \end{bmatrix}, \quad \mathbf{\alpha}_2 = \begin{bmatrix} \sigma_2 & 0 \\ 0 & \sigma_2 \end{bmatrix}, \quad \beta_2 = \begin{bmatrix} \mathbf{1}_2 & 0 \\ 0 & \mathbf{1}_2 \end{bmatrix}. \]

The \( \sigma \)'s in the above matrices themselves represent the well known 2×2 Pauli-spin matrices and \( \mathbf{1} \) is a 2×2 unit matrix. \( \mathbf{\alpha}_1 \) and \( \beta_1 \) operate only on the spinor space of the first electron while \( \mathbf{\alpha}_2 \) and \( \beta_2 \) operate on that of the second electron. \( \mathcal{H}_B(1,2) \) is the Breit interaction hamiltonian given by

\[ \mathcal{H}_B(1,2) = -\frac{e^2}{2\mathbf{r}_1} \alpha_1 \cdot \alpha_2 + (\alpha_1 \cdot \mathbf{r}_1)(\alpha_2 \cdot \mathbf{r}_2). \]  

(2.22)

A complete analysis of the system of more than one electron in terms of the relativistic theory however makes matters quite complicated. Fortunately, it is possible to handle the relativistic effects as a perturbation on the non-relativistic Hamiltonian for the lighter atoms. Such a treatment still provides not only an insight into the physical nature of these effects, but also allows quantitative analyses to be carried out much more easily.

In order to achieve the above, it is necessary first to reduce Eq.(2.21) into an equivalent non-relativistic form involving only the large component spinors for each of the two electrons. Such a non-relativistic reduction of the Breit equation was carried out first by Breit himself\(^{50}\), obtaining an equation in terms of the large components \( \phi(1) \phi(2) \) after eliminating the couplings with the smaller components.
by an iterative reduction procedure\textsuperscript{37}. Alternatively, an extension of the Foldy–Wouthuysen procedure can be applied to eliminate the coupling between the large component and the smaller components\textsuperscript{38}. In this method the relativistic two-particle wave equation involving 16-component spinors are reduced to an approximate 4-component form in two steps. First a sequence of canonical transformations is performed with the help of suitable generating functions. Then twelve components of the wave equation are rejected and only the four upper–upper (or lower–lower) components are retained; namely, that quadruple which describe the states of the system with both particles possessing positive energies. In the resulting transformed Hamiltonian, the non-relativistic equivalent terms of the Breit interaction Hamiltonian can be explicitly identified. Although work presented in the above paper\textsuperscript{38} was applicable only to cases where \( m_1 \neq m_2 \) subsequent development\textsuperscript{39} of the same procedure removed that restriction and therefore could be applied directly to the two-electron system.

Another method of reduction was shown by Bethe and Salpeter\textsuperscript{40}. In this method, Fourier transformation of the Breit equation gives first a set of coupled equations in the momentum space of the large and small component spinors. Expansion of the terms of these equations in powers of \((p/mc)\) up to terms of order of \( c^3 \), elimination of the coupling between the large and the small components by an iterative procedure, and finally an inverse Fourier transformation of the momentum space Hamiltonian thus obtained for the large component spinor space gives the required reduced Hamiltonian in the ordinary position space.

A very direct and simple method is also described by Akheizer and Berestetskii\textsuperscript{41} which is discussed in Appendix–I.

After reduction by any of the above methods the Breit equation can be
written as

\[ H_U(\mathbf{r}_1, \mathbf{r}_2) = [H_0 + \sum_i H_{i,1}] U(\mathbf{r}_1, \mathbf{r}_2), \]  

where

\[ H_0 = \frac{1}{2m} (p_1^2 + p_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r} \]  

\[ H_1 = -\frac{1}{8m^2c^2}(p_1^4 + p_2^4) \]  

\[ H_2 = -\frac{e^2}{2m^2c^2} \left[ \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{r} + \frac{\mathbf{r} \cdot (\mathbf{\hat{r}}_1 \mathbf{\hat{p}}_1 + \mathbf{\hat{r}}_2 \mathbf{\hat{p}}_2)}{r^3} \right] \]

\[ = -\frac{\alpha^2}{2} \left[ \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{r} + \frac{\mathbf{r} \cdot (\mathbf{\hat{r}}_1 \mathbf{\hat{p}}_1 + \mathbf{\hat{r}}_2 \mathbf{\hat{p}}_2)}{r^3} \right] \] in a.u.  

\[ H_3 = \frac{\beta}{4m^2c^2} \left[ \mathbf{\hat{r}}_1 \cdot (\mathbf{\hat{r}}_1 \mathbf{\hat{p}}_1 + 2e \mathbf{\hat{r}}_1 \mathbf{\hat{p}}_2) + \mathbf{\hat{r}}_2 \cdot (\mathbf{\hat{r}}_2 \mathbf{\hat{p}}_2 + 2e \mathbf{\hat{r}}_2 \mathbf{\hat{p}}_1) \right] \]

\[ = \left( \frac{\mu_B}{2mc} \right) \left[ \mathbf{\hat{r}}_1 \cdot (\mathbf{\hat{r}}_1 \mathbf{\hat{p}}_1 + 2e \mathbf{\hat{r}}_1 \mathbf{\hat{p}}_2) + \mathbf{\hat{r}}_2 \cdot (\mathbf{\hat{r}}_2 \mathbf{\hat{p}}_2 + 2e \mathbf{\hat{r}}_2 \mathbf{\hat{p}}_1) \right] \]  

where \( \mathbf{\hat{r}}_1 = -\left( \frac{Ze}{r_1^3} \mathbf{\hat{r}}_1 \right) \) and \( \mathbf{\hat{r}}_2 = -\left( \frac{Ze}{r_2^3} \mathbf{\hat{r}}_2 \right) \) are the effective electric fields at the location of electron-1 and electron-2 respectively,

\[ H_4 = \frac{\pi e^2}{2m^2c^2} \left[ Z \delta^2(\mathbf{r}_1) + Z \delta^2(\mathbf{r}_2) - \delta^2(\mathbf{r}) \right] \]

\[ = \frac{1}{2}Z\pi \alpha^2[\delta^2(\mathbf{r}_1) + \delta^2(\mathbf{r}_2)] - \pi\alpha^2 \delta^2(\mathbf{r}) \] in a.u.  

\[ H_5 = \frac{e^2}{4m^2c^2} \left[ \frac{\mathbf{\hat{r}}_1 \cdot \mathbf{\hat{r}}_2}{r^3} \right] \]

\[ = \frac{1}{4} \alpha^2 \left[ \frac{\mathbf{\hat{r}}_1 \cdot \mathbf{\hat{r}}_2}{r^3} \right] \] in a.u.  

The physical interpretation of these terms is as follows. We can readily see that \( H_0 \) is the usual nonrelativistic Hamiltonian with the additional mutual Coulomb interaction between the two electrons included as part of the potential energy. \( H_1 \) is the relativistic correction that results from the variation of mass with velocity. \( H_2 \) represents the correction due to the retardation of the electromagnetic field produced by one electron at the site of the other. \( H_3 \) describes the spin–orbit effects owing to the nuclear potential as well as the Coulomb potential between the electrons. This in fact can be explicitly expressed as a sum of two distinct parts,
namely the 'spin–orbit' interaction and the 'spin–other–orbit' interactions given by
\[ H_3 = H_3^{(s-o)} + H_3^{(s-o-o)} \]
where
\[ H_3^{(s-o)} = \frac{e^2}{4m^2c^2} \left( \frac{Z}{r_1} \hat{\sigma}_1 \times \hat{p}_1 + \frac{Z}{r_2} \hat{\sigma}_2 \times \hat{p}_2 \right) \cdot \hat{S} \]
\[ = \frac{1}{\alpha^2} \left( \frac{Z}{r_1} \hat{\sigma}_1 \times \hat{p}_1 + \frac{Z}{r_2} \hat{\sigma}_2 \times \hat{p}_2 \right) \cdot \hat{S} \text{ in a.u.} \quad (2.30) \]
\[ H_3^{(s-o-o)} = \frac{e^2}{4m^2c^2} \left[ 3 \hat{\tau} \times (\hat{p}_2 - \hat{p}_1) \cdot \hat{S} \right] \]
\[ = \frac{1}{\alpha^2} \left[ 3 \hat{\tau} \times (\hat{p}_2 - \hat{p}_1) \cdot \hat{S} \right] \text{ in a.u.} \quad (2.31) \]
where \( \hat{S} = \hat{S}_1 + \hat{S}_2 \), \( \hat{S}_1 = \frac{\hat{\sigma}_1}{2} \) and \( \hat{S}_2 = \frac{\hat{\sigma}_2}{2} \). The forms given in Eq (2.30) to (2.31) are strictly valid for the diagonal matrix elements only, in which cases the expectation value of the odd operator \( \langle \hat{S}_1 - \hat{S}_2 \rangle \) is zero. \( H_4 \) is the contact term that arises when we treat the motion of the individual electrons in the field of the nucleus as well as of one another. \( H_5 \) is the spin–spin interaction Hamiltonian. In this, the first two terms can be identified as due to the interaction between two magnetic dipoles separated by a distance \( r \). The Dirac delta function term represents the contact term in the spin–spin interaction.

The relativistic correction for infinite nuclear mass is then given by
\[ \Delta E_{\text{rel}} = \frac{a^2}{8} \left( \langle p_1^4 + p_2^4 \rangle + \langle H_2 \rangle + \langle H_3^{(s-o)} \rangle + \langle H_3^{(s-o-o)} \rangle \right) \]
\[ + \langle H_5 \rangle + \langle Z \delta^2(\hat{r}_1) - \delta^2(\hat{r}) \rangle \pi a^2 \text{ in a.u.} \quad (2.32) \]

The relativistic reduced–mass correction which is the finite mass correction to the Breit interactions is given by\(^{34,35,42}\)
\[ \Delta E_{\text{RR}} = (\Delta E_{\text{RR}})_{M} + (\Delta E_{\text{RR}})_{X}, \quad (2.33) \]
where
\[ (\Delta E_{\text{RR}})_{M} = \Delta_1 + \Delta_2 - \frac{m}{M} \left[ \langle 3H_1 \rangle + 2\{ \langle H_2 \rangle + \langle H_4 \rangle \} \right. \]
\[ \left. \langle H_3^{(s-o-o)} \rangle + \langle H_5 \rangle \} \right] \]
\[ (2.34) \]
with
\[ \Delta_1 = \sum_{i \neq k} \frac{Ze^2}{mmc^2r_k^3} \hat{r}_i \times \hat{p}_i \cdot \hat{S}_k, \quad (2.35) \]
\[ \Delta_2 = -\sum_{k,l} \frac{Ze^2}{2mMC^2r_3} \left[ r_{3k}^2 \beta_k \beta_l + r_{3k} \left( \vec{\beta}_k \cdot \vec{r}_3 \right) \beta_l \right], \]  
\[ \Delta E_{KR} = \langle \Psi_{mp} | \Sigma I_1 | \Psi_{mp} \rangle - \langle \Psi | \Sigma I_1 | \Psi \rangle \]  
where \( \Psi_{mp} \) is the wave function obtained when the mass polarization term \( (\beta_1, \beta_2)_M^\mu \) is included explicitly in the non-relativistic Hamiltonian
\[ H_0 = \frac{1}{2m} (p_1^2 + p_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r}. \]
\( \Delta E_{KR} \) accounts for the second order cross terms between the Breit interaction and the mass polarization operator.

An important improvement in accuracy is obtained by calculating the expectation values for \( \delta^3(\vec{r}_1) \) from the global operator derived by Hiller \textit{et al}. with modifications arising from the \( (\beta_1, \beta_2)_M^\mu \) term in the Hamiltonian. This is given by
\[ \langle \delta^3(\vec{r}_1) \rangle = \frac{1}{2\pi} \left( \frac{Ze}{r_2} - \frac{1}{r_2} \frac{\partial r}{\partial t} \right) - \frac{1}{r_2} \beta_1^2 \]
\[ + \frac{\mu}{M} \left[ \frac{\vec{r}_1 \cdot \vec{v}_2}{r_1} + \frac{\vec{r}_1 \cdot \vec{v}_1}{r_1} \right] \].

In expression (2.38) the operator in the square brackets is the additional contribution due to the mass-polarization. It has been shown by Drake that the use of the above expression accelerates the rate of convergence by about a factor of 20 relative to a direct evaluation of \( \langle \delta^3(\vec{r}_1) \rangle \).

For the P states with \( J=1 \) one has to include an additional correction due to the singlet-triplet mixing given by
\[ \Delta E_{st} = \left| \frac{\langle 3P_1 | H_3 + H_5 | 1P_1 \rangle}{E_{NR} (3P_1) - E_{NR} (1P_1)} \right|^2 \]
which comes from the off-diagonal matrix elements of the spin-dependent Breit interactions.

2.5 Quantum Electrodynamic Corrections

As in the work already presented by Drake the QED energy shift is
taken to be the one-electron energy shift corrected for the electron density at the nucleus, together with explicit two-electron terms dependent on \( \langle \delta^3(\hat{r}) \rangle \) and Q. In this approximation, the energy shift is given by

\[
\Delta E_L = \Delta E_{L,1} + \Delta E_{L,2} .
\]  

(2.40)

In (2.40) the first term on the right is the one-electron Lamb shift given by

\[
\Delta E_{L,1} = \frac{4}{3} Z \alpha^3 \left\{ \ln(Z\alpha)^{-2} + \ln[Z^2\text{Ryd}/\epsilon(n\text{LS})] + \frac{19}{30} 
+ 3\pi Z\alpha \left( \frac{27}{354} - \frac{1}{2}\ln 2 \right) + (Z\alpha)^2 \left[ -\frac{3}{4}\ln^2(Z\alpha)^2 + C_{61}\ln(Z\alpha)^2 + C_{60} \right] 
\right\} \langle \delta^3(\hat{r}_1) + \delta^3(\hat{r}_2) \rangle .
\]  

(2.41)

The second term is given by

\[
\Delta E_{L,2} = \alpha^3 \left( \frac{14}{3} \ln\alpha + \frac{164}{15} \right) \langle \delta^3(\hat{r}) \rangle - \frac{14}{3} \alpha^3 Q
\]  

(2.42)

with

\[ Q = \frac{1}{4\pi} \lim_{r \to 0} \langle r^{-3}(a) + 4\pi(\gamma + \ln a)\delta^3(\hat{r}) \rangle
\]  

(2.43)

where \( \gamma \) is Euler's constant and \( a \) is the radius of a sphere centered at \( r=0 \) which is excluded from the integration over \( r \).

The Bethe logarithms \( \ln[\epsilon(n\text{LS})/Z^2\text{Ryd}] \) is given by

\[
\ln[\epsilon(n\text{LS})/Z^2\text{Ryd}] = \ln[\epsilon_0(n\text{LS})(Z-\sigma)^2/Z^2\text{Ryd}] \tag{44-46}
\]  

(2.44)

where \( \ln[\epsilon_0(n\text{LS})] = \ln(\epsilon(1s)) + \frac{1}{n^3}\ln(\epsilon(nl)) / (1 + n^3\delta_{10}) \). \tag{47,48}

(2.45)

2.6 Anomalous Magnetic Moment Correction

For the \( 2^3\text{P} \) states the anomalous magnetic moment corrections to the spin dependent operators are also to be included. The energy shift due to this is given by

\[
\Delta E_{\text{anom}} = \frac{\alpha}{\pi} \left\{ \langle H_{3}^{(s-o)} \rangle + \frac{2}{3} \langle H_{3}^{(s-o-o)} \rangle + \langle H_{5}^{(s)} \rangle \right\}
\]  

(2.46)

2.7 Finite Nuclear Size Correction:

The correction required due to the finite size of the nucleus is

\[
\Delta E_{\text{nuc}} = \frac{2\pi Z}{3} \langle R/a_0 \rangle \langle \delta^3(\hat{r}_1) + \delta^3(\hat{r}_2) \rangle
\]  

(2.47)

where \( a_0 \) is the Bohr radius \( a_0 = \hbar^2/me^2 \).
Chapter 3
Results and Discussion

In this final chapter, the variational non-relativistic energies of the ground state and the excited 1sns¹S, 1sns³S, 1snp¹P and 1snp³P states of Li⁺ up to n=5 are tabulated in tables 1 through 24. This is supplemented by detailed results of finite nuclear mass, relativistic, QED and other small corrections for the 1s2p¹,³P and 1s2s¹,³S states in tables 25 and 26 respectively. In table-27 the theoretical 2³S-2³P and 2¹S-2¹P transition energies are tabulated and compared with experimental data.

3.0 Discussion of Results

For the 2¹,³S and 2¹,³P states the variational calculations were first carried out with an infinite nuclear mass approximation. These calculations were then repeated by including the mass-polarization operator in the non-relativistic hamiltonian to account for the finite mass of the nucleus. A detailed account of the convergence process of the variational energies, as the basis set is enlarged, is shown in tables 1 through 12. Tables 3, 6, 9, and 12 show the behaviour of the optimized non-linear parameters for these states for various sizes of the basis set. As can be seen from figures 3.1 through 3.7 the non-linear parameters (α₁,β₁) and (α₂,β₂) follow fairly regular trends as the basis set is enlarged. α₁ and β₁ remain nearly constant, close to the corresponding screened hydrogenic values. α₂ and β₂, on the other hand, are well separated from the first set of parameters and increase in a regular manner as the size of the basis set is progressively increased. This allows the optimum values of these parameters to be predicted with good accuracy for
larger basis sets by extrapolation. Ideally, only a few additional iterations are needed to reach the final convergence.

While doing the calculations with large basis sets having more than about 500 terms, it is essential to keep track of every single iteration as the energy steadily goes down. Since the starting values of the non-linear parameters are already quite close to their optimum values, the first derivatives of the energy with respect to those parameters are usually of the order of $10^{-13}$ or less, and slight round-off errors in computation may well take the calculations off the right track. Also, at this level of accuracy, where one is concerned with finding changes in the 14th or 15th figure in the energies, the energies tend to become less sensitive to small changes in the parameters. The energy surface around the minima is so flat that the calculations often tend to terminate at any given values of the input parameters which are close enough to the actual optimum values. A proper extrapolation from the graphs helps avoid this problem to a large extent and to get the real root quickly.

The accuracy of the non-relativistic energies for all of the 2S and 2P states presented in this thesis are better than 1 part in $10^{13}$. For the $2^3S$ state, the result obtained from a 616 term calculation has 15 significant figures. In carrying out the above calculations, particular care was taken to improve the accuracy of the variational wave functions generated in the process. It was found that even when the eigenvalues show fairly good convergence as the basis set is progressively enlarged, the wave function may still contain a few large coefficients $a_i$'s (ref. eq. 2.1), indicating the presence of some numerical cancellation problems. To detect these, all the calculations were repeated in quadruple precision arithmetic (corresponding to 32 figures). To remove numerical cancellation problems, several different truncation schemes were tried, by limiting the maximum powers of $r_1$ and $r$, until the best combination of terms in the wave function was found. For the
$2^13^p$ states, the basis set was truncated by limiting the maximum powers of $r_1$ and $r$ to 8 and 6 respectively. Additional truncation was applied to the second block, corresponding to the non-linear parameters $\alpha_2$ and $\beta_2$, by the constraint $i+j+k+i-j-|i_o-j_o| \leq N2+1$, for $k \geq 1$, where the symbols have their usual meaning and $i_o=0$, $j_o=1$ for the $1snp$ states. For the singlet $2S$ state, the maximum powers of $r_1$ and $r$ were limited to 7 and 6 respectively. Additional truncation of the second block was effected by the constraint $i+j+k+i-j \leq N2+1$, for $k \geq 2$. For the $2^3S$ state, however, it was found best to perform all calculations without any truncation of the basis set.

Table-25 shows the various contributions to the $2P$ states of Li$^+$ relative to Li$^+$(1s) while Table-26 shows the contributions to the $2S$ states. For ease of comparison with existing results, all the energies are presented in units of cm$^{-1}$. All quantities presented in these tables have converged to at least the number of figures quoted. In table-27 the theoretical values for $2^3S$-$2^3P$ transition energies are presented and compared with experimental results. For the $2^3S^1$-$2^3P^0$ transition energy, the theoretical value obtained is 18231.2997514 cm$^{-1}$ as against the experimental values of 18231.30188(19) cm$^{-1}$ and 18231.303(1) cm$^{-1}$. The theoretical $2^3S^1$-$2^3P^1$ transition energy is 18226.1048038 cm$^{-1}$ as against the corresponding experimental values 18226.11206(21) cm$^{-1}$ and 18226.108(1) cm$^{-1}$. For the $2^3S^1$-$2^3P^2$ transition energy, the theoretical value obtained in these calculations is 18228.1941469 cm$^{-1}$ as against the experimental values of 18228.19935(25) cm$^{-1}$ and 18228.198(1) cm$^{-1}$. The calculated value for the $2^1S^0$-$2^1P^1$ transition energy is 10433.9210404 cm$^{-1}$. For this transition no new high precision experimental results are available. The result obtained by Toresson and Edlen$^{51}$ for this transition was 10434.013(109) cm$^{-1}$. 
The slight discrepancies between the theoretical and experimental values can be explained in terms of the higher-order relativistic and QED corrections not included in the theory. For example, the leading terms of the correction of order $\alpha^4$ are of the form

$$\Delta E^{(4)} = \alpha^4 Z^6 \left( C_0 + C_1/Z + \ldots \right) \quad (3.1)$$

where

$$C_0 = \begin{cases} 
-85/1024 & \text{for } 2^3S_1 \\
-85/1024 & \text{for } 2^3P_0 \\
-235/3072 & \text{for } 2^3P_1 \\
-65/1024 & \text{for } 2^3P_2 
\end{cases}$$

and

$$C_1 = \begin{cases} 
0.04323 & \text{for } 2^3S_1 \\
0.14300 & \text{for } 2^3P_0 \\
0.05693 & \text{for } 2^3P_1 \\
-0.001877 & \text{for } 2^3P_2 
\end{cases}$$

in atomic units.$^{52}$

The corrections to the $2^3S$-$2^3P$ transition frequencies are thus

$$\Delta E^{(4)} = \begin{cases} 
0.0151 \text{ cm}^{-1} & \text{for } 2^3S_1-2^3P_0 \\
0.0050 \text{ cm}^{-1} & \text{for } 2^3S_1-2^3P_1 \\
0.0020 \text{ cm}^{-1} & \text{for } 2^3S_1-2^3P_2 
\end{cases}$$

The residual contribution from the higher-order terms is estimated to be $\pm 0.1\alpha^4 Z^4$ a.u.$= \pm 0.005 \text{ cm}^{-1}$. From Table-27, comparing with the experimental results of Riis et al.$^2$, the values obtained for the residual contributions to the higher order corrections to the $2^3S$-$2^3P$ transitions are

$$\Delta E_{\text{res}}^{(4)} = \begin{cases} 
-0.129714 \pm 0.00019 \text{ cm}^{-1} & \text{for } 2^3S_1-2^3P_0 \\
+0.0022562 \pm 0.00021 \text{ cm}^{-1} & \text{for } 2^3S_1-2^3P_1 \\
+0.0032031 \pm 0.00025 \text{ cm}^{-1} & \text{for } 2^3S_1-2^3P_2 
\end{cases}$$

In conclusion, the one- and two-electron Lamb shift corrections to the transition frequencies of about 1 cm$^{-1}$ ($E_{L,1}$ and $E_{L,2}$ in tables 25 and 26) have been confirmed to a precision of $\pm 1\%$ or better. The residual discrepancies are about the order of magnitude one would expect from terms of order $\alpha^4 Z^4$ and higher.
In Tables 13 through 24 the convergence process for the non-relativistic energies of the $1s^2 1S$, $1sn^3S$, $1sn^3P$, ($n=3,4,5$) and $1sn^1S$ ($n=3,4$) are presented. In these preliminary calculations, accuracies of 1 part in $10^{11}$ or better in the non-relativistic energy were obtained. For the S states, the behaviour of the non-linear parameters were found to be fairly regular, and consistent with the observations in the low-lying excited states. For the P states, however, the parameter $\alpha_2$ came out to be greater than $\beta_2$. It is likely that a lower root will most probably be detected, with the non-linear parameters in the second block interchanged, consistent with the behaviour of these parameters in all the other states for which, in general, it was found that $\beta_2 > \alpha_2$.

3.1 Suggestions For Future Work

Since the accuracy of the lower-order terms evaluated for the 2S and 2P states now exceeds the accuracies of the experimental data, the higher order relativistic and QED corrections can be extracted from the latter to the full extent of the experimental precision. A complete two-electron theory for these effects has not yet been fully developed. Further progress on this problem is urgently needed. An immediate task at hand is to determine the spin-independent relativistic effects of order $\alpha^4$. With the information extracted from the existing experimental data in conjunction with present theoretical results, it will be possible to test future calculations of the higher order relativistic and QED effects.

It will also be very useful to have a more detailed study on the ground state of Li$. Accurate calculations of the $2^3S-2^3P$ transition frequencies for other members of the helium-isoelectronic sequence would also be useful, as it is expected that more high precision experimental results on these will be forthcoming in the
near future.

There has been much recent interest in mesomolecules such as $\mu dd$, $\mu dt$ and $\mu tt$ because of their role in muon-catalysed fusion. It would be interesting to apply the multiple basis set methods described here to such systems.
Table 1
1s2s(3S) state of Li

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

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<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies) (in a.u.) ( -E_{\text{bar}} )</th>
<th>Diff. in Energies ( 10^{-7} )</th>
<th>Ratios of Differences</th>
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* N1, N2 are basis set indices such that
  \( i + j + k \leq N1 \), for block no. 1 (\( \alpha_1, \beta_1 \))
  \( i + j + k \leq N2 \), for block no. 2 (\( \alpha_2, \beta_2 \))
Table 2.
1s2s(^2S) state of Li*

Convergence of nonrelativistic eigenvalues for finite nuclear mass

<table>
<thead>
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<th>N1, N2</th>
<th>Block Sizes</th>
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<th>Energies) (in a.u.) -E_{ar}</th>
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* N1,N2 are basis set indices such that
i + j + k ≤ N1, for block no.1 (α_iβ_1)
i + j + k ≤ N2, for block no.2 (α_iβ_2)
Table 3.
$1s2s(^3S)$ state of Li$^+^*$

Variation of the optimized non-linear parameters with size of the basis set

<table>
<thead>
<tr>
<th>$N_{1,N_{2}}$</th>
<th>Total No. of Terms</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
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<td>1.18445</td>
<td>0.96777</td>
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<td>0.95599</td>
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<td>0.95789</td>
<td>1.40680</td>
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Table 4.
1s2s(^1S) state of Li*

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
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<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) (-E_{nr})</th>
<th>Diff. in Energies (10^{-7})</th>
<th>Ratios of Differences</th>
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<tr>
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<td>5.47</td>
</tr>
<tr>
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<td>154, 131</td>
<td>285</td>
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<tr>
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<td>353</td>
<td>(-5.040876745589866)</td>
<td>.00003745</td>
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<tr>
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<td>230, 197</td>
<td>427</td>
<td>(-5.040876745593609)</td>
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<tr>
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<tr>
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<td>321, 281</td>
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<td>(-5.040876745595111)</td>
<td>.00000141</td>
<td>3.72</td>
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</tbody>
</table>

* N1, N2 are basis set indices such that

\(i + j + k \leq N1\), for block no.1 \((\alpha_1, \beta_1)\)

\(i + j + k \leq N2\), for block no.2 \((\alpha_2, \beta_2)\)

Additional truncation is applied to block 2 with the constraint:

\(i + j + k + |i-j| \leq N2 + 1\), for \(k \geq 2\).
Table 5.
1s2s(1S) state of Li⁺

Convergence of nonrelativistic eigenvalues for finite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) -E_{2s}</th>
<th>Diff. in Energies 10⁻⁷</th>
<th>Ratios of Differences</th>
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<td>274, 238</td>
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<td>602</td>
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</table>

* N1, N2 are basis set indices such that

i + j + k ≤ N1, for block no.1 (α₁, β₁)

i + j + k ≤ N2, for block no.2 (α₂, β₂)

Additional truncation is applied to block 2 with the constraint:

i + j + k + |i-j| ≤ N2 + 1, for k ≥ 2.
Table 6.
$1s2s(^1S)$ state of Li$^+$

Variation of the optimized non-linear parameters with size of the basis set

<table>
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<tr>
<th>N1,N2, Total No.of Terms</th>
<th>Infinite Nuclear Mass</th>
<th>Finite Nuclear Mass</th>
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<td>$\alpha_2$</td>
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<td>132 1.00134</td>
<td>0.58868</td>
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<tr>
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<td>0.61926</td>
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<td>227 1.04517</td>
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<tr>
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<td>0.66937</td>
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<td>703 1.01385</td>
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Table 7.
1s2p(^3P) state of Li^+

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>Diff. in Energies 10^{-7}</th>
<th>Ratios of Differences</th>
</tr>
</thead>
<tbody>
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* N1,N2,N3 are basis set indices such that
  
i + j + k ≤ N1, for block no.1 (α1,β1)
i + j + k ≤ N2, for block no.2 (α2,β2)
i + j + k ≤ N3, for block no.3 (α1,β1)

Additional truncation is applied to block 2 with the constraint:
  
i + j + k + (|i−j| − |i_0−j_0|) ≤ N2 + 1, for k > 1.
Table 8.
$1s2p(^3P)$ state of Li$^+$

Convergence of nonrelativistic eigenvalues for finite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) $-\varepsilon_{\text{ref}}$</th>
<th>Diff. in Energies $10^{-7}$</th>
<th>Ratios of Differences</th>
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</table>

* N1,N2,N3 are basis set indices such that
  $i + j + k \leq N1$, for block no.1 ($\alpha_1,\beta_1$)
  $i + j + k \leq N2$, for block no.2 ($\alpha_2,\beta_2$)
  $i + j + k \leq N3$, for block no.3 ($\alpha_1,\beta_1$)

Additional truncation is applied to block 2 with the constraint:

$$i + j + k + (|i-j| - |i_0-j_0|) \leq N2 + 1,$$
for $k_2 1$. 
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<th>β₁</th>
<th>β₂</th>
<th>α₁</th>
<th>α₂</th>
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</tr>
<tr>
<td>9, 9, 4</td>
<td>420</td>
<td>1.00000</td>
<td>0.65466</td>
<td>1.61176</td>
<td>1.77142</td>
<td>1.00000</td>
<td>0.65424</td>
<td>1.59900</td>
<td>1.76410</td>
</tr>
<tr>
<td>10,10,4</td>
<td>523</td>
<td>1.00000</td>
<td>0.66150</td>
<td>1.70343</td>
<td>1.81378</td>
<td>1.00000</td>
<td>0.66119</td>
<td>1.69965</td>
<td>1.83154</td>
</tr>
<tr>
<td>11,11,4</td>
<td>633</td>
<td>1.00000</td>
<td>0.68915</td>
<td>1.83936</td>
<td>1.85706</td>
<td>1.00000</td>
<td>0.65997</td>
<td>1.77460</td>
<td>1.94000</td>
</tr>
<tr>
<td>11,12,4</td>
<td>699</td>
<td>1.00000</td>
<td>0.67969</td>
<td>1.85107</td>
<td>2.05560</td>
<td>1.00000</td>
<td>0.65686</td>
<td>1.90796</td>
<td>2.04419</td>
</tr>
<tr>
<td>11,13,4</td>
<td>768</td>
<td>1.00000</td>
<td>0.66925</td>
<td>1.81830</td>
<td>2.06714</td>
<td>1.00000</td>
<td>0.66266</td>
<td>1.87305</td>
<td>2.09998</td>
</tr>
</tbody>
</table>
Table 10.
\(1s2p(^1P)\) state of Li$^+$

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>(N1,N2,N3)</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) (-E_{\text{ar}})</th>
<th>Diff. in Energies (10^7)</th>
<th>Ratios of Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>4, 4, 4</td>
<td>(35, 33, 35)</td>
<td>103</td>
<td>(-4.993351060470619)</td>
<td>.15077642</td>
<td></td>
</tr>
<tr>
<td>5, 5, 4</td>
<td>(56, 50, 35)</td>
<td>141</td>
<td>(-4.993351075548268)</td>
<td>.01956645</td>
<td>7.71</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>(84, 74, 35)</td>
<td>193</td>
<td>(-4.993351077504906)</td>
<td>.008222665</td>
<td>7.51</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>(119,101,35)</td>
<td>255</td>
<td>(-4.993351077727571)</td>
<td>.00644491</td>
<td>8.79</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>(161,137,35)</td>
<td>333</td>
<td>(-4.993351077772062)</td>
<td>.00046049</td>
<td>5.00</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>(209,176,35)</td>
<td>420</td>
<td>(-4.993351077778111)</td>
<td>.00006049</td>
<td>7.36</td>
</tr>
<tr>
<td>10,10,4</td>
<td>(252,226,35)</td>
<td>523</td>
<td>(-4.99335107777929)</td>
<td>.00001518</td>
<td>3.98</td>
</tr>
<tr>
<td>11,11,4</td>
<td>(319,279,35)</td>
<td>633</td>
<td>(-4.993351077779917)</td>
<td>.00000288</td>
<td>5.27</td>
</tr>
<tr>
<td>11,12,4</td>
<td>(319,345,35)</td>
<td>699</td>
<td>(-4.993351077779971)</td>
<td>.00000054</td>
<td>5.33</td>
</tr>
<tr>
<td>11,13,4</td>
<td>(319,414,35)</td>
<td>768</td>
<td>(-4.993351077779996)</td>
<td>.00000025</td>
<td>2.18</td>
</tr>
</tbody>
</table>

* \(N1,N2,N3\) are basis set indices such that:

- \(i + j + k \leq N1\), for block no.1 \((\alpha_1, \beta_1)\)
- \(i + j + k \leq N2\), for block no.2 \((\alpha_2, \beta_2)\)
- \(i + j + k \leq N3\), for block no.3 \((\alpha_1, \beta_1)\)

Additional truncation is applied to block 2 with the constraint:

\[ i + j + k + (|i-j| - |i_0-j_0|) \leq N2 + 1, \text{ for } k \geq 1. \]
Table 11.

1s2p(P) state of Li*  

Convergence of nonrelativistic eigenvalues for finite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) $\Delta E_{nr}$</th>
<th>Diff. in Energies $10^{-7}$</th>
<th>Ratios of Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>4, 4, 4</td>
<td>(35, 33, 35)</td>
<td>103</td>
<td>-4.993331421793429</td>
<td>.15057442</td>
<td></td>
</tr>
<tr>
<td>5, 5, 4</td>
<td>(56, 50, 35)</td>
<td>141</td>
<td>-4.993331436850871</td>
<td>.01954643</td>
<td>7.70</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>(84, 74, 35)</td>
<td>193</td>
<td>-4.993331438805514</td>
<td>.00222769</td>
<td>8.77</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>(119,101,35)</td>
<td>255</td>
<td>-4.993331439028283</td>
<td>.00044357</td>
<td>5.02</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>(161,137,35)</td>
<td>333</td>
<td>-4.993331439072640</td>
<td>.00066129</td>
<td>7.24</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>(209,176,35)</td>
<td>420</td>
<td>-4.993331439078770</td>
<td>.00001264</td>
<td>4.85</td>
</tr>
<tr>
<td>10,10,4</td>
<td>(262,226,35)</td>
<td>523</td>
<td>-4.993331439080034</td>
<td>.00000345</td>
<td>3.67</td>
</tr>
<tr>
<td>11,11,4</td>
<td>(319,279,35)</td>
<td>633</td>
<td>-4.993331439080378</td>
<td>.00000062</td>
<td>5.54</td>
</tr>
<tr>
<td>11,12,4</td>
<td>(319,345,35)</td>
<td>699</td>
<td>-4.993331439080464</td>
<td>.00000024</td>
<td>2.59</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that

\[ i + j + k \leq N1, \text{ for block no.1 } (\alpha_1, \beta_1) \]

\[ i + j + k \leq N2, \text{ for block no.2 } (\alpha_2, \beta_2) \]

\[ i + j + k \leq N3, \text{ for block no.3 } (\alpha_3, \beta_3) \]

Additional truncation is applied to block 2 with the constraint:

\[ i + j + k + (|i-j| - |i_0-j_0|) \leq N2 + 1, \text{ for } k \geq 1. \]
Table 12.
1s2p(1P) state of Li

Variation of the optimized non-linear parameters with size of the basis set

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Total No. of Terms</th>
<th>Infinite Nuclear Mass</th>
<th>Finite Nuclear Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α1</td>
<td>α2</td>
<td>β1</td>
</tr>
<tr>
<td>4, 4, 4</td>
<td>103</td>
<td>1.00000</td>
<td>0.62579</td>
</tr>
<tr>
<td>5, 5, 4</td>
<td>141</td>
<td>1.00000</td>
<td>0.65356</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>193</td>
<td>1.00000</td>
<td>0.65399</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>255</td>
<td>1.00000</td>
<td>0.66083</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>333</td>
<td>1.00000</td>
<td>0.65656</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>420</td>
<td>1.00000</td>
<td>0.69299</td>
</tr>
<tr>
<td>10,10,4</td>
<td>523</td>
<td>1.00000</td>
<td>0.68347</td>
</tr>
<tr>
<td>11,11,4</td>
<td>633</td>
<td>1.00000</td>
<td>0.67493</td>
</tr>
<tr>
<td>11,12,4</td>
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</tr>
<tr>
<td>11,13,4</td>
<td>768</td>
<td>1.00000</td>
<td>0.67218</td>
</tr>
</tbody>
</table>
Table 13.

$1s^2(^1S)$ state of Li

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) $-E_n$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9, 9</td>
<td>(122,105)</td>
<td>227</td>
<td>7.279913412647146</td>
<td>1.53789</td>
<td>1.34839</td>
<td>3.10077</td>
<td>3.40417</td>
</tr>
<tr>
<td>10,10</td>
<td>(154,131)</td>
<td>285</td>
<td>7.279913412665466</td>
<td>1.41550</td>
<td>1.41467</td>
<td>3.21667</td>
<td>3.67737</td>
</tr>
<tr>
<td>11,11</td>
<td>(190,163)</td>
<td>353</td>
<td>7.279913412667910</td>
<td>1.39642</td>
<td>1.40118</td>
<td>3.56708</td>
<td>3.87775</td>
</tr>
<tr>
<td>12,12</td>
<td>(230,197)</td>
<td>427</td>
<td>7.279913412668792</td>
<td>1.44891</td>
<td>1.41241</td>
<td>3.67310</td>
<td>4.10071</td>
</tr>
<tr>
<td>13,13</td>
<td>(274,238)</td>
<td>512</td>
<td>7.279913412669052</td>
<td>1.50348</td>
<td>1.46631</td>
<td>3.91895</td>
<td>4.23737</td>
</tr>
<tr>
<td>14,14</td>
<td>(321,281)</td>
<td>602</td>
<td>7.279913412669205</td>
<td>1.48212</td>
<td>1.55170</td>
<td>4.08044</td>
<td>4.49133</td>
</tr>
<tr>
<td>15,15</td>
<td>(371,332)</td>
<td>703</td>
<td>7.279913412669238</td>
<td>1.47998</td>
<td>1.55292</td>
<td>4.31000</td>
<td>4.84998</td>
</tr>
</tbody>
</table>

* N1 and N2 are basis set indices such that

$i + j + k \leq N1$, for block no.1 ($\alpha_1, \beta_1$)

$i + j + k \leq N2$, for block no.2 ($\alpha_2, \beta_2$)
Table 14.

1s3p(2P) state of Li^+

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>α₁</th>
<th>α₂</th>
<th>β₁</th>
<th>β₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5, 4</td>
<td>(56, 50, 35)</td>
<td>141</td>
<td>4.730459674381721</td>
<td>1.00000</td>
<td>0.33374</td>
<td>1.25275</td>
<td>0.84747</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>(84, 74, 35)</td>
<td>193</td>
<td>4.730459678225427</td>
<td>1.00000</td>
<td>0.34467</td>
<td>1.29718</td>
<td>1.02539</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>(119,101,35)</td>
<td>255</td>
<td>4.730459678748554</td>
<td>1.00000</td>
<td>0.36609</td>
<td>1.40576</td>
<td>1.12933</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>(161,137,35)</td>
<td>333</td>
<td>4.730459678918180</td>
<td>1.00000</td>
<td>0.37378</td>
<td>1.43030</td>
<td>1.13489</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>(209,176,35)</td>
<td>420</td>
<td>4.730459678934272</td>
<td>1.00000</td>
<td>0.38513</td>
<td>1.47510</td>
<td>1.26093</td>
</tr>
<tr>
<td>10,10,4</td>
<td>(262,226,35)</td>
<td>523</td>
<td>4.730459678938604</td>
<td>1.00000</td>
<td>0.39545</td>
<td>1.57489</td>
<td>1.45886</td>
</tr>
<tr>
<td>11,11,4</td>
<td>(319,279,35)</td>
<td>633</td>
<td>4.730459678939487</td>
<td>1.00000</td>
<td>0.40930</td>
<td>1.71515</td>
<td>1.42963</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that
  i + j + k ≤ N1, for block no.1 (α₁ β₁)
  i + j + k ≤ N2, for block no.2 (α₂ β₂)
  i + j + k ≤ N3, for block no.3 (α₃ β₃)
Table 15.
ls4p(3P) state of Li*

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>α₁</th>
<th>α₂</th>
<th>β₁</th>
<th>β₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5, 4</td>
<td>(54, 54, 35)</td>
<td>143</td>
<td>4.628463569063415</td>
<td>1.01501</td>
<td>0.22009</td>
<td>1.16577</td>
<td>0.80457</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>(76, 78, 35)</td>
<td>189</td>
<td>4.62846357224766</td>
<td>0.98645</td>
<td>0.22198</td>
<td>1.26508</td>
<td>0.83643</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>(100,110,35)</td>
<td>245</td>
<td>4.62846357287885</td>
<td>1.00476</td>
<td>0.23334</td>
<td>1.29834</td>
<td>0.99634</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>(125,146,35)</td>
<td>306</td>
<td>4.62846357285665</td>
<td>0.98413</td>
<td>0.23669</td>
<td>1.40698</td>
<td>1.01007</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>(150,192,35)</td>
<td>377</td>
<td>4.62846357288311</td>
<td>0.99570</td>
<td>0.24750</td>
<td>1.40356</td>
<td>1.19189</td>
</tr>
<tr>
<td>10,10,4</td>
<td>(175,242,35)</td>
<td>452</td>
<td>4.628463572872954</td>
<td>0.98395</td>
<td>0.25342</td>
<td>1.50897</td>
<td>1.17920</td>
</tr>
<tr>
<td>11,11,4</td>
<td>(200,304,35)</td>
<td>539</td>
<td>4.628463572873717</td>
<td>0.98975</td>
<td>0.25562</td>
<td>1.60754</td>
<td>1.25525</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that

i + j + k ≤ N1, for block no.1 (α₁, β₁)

i + j + k ≤ N2, for block no.2 (α₂, β₂)

i + j + k ≤ N3, for block no.3 (α₃, β₃)
Table 16.
1s5p(^3P) state of Li*

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) -E_{ar}</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \beta_1 )</th>
<th>( \beta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5, 4</td>
<td>(54, 54, 35)</td>
<td>139</td>
<td>4.581768407413421</td>
<td>0.99042</td>
<td>0.15533</td>
<td>1.17236</td>
<td>0.58585</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>(76, 78, 35)</td>
<td>189</td>
<td>4.581768417212797</td>
<td>1.00903</td>
<td>0.16199</td>
<td>1.27899</td>
<td>0.69446</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>(100,110,35)</td>
<td>239</td>
<td>4.581768417932077</td>
<td>0.98206</td>
<td>0.16809</td>
<td>1.34106</td>
<td>0.76160</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>(125,146,35)</td>
<td>306</td>
<td>4.581768418098041</td>
<td>1.00641</td>
<td>0.17786</td>
<td>1.36914</td>
<td>0.92084</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>(150,192,35)</td>
<td>377</td>
<td>4.581768418113075</td>
<td>0.97998</td>
<td>0.17926</td>
<td>1.45325</td>
<td>0.93585</td>
</tr>
<tr>
<td>10,10,4</td>
<td>(175,242,35)</td>
<td>452</td>
<td>4.581768418118901</td>
<td>1.00385</td>
<td>0.18713</td>
<td>1.48364</td>
<td>1.05988</td>
</tr>
<tr>
<td>11,11,4</td>
<td>(200,304,35)</td>
<td>539</td>
<td>4.581768418119575</td>
<td>0.99933</td>
<td>0.19305</td>
<td>1.51367</td>
<td>1.06671</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that

\[ i + j + k \leq N1, \text{ for block no.1 } (\alpha_1, \beta_1) \]
\[ i + j + k \leq N2, \text{ for block no.2 } (\alpha_2, \beta_2) \]
\[ i + j + k \leq N3, \text{ for block no.3 } (\alpha_1, \beta_1) \]
Table 17.  
$1s3p(^1P)$ state of Li$^+$

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3 Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) $-E_{1r}$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7, 7, 4 (75, 110, 31)</td>
<td>216</td>
<td>4.720206887295567</td>
<td>0.95184</td>
<td>0.35236</td>
<td>1.42181</td>
<td>1.14209</td>
</tr>
<tr>
<td>8, 8, 4 (90, 146, 31)</td>
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<td>4.720206887388893</td>
<td>0.95490</td>
<td>0.36554</td>
<td>1.51843</td>
<td>1.15039</td>
</tr>
<tr>
<td>9, 8, 4 (105,146,31)</td>
<td>282</td>
<td>4.720206887400468</td>
<td>0.95483</td>
<td>0.39166</td>
<td>1.67542</td>
<td>1.14874</td>
</tr>
<tr>
<td>10,9, 4 (120,192,31)</td>
<td>343</td>
<td>4.720206887430910</td>
<td>0.96038</td>
<td>0.37701</td>
<td>1.75580</td>
<td>1.12726</td>
</tr>
<tr>
<td>11,10,4 (200,242,35)</td>
<td>477</td>
<td>4.720206887446368</td>
<td>1.01575</td>
<td>0.41168</td>
<td>1.78290</td>
<td>1.41815</td>
</tr>
<tr>
<td>11,11,4 (200,304,35)</td>
<td>539</td>
<td>4.720206887446922</td>
<td>1.01001</td>
<td>0.41486</td>
<td>1.83844</td>
<td>1.50525</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that

$i + j + k \leq N1$, for block no.1 ($\alpha_1, \beta_1$)

$i + j + k \leq N2$, for block no.2 ($\alpha_2, \beta_2$)

$i + j + k \leq N3$, for block no.3 ($\alpha_1, \beta_1$)
Table 18
1s4p(^1P) state of Li*

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3 Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) (-E_{nr})</th>
<th>(\alpha_1)</th>
<th>(\alpha_2)</th>
<th>(\beta_1)</th>
<th>(\beta_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5, 4 (54, 54, 35)</td>
<td>143</td>
<td>4.62415142305136</td>
<td>1.00092</td>
<td>0.22437</td>
<td>1.05591</td>
<td>0.95819</td>
</tr>
<tr>
<td>6, 6, 4 (76, 78, 35)</td>
<td>189</td>
<td>4.624151425835921</td>
<td>0.98090</td>
<td>0.23279</td>
<td>1.15424</td>
<td>1.00128</td>
</tr>
<tr>
<td>7, 7, 4 (100,110,35)</td>
<td>245</td>
<td>4.624151426420320</td>
<td>1.00281</td>
<td>0.24042</td>
<td>1.19910</td>
<td>1.14142</td>
</tr>
<tr>
<td>8, 8, 4 (125,146,35)</td>
<td>306</td>
<td>4.624151426499488</td>
<td>0.96857</td>
<td>0.24725</td>
<td>1.30774</td>
<td>1.20569</td>
</tr>
<tr>
<td>9, 9, 4 (150,192,35)</td>
<td>377</td>
<td>4.624151426516476</td>
<td>0.99731</td>
<td>0.25726</td>
<td>1.42615</td>
<td>1.30339</td>
</tr>
<tr>
<td>10,10,4 (175,242,35)</td>
<td>452</td>
<td>4.624151426520795</td>
<td>0.97455</td>
<td>0.26447</td>
<td>1.46967</td>
<td>1.36469</td>
</tr>
<tr>
<td>11,11,4 (200,305,35)</td>
<td>540</td>
<td>4.6241514265421619</td>
<td>0.97992</td>
<td>0.27338</td>
<td>1.55526</td>
<td>1.40552</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that
  
i + j + k \leq N1, for block no.1 \((\alpha_1,\beta_1)\)
  
i + j + k \leq N2, for block no.2 \((\alpha_2,\beta_2)\)
  
i + j + k \leq N3, for block no.3 \((\alpha_3,\beta_3)\)
Table 19.

$1s^2p^1(1P)$ state of Li$^*$

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1,N2,N3</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) $-E_{ar}$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5, 4</td>
<td>(54, 54, 35)</td>
<td>143</td>
<td>4.579566517819179</td>
<td>0.99084</td>
<td>0.16028</td>
<td>1.16083</td>
<td>0.76178</td>
</tr>
<tr>
<td>6, 6, 4</td>
<td>(76, 78, 35)</td>
<td>189</td>
<td>4.579566523544275</td>
<td>1.00299</td>
<td>0.17230</td>
<td>1.21155</td>
<td>0.88184</td>
</tr>
<tr>
<td>7, 7, 4</td>
<td>(100,110,35)</td>
<td>245</td>
<td>4.579566524227733</td>
<td>0.98102</td>
<td>0.17365</td>
<td>1.27747</td>
<td>0.92419</td>
</tr>
<tr>
<td>8, 8, 4</td>
<td>(125,146,35)</td>
<td>306</td>
<td>4.579566524365640</td>
<td>1.00299</td>
<td>0.18433</td>
<td>1.25934</td>
<td>1.08130</td>
</tr>
<tr>
<td>9, 9, 4</td>
<td>(150,192,35)</td>
<td>377</td>
<td>4.579566524388801</td>
<td>0.97567</td>
<td>0.18585</td>
<td>1.40997</td>
<td>1.10944</td>
</tr>
<tr>
<td>10,10,4</td>
<td>(175,242,35)</td>
<td>452</td>
<td>4.579566524394834</td>
<td>1.00018</td>
<td>0.19495</td>
<td>1.39734</td>
<td>1.24072</td>
</tr>
<tr>
<td>11,11,4</td>
<td>(200,304,35)</td>
<td>539</td>
<td>4.579566524395987</td>
<td>0.98401</td>
<td>0.19958</td>
<td>1.46503</td>
<td>1.25769</td>
</tr>
</tbody>
</table>

* N1,N2,N3 are basis set indices such that

\[ i + j + k \leq N_1 \], for block no.1 ($\alpha_1, \beta_1$)
\[ i + j + k \leq N_2 \], for block no.2 ($\alpha_2, \beta_2$)
\[ i + j + k \leq N_3 \], for block no.3 ($\alpha_1, \beta_1$)
Table 20.
1s3s(^3S) state of Li'

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \beta_1 )</th>
<th>( \beta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6, 6</td>
<td>(49, 50)</td>
<td>099</td>
<td>4.733756113097471</td>
<td>1.00740</td>
<td>0.34700</td>
<td>1.28150</td>
<td>1.23530</td>
</tr>
<tr>
<td>7, 7</td>
<td>(70, 70)</td>
<td>140</td>
<td>4.733756130215415</td>
<td>0.97720</td>
<td>0.32680</td>
<td>1.44680</td>
<td>1.48289</td>
</tr>
<tr>
<td>8, 8</td>
<td>(94, 95)</td>
<td>189</td>
<td>4.733756132160908</td>
<td>0.98950</td>
<td>0.34450</td>
<td>1.49820</td>
<td>1.73780</td>
</tr>
<tr>
<td>9, 9</td>
<td>(122,125)</td>
<td>247</td>
<td>4.733756132535957</td>
<td>1.00520</td>
<td>0.35800</td>
<td>1.59900</td>
<td>1.95530</td>
</tr>
<tr>
<td>10,10</td>
<td>(154,161)</td>
<td>315</td>
<td>4.733756132612588</td>
<td>1.00140</td>
<td>0.36030</td>
<td>1.68740</td>
<td>2.13410</td>
</tr>
<tr>
<td>11,11</td>
<td>(190,203)</td>
<td>393</td>
<td>4.733756132637839</td>
<td>1.01880</td>
<td>0.37540</td>
<td>1.76630</td>
<td>2.36560</td>
</tr>
<tr>
<td>12,12</td>
<td>(230,252)</td>
<td>482</td>
<td>4.733756132644032</td>
<td>1.03890</td>
<td>0.37420</td>
<td>1.89480</td>
<td>2.50400</td>
</tr>
<tr>
<td>13,13</td>
<td>(274,308)</td>
<td>582</td>
<td>4.733756132646075</td>
<td>0.99130</td>
<td>0.36630</td>
<td>1.98550</td>
<td>2.73850</td>
</tr>
</tbody>
</table>

* N1 and N2 are basis set indices such that

\[ i + j + k \leq N1, \text{ for block no.1 (} \alpha_1, \beta_1 \) \]

\[ i + j + k \leq N2, \text{ for block no.2 (} \alpha_2, \beta_2 \) \]
Table 21.
1s4s(1S) state of Li

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>α1</th>
<th>α2</th>
<th>β1</th>
<th>β2</th>
</tr>
</thead>
<tbody>
<tr>
<td>6, 6</td>
<td>(50, 50)</td>
<td>100</td>
<td>4.629783608733150</td>
<td>0.99310</td>
<td>0.21710</td>
<td>1.01420</td>
<td>1.12830</td>
</tr>
<tr>
<td>7, 7</td>
<td>(70, 70)</td>
<td>142</td>
<td>4.629783632832081</td>
<td>1.00000</td>
<td>0.22730</td>
<td>1.11500</td>
<td>1.19410</td>
</tr>
<tr>
<td>8, 8</td>
<td>(94, 95)</td>
<td>189</td>
<td>4.629783637002549</td>
<td>0.95460</td>
<td>0.22470</td>
<td>1.28150</td>
<td>1.40270</td>
</tr>
<tr>
<td>9, 9</td>
<td>(122,125)</td>
<td>147</td>
<td>4.629783637680292</td>
<td>0.94790</td>
<td>0.23100</td>
<td>1.37080</td>
<td>1.62270</td>
</tr>
<tr>
<td>10,10</td>
<td>(154,161)</td>
<td>315</td>
<td>4.629783637826947</td>
<td>0.95250</td>
<td>0.23340</td>
<td>1.49620</td>
<td>1.74170</td>
</tr>
<tr>
<td>11,11</td>
<td>(190,203)</td>
<td>393</td>
<td>4.629783637861579</td>
<td>0.96050</td>
<td>0.24020</td>
<td>1.57940</td>
<td>1.87800</td>
</tr>
<tr>
<td>12,12</td>
<td>(230,252)</td>
<td>482</td>
<td>4.629783637871640</td>
<td>0.96710</td>
<td>0.23580</td>
<td>1.69510</td>
<td>1.95910</td>
</tr>
<tr>
<td>13,13</td>
<td>(274,308)</td>
<td>582</td>
<td>4.629783637874488</td>
<td>0.93840</td>
<td>0.23170</td>
<td>1.81730</td>
<td>2.08980</td>
</tr>
</tbody>
</table>

*N1 and N2 are basis set indices such that
i + j + k ≤ N1, for block no.1 (α1,β1)
i + j + k ≤ N2, for block no.2 (α2,β2)
Table 22.
1s3s(^3S) state of Li⁺

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>α₁</th>
<th>α₂</th>
<th>β₁</th>
<th>β₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 5</td>
<td>(34, 34)</td>
<td>68</td>
<td>4.752076453042607</td>
<td>0.98690</td>
<td>0.29200</td>
<td>0.82220</td>
<td>0.91150</td>
</tr>
<tr>
<td>6, 6</td>
<td>(50, 50)</td>
<td>100</td>
<td>4.752076455515084</td>
<td>0.99430</td>
<td>0.31480</td>
<td>0.87060</td>
<td>0.95360</td>
</tr>
<tr>
<td>7, 7</td>
<td>(70, 70)</td>
<td>140</td>
<td>4.752076456006734</td>
<td>0.98370</td>
<td>0.31600</td>
<td>1.00780</td>
<td>1.15430</td>
</tr>
<tr>
<td>8, 8</td>
<td>(94, 95)</td>
<td>189</td>
<td>4.752076456036935</td>
<td>0.98920</td>
<td>0.32510</td>
<td>1.11550</td>
<td>1.19390</td>
</tr>
<tr>
<td>9, 9</td>
<td>(122,125)</td>
<td>247</td>
<td>4.752076456044674</td>
<td>0.97350</td>
<td>0.32520</td>
<td>1.11990</td>
<td>1.22150</td>
</tr>
<tr>
<td>10,10</td>
<td>(154,161)</td>
<td>315</td>
<td>4.752076456045370</td>
<td>0.97870</td>
<td>0.32870</td>
<td>1.12570</td>
<td>1.27930</td>
</tr>
<tr>
<td>11,11</td>
<td>(190,203)</td>
<td>393</td>
<td>4.752076456045535</td>
<td>0.99080</td>
<td>0.32870</td>
<td>1.14130</td>
<td>1.33960</td>
</tr>
<tr>
<td>12,12</td>
<td>(230,252)</td>
<td>482</td>
<td>4.752076456045535</td>
<td>0.98040</td>
<td>0.34080</td>
<td>1.17170</td>
<td>1.42160</td>
</tr>
<tr>
<td>13,13</td>
<td>(274,308)</td>
<td>582</td>
<td>4.752076456045583</td>
<td>0.98050</td>
<td>0.33200</td>
<td>1.20190</td>
<td>1.50550</td>
</tr>
</tbody>
</table>

* N1 and N2 are basis set indices such that
  
i + j + k ≤ N1, for block no.1 (α₁,β₁)
  
i + j + k ≤ N2, for block no.2 (α₂,β₂)
Table 23.
1s4s(^2S) state of Li⁺

Convergence of nonrelativistic eigenvalues for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.) -E_n</th>
<th>α₁</th>
<th>α₂</th>
<th>β₁</th>
<th>β₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,9</td>
<td>(122,125)</td>
<td>147</td>
<td>4.637136595004172</td>
<td>1.000000</td>
<td>0.19550</td>
<td>0.99990</td>
<td>1.11710</td>
</tr>
<tr>
<td>10,10</td>
<td>(154,161)</td>
<td>315</td>
<td>4.637136595009255</td>
<td>1.000000</td>
<td>0.19560</td>
<td>1.03930</td>
<td>1.12700</td>
</tr>
<tr>
<td>11,11</td>
<td>(190,203)</td>
<td>393</td>
<td>4.637136595010467</td>
<td>1.000000</td>
<td>0.19540</td>
<td>1.08080</td>
<td>1.14830</td>
</tr>
<tr>
<td>12,12</td>
<td>(230,252)</td>
<td>482</td>
<td>4.637136595010677</td>
<td>1.000000</td>
<td>0.19550</td>
<td>1.10800</td>
<td>1.16820</td>
</tr>
<tr>
<td>13,13</td>
<td>(274,308)</td>
<td>582</td>
<td>4.637136595010731</td>
<td>1.000000</td>
<td>0.19550</td>
<td>1.10930</td>
<td>1.19690</td>
</tr>
</tbody>
</table>

* N1 and N2 are basis set indices such that

i + j + k ≤ N1, for block no.1 (α₁, β₁)
i + j + k ≤ N2, for block no.2 (α₂, β₂)
### Table 24.

**1s5s(3S) state of Li**

Convergence of nonrelativistic eigen values for infinite nuclear mass

<table>
<thead>
<tr>
<th>N1, N2</th>
<th>Block Sizes</th>
<th>Total No. of Terms</th>
<th>Energies (in a.u.)</th>
<th>α₁</th>
<th>α₂</th>
<th>β₁</th>
<th>β₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>6, 6</td>
<td>(50, 50)</td>
<td>100</td>
<td>4.586092669687876</td>
<td>1.00040</td>
<td>0.15400</td>
<td>0.73970</td>
<td>0.84280</td>
</tr>
<tr>
<td>7, 7</td>
<td>(70, 70)</td>
<td>140</td>
<td>4.586092670300881</td>
<td>0.98990</td>
<td>0.15460</td>
<td>0.75118</td>
<td>0.92920</td>
</tr>
<tr>
<td>8, 8</td>
<td>(94, 95)</td>
<td>189</td>
<td>4.586092670429146</td>
<td>1.00040</td>
<td>0.15760</td>
<td>0.72660</td>
<td>1.05520</td>
</tr>
<tr>
<td>9, 9</td>
<td>(122,125)</td>
<td>247</td>
<td>4.586092670440790</td>
<td>0.99490</td>
<td>0.15940</td>
<td>0.76430</td>
<td>1.10580</td>
</tr>
<tr>
<td>10,10</td>
<td>(154,161)</td>
<td>315</td>
<td>4.586092670442780</td>
<td>0.98810</td>
<td>0.15820</td>
<td>0.77770</td>
<td>1.09830</td>
</tr>
<tr>
<td>11,11</td>
<td>(190,203)</td>
<td>393</td>
<td>4.586092670443432</td>
<td>0.99090</td>
<td>0.15280</td>
<td>0.82150</td>
<td>1.11090</td>
</tr>
<tr>
<td>12,12</td>
<td>(230,252)</td>
<td>482</td>
<td>4.586092670443614</td>
<td>1.01080</td>
<td>0.15740</td>
<td>0.84840</td>
<td>1.11870</td>
</tr>
<tr>
<td>13,13</td>
<td>(274,308)</td>
<td>582</td>
<td>4.586092670443662</td>
<td>0.99080</td>
<td>0.16060</td>
<td>0.85140</td>
<td>1.14130</td>
</tr>
</tbody>
</table>

* N1 and N2 are basis set indices such that
  
i + j + k ≤ N1, for block no.1 (α₁, β₁)  
i + j + k ≤ N2, for block no.2 (α₂, β₂)
Table 25.

Contributions to the $2^1P$ and $2^3P$ state energies of Li$^+$ relative to Li$^+(1s)$:

(units are in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Term</th>
<th>$2^1P_1$</th>
<th>$2^3P_0$</th>
<th>$2^3P_1$</th>
<th>$2^3P_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{or}$</td>
<td>$-108269.5783923$</td>
<td>$-115811.1472929$</td>
<td>$-115811.1472929$</td>
<td>$-115811.1472929$</td>
</tr>
<tr>
<td>$EM(1)$</td>
<td>$4.3107906$</td>
<td>$-5.2365928$</td>
<td>$-5.2365928$</td>
<td>$-5.2365928$</td>
</tr>
<tr>
<td>$EM(2)$</td>
<td>$-0.0009314$</td>
<td>$-0.0010066$</td>
<td>$-0.0010066$</td>
<td>$-0.0010066$</td>
</tr>
<tr>
<td>$E_{rel}$</td>
<td>$-5.6359686$</td>
<td>$3.6649556$</td>
<td>$-1.5163207$</td>
<td>$0.5578166$</td>
</tr>
<tr>
<td>$E_{anom}$</td>
<td>$0.00000090$</td>
<td>$0.0015139$</td>
<td>$-0.0072500$</td>
<td>$0.0040532$</td>
</tr>
<tr>
<td>$E_{et}$</td>
<td>$0.0044613$</td>
<td>$0.0000000$</td>
<td>$-0.0044613$</td>
<td>$0.0000000$</td>
</tr>
<tr>
<td>$E_{RR}(N)$</td>
<td>$-0.0020271$</td>
<td>$0.0013573$</td>
<td>$0.0018786$</td>
<td>$0.0009716$</td>
</tr>
<tr>
<td>$E_{RR}(X)$</td>
<td>$0.0009509$</td>
<td>$0.0008656$</td>
<td>$-0.0000089$</td>
<td>$0.0004967$</td>
</tr>
<tr>
<td>$E_{auc}$</td>
<td>$0.0000606$</td>
<td>$-0.0004009$</td>
<td>$0.0004009$</td>
<td>$-0.0004009$</td>
</tr>
<tr>
<td>$E_{L,1}$</td>
<td>$0.0345662$</td>
<td>$-0.2281888$</td>
<td>$-0.2281914$</td>
<td>$-0.2236568$</td>
</tr>
<tr>
<td>$E_{L,2}$</td>
<td>$-0.0187005$</td>
<td>$-0.0099266$</td>
<td>$-0.0099266$</td>
<td>$-0.0099266$</td>
</tr>
<tr>
<td>Total</td>
<td>$-108270.8851902$</td>
<td>$-115812.9546359$</td>
<td>$-115818.1495835$</td>
<td>$-115816.0602384$</td>
</tr>
</tbody>
</table>

Table 26.

Contributions to the $2^1S$ and $2^3S$ state energies of Li$^+$ relative to Li$^+(1s)$:

(units are in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Term</th>
<th>$2^1S_0$</th>
<th>$2^3S_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-E_{or}$</td>
<td>$-118699.4411187$</td>
<td>$-134028.6828569$</td>
</tr>
<tr>
<td>$EM(1)$</td>
<td>$0.3724903$</td>
<td>$0.3015034$</td>
</tr>
<tr>
<td>$EM(2)$</td>
<td>$-0.0007049$</td>
<td>$-0.0002414$</td>
</tr>
<tr>
<td>$E_{rel}$</td>
<td>$-6.5137745$</td>
<td>$-16.8876120$</td>
</tr>
<tr>
<td>$E_{RR}(N)$</td>
<td>$-0.0019942$</td>
<td>$-0.0006951$</td>
</tr>
<tr>
<td>$E_{RR}(X)$</td>
<td>$0.0013672$</td>
<td>$0.0002143$</td>
</tr>
<tr>
<td>$E_{auc}$</td>
<td>$0.0014306$</td>
<td>$0.0017208$</td>
</tr>
<tr>
<td>$E_{L,1}$</td>
<td>$0.6394729$</td>
<td>$1.0197730$</td>
</tr>
<tr>
<td>$E_{L,2}$</td>
<td>$-0.0633996$</td>
<td>$-0.0061934$</td>
</tr>
<tr>
<td>Total</td>
<td>$-118704.3062306$</td>
<td>$-134044.2543873$</td>
</tr>
</tbody>
</table>

$R_\infty = 109737.315709$, $R_m = 109728.734028$, $\mu_u/M = 7.8202030000\times10^{-5}$,

Nuclear Radius = 2.5600 fm, $\frac{1}{\alpha} = 137.0359896$
Table 27.
Comparison of theoretical and experimental \((2^3S-2^3P)\) and \((2^1S-2^1P)\) transition energies.
\(\text{(units are in cm}^{-1}\text{)}\)

<table>
<thead>
<tr>
<th>Present Work</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2^3S_1 - 2^3P_0)</td>
<td>18231.303(1)a</td>
</tr>
<tr>
<td>18231.2997514</td>
<td>18231.30188(19)b</td>
</tr>
<tr>
<td>(2^3S_1 - 2^3P_1)</td>
<td>18226.108(1)a</td>
</tr>
<tr>
<td>18226.1048038</td>
<td>18226.11206(21)b</td>
</tr>
<tr>
<td>(2^3S_1 - 2^3P_2)</td>
<td>18228.198(1)a</td>
</tr>
<tr>
<td>18228.1941469</td>
<td>18228.19935(25)b</td>
</tr>
<tr>
<td>(2^1S_0 - 2^1P_1)</td>
<td>10434.013(109)c</td>
</tr>
<tr>
<td>10433.9210404</td>
<td></td>
</tr>
</tbody>
</table>


\(b\)E. Riis, H.G.Berry, O.Poulsen, S.A.Lee, and S.Y.Tang

\(c\)Y.G.Toresson and B.Edlen
Arkiv Fysik 23, 117(1962).
Figure 3.1  Variation of the optimized non-linear parameters for the $2^3S$ state of Li* as the basis set is enlarged.
Figure 3.2 Variation of the optimized non-linear parameters for the $2^1S$ state of Li$^+$ as the basis set is enlarged.
Figure 3.3  Variation of the optimized non-linear parameters for the $2^1S$ state of Li$^+$ as the basis set is enlarged.
Figure 3.4 Variation of the optimized non-linear parameters for the $2^3P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.5  Variation of the optimized non-linear parameters for the $2^3P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.6 Variation of the optimized non-linear parameters for the $2^1P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.7 Variation of the optimized non-linear parameters for the $2^1\text{P}$ state of Li$^+$ as the basis set is enlarged.
Figure 3.8 Variation of the optimized non-linear parameters for the $1^1S$ state of Li$^+$ as the basis set is enlarged.
Figure 3.9  Variation of the optimized non-linear parameters for the $3^p$ state of Li$^+$ as the basis set is enlarged.
Figure 3.10 Variation of the optimized non-linear parameters for the $4^3P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.11 Variation of the optimized non-linear parameters for the $5^3P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.12  Variation of the optimized non-linear parameters for the $3^1P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.13  Variation of the optimized non-linear parameters for the $4^1P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.14  Variation of the optimized non-linear parameters for the $5^1P$ state of Li$^+$ as the basis set is enlarged.
Figure 3.15 Variation of the optimized non-linear parameters for the $3^1S$ state of Li$^+$ as the basis set is enlarged.
Figure 3.16  Variation of the optimized non-linear parameters for the $4^1S$ state of Li$^+$ as the basis set is enlarged.
Figure 3.17  Variation of the optimized non-linear parameters for the 3²S state of Li⁺ as the basis set is enlarged.

Figure 3.18  Variation of the optimized non-linear parameters for the 5²S state of Li⁺ as the basis set is enlarged.
Figure 3.19  Variation of the optimized non-linear parameters for the $4^3S$ state of Li$^+$ as the basis set is enlarged.
Appendix-I

In this appendix, the Breit equation for a two electron system is reduced to and equivalent non-relativistic form, thereby obtaining the Breit-Pauli operators, which are the non-relativistic correction operators for the relativistic effects in the two-electron system.

The effective interaction between two electrons is represented by the Breit interaction formula given by

$$\mathcal{V}_{\text{Breit}} = e^2\left[\frac{1}{r} - \frac{\mathbf{\alpha}_1 \cdot \mathbf{\alpha}_2 + (\mathbf{\delta}_1 \cdot \mathbf{\hat{r}})(\mathbf{\delta}_2 \cdot \mathbf{\hat{r}})}{2r}\right].$$  \hspace{1cm} (I.1)

The matrix element for the effective interaction energy is given by

$$E_{\text{Breit}} = \langle \psi_c \psi_d | \mathcal{V}_{\text{Breit}} | \psi_a \psi_b \rangle$$

$$= e^2 \int \psi_c^\dagger \psi_d^\dagger \mathcal{V}_{\text{Breit}} \psi_a \psi_b \, d\mathbf{r}_1 d\mathbf{r}_2$$  \hspace{1cm} (I.2)

where $\psi_a$ and $\psi_c$ are the initial and the final relativistic wave functions of the electron-1 and $\psi_b$ and $\psi_d$ are the initial and the final relativistic wave functions of the electron-2. In order that the expression (I.2) may be reduced to an equivalent non-relativistic form these wave functions are to be taken in the form $\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$ with

$$\chi = \frac{\mathbf{p}}{2mc}.$$  

Thus we have,

$$\psi_a = \begin{pmatrix} \phi_a \\ (\mathbf{\delta}_1 \cdot \mathbf{\hat{p}}_1) \phi_a \end{pmatrix}, \quad \psi_c = \begin{pmatrix} \phi_c \\ (\mathbf{\delta}_1 \cdot \mathbf{\hat{p}}_1) \phi_c \end{pmatrix}, \quad \psi_b = \begin{pmatrix} \phi_b \\ (\mathbf{\delta}_2 \cdot \mathbf{\hat{p}}_2) \phi_b \end{pmatrix}, \quad \psi_d = \begin{pmatrix} \phi_d \\ (\mathbf{\delta}_2 \cdot \mathbf{\hat{p}}_2) \phi_d \end{pmatrix}. $$
With these wave functions in expression (1.2) we first expand the integrand by ordinary matrix multiplication. In doing so, we obtain a number of integrals of the form

\[
\int (\sigma_{i_1} \beta_{i_1} \phi)^\dagger \phi' \, d\mathbf{r}_1,
\]

which on integration by parts becomes

\[
= \int (\sigma_{i_1} \nabla_{i_1} \phi)^\dagger \phi' \, d\mathbf{r}_1.
\]

\[
= \int \left( \frac{\partial \phi^*}{\partial x_i} \sigma_{i_1} + \frac{\partial \phi^*}{\partial y_i} \sigma_{y_i} + \frac{\partial \phi^*}{\partial z_i} \sigma_{z_i} \right) \phi' \, dx_1 \, dy_1 \, dz_1.
\]

\[
= \left\{ \iint \phi^* \sigma_{i_1} \phi' \, dx_1 \, dy_1 \, dz_1 - \iint \phi^* \sigma_{y_i} \frac{\partial \phi'}{\partial y_i} \, dx_1 \, dy_1 \, dz_1 - \iint \phi^* \sigma_{z_i} \frac{\partial \phi'}{\partial z_i} \, dx_1 \, dy_1 \, dz_1 \right\}
\]

\[
= -\iint \phi^* (\sigma_{i_1} \nabla_{i_1} \phi') \, dx_1 \, dy_1 \, dz_1
\]

\[
= \iint \phi^* (\sigma_{i_1} \beta_{i_1} \phi') \, dx_1 \, dy_1 \, dz_1
\]

Thus, for example we can write,

\[
\iint \psi_c^\dagger \psi_d^\dagger \, A_{i_1} \psi_{i_1} \, d\mathbf{r}_1 \, d\mathbf{r}_2
\]

\[
= \iint \left[ \phi_c^* \phi_{i_1}^*, \phi_c^* \phi_{i_1}^* \frac{\sigma_{i_1} \beta_{i_1}}{2mc}, \phi_c^* \phi_{i_1}^* \frac{\sigma_{i_1} \beta_{i_1}}{2mc}, \phi_c^* \phi_{i_1}^* \frac{\sigma_{i_1} \beta_{i_1}}{2mc}, \phi_c^* \phi_{i_1}^* \frac{\sigma_{i_1} \beta_{i_1}}{2mc} \right] A_{i_1} \psi_{i_1} \, d\mathbf{r}_1 \, d\mathbf{r}_2
\]
where,

\[
\psi_a \psi_b = \begin{bmatrix}
\phi_a \phi_b \\
\frac{\varphi_1 \cdot \varphi_1}{2mc} \phi_a \phi_b \\
\frac{\varphi_2 \cdot \varphi_2}{2mc} \phi_a \phi_b \\
\frac{(\varphi_1 \cdot \varphi_1)(\varphi_2 \cdot \varphi_2)}{(2mc)^2} \phi_a \phi_b
\end{bmatrix}
\]

and

\[
\psi_c \psi_d = [ \phi_c \phi_d, \phi_c \phi_d \frac{\varphi_1 \cdot \varphi_1}{2mc}, \phi_c \phi_d \frac{\varphi_2 \cdot \varphi_2}{2mc}, \phi_c \phi_d \frac{(\varphi_1 \cdot \varphi_1)(\varphi_2 \cdot \varphi_2)}{(2mc)^2} ].
\]

Here A is any operator operating towards the right.

Thus, unless the terms in the integrands become singular at any point in space the reduction of (I.2) to an integral involving the components \( \phi \)'s and then transformation to the non-relativistic wave functions \( \Phi \) by using the approximate relation

\[
\phi = (1 - \frac{\mathbf{p}^2}{8m^2 c^2}) \Phi
\]

is quite straightforward. Such a reduction is shown below.

First consider \( \psi_c \psi_d \left[ \frac{\alpha_1 \cdot \alpha_2}{2r} \right] \psi_a \psi_b \).

Since

\[
\alpha_1 \cdot \alpha_2 = \begin{bmatrix}
0 & 0 & 0 & \varphi_1 \cdot \varphi_2 \\
0 & 0 & \varphi_1 \cdot \varphi_2 & 0 \\
0 & \varphi_1 \cdot \varphi_2 & 0 & 0 \\
\varphi_1 \cdot \varphi_2 & 0 & 0 & 0
\end{bmatrix},
\]

therefore,

\[
(\alpha_1 \cdot \alpha_2) \psi_a \psi_b = \begin{bmatrix}
\frac{\varphi_1 \cdot \varphi_2 (\varphi_1 \cdot \varphi_1)(\varphi_2 \cdot \varphi_2)}{(2mc)^2} \phi_a \phi_b \\
\frac{\varphi_1 \cdot \varphi_2 (\varphi_2 \cdot \varphi_2)}{2mc} \phi_a \phi_b \\
\frac{\varphi_1 \cdot \varphi_2 (\varphi_1 \cdot \varphi_1)}{2mc} \phi_a \phi_b \\
(\varphi_1 \cdot \varphi_2) \phi_a \phi_b
\end{bmatrix}.
\]
\[ \psi_c^+ \psi_d^+ \alpha_1 \alpha_2 \frac{\alpha_1 \alpha_2}{r} \psi_a \psi_b \]

\[ = \phi_c^+ \phi_d^+ \frac{\bar{\sigma}_1 \bar{\sigma}_2 (\bar{\sigma}_1 \cdot \bar{p}_1) (\bar{\sigma}_2 \cdot \bar{p}_2)}{r (2mc)^2} \phi_a \phi_b \]

\[ + \phi_c^+ \phi_d^+ \frac{1}{(2mc)^2} \left\{ \left[ \frac{1}{r^2} \right] (\bar{\sigma}_1 \cdot \bar{p}_1) (\bar{\sigma}_1 \cdot \bar{p}_2) \phi_a \phi_b \right\} \]

\[ + \phi_c^+ \phi_d^+ \frac{1}{(2mc)^2} \left\{ \left[ \frac{1}{r^2} \right] (\bar{\sigma}_2 \cdot \bar{p}_2) \phi_a \phi_b \right\} \]

\[ + (\bar{\sigma}_1 \cdot \bar{p}_1) (\bar{\sigma}_2 \cdot \bar{p}_2) \phi_a \phi_b \}

\text{(1.3)}

Using \( \bar{p} = -i \hbar \bar{\nabla} \), the right hand side of (1.3) becomes

\[ = \phi_c^+ \phi_d^+ \frac{\bar{\sigma}_1 \bar{\sigma}_2 (\bar{\sigma}_1 \cdot \bar{p}_1) (\bar{\sigma}_2 \cdot \bar{p}_2)}{r (2mc)^2} \phi_a \phi_b \]

\[ + \phi_c^+ \phi_d^+ \frac{1}{(2mc)^2} \left\{ \left[ \frac{1}{r^2} \right] \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) + \frac{1}{r} \sigma_1 \sigma_2 (\sigma_2 \cdot p_2) \right\} \]

\[ + \left\{ \frac{1}{r^2} \right\} \sigma_1 \sigma_2 \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) + \frac{1}{r} \sigma_2 \sigma_1 \sigma_2 \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) \}

\text{(1.3)}

\[ = \phi_c^+ \phi_d^+ \frac{\bar{\sigma}_1 \bar{\sigma}_2 (\bar{\sigma}_1 \cdot \bar{p}_1) (\bar{\sigma}_2 \cdot \bar{p}_2)}{r (2mc)^2} \phi_a \phi_b \]

\[ + \phi_c^+ \phi_d^+ \frac{1}{(2mc)^2} \left\{ \left[ \frac{1}{r^2} \right] \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) + \frac{1}{r} \sigma_1 \sigma_2 (\sigma_2 \cdot p_2) \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) \right\} \]

\[ + \left\{ \frac{1}{r^2} \right\} \sigma_1 \sigma_2 \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) + \frac{1}{r} \sigma_2 \sigma_1 \sigma_2 \sigma_1 \sigma_2 (\sigma_1 \cdot p_1) \}

\text{(1.3)}
\[ = \phi^c \phi^a \frac{1}{2mc^2} \left\{ \frac{2}{\Gamma} (\hat{\varpi}_1 \hat{\varpi}_2 - i \hat{\varpi}_2 \hat{\varpi}_1 \times \hat{\varpi}_1) \phi_a \phi_b \right. \\
\left. \frac{3}{\Gamma} (\hat{\varpi}_2 \hat{\varpi}_1 \times \hat{\varpi}_1 \times \hat{\varpi}_2) \left( \hat{\varpi}_1 \hat{\varpi}_2 + \frac{1}{\Gamma} (\varpi_1^2 - 2 \varpi_1 \varpi_2) \right) \\
+ \frac{2}{\Gamma} (\hat{\varpi}_1 \hat{\varpi}_2 - \varpi_1 \varpi_2) \left( \hat{\varpi}_1 \hat{\varpi}_2 - \varpi_1 \varpi_2 \right) \phi_a \phi_b \right\} \]

\[ = \phi^c \phi^a \frac{1}{2mc^2} \left\{ \frac{2}{\Gamma} (\hat{\varpi}_1 \hat{\varpi}_2 - i \hat{\varpi}_2 \hat{\varpi}_1 \times \hat{\varpi}_1) \phi_a \phi_b \right. \\
\left. \frac{3}{\Gamma} (\hat{\varpi}_2 \hat{\varpi}_1 \times \hat{\varpi}_1 \times \hat{\varpi}_2) \left( \hat{\varpi}_1 \hat{\varpi}_2 + \frac{1}{\Gamma} (\varpi_1^2 - 2 \varpi_1 \varpi_2) \right) \\
+ \frac{2}{\Gamma} (\hat{\varpi}_1 \hat{\varpi}_2 - \varpi_1 \varpi_2) \left( \hat{\varpi}_1 \hat{\varpi}_2 - \varpi_1 \varpi_2 \right) \phi_a \phi_b \right\} \]

\[ \therefore \psi^c \psi^a \left[ - \frac{1}{2} \alpha_1 \alpha_2 \right] \psi^a \psi^b \]

\[ = - \phi^c \phi^a \frac{1}{2mc^2} \left\{ \frac{2}{\Gamma} (\hat{\varpi}_1 \hat{\varpi}_2 - i \hat{\varpi}_2 \hat{\varpi}_1 \times \hat{\varpi}_1) \phi_a \phi_b \right. \\
\left. \frac{3}{\Gamma} (\hat{\varpi}_2 \hat{\varpi}_1 \times \hat{\varpi}_1 \times \hat{\varpi}_2) \left( \hat{\varpi}_1 \hat{\varpi}_2 + \frac{1}{\Gamma} (\varpi_1^2 - 2 \varpi_1 \varpi_2) \right) \\
+ \frac{2}{\Gamma} (\hat{\varpi}_1 \hat{\varpi}_2 - \varpi_1 \varpi_2) \left( \hat{\varpi}_1 \hat{\varpi}_2 - \varpi_1 \varpi_2 \right) \phi_a \phi_b \right\} \]

\[ \text{(I.4)} \]

We note that when we transform from \( \phi \to \Phi \) by using \( \phi = (1 - p^2 / 2m^2 c^2)^2 \Phi \), none of the above terms survive the \( p^2 \)-operation because of the factor \( c^{-4} \) that come in as a result.

Again,

\[ (\hat{\varpi}_1 \hat{\varpi}_2)(\hat{\varpi}_1 \hat{\varpi}_2) = \begin{bmatrix} 0 & 0 & 0 & (\hat{\varpi}_1 \hat{\varpi}_2)(\hat{\varpi}_1 \hat{\varpi}_2) \\ 0 & 0 & (\hat{\varpi}_1 \hat{\varpi}_2)(\hat{\varpi}_1 \hat{\varpi}_2) & 0 \\ 0 & (\hat{\varpi}_1 \hat{\varpi}_2)(\hat{\varpi}_1 \hat{\varpi}_2) & 0 & 0 \\ (\hat{\varpi}_1 \hat{\varpi}_2)(\hat{\varpi}_1 \hat{\varpi}_2) & 0 & 0 & 0 \end{bmatrix} \]

\[ \therefore (\hat{\varpi}_1 \hat{\varpi}_2)(\hat{\varpi}_1 \hat{\varpi}_2) \psi_a \psi_b = \begin{bmatrix} \frac{1}{3m^2 c^2} (\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2) \phi_a \phi_b \\ \frac{1}{2mc^2} (\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2) \phi_a \phi_b \\ \frac{1}{2mc^2} (\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2)(\varpi_1 \hat{\varpi}_2) \phi_a \phi_b \\ (\varpi_1)(\varpi_1) \phi_a \phi_b \end{bmatrix} \]
\[ \psi_{\text{c}}\phi_{\text{c}}^{*}
abla_{1} T^{2}(\partial_{2}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{1}) \psi_{\text{a}} \psi_{\text{b}} \]
\[ = \phi_{\text{c}} \phi_{\text{c}}^{*} \frac{1}{4m^{2}c^{2}} \left[ \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{1}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \right. \]
\[ + \phi_{\text{c}} \phi_{\text{c}}^{*} \frac{1}{4m^{2}c^{2}} \left\{ \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{1}) (\partial_{2}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \right. \]
\[ \left. + (\partial_{2}, \bar{\phi}_{2}) \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{1}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \right\} \]
\[ (\partial_{1}, \bar{\phi}_{1}) (\partial_{2}, \bar{\phi}_{2}) \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{1}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \]  

(1.5)

Now,

(a):
\[ \sigma_{1} \bar{\phi}_{1} \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \]
\[ = \frac{1}{r^{3}} [ -i \sigma_{1} \bar{\phi}_{2} (\partial_{1}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{2}) + 2 (\partial_{1}, \bar{\phi}_{2}) (\partial_{1}, \bar{\phi}_{1}) ] \phi_{\text{a}} \phi_{\text{b}} \]

(b):
\[ \sigma_{2} \bar{\phi}_{2} \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{2}) (\partial_{1}, \bar{\phi}_{1}) \phi_{\text{a}} \phi_{\text{b}} \]
\[ = \frac{1}{r^{3}} [ -i \sigma_{2} \bar{\phi}_{1} (\partial_{1}, \bar{\phi}_{1}) (\partial_{2}, \bar{\phi}_{2}) + 2 (\partial_{1}, \bar{\phi}_{1}) (\partial_{1}, \bar{\phi}_{1}) ] \phi_{\text{a}} \phi_{\text{b}} \]

(c):
\[ (\sigma_{1} \bar{\phi}_{1}) (\sigma_{2} \bar{\phi}_{2}) \frac{1}{r^{3}} (\partial_{1}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \]
\[ = (\sigma_{1} \bar{\phi}_{1}) \left\{ \frac{3}{r^{5}} (\partial_{2}, \bar{\phi}_{2}) (\partial_{1}, \bar{\phi}_{1}) - \frac{1}{r^{3}} \sigma_{2} \bar{\phi}_{1} (\partial_{2}, \bar{\phi}_{2}) - \frac{1}{r^{3}} \sigma_{2} (\partial_{1}, \bar{\phi}_{1}) \right\} \]
\[ + \frac{1}{r^{3}} \sigma_{2} (\partial_{1}, \bar{\phi}_{2}) (\partial_{2}, \bar{\phi}_{2}) \phi_{\text{a}} \phi_{\text{b}} \]

Expanding the terms further, using properties of the Pauli-srin matrices, we
finally obtain the right hand side of (c) as

\[
\begin{align*}
&= \left\{-\frac{3}{\Gamma_0}(\hat{\sigma}_1 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{\tau}) + \frac{2}{\Gamma_3} \hat{\sigma}_1 \cdot \hat{\sigma}_2 - \frac{4}{\Gamma_3} \hat{\tau} \cdot \hat{p}_1 + \frac{2}{\Gamma_3}(\hat{\sigma}_2 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{p}_1)
\right. \\
&\quad + \frac{1}{\Gamma_3} \hat{\sigma}_2 \cdot \hat{\sigma}_1(\hat{\sigma}_2 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{p}_1) + \frac{4}{\Gamma_3} \hat{\tau} \cdot \hat{p}_2 - \frac{2}{\Gamma_3}(\hat{\sigma}_1 \cdot \hat{\tau})(\hat{\sigma}_1 \cdot \hat{p}_2)
\end{align*}
\]

\[
+ \frac{4}{\Gamma_3} \hat{\tau} \cdot (\hat{\tau} \cdot \hat{p}_2) \hat{p}_1 - \frac{2}{\Gamma_3}(\hat{\sigma}_1 \cdot \hat{\tau}) \hat{\tau} \cdot (\hat{\sigma}_1 \cdot \hat{p}_1) - \frac{2}{\Gamma_3}(\hat{\sigma}_2 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{p}_2)
\]

\[
+ \frac{1}{\Gamma_3} \hat{\tau} \cdot (\hat{\sigma}_1 \cdot \hat{\tau}) \hat{p}_1(\hat{\sigma}_2 \cdot \hat{p}_2) - \frac{2}{\Gamma_3}(\hat{\tau} \cdot \hat{p}_2) \hat{p}_1(\hat{\sigma}_2 \cdot \hat{p}_2) + \frac{2}{\Gamma_3}(\hat{\sigma}_2 \cdot \hat{p}_2) + \frac{1}{\Gamma_3}(\hat{\sigma}_1 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{p}_1)(\hat{\sigma}_2 \cdot \hat{p}_2)\phi_a \phi_b
\]

(I.6)

Substituting (a), (b), and (c) in (I.5) we have

\[
\psi_c \phi_0 \left[ \frac{1}{\Gamma_0}(\hat{x}_1 \cdot \hat{\tau})(\hat{x}_2 \cdot \hat{\tau}) \right] \psi_a \phi_b
\]

\[
= \phi_c^* \phi_a \left\{-\frac{1}{8m^2C^2} \left\{-\frac{1}{\Gamma_3} \hat{\sigma}_1 \cdot \hat{\sigma}_2 + \frac{3}{\Gamma_3}(\hat{\sigma}_1 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{\tau}) - \frac{2}{\Gamma_3}(\hat{\tau} \cdot \hat{p}_1 - \hat{\tau} \cdot \hat{p}_2)
\right.
\end{align*}
\]

\[
+ \frac{2}{\Gamma_3}(\hat{p}_2 \cdot \hat{\tau} \cdot \hat{p}_1) - \hat{\sigma}_1 \cdot (\hat{\tau} \cdot \hat{p}_2) + \frac{4}{\Gamma_3} \hat{\tau} \cdot (\hat{\tau} \cdot \hat{p}_2) \hat{p}_1 \right\} \phi_a \phi_b
\]

(I.7)

\[
(\text{I.4}) + (\text{I.7}) \Rightarrow \quad \\
\psi_c \phi_0 \left[ \frac{1}{\Gamma_0}(\hat{x}_1 \cdot \hat{\tau})(\hat{x}_2 \cdot \hat{\tau}) \right] \psi_a \phi_b
\]

\[
= -\frac{1}{2m^2C^2} \phi_c^* \phi_a \left\{ \frac{1}{\Gamma_0} \hat{p}_1 \cdot \hat{p}_2 - \frac{1}{\Gamma_3} \hat{\sigma}_1 \cdot \hat{\sigma}_2 - \frac{3}{\Gamma_3}(\hat{\sigma}_1 \cdot \hat{\tau})(\hat{\sigma}_2 \cdot \hat{\tau})
\right.
\]

\[
+ \frac{1}{\Gamma_3}(\hat{\tau} \cdot \hat{p}_1) - \hat{\sigma}_1 \cdot (\hat{\tau} \cdot \hat{p}_2) + \frac{1}{\Gamma_3} \hat{\tau} \cdot (\hat{\tau} \cdot \hat{p}_2) \hat{p}_1 \right\} \phi_a \phi_b
\]

(I.8)

Finally,

\[
\psi_c \phi_0 \left[ \frac{1}{\Gamma_0}(\hat{x}_1 \cdot \hat{\tau})(\hat{x}_2 \cdot \hat{\tau}) \right] \psi_a \phi_b
\]

\[
= \phi_c^* \phi_a(1/\Gamma_0) \phi_a \phi_b + \frac{1}{4m^2C^2} \phi_c^* \phi_a \hat{\sigma}_1 \cdot \hat{p}_1 \left[ \frac{1}{\Gamma_0}(\hat{x}_2 \cdot \hat{\tau}) \phi_a \phi_b \right]
\]

\[
+ \frac{1}{4m^2C^2} \phi_c^* \phi_a \hat{\sigma}_2 \cdot \hat{p}_2 \left[ \frac{1}{\Gamma_0}(\hat{x}_2 \cdot \hat{\tau}) \phi_a \phi_b \right]
\]

(I.9)
where all terms smaller than the order of $c^{-2}$ have been neglected. Here $I$ is a 16×16 unit matrix.

Expanding further, the right-hand side of (1.9) can be written as

$$\phi^*_c \phi^*_d (1/r) \phi_a \phi_b$$

$$+ \frac{1}{4m^2 c^2 \phi^*_c \phi^*_d [\frac{1}{r^3} (\hat{s}_1 \cdot \hat{r}) (\hat{s}_1 \cdot \hat{p}_1) + \frac{1}{r} p_1^2] \phi_a \phi_b}$$

$$+ \frac{1}{4m^2 c^2 \phi^*_c \phi^*_d [\frac{1}{r^3} (\hat{s}_2 \cdot \hat{r}) (\hat{s}_2 \cdot \hat{p}_2) + \frac{1}{r} p_2^2] \phi_a \phi_b}$$

The terms involving the operators $p_1^2$ and $p_2^2$ above are eventually canceled when we perform the $p_1^2$ and $p_2^2$ operations in the transformations $\phi_a \rightarrow \Phi_a$, $\phi_c \rightarrow \Phi_c$ and $\phi^*_b \rightarrow \Phi_b$, $\phi_d \rightarrow \Phi_d$ respectively in the first term above.

Again remembering that only terms up to the order $c^{-2}$ will be considered, other terms which come from $p^2$ operations on $\Phi^*_c$ and $\Phi^*_d$ are:

$$- \frac{1}{8m^2 c^2 \phi^*_c \phi^*_d [p_1^2 (\frac{1}{r}) \Phi_a \Phi_b + 2 \hat{p}_1 (\frac{1}{r}) \cdot \hat{p}_1 \Phi_a \Phi_b]}$$

$$= - \frac{1}{8m^2 c^2 \phi^*_c \phi^*_d [\hat{p}_1 (\frac{1}{r}) \Phi_a \Phi_b - \frac{2}{r} \hat{p}_1 \Phi_a \Phi_b]}$$

$$= - \frac{1}{8m^2 c^2 \phi^*_c \phi^*_d [\hat{p}_1 (\frac{1}{r}) \Phi_a \Phi_b - \frac{2}{r} \hat{p}_1 \Phi_a \Phi_b]}$$

and,

$$- \frac{1}{8m^2 c^2 \phi^*_c \phi^*_d [p_2^2 (\frac{1}{r}) \Phi_a \Phi_b + 2 \hat{p}_2 (\frac{1}{r}) \cdot \hat{p}_2 \Phi_a \Phi_b]}$$

$$= - \frac{1}{8m^2 c^2 \phi^*_c \phi^*_d [\hat{p}_2 (\frac{1}{r}) \Phi_a \Phi_b - \frac{2}{r} \hat{p}_2 \Phi_a \Phi_b]}$$

Therefore, collecting all the above terms together we finally have

$$\int \psi^* \psi \frac{e^2}{2 \hbar} \{ \alpha_1, \alpha_2 + (\hat{a}_1 \cdot \hat{r}) (\hat{a}_2 \cdot \hat{r}) \} + \frac{e^2}{\hbar} \psi_a \psi_b \ d\hat{r}_1 \ d\hat{r}_2$$

$$= \int \Phi^*_c \Phi^*_d \ U_{\text{eff}} \ \Phi_a \Phi_b \ d\hat{r}_1 \ d\hat{r}_2$$

(I.10)

where

$$U_{\text{eff}} = \frac{e^2}{\hbar} - \frac{\pi \hbar^2 \delta^3(\hat{r})}{m^2 c^2} + \frac{e^2}{4m^2 c^2 \hbar^3} [\delta_1 \cdot \delta_2 - 3 (\delta_1 \cdot \hat{r}) (\delta_2 \cdot \hat{r}) - \frac{8\pi}{3} \delta_1 \cdot \delta_2 \delta^3(\hat{r})]$$

$$- \frac{e^2}{4m^2 c^2 \hbar^3} [\delta_1 \cdot (\hat{r} \times \hat{p}_1) - \delta_2 \cdot (\hat{r} \times \hat{p}_2) + 2 \delta_2 \cdot (\hat{r} \times \hat{p}_1) - 2 \delta_1 \cdot (\hat{r} \times \hat{p}_2)]$$

$$- \frac{e^2}{2m^2 c^2 \hbar^3} [\frac{1}{r} (\hat{p}_1 \cdot \hat{p}_2) + \frac{1}{r^3} \cdot (\hat{r} \times \hat{p}_2) \hat{p}_1],$$

(I.11)
where the delta function term inside the first square bracket arises due to the following reason:

The integrand involving the spin-spin interactions contain high powers of $r^{-1}$ and therefore become singular at the origin (i.e., at points in space where $\vec{r}_1 = \vec{r}_2$). Therefore, while integrating over whole space the origin has to be excluded. The surface integral over a sphere of radius $r$ surrounding the origin ($r\to 0$) that takes care of this requirement has a finite value only at the origin and hence can be expressed as a volume integral over the whole space containing the delta function $\delta^3(\vec{r})$ such that this term can also be included with the rest in $U_{\text{eff}}$.

Again, the one-electron part of the Breit equation, when reduced to equivalent non-relativistic form yields the following Hamiltonians

$$U_1 = p_1^2/2m - p_1^4/8m^3c^2 - \frac{e}{4m^2c^2}(\vec{\sigma}_1 \cdot \vec{\sigma}_1 \times \vec{\sigma}_1) + \frac{e}{8m^2c^2} \nabla_1^2 A_0^{(1)} - \frac{Ze^2}{r_1}$$

$$= p_1^2/2m - p_1^4/8m^3c^2 - \frac{e}{4m^2c^2}(\vec{\sigma}_1 \cdot \vec{\sigma}_1 \times \vec{\sigma}_1) + \frac{4\pi e^2}{8m^2c^2} Z \delta^3(\vec{r}_1) - \frac{Ze^2}{r_1} \tag{I.12}$$

and,

$$U_2 = p_2^2/2m - p_2^4/8m^3c^2 - \frac{e}{4m^2c^2}(\vec{\sigma}_2 \cdot \vec{\sigma}_2 \times \vec{\sigma}_2) + \frac{e}{8m^2c^2} \nabla_2^2 A_0^{(2)} - \frac{Ze^2}{r_2}$$

$$= p_2^2/2m - p_2^4/8m^3c^2 - \frac{e}{4m^2c^2}(\vec{\sigma}_2 \cdot \vec{\sigma}_2 \times \vec{\sigma}_2) + \frac{4\pi e^2}{8m^2c^2} Z \delta^3(\vec{r}_2) - \frac{Ze^2}{r_2} \tag{I.13}$$

where,

$$\vec{\sigma}_1 = -\frac{Ze}{r_1^3} \vec{r}_1, \quad \vec{\sigma}_2 = -\frac{Ze}{r_2^3} \vec{r}_2, \quad A_0^{(1)} = -\frac{Ze}{r_1} \quad \text{and} \quad A_0^{(2)} = -\frac{Ze}{r_2}.$$

Combining (I.11), (I.12) and (I.13), the total effective non-relativistic reduced form of the Hamiltonian is obtained as
\[ H_{\text{rel}} = \frac{(p_1^2 + p_2^2)}{2m} - \frac{(p_1^4 + p_2^4)}{\delta m^3 c^2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} \]
\[ + \frac{e^2}{\delta m^2 c^2} \frac{\pi e^2}{2m c^2} \delta^3(\vec{r}) + \frac{4\pi e^2}{\delta m^2 c^2} Z[\delta^3(\vec{r}_2) + \delta^3(\vec{r}_2)] \]
\[ + \frac{e^2}{4m^2 c^2} \left[ \frac{Z}{r_1} \vec{\sigma}_{1} \times \vec{p}_1 + \frac{Z}{r_2} \vec{\sigma}_{2} \times \vec{p}_2 - \left( \frac{1}{r_3} \vec{\sigma}_1 \times \vec{p}_1 - \frac{1}{r_3} \vec{\sigma}_2 \times \vec{p}_2 \right) \right] \]
\[ - \frac{e^2}{4m^2 c^2} \left( \frac{2}{r_3} \vec{\sigma}_2 \times \vec{p}_1 - \frac{2}{r_3} \vec{\sigma}_1 \times \vec{p}_2 \right) \]
\[ + \frac{e^2}{4m^2 c^2} \left( \frac{\vec{\sigma}_1 \cdot \vec{\sigma}_2}{r^3} - \frac{3(\vec{\sigma}_1 \cdot \vec{r})(\vec{\sigma}_2 \cdot \vec{r})}{r^5} - \frac{8\pi}{3} \delta^3(\vec{r}) \right) \]
\[ - \frac{e^2}{2m^2 c^2} \left[ \frac{\vec{\sigma}_1 \cdot \vec{p}_2}{r} + \frac{\vec{r} \cdot (\vec{r} \cdot \vec{p}_1) \vec{p}_2}{r^3} \right] \]
\[ = \frac{(p_1^2 + p_2^2)}{2m} - \frac{(p_1^4 + p_2^4)}{\delta m^3 c^2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{\delta m^2 c^2} \left[ \frac{\vec{\sigma}_1 \cdot \vec{p}_2}{r} + \frac{\vec{r} \cdot (\vec{r} \cdot \vec{p}_1) \vec{p}_2}{r^3} \right] \]
\[ + \frac{e^2}{4m^2 c^2} \left[ \vec{\sigma}_1 \cdot \vec{p}_2 - \frac{3(\vec{\sigma}_1 \cdot \vec{r})(\vec{\sigma}_2 \cdot \vec{r})}{r^5} - \frac{8\pi}{3} \delta^3(\vec{r}) \right] \]
\[ + \frac{e}{4m^2 c^2} \left[ \vec{\sigma}_1 \cdot (-\vec{\sigma}_1 \times \vec{p}_1 + \frac{2e}{r_3} \vec{r} \times \vec{p}_2) + \vec{\sigma}_2 \cdot (-\vec{\sigma}_2 \times \vec{p}_2 - \frac{2e}{r_3} \vec{r} \times \vec{p}_1) \right] \]
\[ + \frac{4\pi e^2}{\delta m^2 c^2} \left[ Z\delta^3(\vec{r}_2) + Z\delta^3(\vec{r}_2) - 2\delta^3(\vec{r}) \right] \]

where \( \vec{\sigma}_1 \) and \( \vec{\sigma}_2 \) are the effective electric fields at the location of the electron-1 and electron-2 respectively.

Thus finally we can write the total Hamiltonian as:

\[ H = H_0 + \sum_{i=1}^{\delta} H_i \]

where \( H_i \ (i=1 \text{ to } \delta) \) are the six well known Breit-Pauli operators given in Chapter-2.
Appendix II.

General Theory for Calculation of Two-Electron Matrix Elements

In this appendix the general formalism developed by Drake\textsuperscript{31} for reduction of two-electron matrix elements involving Hylleraas co-ordinates to finite sums of radial integrals is discussed in brief.

To use Hylleraas co-ordinates \( r_1, r_2, r = |\vec{r}_1 - \vec{r}_2| \) to construct the variational trial functions, one requires six independent variables \( r_1, r_2, r, \theta_1, \phi_1 \) and \( \chi \), to specify the configuration of the two-electrons system in space. Here \( \theta_1, \phi_1 \) and \( \chi \) are the three independent angular variables which determine the orientation in space of the triangle formed by \( \vec{r}_1, \vec{r}_2 \) and \( \vec{r} \).

II.A Calculation of General Matrix Elements

In solving the two-electron problem, one needs to calculate integrals of the general form

\[
I(T^Q_{k_1, k_2, k}) = I = \int d\vec{r}_1 d\vec{r}_2 \ R'(\mathcal{J}^M_{l_1, l_2, L})^* T^Q_{k_1, k_2, k} R^M_{l_1, l_2, L} \tag{II.1}
\]

where

\[
\mathcal{J}^M_{l_1, l_2, L} = \sum_{m_1, m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle Y^m_{l_1}(\hat{r}_1) Y^m_{l_2}(\hat{r}_2) \tag{II.2}
\]

and

\[
T^Q_{k_1, k_2, k} = \sum_{q_1, q_2} \langle k_1 k_2 q_1 q_2 | kQ \rangle Y^{q_1}_{k_1}(\hat{r}_1) Y^{q_2}_{k_2}(\hat{r}_2) \tag{II.3}
\]

Here \( \langle l_1 l_2 m_1 m_2 | LM \rangle \) and \( \langle k_1 k_2 q_1 q_2 | kQ \rangle \) are Clebsch-Gordan coefficients. The volume
element \( d\vec{r}_1 d\vec{r}_2 \) is given by

\[
d\vec{r}_1 d\vec{r}_2 = r_1^2 dr_1 \sin \theta_1 d\theta_1 d\phi_1 r_2^2 dr_2 \sin \theta_2 d\theta_2 d\phi_2.
\]

Making repeated use of the spherical harmonic addition formula

\[
Y_{l_1}^{m_1}(\hat{r}_1)Y_{l_2}^{m_2}(\hat{r}_1) = \sum_{l_m} \left[ \frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} Y_l^m(\hat{r}_1)^* \tag{II.5}
\]

where \( Y_l^m(\hat{r}_1)^* = (-1)^m Y_l^{-m}(\hat{r}_1) \) and \( \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \) is a 3j-symbol which is given by

\[
\begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} = (-1)^{l_1-l_2-m} (2l+1)^{-\frac{1}{2}} \langle l_1 l_2 m_1 m_2 | l, -m \rangle,
\]

to combine the three spherical harmonics corresponding to \( \hat{r}_1 \) into a series of a single spherical harmonics of order \( \Lambda \), say, and the three spherical harmonics corresponding to \( \hat{r}_2 \) into another series of single spherical harmonics of order \( \Lambda' \), say, and also remembering that it is possible to transform \( Y_{\Lambda'}^{n'}(\hat{r}_2) \) into the independent coordinates with the help of proper rotation matrices such that it can be expressed as

\[
Y_{\Lambda'}^n(\theta_2, \phi_2) = \sum_i Y_{\Lambda'}^i(\theta_{12}, \phi_{12}) (S_{\Lambda', \Lambda}^{1, i} (\phi_1, \theta_1, \chi))^*, \tag{II.6}
\]

we can finally carry out the angular integrations over \( \theta_1, \phi_1 \) and \( \chi \) to obtain

\[
\int_0^{2\pi} \int_0^\pi \int_0^\pi Y_{\Lambda}^{m}(\theta_1, \phi_1)Y_{\Lambda'}^{n'}(\theta_2, \phi_2) \sin \theta_1 d\theta_1 d\phi_1 d\chi
\]

\[
= (-1)^m 2\pi \delta_{-m, m'} \delta_{\Lambda \Lambda'} P_{\Lambda}(\cos \theta_{12}) \tag{II.7}
\]
In (II.7) \( P_\Lambda(\cos \theta_{12}) \) is a Legendre Polynomial. \( \theta_{12} \) is the angle between \( \hat{r}_1 \) and \( \hat{r}_2 \).

The original integral (II.1) can now be expressed as

\[
I = \sum_{m_1', m_2', \mu_1, \mu_2} \sum_{m_1, m_2} \sum_{\lambda_1, m} \sum_{\lambda_2, n} \int_{r_1 dr_1} \int_{r_2 dr_2} r_1^{\lambda_1 + \lambda_2} r_2^{\lambda_1 + \lambda_2} r dr R R' P_\Lambda(\cos \theta_{12}) \times \\
\frac{1}{(2\pi)^2 (-1)^{m_1' - l_1' + M_1' + k_1 - k_2 + Q + l_2 + M}} (l_1', l_2', \Lambda_1', k_1, l_1, l_1', k_2, l_2, l_2', \Lambda_2') \frac{1}{2} \times \\
\begin{pmatrix} l_1' & l_2' & L_1' \\ m_1' & m_2' & M_1' \end{pmatrix} \begin{pmatrix} k_1 & k_2 & K \\ \mu_1 & \mu_2 & -Q \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} k_1 & l_1 & \lambda_1 \\ \mu_1 & m_1 & m \end{pmatrix} \begin{pmatrix} l_1' & \lambda_1 & \Lambda_1 \\ m_1' & m & m' \end{pmatrix} \times \\
\begin{pmatrix} k_2 & l_2 & \lambda_2 \\ \mu_2 & m_2 & n \end{pmatrix} \begin{pmatrix} l_2' & \lambda_2 & \Lambda_2 \\ m_2' & n & n' \end{pmatrix} \begin{pmatrix} k_1 & l_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & \lambda_1 & \Lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k_2 & l_2 & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \times \\
\begin{pmatrix} l_2' & \lambda_2 & \Lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \frac{2\pi}{\delta_{m_1', n} \delta_{\Lambda_1'}} \tag{II.8}
\]

\[
= \sum_{m_1', m_2', \mu_1, \mu_2} \sum_{m_1, m_2} \sum_{\lambda_1, m} \sum_{\lambda_2, n} \int_{r_1 dr_1} \int_{r_2 dr_2} r_1^{\lambda_1 + \lambda_2} r_2^{\lambda_1 + \lambda_2} r dr R R' P_\Lambda(\cos \theta_{12}) \times \\
\times (8\pi)^{-1} (-1)^{m_1' - l_1' + M_1' + k_1 - k_2 + Q + l_2 + M} (l_1', l_2', \Lambda_1', k_1, l_1, l_1', k_2, l_2, l_2') \frac{1}{2} \times \\
\begin{pmatrix} l_1' & l_2' & L_1' \\ m_1' & m_2' & M_1' \end{pmatrix} \begin{pmatrix} k_1 & k_2 & K \\ \mu_1 & \mu_2 & -Q \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} k_1 & l_1 & \lambda_1 \\ \mu_1 & m_1 & m \end{pmatrix} \begin{pmatrix} l_1' & \lambda_1 & \Lambda_1 \\ m_1' & m & m' \end{pmatrix} \times \\
\begin{pmatrix} k_2 & l_2 & \lambda_2 \\ \mu_2 & m_2 & n \end{pmatrix} \begin{pmatrix} l_2' & \lambda_2 & \Lambda_2 \\ m_2' & n & n' \end{pmatrix} \begin{pmatrix} k_1 & l_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1' & \lambda_1 & \Lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k_2 & l_2 & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \times \\
\begin{pmatrix} l_2' & \lambda_2 & \Lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \tag{II.9}
\]

where the \( \delta j \) symbols appear as a result of applying Eq.(II.5) repeatedly. The sum of the products of the seven \( \delta j \) symbols in (II.9) with non-zero elements in the bottom rows can be reduced further to express it as the product of a \( \delta j \), a \( \delta j \) and a \( \delta j \) symbol\(^31,32\) as in the following equation.
\[ \sum_{m_1', m_2'} \sum_{\mu_1, \mu_2} \sum_{m_1, m_2} \sum_{m, n, m'} \left\{ (-1)^{m' + l_1' + l_2' + L'} + k_1 - k_2 + Q + l_1 - l_2 + M_x \right\} \]

\[ \times \left( \begin{array}{ccc} l_1' & l_2' & L' \\ m_1' & m_2' & -M' \end{array} \right) \left( \begin{array}{ccc} k_1 & k_2 & K \\ \mu_1 & \mu_2 & -\mu \end{array} \right) \left( \begin{array}{ccc} l_1 & l_2 & L \\ m_1 & m_2 & -m \end{array} \right) \left( \begin{array}{ccc} k_1 & l_1 & \lambda_1 \\ \mu_1 & m_1 & m' \end{array} \right) \]

\[= (-1)^{l_1' + l_2' + L' + \Lambda} (-1)^{l_1' + L'} \left( \begin{array}{ccc} L' & K & L \\ -M' & Q & M \end{array} \right) \left( \begin{array}{ccc} l_1' & l_2' & L' \\ \lambda_1 & \lambda_2 \end{array} \right) \left( \begin{array}{ccc} l_1 & l_2 & L \\ \lambda_1 & \lambda_2 & L \end{array} \right). \]  

(II.10)

Defining

\[ I_{\Lambda}(R', R) = \int_{r_1}^{r_2} \int_{r_2}^{r_1} r dr R R P(\cos \theta_{12}), \]

(II.11)

\[ X_{\lambda_1, \lambda_2, \Lambda} = (-1)^{l_1' + l_2' + L' + \Lambda} \times (8\pi)^{-1}(\lambda_1, \lambda_2, \Lambda)(L', K, L, k_1, l_1, l_1', k_2, l_2, l_2') \frac{1}{2} \times \]

\[ \times \left( \begin{array}{ccc} l_1 & k_1 & \lambda_1 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_1' & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_2 & k_2 & \lambda_2 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_2 & \lambda_2 & \Lambda \end{array} \right), \]

we can finally write

\[ I = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(R', R). \]  

(II.12)

The angular coefficients \( C_{\Lambda} \) are given by

\[ C_{\Lambda} = \sum_{\lambda_1', \lambda_2'} C_{\lambda_1, \lambda_2} \delta_{\lambda_1, \lambda_1'} \delta_{\lambda_2, \lambda_2'}. \]  

(II.13)
where
\[ C_{\lambda_1, \lambda_2, \Lambda} = (-1)^{L' - M'} \begin{pmatrix} L' & K & L \\ -M' & Q & M \end{pmatrix} \frac{H}{X_{\lambda_1, \lambda_2, \Lambda} D_{\lambda_1, \lambda_2, \Lambda}}. \]  

(II.14)

Thus the matrix elements of a wide variety of operators may be conveniently reduced to sums of radial integrals (II.11). Evaluating each and every integral from first principles, however, would be a laborious task. Fortunately, recurrence relations for these integrals exist so that once the fundamental integrals corresponding to \( \Lambda = 0 \) and \( \Lambda = 1 \) are known, the rest can be evaluated quite easily.

II.B Recurrence Relations for Radial Integrals

Let us consider a general radial integral of the form,

\[ I_l(\mathcal{R}) = \int d\tau_r \mathcal{R} P_l(\cos \theta), \]  

(II.15)

where \( \mathcal{R}(r_1, r_2, r) \) is a function of the radial coordinates only, and

\[ d\tau_r = r_1 dr_1 r_2 dr_2 \quad d\tau_r. \]  

(II.16)

Now,

\[ P_l(x) = \frac{1}{2l+1} \left[ P_{l+1}(x) - P_{l-1}(x) \right], \]  

(II.17)

where

\[ P_l'(x) = \frac{d}{dx}[P_l(x)]. \]

Taking \( x = \cos \theta \) and using (II.17), one can rewrite (II.15) as

\[ I_l(\mathcal{R}) = \frac{1}{2l+1} \int d\tau_r \mathcal{R} \left( -\frac{r_1 r_2}{r} \frac{d}{dr} \left[ P_{l+1}(\cos \theta) - P_{l-1}(\cos \theta) \right] \right), \]  

(II.18)

since

\[ \cos \theta = \frac{r_1^2 + r_2^2 - r^2}{2r_1 r_2}, \quad \text{and} \quad \frac{d}{d\cos \theta} = -\frac{r_1 r_2}{r} \frac{d}{dr}. \]
Writing \( \mathcal{R} = f(r_1, r_2) g(r) \), the \( r \)-part of the above integral gives

\[
\int_{r_1 - r_2}^{r_1 + r_2} r \, dr \, g(r)(-\frac{r_1 r_2}{r}) \frac{d}{dt} [P_{l+1}(\cos \theta) - P_{l-1}(\cos \theta)]
\]

\[
= g(r)(-r_1 r_2)[P_{l+1}(\cos \theta) - P_{l-1}(\cos \theta)]\bigg|_{r_1 - r_2}^{r_1 + r_2}
\]

\[
- \int_{r_1 - r_2}^{r_1 + r_2} dr \, (-r_1 r_2) \frac{d}{dr} g(r) \left[ P_{l+1}(\cos \theta) - P_{l-1}(\cos \theta) \right].
\]

The first term on the right hand side of (II.19) vanishes since \( \theta = 0 \) and \( \pi \) when \( r \) is equal to \( |r_1 - r_2| \) and \( (r_1 + r_2) \) respectively, and \( P_{l+1}(1) = 1 \) and \( P_{l-1}(-1) = (-1)^l \).

Therefore, (II.18) and (II.9) give

\[
I_{l+1}^{(r_1 r_2)}(\mathcal{R}) = (2l+1)I_{l+1}^{(r_1 r_2)}(\mathcal{R}) + I_{l-1}^{(r_1 r_2)}(\mathcal{R})
\]

where \( \mathcal{R}' = \frac{d}{dr} [f(r_1, r_2) g(r)] \).

Equation (II.20) generates a wide variety of integral recurrence relations depending on the choice made for the function \( g(r) \). If we consider the case \( g(r) = r^{c+g} \) and \( \mathcal{R} = r_1^{a-l} r_2^{b-l} r^{c+g} \exp(-ar_1 - br_2) \), then (II.20) gives the particular recurrence relation

\[
I_{l+1}^{(r_1 r_2)}(\mathcal{R}) = \frac{2l+1}{c+2} I_{l+1}^{(r_1 r_2)}(\mathcal{R}) + I_{l-1}^{(r_1 r_2)}(\mathcal{R}).
\]

Except for the case \( c = -2 \), relation (II.21) is valid whenever the integrals exist. Using it, one can evaluate all the integrals provided the integrals \( I_0 \) and \( I_1 \) are known. Again, \( I_1 \) itself can be calculated in terms of \( I_0 \), since we also have the
relation

\[ I_j(r_1^a r_2^b r^c) = \frac{j}{2} [I_0(r_1^{a+1} r_2^{b-1} r^c) + I_0(r_1^{a-1} r_2^{b+1} r^c) - I_0(r_1^{a-1} r_2^{b-1} r^{c+2})] \]  \( (II.22) \]

which follows directly from (II.15) when the substitution

\[ P_j(cos \theta) = \cos \theta = \frac{r_1^2 + r_2^2 - r^2}{2 r_1 r_2} \]

is made in it.

The analytic calculations of the fundamental integrals \( I_0 \) are shown in the following. From definition, we have

\[ I_0(a,b,c) = \int_0^{\infty} r_1 \int_0^{\infty} r_2 \int_{r_2}^{r_1+r_2} r dr r_1^a r_2^b r^c \exp(-\alpha r_1 - \beta r_2) \]

\[ + \int_0^{\infty} r_2 dr \int_0^{\infty} r_1 dr \int_{r_1}^{r_1+r_2} r dr r_1^a r_2^b r^c \exp(-\alpha r_1 - \beta r_2) \]

\( (II.23) \)

Now,

\[ \int_{r_2}^{r_1+r_2} r^{c+1} dr = \frac{2}{c+2} \sum_{i=0}^{w} \left( \frac{c+2}{2i+1} \right) \frac{r_1^{c+1} - 2i \cdot r_2^{c+1}}{r_1^{c+1}} \]

\( (II.24a) \)

and

\[ \int_{r_1}^{r_1+r_2} r^{c+1} dr = \frac{2}{c+2} \sum_{i=0}^{w} \left( \frac{c+2}{2i+1} \right) \frac{r_2^{c+1} - 2i \cdot r_2^{c+1}}{r_2^{c+1}} \]

\( (II.24b) \)

where \( w = (c+1)/2 \).

Inserting (II.24a) and (II.24b) in (II.23), and also remembering that

\[ \int_{x}^{\infty} y^n e^{-\alpha y} dy = \frac{n!}{\alpha^{n+1}} e^{-\alpha x} \sum_{j=0}^{n} \frac{(\alpha x)^j}{j!} \]

\( (II.25) \)
we finally get the result

\[
I_0(a, b, c) = \frac{\beta}{c+2} \left[ \sum_{i=0}^{u} \binom{c+2}{2i+j} \left\{ \frac{q!}{\beta^{q+i}(\alpha+\beta)^{p+j}} \sum_{j=0}^{q} \binom{p+j}{j} \left( \frac{\beta}{\alpha+\beta} \right)^j \right. \\
\left. + \frac{q'!}{\alpha^{q'+i}(\alpha+\beta)^{p'+j}} \sum_{j=0}^{q'} \binom{p'+j}{j} \left( \frac{\alpha}{\alpha+\beta} \right)^j \right\} \right]
\]

(II.26)

where

\[
q = (b + c + 2 - 2i) \\
p = (a + 2 + 2i) \\
p' = (b + 2 + 2i) \\
q' = (a + c + 2 - 2i).
\]

II.C Matrix Elements of Scalar Operators

In the two-electron problem one encounters many scalar operators for which matrix elements have to be calculated to find the variational energy. Therefore it becomes convenient for later use if we treat the above general theory for the special class of the scalar operators of the form \(T_{k,k',0}^0(\vec{r}_1,\vec{r}_2)\) in more detail. In this case the \(9j\) symbol in (II.10) reduces to a \(6j\) symbol and the angular coefficients \(C_{\lambda_1,\lambda_2,\lambda}^\lambda\) can be expressed as

\[
C_{\lambda_1,\lambda_2,\lambda}^\lambda (T_{k,k',0}^0) = (-1)^{l_1'+l_2'+L'} (8\pi)^{-1}(\lambda_1,\lambda_2,\lambda)(L,0,L,k,l_1,l_1',k,l_2,l_2')^{1/2} \times
\]

\[
\times \left( \begin{array}{ccc}
  l_1 & k & \lambda_1 \\
  0 & 0 & 0
\end{array} \right) \left( \begin{array}{ccc}
  l_1' & \lambda_1 & \Lambda_1 \\
  0 & 0 & 0
\end{array} \right) \left( \begin{array}{ccc}
  l_2 & k & \lambda_2 \\
  0 & 0 & 0
\end{array} \right) \left( \begin{array}{ccc}
  l_2' & \lambda_2 & \Lambda
\end{array} \right)_\lambda
\]
\[
\times (-1)^{L-M} \begin{bmatrix} L & 0 & L \\ -M & 0 & M \end{bmatrix} \begin{bmatrix} L & l'_{1} & l'_{2} \\ \lambda_{1} & \lambda_{1}' & \lambda_{2}' \end{bmatrix} \begin{bmatrix} l_{1} & l_{2} & L \\ k & k & 0 \end{bmatrix} \begin{bmatrix} \lambda_{1} & \lambda_{2} & L \end{bmatrix} \delta_{L'L} \delta_{M'M'}
\]
\[
= (-1)^{\Lambda} \times (8\pi)^{-1} (\lambda_{1}, \lambda_{2}, \Lambda) (k, l_{1}, l_{1}', l_{2}, l_{2}')^{\frac{1}{2}} \times
\]
\[
\times \begin{bmatrix} l_{1} & k & l_{1}' \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{1} & \lambda_{1} & l_{1}' \Lambda \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{2} & k & l_{2}' \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{2} & \lambda_{2} & l_{2}' \Lambda \\ 0 & 0 & 0 \end{bmatrix} \times
\]
\[
\times \begin{bmatrix} L & \lambda_{1} & \lambda_{2} \\ \Lambda & l_{1}' & l_{1}' \end{bmatrix} \begin{bmatrix} L & \lambda_{1} & \lambda_{2} \\ k & l_{2}' & l_{2}' \end{bmatrix} \delta_{LL'} \delta_{MM'}.
\]
(II.27)

The final result for the integral \( I(T_{k,k,0}^{\theta}) \) can be written as

\[
I(T_{k,k,0}^{\theta}) = \frac{1}{4\pi} \sum_{\Lambda} C_{\Lambda}(\theta) I_{\Lambda}[R'R P_{k}(\cos \theta)]
\]
(II.28)

where

\[
C_{\Lambda}(\theta) = (-1)^{L+\Lambda} (2\Lambda+1) (l_{1}, l_{1}', l_{2}, l_{2}')^{\frac{1}{2}} \begin{bmatrix} l_{1}' & l_{1} & \Lambda \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{2}' & l_{2} & \Lambda \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} L & l_{1} & l_{2} \\ \Lambda & l_{1}' & l_{2}' \end{bmatrix}.
\]
(II.29)

An Example of application of the above technique: Angular coefficients in the matrix element of the operator \( \mathbf{V}_{1}^{2} \).

In terms of \( r_{1}, r_{2}, r, \theta_{1}, \phi_{1} \) the \( \mathbf{V}_{1}^{2} \) operator can be expressed as

\[
\mathbf{V}_{1}^{2} = \frac{1}{r_{1}^{2}} \frac{\partial}{\partial r_{1}} \left( r_{1}^{2} \frac{\partial}{\partial r_{1}} \right) + \frac{1}{r^{2}} \frac{\partial}{\partial r} \left( r^{2} \frac{\partial}{\partial r} \right) + \frac{2}{r} (r_{1} - r_{2} \cos \theta) \frac{\partial}{\partial \theta_{1}} \left( \frac{\partial}{\partial \theta_{1}} \right) - \frac{2}{r} \mathbf{V}_{y}^{2} \frac{\partial}{\partial \theta_{1}}.
\]
(II.30)

Here, the operator \((\ell_{1} \mathbf{y})^{2}\), like the operator \( \mathbf{V}_{y} \), operates only on the spherical harmonics corresponding to the electron \(-1\).

Except for the last term on the right hand side of (II.30), the angular integrations to find out the coefficients \( C_{\lambda_{1}' \lambda_{2}' \Lambda} \) can be performed directly by the method given in
section II.A. As for the angular part in the last term, we note that it is a scalar operator of the form $(\hat{\mathbf{V}}_{1\cdot 2})^0_{110}$. From definition we have

$$C_{\lambda_1, \lambda_2, \Lambda}(T^0_{110}) = (-1)^\Lambda \times (8\pi)^{-1}(\lambda_1, \lambda_2, \Lambda)(l_1, l_1', l_2, l_2') \times$$

$$\times \begin{pmatrix} l_1 & l_1 & l_1 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \end{pmatrix} \begin{pmatrix} l_2 & l_2 & \Lambda \end{pmatrix} \times$$

$$\times \begin{pmatrix} L & \lambda_1 & \lambda_2 \\ L & \lambda_1 & \lambda_2 \\ l_2 & l_2 & l_1^2 \end{pmatrix} \begin{pmatrix} l_1 & \lambda_1 & \lambda_2 \\ l_1 & \lambda_1 & \lambda_2 \\ l_1 & l_2 & l_1 \end{pmatrix} \delta_{LL'} \delta_{\Lambda \Lambda'} .$$

(II.31)

The right hand side of (II.31) is non-zero only for $\lambda_i = \lambda_i^\mp \Lambda$ and $l_i^\mp l_i$.

Also,

$$\hat{r}_1 \cdot \hat{r}_2 = (-4\pi/\sqrt{3}) T^0_{110}(\hat{r}_1, \hat{r}_2).$$

(II.32)

therefore,

$$C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1, \hat{r}_2) = (-4\pi/\sqrt{3}) C_{\lambda_1, \lambda_2, \Lambda}(T^0_{110})$$

(II.33)

Further, the coefficients $C_{\lambda_1, \lambda_2, \Lambda}(\hat{\mathbf{V}}_{1\cdot 2})$ are related to $C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1, \hat{r}_2)$ by

$$C_{\lambda_1, \lambda_2, \Lambda}(\hat{\mathbf{V}}_{1\cdot 2}) = b_{\lambda_1} C_{\lambda_1, \lambda_2, \Lambda}(\hat{r}_1, \hat{r}_2)$$

(II.34)

where

$$b_{\lambda_1} = \begin{cases} -l_1 & \text{if } \lambda_1 = l_1^\mp \Lambda \\ l_1^\mp l_1 & \text{if } \lambda_1 = l_1^\mp \Lambda . \end{cases}$$

(II.35)

Therefore,

$$C_{\lambda_1, \lambda_2, \Lambda}(\hat{\mathbf{V}}_{1\cdot 2}) = \hat{r}_2 \frac{r_1}{r_1^2} b_{\lambda_1} (-4\pi/\sqrt{3}) C_{\lambda_1, \lambda_2, \Lambda}(T^0_{110})$$

(II.36)

where $(-4\pi/\sqrt{3}) C_{\lambda_1, \lambda_2, \Lambda}(T^0_{110})$ is obtained from (II.31).
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