# Calculations of lithium in magnetic fields with a modified freezing full-core method

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A modified freezing full-core method is introduced and applied to calculations of lithium in strong magnetic fields up to $10^{10}$ G. The accuracy of results is higher than that from unrestricted Hartree-Fock calculations. In the absence of magnetic fields, our results agree with the most accurate calculations to within 0.02%. We also discussed the effect of strong magnetic fields on core electrons.

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## I. INTRODUCTION

Theoretical studies of atoms and ions in strong magnetic fields attract great interest, because of the discovery of magnetic fields comparable in strength to the Coulomb potential of the atomic nucleus on the surfaces of neutron stars and white dwarfs [1], and the observations of excitons with small effective masses and large dielectric constants in semiconductors [2]. The detailed work on the spectrum of hydrogen in strong magnetic fields that was done by Rösner *et al.* [3] has been successfully applied to study spectra from many magnetic white dwarf stars [4]. However, the spectra from these stars with very large magnetic fields cannot be completely accounted for with hydrogen atoms; therefore, detailed studies of heavier atoms in strong magnetic fields are necessary. Our knowledge of energy levels and transition strengths of low-lying states of heavier atoms and ions in strong magnetic fields is much more limited and less accurate than for hydrogen. Because of the combination of electronic correlation and the magnetic fields, theoretical studies of multielectronic atoms and ions in strong magnetic fields have a very high level of complexity. Up to now, theoretical studies on these systems have concentrated on twoelectron atoms and ions [5–19]. For lithium, a quartet system has been established by studying optical spectra from beam-foil measurements [20], but calculations of lithium in strong magnetic fields are very scarce. Within a flexible implementation of the spin-unrestricted Hartree-Fock (UHF) formula, ground-state and low-lying excited-state properties have been presented for first-row atoms He, Li, and C, and the ion $H^-$ by Jones *et al.* [14], but the accuracy of their results is not very high, because the correlation between electrons was not fully considered.

When magnetic fields are as strong as $10^{10}$ G, they can be compared to the atomic Coulomb potential for ground and low-lying excited states. It is clear that the magnetic fields cannot be treated as negligible in comparison to the Coulomb fields even near the nucleus. Therefore, the multichannel quantum defect theory (MQDT) cannot be used to solve the problem. With the configuration interaction (CI) method, a very large basis set has to be used in order to obtain high accuracy of results. This necessitated a higher level of complexity than that of CI method used for theoretical studies of two-electron atomic systems. Up to now, results on lithium in strong magnetic fields obtained with a CI method have not been reported to our knowledge.

In this paper, a modified freezing full-core method that can be applied to systems with a $1s^2$ core is presented, and applied to compute the energies of the ground state and low-lying excited states of lithium in strong magnetic fields. Highly accurate results were obtained with a small basis set and simple calculations.

## II. THEORY AND METHOD

The Hamiltonian for a three-electron atomic system in combined Coulomb and uniform magnetic fields is

$$\hat{H}=\sum_{i=1}^{3}\left(-\frac{1}{2}\frac{\partial^2}{\partial r_i^2}-\frac{1}{r_i}\frac{\partial}{\partial r_i}+\frac{\hat{L}_i^2}{2r_i^2}-\frac{Z_e}{r_i}+\tfrac{1}{2}\beta^2 r_i^2\sin^2\theta_i\right)+\beta(M_L+2M_S)+V(1,2,3). \tag{1}$$

When the magnetic fields strength $\vec{B}$ is uniform and oriented along the $Z$ axis, it can be represented by $\beta$,

$$\beta=\frac{B\ (\mathrm{G})}{4.701\,13\times10^9\ \mathrm{G}}. \tag{2}$$

$Z_e$ is the atomic charge and $M_L$ and $M_S$ represent the components along the $Z$ direction of the total orbital and spin angular momenta $L$ and $S$, respectively. $V(1,2,3)$ is the electron-electron exclusionary potential

$$V(1,2,3)=\frac{1}{r_{12}}+\frac{1}{r_{23}}+\frac{1}{r_{13}}, \tag{3}$$

$$\frac{1}{r_{ij}}=\frac{1}{|\vec{r_i}-\vec{r_j}|}=\sum_{\lambda=0}^{\infty}\frac{4\pi}{2\lambda+1}\frac{r_<^\lambda}{r_>^{\lambda+1}}\sum_{q=-\lambda}^{\lambda}Y_{\lambda q}^*(\Omega_i)Y_{\lambda q}(\Omega_j), \tag{4}$$

$$r_>=\max(r_i,r_j),\ r_<=\min(r_i,r_j), \tag{5}$$

 

TABLE I. The variational exponents of $1s^2\,{}^1S$ core wave functions for each strength of magnetic field $\beta$.

| $\beta$ | $\mu_1$ | $\nu_1$ | $\mu_2$ | $\nu_2$ | $\mu_3$ | $\nu_3$ |
|---|---|---|---|---|---|---|
| 0.0000 | 6.586 247 | 3.406 921 | 5.712 888 | 4.279 717 | 6.242 560 | 5.760 577 |
| 0.0009 | 5.621 526 | 4.098 943 | 5.697 294 | 5.126 798 | 6.419 028 | 6.426 276 |
| 0.0045 | 5.617 683 | 4.100 362 | 5.689 635 | 5.138 457 | 6.419 267 | 6.425 832 |
| 0.0090 | 5.608 776 | 4.118 347 | 5.693 947 | 5.144 898 | 6.414 489 | 6.419 957 |
| 0.0270 | 5.548 192 | 4.114 642 | 5.090 123 | 5.552 433 | 6.419 934 | 6.423 496 |
| 0.0630 | 5.568 836 | 4.115 254 | 5.693 504 | 5.142 759 | 6.408 327 | 6.415 178 |
| 0.0900 | 5.513 763 | 4.132 026 | 5.082 765 | 5.547 887 | 6.406 058 | 6.408 232 |
| 0.2700 | 5.635 528 | 4.246 676 | 5.731 000 | 5.169 057 | 6.378 321 | 6.372 187 |
| 0.4500 | 5.855 404 | 4.455 317 | 5.774 624 | 5.240 504 | 5.953 541 | 5.856 187 |
| 0.6300 | 6.034 958 | 4.689 980 | 5.851 017 | 5.335 711 | 5.72 1078 | 3.631 067 |
| 0.9000 | 6.343 053 | 5.030 729 | 5.954 010 | 5.51 1897 | 5.471 858 | 3.382 403 |
| 1.8000 | 7.535 653 | 4.366 918 | 6.047 630 | 6.363 962 | 5.539 300 | 3.806 184 |
| 2.7000 | 8.163 557 | 4.892 979 | 6.807 715 | 6.918 832 | 5.976 501 | 4.371 965 |

where $i,j=1,3$ and $i<j$, and $Y$ are spherical harmonics.

In our calculations, the trial wave function was expanded in the form

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3)=\sum_{i=1}^{N_1} C_i\phi_i, \tag{6}$$

$$\phi_i=\hat{A}[\psi_{12}(\vec{r}_1,\vec{r}_2)r_3^{f_i}\exp(-\tau_i r_3)Y_{l_{3i}m_{3i}}(\Omega_3)\chi(3)], \tag{7}$$

where $\hat{A}$ is the antisymmetrization operator, the nonlinear parameters $\tau_i$ were optimized for each strength $\beta$ of the magnetic fields in our calculations, $\chi(3)$ is the spin wave function of the third electron, and $\psi_{12}(\vec{r}_1,\vec{r}_2)$ is the $1s^21s^1S$ core wave function, obtained by solving the Schrödinger equation for the ${}^1S$ state of $Li^+$ in magnetic fields. The core wave function is given by

$$\psi_{12}(\vec{r}_1,\vec{r}_2)=\sum_{n=1}^{N_2} d_n[r_1^{a_n}r_2^{b_n}\exp(-\eta_n r_1-\sigma_n r_2)\times\Lambda^{L_n0}_{l_{1n}l_{2n}}(\Omega_1,\Omega_2)(\vec{r}_1\Leftrightarrow\vec{r}_2)]\chi(1,2), \tag{8}$$

where the second term is obtained from the first term by interchanging $\vec{r}_1$ and $\vec{r}_2$, and $\Lambda$ are superspherical harmonics,

$$\Lambda^{LM}_{l_1l_2}(\Omega_1,\Omega_2)=\sum_{m_1m_2}\langle l_1m_1l_2m_2|LM\rangle Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2). \tag{9}$$

$\chi(1,2)$ is the spin wave function of the first and second electrons, and $\eta_n$ and $\sigma_n$ are arbitrary nonlinear parameters. In Eq. (6) and Eq. (8), the linear expansion coefficients $C_i$ and $d_n$ can be obtained from solution of a finite-dimensional eigenproblem, and $f_i$, $a_n$, and $b_n$ are integers, their values ranging from 0 to 6 in this paper. In our calculations, the number of linear coefficients $N_1$ and $N_2$ was 19 and 100, respectively.

## III. RESULTS AND DISCUSSION

The basis set used in our calculations is given in Eq. (7). In this work, the $1s^2\,{}^1S$ core wave funtion was prepared by using 100 terms in $8l$ components. Each $l$ component is represented by $(l_1,l_2)L$; the first is $(0,0)0$, which was expanded with 27 terms of radial functions. These radial functions were selected by the rule

$$0\leqslant a_n\leqslant 5,\quad 0\leqslant b_n\leqslant 6,\quad a_n\leqslant b_n, \tag{10}$$

$$\eta_n=\mu_1,\quad \sigma_n=\nu_1,\quad n=1,2,\ldots,27. \tag{11}$$

The second $l$ component is $(1,1)0$, which was expanded with 13 terms of radial functions, selected by the rule

$$0\leqslant a_n\leqslant 3,\quad 0\leqslant b_n\leqslant 4,\quad a_n\leqslant b_n,\quad a_n+b_n\leqslant 6, \tag{12}$$

$$\eta_n=\mu_2,\quad \sigma_n=\nu_2,\quad n=28,29,\ldots,40. \tag{13}$$

The third to the eighth $l$ components are $(2,2)0$, $(3,3)0$, $(4,4)0$, $(5,5)0$, $(6,6)0$, and $(0,2)2$, respectively. They were all expanded with 10 terms of radial functions, selected by the rule

$$0\leqslant a_n\leqslant 3,\quad 0\leqslant b_n\leqslant 3,\quad a_n\leqslant b_n, \tag{14}$$

$$\eta_n=\mu_3,\quad \sigma_n=\nu_3,\quad n=41,42,\ldots,100. \tag{15}$$

$\mu_i$ and $\nu_i$ $(i=1,3)$ are variational parameters, all optimized for each strength of the magnetic field $\beta$. These exponents for each $\beta$ are presented in Table I. The core wave function given by the above method may not be very accurate, but the accuracy is enough for our calculations of lithium in strong magnetic fields. For example, the energy of the $1s^2\,{}^1S$ core in the absence of a magnetic field was $-7.279\,55$ a.u. from our calculations, it is close to the result of $-7.279\,98$ a.u. obtained with 318 terms of Slater-type orbitals by Chung [21].

Our results are presented in Tables II and III. In this paper, the states are labeled by the dominant configuration in the absence of a magnetic field. For each energy value, all figures but the last one were stable when advanced optimizations of those nonlinear parameters were performed, and

TABLE II. The energies of $1s^2 2s$ and $1s^2 3d$ states of lithium in strong magnetic fields, $E$(UHF) are results obtained from UHF calculations [14].

| $\beta$ | $1s^2 2s$ $E$(UHF) | $1s^2 2s$ $E$ | $1s^2 3d$ $E$ |
|---|---|---|---|
| 0.0000 | −7.4327 | −7.477 655 | −7.334 949 |
| 0.0009 | −7.4337 | −7.476 529 | −7.336 723 |
| 0.0045 | −7.4371 | −7.480 008 | −7.347 394 |
| 0.0090 | −7.4412 | −7.484 132 | −7.357 920 |
| 0.0270 | −7.4553 | −7.498 242 | −7.388 991 |
| 0.0630 | −7.4739 | −7.516 924 | −7.428 939 |
| 0.0900 | −7.4814 | −7.524 862 | −7.450 817 |
| 0.2700 | −7.4731 | −7.515 338 | −7.530 911 |
| 0.4500 | −7.4240 | −7.459 652 | −7.557 268 |
| 0.6300 | −7.3609 | −7.380 319 | −7.550 667 |
| 0.9000 | | | −7.499 568 |
| 1.8000 | | | −7.087 585 |
| 2.7000 | | | −6.408 515 |

all figures but the last two were stable when the basis set was enlarged. The basis-set truncation errors are of the order of about $10^{-4}$. According to the work of Chung [21] and our calculations, the main errors of our results are from approximations for the freezing core; they are of the order of $10^{-3}$. Therefore, it may not be necessary to further decrease the basis-set truncation errors. In Tables II and III, we also list the results of other calculations for comparison. It can be seen that our results are more accurate than those obtained by the UHF method [14]. In the absence of magnetic fields, the energies of the $1s^2 2s$ and $1s^2 2p$ states are −7.477 655 and −7.408 562 a.u., respectively. The most accurate results obtained with Hylleraas calculations are −7.478 060 3 and −7.410 156 5 a.u. [22,23]; so our results agree with the best calculations to within 0.0054% and 0.022%, respectively.

TABLE III. The energies of the $1s^2 2p$ state of the lithium in strong magnetic fields, $E$(UHF) are results obtained from Ref. [14], $E$(SFC) are those obtained by the standard freezing core method, $E$(MFC) are those obtained by the modified freezing full-core method, and $E_C$ are energies of the $1s^2\,{}^1S$ core as well as the energies of the ground $^1S$ state of $Li^+$ in strong magnetic fields.

| $\beta$ | $E$(UHF) | $E$(SFC) | $E$(MFC) | $E_C$ |
|---|---|---|---|---|
| 0.0000 | −7.3651 | −7.408 562 | −7.408 562 | −7.279 551 |
| 0.0009 | −7.3669 | −7.409 685 | −7.409 748 | −7.279 405 |
| 0.0045 | −7.3738 | −7.416 663 | −7.416 726 | −7.279 400 |
| 0.0090 | −7.3832 | −7.424 977 | −7.425 040 | −7.279 381 |
| 0.0270 | −7.4114 | −7.454 204 | −7.454 267 | −7.279 190 |
| 0.0630 | −7.4565 | −7.499 253 | −7.499 309 | −7.278 225 |
| 0.0900 | −7.4832 | −7.526 003 | −7.526 048 | −7.276 999 |
| 0.2700 | −7.5965 | −7.638 885 | −7.639 002 | −7.257 863 |
| 0.4500 | −7.6563 | −7.696 069 | −7.696 831 | −7.220 237 |
| 0.6300 | −7.6820 | −7.719 946 | −7.720 152 | −7.165 522 |
| 0.9000 | −7.6747 | −7.705 084 | −7.708 285 | −7.054 484 |
| 1.8000 | −7.3627 | −7.281 622 | −7.397 531 | −6.486 132 |
| 2.7000 | −6.7747 | −6.313 277 | −6.810 567 | −5.702 614 |

Because the correlation effects were not taken into account, the accuracy of the results in the UHF calculation was not very high. For a lithiumlike system with a $1s^2\,{}^1S$ core, the dominant part of the correlation effect comes from the two inner electrons; the correlation between the inner and outer electrons can be seen to be negligible in comparison to the whole energy. In the freezing full-core method used in our calculations, correlation between inner electrons is accounted for in the core wave function. Therefore, the dominant part of the correlation effect was accounted for with a small basis set, and highly accurate results were obtained with simple calculations.

The core wave function is obtained from the ground $^1S$ state of $Li^+$ in the absence of magnetic fields in standard freezing-core calculations. But when the strong magnetic fields can be compared to the atomic Coulomb potential, the contribution of the magnetic fields to the core wavefunction cannot be neglected. Thus, the effects of strong magnetic fields are poorly represented by the standard freezing core and MQDT methods. In our calculations, the core wave functions were obtained from the Schrödinger equation of the ground $^1S$ state of $Li^+$ in magnetic fields. For the $1s^2 2p$ state of lithium, the energies obtained from different methods are presented in Table III. The results from modified freezing full-core calculations are in agreement with those from the standard freezing core method when $\beta \leqslant 0.45$, but the differences increase with the field strength, and agreement is poor when $\beta > 0.63$.

On the other hand, the CI method provides a technique to obtain more accurate results, but the accuracy in a CI calculation will depend on the number of radial functions and different angular configurations included in the basis set. For two-electron systems, the number of configurations was 1997 in Scrinzi's work [17]; in the simpler calculations of Ref. [19], the number was 1134. Thus, for lithium, a much larger basis set has to be used. This causes a very high level of complexity in numerical calculations. In our work, only 19 configurations were included in the basis set, and a high accuracy of results was obtained.

## IV. CONCLUSION

A modified freezing full-core method, which can be effectively used in three-electron atomic systems with a $1s^2\,{}^1S$ core in strong magnetic fields, was described in this paper. Because the dominant part of the correlation was accounted for with a small basis set, highly accurate results were obtained with simple calculations. But at very high magnetic fields, when spherical symmetry is mostly broken, our basis set may be insufficient again. A basis in cylindrical coordinates might be expected to give better results.

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