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Combined perturbation and configuration-interaction calculation for the fine-structure level splittings of the $1s4f$ states of helium

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We present a combined application of perturbation and configuration-interaction calculation for the nonrelativistic electrostatic energy for the He $1s4f\,^{1,3}F$ multiplets with particular emphasis given to the contributions beyond the second order from perturbation calculation. The numerical efficiency and the quantitative accuracy of our *ab initio* calculation are greatly improved with the use of a *finite* basis set constructed from the B splines. The calculated fine-structure level splittings for the $1s4f\,^{1,3}F$ multiplets compare very well with the result from the most recent rf electric-resonance experiment.

I. INTRODUCTION

The early high-precision microwave-optical-resonance measurement by Wing and his co-workers[1] on the fine-structure level splittings (FSLS) for the high-angular-momentum Rydberg states of helium with one highly excited electron in a high-l orbit screened by a tightly bound inner $1s$ electron has inaugurated a series of similar experiments[2–4] with ever increasing precision which is capable of testing smaller physical effects beyond the usual spin-dependent interactions.[4] For state with its total orbital angular momentum $L \le 2$, it is well known[1] that the spin-dependent contribution to FSLS is small compared to the contribution from the electrostatic exchange interaction. As L increases, the exchange interaction decreases much more rapidly than the spin-dependent interactions. In particular, for the $L=3$ F state, these two contributions to FSLS are comparable. For states with $L \ge 4$, the FSLS is dominated by the contribution from the spin-dependent interactions.

The early theoretical interpretation for the FSLS for a two-electron atomic system, which takes into account both the electrostatic and spin-dependent interactions (i.e., the spin-orbit, the spin-other-orbit, and the spin-spin interactions in the Breit-Pauli approximation[5]), was first developed by Araki[6] and later extended by Parish and Mires.[7] Subsequently, an alternative description has been suggested by Cok and Lundeen.[8] More recently, high-precision variational procedures have also been applied to achieve quantitative accuracy comparable to the experimental results.[9–11]

For the high Rydberg states, the tightly bound inner $1s$ electron and the highly excited high-l outer electron are both well approximated by the one-electron hydrogenic orbitals subject to Z and $Z-1$ nuclear charge, respectively. Following Araki's original derivation[6] and the subsequent work of Parish and Mires,[7] the relative energies of the four fine-structure levels (i.e., $1snl\,^{1,3}L_J$ multiplets) can be expressed by a set of simple analytical formulas, i.e.,

$$\varepsilon_1 \simeq -K-(l+1)\left[1-\frac{(6l-1)}{Z(2l-1)}\right]\lambda, \quad J=L-1\ , \tag{1}$$

$$\varepsilon_2 \simeq -\frac{1}{2}\left[\left[2K+\lambda\frac{Z-1}{Z}\right]^2 +4l(l+1)\left[\frac{Z+1}{Z}\right]^2\lambda^2\right]^{1/2} -\tfrac{1}{2}\lambda\frac{Z-1}{Z}, \quad J=L\ , \tag{2}$$

$$\varepsilon_3 \simeq -K+l\left[1-\frac{(6l+7)}{Z(2l+3)}\right]\lambda, \quad J=L+1\ , \tag{3}$$

$$\varepsilon_4 \simeq \frac{1}{2}\left[\left[2K+\lambda\frac{Z-1}{Z}\right]^2 +4l(l+1)\left[\frac{Z+1}{Z}\right]^2\lambda^2\right]^{1/2} -\tfrac{1}{2}\lambda\frac{Z-1}{Z}, \quad J=L\ , \tag{4}$$

where

$$\lambda=\tfrac{1}{2}\alpha^2 Z(Z-1)^3/[n^3 l(l+1)(2l+1)] \tag{5}$$

is in atomic units, α is the fine-structure constant, and K is the electrostatic exchange energy. Equations (1)–(3) represent the relative energies for the three triplet levels and Eq. (4) represents the energy for the singlet level in the usual LS coupling. Equations (1)–(4) are derived from the theoretical results of Parish and Mires[7] for the $L \ge 2$ states [i.e., Eqs. (48)–(51) in Ref. 7] by employing the approximation that

$$\xi \simeq \lambda/Z\ , \tag{6}$$

$$\eta \simeq \lambda/[Z(2l-1)(2l+3)]\ , \tag{7}$$

and neglecting the small contributions from ξ' and η'.

TABLE I. The fine-structure level splittings (in MHz) for the He 10*G* and 10*H* states. The experimental uncertainty is given in parentheses.

Level splittings	Present	Drachman (Ref. 12)	Hessels *et al.* (Ref. 2)	Farley *et al.* (Ref. 3)
${}^1G_4$-${}^3G_4$	26.130	26.168	26.178(14)	26.27(14)
${}^3G_3$-${}^3G_4$	19.807	19.760	19.755(14)	19.92(17)
${}^2G_5$-${}^3G_4$	10.367	10.333	10.345(20)	10.54(26)
${}^1H_5$-${}^3H_5$	17.452	17.478	17.489(15)	
${}^3H_4$-${}^3H_5$	12.884	12.897	12.905(14)	
${}^3H_6$-${}^3H_5$	6.746	6.763	6.764(22)	

For $L \geq 4$ states, the electrostatic exchange energy K is at least 2 orders of magnitude smaller than the spin-dependent interactions. Table I compares the most accurate measured FSLS values for the 10*G* and 10*H* states to the calculated values. The present result is obtained from Eqs. (1)–(4) by setting $K=0$. In spite of its simplicity and the approximation that $K=0$, estimation from Eqs. (1)–(4) has led to FSLS values accurate to about 0.05 MHz or better for states with $L \geq 4$ although not as accurate as the more elaborate calculation by Drachman.[12]

The study of the FSLS of He $1snf$ ${}^{1,3}F$ multiplets is particularly interesting due to the strong singlet-triplet mixing as a result of comparable contributions from the exchange interaction and the spin-dependent interactions. All earlier works have shown that the first-order exchange energy is about a factor of 2 larger than its observed value. The large cancellation to the first-order exchange energy due to the second-order contribution found in our earlier perturbation calculation[13] suggests that a more definitive calculation should at least include an estimation of the higher-order contribution. Experimentally, in a recent rf electric-resonance experiment, Schilling *et al.*[14] have derived the exchange energy K for the He $1s4f$ multiplets from the measured fine-structure intervals between the ${}^1F_3$ and the ${}^3F_J$ levels. Their experimental K value is in agreement with the most recent variational configuration-interaction–Hylleraas (CI-H) result by Sims and Martin[10] but about 13% larger than the value from our earlier perturbation calculation.[13] In this paper we will report the result of our renewed theoretical effort which has led to a substantial improvement in the quantitative accuracy of the electrostatic exchange energy K over our previous perturbation calculation.

II. PERTURBATION CALCULATION AND THE FINITE BASIS SET FROM *B* SPLINES

Similar to our early study,[13] we have selected the one-electron hydrogenic wave functions subject to a nuclear charge Z for the inner electron and a charge of $(Z-1)$ for the outer electron. The hydrogenic wave function U_{nlmm_s} is expressed in terms of the product of the radial part $\chi_{nl}(r)$, the angular part Y_{lm}, i.e., the spherical harmonics, and the spin function $\sigma(m_s)$

$$U_{nlmm_s}=\frac{\chi_{nl}(r)}{r}Y_{nl}(\Omega)\sigma(m_s) \ . \tag{8}$$

The first-order electrostatic exchange energy K_1 is given by

$$K_1=\frac{1}{2l+1}\langle 1s|Y_l(nl,1s;r)|nl\rangle \ , \tag{9}$$

where

$$\langle n_1l_1|Y_k(n_2l_2,n_3l_3;r)|n_4l_4\rangle = \int_0^\infty dr\,\chi_{n_1l_1}(r)Y_k(n_2l_2,n_3l_3;r)\chi_{n_4l_4}(r) \tag{10}$$

and

$$Y_k(nl,n'l';r)=r^{-(k+1)}\int_0^r s^k ds\,\chi_{nl}(s)\chi_{n'l'}(s) + r^k\int_r^\infty s^{-(k+1)}ds\,\chi_{nl}(s)\chi_{n'l'}(s) \ . \tag{11}$$

The second-order electrostatic exchange energy K_2 is given by

$$K_2=2\sum_{n_1l_1}\sum_{n_2l_2}\frac{V_d(n_1l_1,n_2l_2)V_{\rm ex}(n_1l_1,n_2l_2)}{\Delta D(n_1l_1,n_2l_2)} \tag{12}$$

where the complete set of intermediate-state n_1l_1, representing both the *bound* and the *continuum* components, are included in the summation. The double summation is taken over all allowed two-electron configurations except $1snl$. The direct and exchange integrals V_d and $V_{\rm ex}$ are given by

$$V_d(n_1l_1,n_2l_2) = \begin{cases} \eta_{l_1}(0ll_1l_2;L)\langle 1s|Y_{l_1}(nl,n_2l_2;r)|n_1l_1\rangle, & n_1l_1\neq 1s \\ \delta_{ll_2}\langle nl|Y_0(1s,1s;r)-1/r|n_2l_2\rangle, & n_1l_1=1s \end{cases} \tag{13}$$

and

$$V_{\rm ex}(n_1l_1,n_2l_2)=\eta_{l_2}(0ll_2l_1;L) \times\langle 1s|Y_{l_2}(nl,n_1l_1;r)|n_2l_2\rangle \ , \tag{14}$$

where the angular factor η_k is given elsewhere.[15] The energy denominator ΔD is given by

$$\Delta D(n_1l_1,n_2l_2)=\varepsilon_{1s}(Z)+\varepsilon_{nl}(Z-1) -\varepsilon_{n_1l_1}(Z)-\varepsilon_{n_2l_2}(Z-1) \tag{15}$$

with the choice that $l_2>l_1$ and n_1l_1 and n_2l_2 represent the orbitals for the inner and outer electron, respectively.

Like all many-body perturbation calculations, the most time-consuming part of the numerical works is the summing over the complete intermediate basis included in the double summation in Eq. (12). In our previous calculation,[13] we first carried out one of the summations, e.g., the sum over basis set n_2l_2, by solving the effective inhomogeneous differential equation with the Dalgarno-Lewis technique[16] for each n_1l_1 orbit. This is followed by a direct sum over the *bound* contribution and the integration over the *continuum* contribution for the second intermediate basis set n_1l_1. Such a procedure is particularly difficult for higher nl Rydberg states as orbitals extending to very large distances are required in the calculation. In the present calculation, we have, instead, replaced the complete intermediate basis with a *finite* basis set constructed from B splines.[17] The finite basis set constructed from B splines has been applied successfully in the recent relativistic many-body perturbation calculation by Johnson *et al.*[18] Its extension to the nonrelativistic calculation is trivial. We will only briefly outline in this section the construction of the finite basis set from B splines for the nonrelativistic calculation. Basic properties associated with the B splines are discussed in detail elsewhere.[17,18]

The radial function χ in this calculation satisfies the eigenequation

$$-\frac{1}{2}\frac{d^2\chi}{dr^2}+V(r)\chi=\varepsilon\chi\ , \tag{16}$$

where

$$V(r)=-\zeta/r+\tfrac{1}{2}l(l+1)/r^2 \tag{17}$$

is the hydrogenic potential with $\zeta=Z$ for the inner electron and $\zeta=Z-1$ for the outer electron. The solution χ is expanded in terms of a set of B splines of order k, total number n, and a knot sequence between $r=0$ and $r=R$, i.e.,

$$\chi(r)=\sum_{i=1}^{n} c_i B_i(r)\ . \tag{18}$$

For simplicity, n and k are omitted from the functions B_i. At the endpoint $r=0$, all B splines equal to zero except for B_1 and at the other endpoint $r=R$, all B splines also equal to zero except for B_n, i.e.,

$$B_1(0)=1,\quad B_n(R)=1\ . \tag{19}$$

The boundary conditions that χ equals to zero at $r=0$ and R require that

$$c_1=c_n=0\ . \tag{20}$$

An exponential knot sequence is employed in the present calculation similar to the one used in the relativistic calculation by Johnson *et al.*[18] With the expansion in the form of Eq. (18) and the boundary conditions Eq. (20), the eigenequation Eq. (16) can be expressed as a $(n-2)\times(n-2)$ symmetric generalized eigenvalue equation

$$HC=\varepsilon AC\ , \tag{21}$$

where H and A are $(n-2)\times(n-2)$ symmetric matrices given by

$$H_{ij}=-\tfrac{1}{2}\left\langle B_i\left|\frac{d^2}{dr^2}\right|B_j\right\rangle+\langle B_i|V|B_j\rangle,\quad i,j=2,\ldots,(n-1) \tag{22}$$

$$A_{ij}=\langle B_i|B_j\rangle,\quad i,j=2,\ldots,(n-1)\ . \tag{23}$$

The eigenvector χ_v corresponding to the energy eigenvalue ε_v, i.e.,

$$\chi_v=\sum_{i=2}^{n-1} c_i B_i(r) \tag{24}$$

is constructed from the $n-2$ coefficients c_i from the eigenvector

TABLE II. Calculated first- and second-order perturbation contribution to the electrostatic exchange energy $2K$ (in 10^{-8} Ry) for the He $1s4f$ multiplets.

Energy	Orbital angular momenta $l_i(Z=2)$	 $l_o(Z=1)$	Electrostatic exchange energy $2K$ (in 10^{-8} Ry) B-spline basis	 H-like bound states (up to $n=18$)
First order ($2K_1$)			10.2555	10.2555
Second order	0	3	0.2934	0.0001
	1	2	−4.8483	−3.6293
	1	4	−1.1877	−0.0075
	2	3	−0.6570	−0.0072
	2	5	−0.3299	−0.0001
	3	4	−0.1963	0.0000
	3	6	−0.1307	0.0000
	4	5 and 7	−0.1412	0.0000
	5	6 and 8	−0.0705	0.0000
	6	7 and 9	−0.0388	0.0000
	7	8 and 10	−0.0226	0.0000
	8	9 and 11	−0.0139	0.0000
	9	10 and 12	−0.0092	0.0000
	10	11 and 13	−0.0061	0.0000
	11	12 and 14	−0.0041	0.0000
	12	13 and 15	−0.0027	0.0000
Total ($2K_2$)			−7.3641	−3.6440
$2K_1+2K_2$			2.8914 (95.11 MHz)	6.6115 (217.48 MHz)

$$C_v=(c_2,c_3,\ldots,c_{n-1}) \ . \tag{25}$$

In the present calculation, the numerical eigenvalues of the first few lowest negative-energy solutions agree to the hydrogenic values to 10^{-10} Ry. The *quasicomplete* set of eigenfunctions constructed from B splines are then used in the calculation of the second-order exchange energy $2K_2$.

The calculated exchange interactions up to second order are listed in Table II. The basis functions χ are constructed from sets of B splines of n ranging from 27 to 62 and k ranging from 7 to 11. The numerical results listed in Table II are the converged results of various combinations of n and k as we vary the radius R from $90a_0$ to $200a_0$. The individual contribution from each (l_1,l_2) combination, i.e., $l_1=l_i$ for the *inner* electron and $l_2=l_o$ for the *outer* electron, are tabulated in detail to illustrate the slow convergence in the second-order calculation. In particular, we note that the present calculation up to $(l_il_o)=(2,3)$ combination agree well with our early perturbation calculation[13] which did not include the contributions from other higher (l_il_o) combinations. Similar to our earlier calculation,[13] the present calculation also shows that the contribution from the *continuum* part of the intermediate basis set is substantial as indicated by the large difference between the *more complete* second-order calculation and the one which includes only the *bound* component shown in Table II. With an uncertainty of about 0.18 MHz or less, the sum of the first- and second-order exchange energies is about 95.11 MHz which is substantially smaller than the measured value of 158±3 MHz by Schilling *et al.*[14]

III. COMBINED PERTURBATION AND CONFIGURATION-INTERACTION CALCULATION

The larger discrepancy in the exchange energy between the experimental value and the more complete first- and second-order perturbation results clearly indicates the need to carry out theoretical calculation beyond second order. The obvious choice would be an extension of the perturbation calculation to include higher-order contributions. Such an approach would require an enormous numerical effort with little advanced assurance that the perturbation series would converge any faster than its convergence up to second order. Alternatively, we could include contributions up to infinite orders in a configuration-interaction (CI) calculation if only limited configurations contribute significantly and a high numerical accuracy can be achieved to about 10^{-10} Ry or better in calculating the energy difference between separate calculations for the ^1F and ^3F states. A straightforward *nonvariational* CI calculation would also require enormous numerical effort with no assurance that the contributions from two-electron configurations corresponding to higher (l_il_o) combination could be calculated at the same level of numerical accuracy.

To minimize the numerical effort in the estimation of higher-order contributions, we started exploring the possibility of a combined perturbation and CI calculation after recognizing that the larger individual second-order contribution comes predominantly from configurations with $l_i=1$. Typically, the direct integrals V_d involving such configurations are few orders of magnitude larger than those with l_i other than 1. In particular, we have examined the second-order contribution from each configuration series $n_il_il_o$ [i.e., a set of configurations with a fixed inner electron orbit n_il_i combined with outer electron in orbits consisting of the complete set of solutions χ of Eq. (16) corresponding to the fixed l_o] and concluded that the contributions from the first few configuration series with a $(l_il_o)=(1,2)$ or *pd* combination and the first few configuration series with a $(l_il_o)=(1,4)$ or *pg* combination are about 2 orders of magnitude larger than the individual contribution from other configuration series. In our combined perturbation and CI calculation, we first carried out separate CI calculation for both $1s4f\ ^1F$ and $1s4f\ ^3F$ states by including a selected number of dominating *npd* and *npg* configuration series in addition to the $2sf$ series which also contributes significantly. The singlet-triplet energy separation from the CI calculation is then subtracted from the calculated first-order value $2K_1$ to determine the second- and higher-order contribution to $2K$ due to the configuration series included in the CI calculation. The second-order perturbation contribution from all other configurations *not* included in the CI calculation are then added to the contribution from CI calculation to get our final calculated $2K$ value.

As the number of configuration series included in the CI calculation increases, the calculated $2K$ value slowly converges to the experimental value. The calculated singlet-triplet separation Δ from the CI calculation including contribution from $2sf$ series and all *npd* and *npg* series is determined by extrapolating the calculated Δ_N with increasing number of configuration series N according to the limiting expression

$$\Delta_N=\Delta(1-e^{-\mu(N-\delta)}) \ , \tag{26}$$

where μ and δ are fitting parameters which are adjusted to get the best fit as N approaches the limiting value. Figure 1 shows the numerical fit of Δ from the calculated

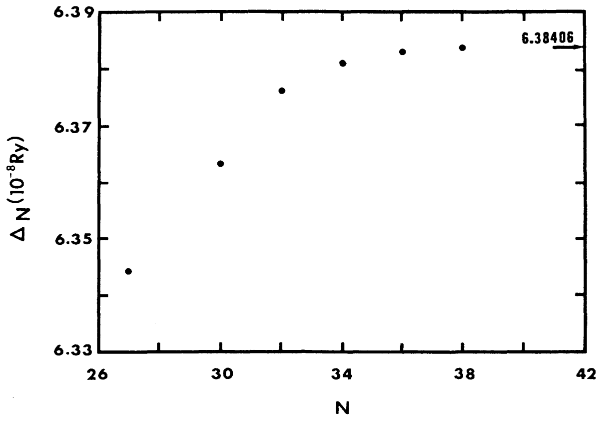

FIG. 1. The extrapolated $1s4f$ singlet-triplet separation $\Delta=6.384\,06\times10^{-8}$ Ry from the calculated Δ_N as function of increasing number of configuration series N following Eq. (26).

TABLE III. The combined CI (configuration interaction) and perturbation contribution to the exchange energy $2K$ for He $1s4f$ multiplets.

Contributing term	Electrostatic exchange energy $2K$ (10^{-8} Ry)	(MHz)
First order ($2K_1$)	10.2555	337.34
CI contribution	−3.8714	−127.35
Second order excluding configurations in CI calculation	−1.5868	−52.19
Total	4.7973	157.80
Sims and Martin[a]		158.02
Experiment[b]		158±3

[a] Reference 10.

[b] Reference 14.

Δ_N ranging from $N=27$ to 38 to the Eq. (26). The limiting value $\Delta=6.38406\times10^{-8}$ Ry is used to derive the CI contribution of -3.8714×10^{-8} Ry listed in Table III. We have estimated an uncertainty of approximately 0.10 MHz due to the extrapolation from Fig. 1. Table III lists the first-order value $2K_1$, the CI contribution, and the second-order contribution from all other configurations *not* included in the CI calculation. The sum of these three contributions leads to a value of $2K=157.80\pm0.28$ MHz which compares very well with the theoretical value from Sims and Martin[10] and the experimental value from Schilling *et al.*[14] Finally, from Eqs. (1)–(4), we find $\nu_{12}=231.88\pm0.34$ MHz, $\nu_{14}=490.37\pm0.34$ MHz, and $\nu_{13}=703.46\pm0.58$ MHz which are also in excellent agreement with the observed values[14] of 232.8±2.0 MHz, 490.8±2.0 MHz, and 704.3±1.0 MHz, respectively.

The present calculation has shown that the combined application of the perturbation and CI calculation can indeed offer an effective alterative to a separate perturbation or CI calculation if the dominating contributions can be identified in detail. Our calculation has also shown that the *finite* basis set constructed from B splines can be applied very effectively to the nonrelativistic perturbation and CI calculations.

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