Vol 15 No 5, May 2006
1009-1963/2006/15(05)/0992-06

Chinese Physics

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Analytic variationally optimized internally orthogonalized modified Laguerre orbitals in accurate atomic configuration interaction calculation*

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(Received 17 October 2005; revised manuscript received 31 December 2005)

An analytic configuration interaction method based on variationally optimized internally orthogonalized modified Laguerre orbitals is presented. We have developed the corresponding computer code. For application, we study the 1s2s ^1S isoelectronic sequence from helium to neon, and compare with other methods. By taking into account the Eckart upper-bound theorem, we obtained more accurate and more intuitively understandable results than Hartree–Fock and multi-configuration Hartree–Fock reported results.

Keywords: atomic excited states, analytic basis function, configuration interaction, variational computation

PACC: 3120A, 3120B, 3150

1. Introduction

Among various configuration interaction methods for the calculation of the electronic structure of atoms based on the variational principle, the numerical multi-configuration Hartree–Fock (NMCHF) is very efficient and accurate because it describes the electronic state with few simple orbitals, rich in physical meaning, whereas other methods are based on large basis sets which complicate the description. However, since NMCHF is numerical, it leads to an energy minimum, indifferently global or local, usually the widest (which is sometimes misinterpreted): i.e., it may suffer from the 'variational collapse' that it iteratively to states different then the desired one, or may diverge at all.[1]

The configuration interaction (CI) variational method using basis functions that are antisymmetrized products of one-electron spin orbitals, unlike, e.g. Hylleraas's treatment, which has been easily extended to many-electron systems, was developed since 1930. The functions chosen to represent the atomic orbitals are usually combinations of spherical harmonics and one of the following radial orbitals: hydrogenlike orbitals, Laguerre orbitals, Slater type orbitals (STO) and Gaussian type orbitals (GTO). Among these, the hydrogenlike orbitals are intuitively transparent but converge rather slowly and Laguerre orbitals are very closely concentrated in space and lead to rather rapid convergence.[2]

It would be interesting to invent *analytic* orbitals similar to NMCHF, describing the state in an equally simple and concise way with comparable accuracy. In this paper, we present more general one-electron functions, namely, optimized internally orthogonalized modified Laguerre orbitals, the central idea is to adopt the usual Laguerre orbitals and start moving variationally the nodes and the extent of their radial function, until the minimum of the energy is reached. Thus we can both have an adequately precise and simple intuitive physical picture of the electronic state and we can efficiently incorporate charge correlation and radial correlation. Since our orbitals are analytic, all energy minima can be located, at least in principle, and because of the simplicity, and of the immediate recognizability of the physical content of the

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orbitals, the most representative description of the CI expansion can be chosen, therefore it is free from the variational collapse.

We present a method which introduces these orbitals in CI atomic calculations. We have developed the computer code implementing this method.[3–5] Using this method, we study the 1s2s ^1S isoelectronic sequence of atoms from helium to neon. Unlike configuration Hartree–Fock (NHF) and NMCHF calculations as reported,[6] our method is capable of making this state orthogonalize in zero-order exactly to the ground state and we shall see that it is possible to maintain this orthogonality quite satisfactorily when dealing with many configurations, thus satisfying the Eckart upper bound theorem.[7]

2. Theory and method

Given the atom with $n = n_{\rm elec}$ electrons, the symmetry, and the electron occupancy, the desired n-electron normalized wave function, consisting of $n_{\rm conf}$ (predetermined) configurations are respectively,

$$\Psi(r_1 s_1, ..., r_n s_n) = \sum_{p=1}^{n_{\rm conf}} c_p \Gamma_p(r_1 s_1, ..., r_n s_n),$$
$$|\Psi|^2 = 1,$$
$$\Gamma_p = \sum_{i=1}^{n_{\rm det}} a_{ip} D_i, \qquad (1)$$

where the linear parameters c_p are determined from the lowest root of the secular equation

$$\det|H_{p,q} - S_{p,q}E| = 0, \qquad (2)$$

where

$$H_{p,q} = \sum_{i,j=1}^{n_{\rm det}} a_{ip} a_{jq} \langle D_i | H | D_j \rangle, \qquad (3)$$

$$H = -\frac{1}{2}\sum_{i=1}^{n_{\rm elec}} \left(\nabla_i^2 + \frac{Z_n}{r_i}\right) + \sum_{i>j}^{n_{\rm elec}} \frac{1}{r_{ij}}$$
(Z_n being the nuclear charge), (4)

and $S_{p,q} = \langle D_i | D_j \rangle$ is the overlap matrix.

Here D_i are all ($n_{\rm det}$) consistent with the Slater determinants formed out of the $n_{\rm orb}$ (predetermined) orbitals to be optimized, and the a_{ip} are all ($n_{\rm det} \times n_{\rm conf}$) corresponding consistent coefficients which we determine by applying Schaffer and Harris's method.[8] The D_i is constructed from the modified Laguerre orbitals of the form

$$R_{n,l}(r, z_{n,l}) = A \exp\left(-\frac{z_{n,l} r}{n}\right) r^l L_{n,l,z_{n,l}}(\{g\}, r)$$
(in a.u.), (5)

where A is a normalization constant, and

$$L_{n,l,z_{n,l}}(\{g\}, r) = \sum_{k=0}^{n-l-1} c_k(n, l, z_{n,l}) g(n, l, k, \{z_{i,l}\}_{i=1}^n) r^k \qquad (6)$$

and

$$c_k(n, l, z_{n,l}) = \frac{(-1)^{k+1}(n+l)!}{(n-l-1-k)!(2l+k+1)!k!}\left(\frac{2z_{n,l}}{n}\right)^k. \qquad (7)$$

The parameters $z_{n,l}$ (different from the nuclear charge Z_n) are effective nuclear charges resulting from the (non-linear variational) minimization of the desired (usually the lowest) root of Eq.(2) and determines the extent of the orbital. Our new approach is to introduce the g-functions, $g(n, l, k, \{z_{i,l}\}_{i=1}^n)$, which are determined by intrinsic orthogonalization among the orbitals. These have the advantage to provide a good and simple intuitive physical description of the state.

When we choose $g(n, l, k, \{z_{i,l}\}_{i=1}^n) = 1$, the $L_{n,l,z_{n,l}}(\{g\}, r)$ is reduced to a Laguerre polynomial. In this case, it is worth to note that our Laguerre orbitals in Eq.(5) have the following properties:

If $z_{n,l} = Z_n$, then Eq.(5) reduces to hydrogenlike orbitals.

If $z_{n,l}$ is varied and is chosen to be the same for all orbitals, then Eq.(5) reduces to Laguerre orbitals, which are orthogonal and converge faster than hydrogenlike orbitals and Gaussian-type orbitals.

The effect of our g-functions is to move the orbital nodes. In general, our orbitals in Eq.(5) are not orthogonal since $z_{n,l}$ is different for different orbitals $R_{n,l}(r, z_{n,l})$. However, by finding out appropriate $g(n, l, k, \{z_{i,l}\}_{i=1}^n)$, we can orthogonalize them by directly solving

$$\langle R_{i,l} | R_{j,l} \rangle = \delta_{i,j}, \quad (i, j = 1, n_{\rm orb}).$$

For example, for our 1s and 2s orbitals, Eq.(5) gives

$$R_{1\rm s} = A_{1\rm s} g(1, \rm s, 0) \exp(-z_{1\rm s} r),$$

$$R_{2\rm s} = A_{2\rm s}(2g(2, \rm s, 0) - r g(2, \rm s, 1) z_{2\rm s}) \exp(-z_{2\rm s} r/2).$$

By a redefinition of the normalization factor we can have

$$g(1, \rm s, 0) = 1,$$

$$g(2, \rm s, 1) = 1,$$

and through solving the equation $\langle R_{1s}|R_{2s}\rangle = 0$, we get

$$g(2,s,0) = \frac{3z_{2s}}{2z_{1s}+z_{2s}}. \quad (8)$$

In the appendix, similarly, we give g-functions for 3s and 3p. In the same way, we calculated the g-factors for $n = 4$, but the formulas are too lengthy to be given here.

Unlike the Gram–Schmidt orthogonalization, which combines unmodified orbitals, our orthogonalization modifies the orbitals themselves through the g-functions, with the result that our orbitals have a clear interpretation.

If the orbital has only one g-function (=1), we simulate the NMCHF orbitals by adding more orbitals with the same quantum numbers and by adjusting their shapes appropriate to the desired states according to the variational principle. Especially for 1s orbital that is necessary for example, we use 1s' with larger z to describe that the outer electron push the inner electrons closer to nucleus and improve by radial (via nodes) and angular (via lobes) correlation in order to simulate the cusp conditions.

From our test (atomic unit are used), for He ground ^1S using the orbitals up to 4f, we get the total energy –2.9031037, comparable with NMCHF up to 4f, –2.9031173,[9] and the exact value is –2.9037244.[10]

For the lithium ground state $1s^2 2s\ ^2S$, using the orbital up to 4f, we get the total energy –7.4766718, comparable with –7.4762030 of NMCHF.[11] And the exact value is –7.48.[12]

For the lithium excited state $1s^2 2p\ ^2P$, using the orbital up to 4f, we get the total energy –7.4077968, comparable with experiment value –7.4099.[12]

3. Application for 1s2s ^1S from He to Ne

For application, we investigated one of the most interesting of the singly excited states of He, as well as one of the most difficult to treat, the 2s state of parahelium.[13] Between 1936 and 1997, there have been many publications on this subject.[14–19] The most accurate calculations, by variational method using trial functions which include the interelectronic distance as an independent variable first carried out by Hylleraas,[18] have been performed by the Perkeris and his group.[19] However, their methods are of a noncentral field type which cannot easily be extended to more complex systems, and their wavefunctions, having more then 220 terms, do not provide a simple understanding of this relatively simple state. Fischer has performed NMCHF calculations of 1s2s ^1S isoelectronic sequence from helium to neon.[6] Here we study 1s2s ^1S for the same sequence by our method. We shall see that our method is simpler and of comparable accuracy with NMCHF. First we study the zero-order case and compare with Fischer's HF treatment.

According to the Eckart upper-bound theorem,[7] instead of using free nonorthogonal orbitals, we introduce the orthogonality between the 1s orbital of ground state and 2s orbital of excited state such that the whole ground $1s^2\ ^1S$ is orthogonalized to 1s2s ^1S state, i.e.

$$\text{If} \quad \langle 1s_g|2s_e\rangle = 0, \quad (9)$$

$$\text{then} \quad \langle 1s_g^2|1s_e 2s_e\rangle = 0, \quad (10)$$

where, from now on, the subscript g indicates the ground state and e indicates the excited state.

In practice, we first calculate the zero-order $1s^2\ ^1S$ and get the optimum z_{1sg}, and replace z_{1s} by z_{1sg} in the Eq.(8) in order to determine the g-functions of our $2s_e$ for every varied value of z_{1s}, z_{2s}.

Table 1 show our zero-order results 1s2s ^1S isoelectronic sequence from helium to neon compared with other calculations (in a.u.).

Table 1. Our zero-order CI calculation results for 1s2s ^1S isoelectronic sequence from helium to neon compared with other calculations (in a.u.).

	Our results (zero-order)	Exact[10]	MCHF[6]) (two-config.)	HF[6] (nonorthogonal)	HF[6] (orthogonal)	Z_{1sg}
He I	2.14545	2.14597	2.14347	2.14348	2.16985	1.68750
Li II	5.03809	5.04087	5.03622	5.03644	5.09922	2.68750
Be III	9.18044	9.18487	9.17886	9.17919	9.27960	3.68750
B IV	14.57268	14.57853	14.57163	–	14.71032	4.68750
C V	21.21520	21.22202	21.21449	–	21.39118	5.68750
N VI	29.10796	29.11542	29.10743	–	29.32213	6.68750
O VII	38.25104	38.25876	38.25043	–	38.50313	7.68750
F VIII	48.64364	48.65206	48.64346	–	48.93416	8.68750
Ne IX	60.28661	60.29534	60.28652	–	60.61521	9.68750

From this table, one can see that our zero-order results are closer to the exact energies than Fischer's results (MCHF (two-config.) and HF (nonorthogonal)).[6] Our method thus provides a clearer and simpler physical understanding, because it applies the Eckart upper bound theorem rigorously and in a very simple way.

Figure 1 shows our 1s2s ^1S He orbitals indicated by ($1s_e$, $2s_e$) compared with He^+1s orbital (1s) and 1s2s ^1S (1s, 2s) (orthogonal to each other) orbitals which gives an energy below the experiment like the HF orthogonal case. One can see that our $1s_e$ orbital is similar to the He^+1s orbital and orthogonality with the ground state, i.e. $2s_e \perp 1s_g$, pushes the $2s_e$ electron farther from the nucleus than the solely excited orthogonality, i.e. $2s \perp 1s$ therefore giving an upper bound energy according to the Eckart theorem.[7]

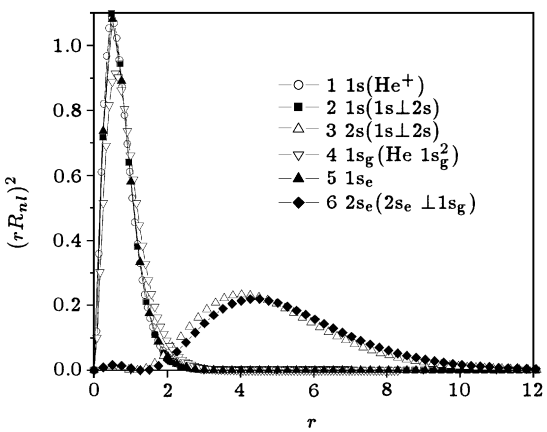


Fig.1. Our He 1s2s ^1S orbitals indicated by ($1s_e$, $2s_e$) compared with He^+1s orbital and 1s, 2s (which there are orthogonal to each other).

Figure 2 shows the He 1s2s ^1S energy as a function of $g = g$ (2,s,0) and z_{1s}. One can see that the g-factor plays a critical role for the variation method reaching the correct energy because only on the g=0.7433 plane, by finding the partial minimum, we get the upper bound energy –2.1454558. The global minimum corresponds to an approximation of He $1s^2$ ^1S instead of 1s2s ^1S. Without the g-factor (i.e. by using Laguerre functions), our 1s2s ^1S calculated energy is −2.1704711, which is lower then the exact energy as well as the HF (orthogonal) value.

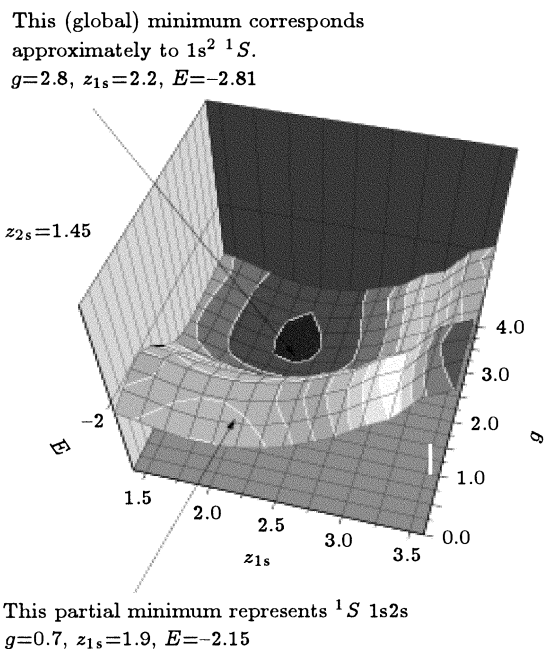


Fig.2. Our He 1s2s ^1S energy surface as function of $g = g$ (2, s, 0) and z_{1s}.

For the CI calculation, it is difficult to apply the Eckart upper-limit theorem rigorously, because generally the relation $\langle (nl)_g | (nl)_e \rangle = 0$ does not hold. However, by using enough orbitals a thorough investigation of the energy surface in the effective z parameter space reveals that there are many local minima with the same energy down to 3rd decimal place. These minima correspond to slightly different linear combinations of configurations, whose coefficients change slightly from minimum to minimum. So for both the ground and the excited states, we choose the minimum of the energy function, which maximizes the coefficient in the main configuration and minimizes the second largest coefficient, then through $\langle 1s_g | 2s \rangle = 0$ and $\langle n_s | 2s \rangle = \delta_{n,2}$, we make $\langle \Psi_g(\mathrm{CI}) | \Psi_e(\mathrm{CI}) \rangle$ as close to zero as possible, so the Eckart upper bound theorem can hold approximately with a satisfactory accuracy, e.g. 10^{-4}.

For the ground of He $1s^2$ correlated in full CI by 2s3s4s2p3p4p3d4d4f, various significant candidate minima tabulated in Table 2 were found, from which we choose the z_{1sg}=1.6297 (a.u). As explained above, then we calculate the excited state 1s2s ^1S (+3s4s2p3p4p3d4d4f), from many minima, we report

the one which has the largest coefficient on the 1s2s configuration and the smallest second largest coefficients. The corresponding orbitals are plotted in Fig.3. One can see the virtual orbitals 2p, 3d, 4f, etc. introduced an angular separation between 1s, 2s electrons and the 3s, 4s orbitals introduced nodes, i.e. a radial separation between the 1s, 2s electrons.

Table 2g. The various significant candidate minima (in a.u.) for He $1s^2$ ground state ^1S for full CI expansion up to 4f.

Most important CI	Z_{1sg}	Energy
$0.98[1s^2]-0.17[1s2s]+\ldots$	1.4080	−2.9028111
$0.98[1s^2]-0.16[1s2s]+\ldots$	1.4057	−2.9013973
$0.99[1s^2]-0.08[1s2s]+\ldots$	1.6297	−2.9027040

Table 2e. The various significant candidate minima (in a.u.) for He 1s2s excited state ^1S for full CI expansion up to 4f.

Most important CI	Energy
$0.999[1s2s]+0.017[2p3p]+\ldots$	−2.14604
$0.999[1s2s]+0.010[3s^2]+\ldots$	−2.14596
$0.936[1s2s]+0.350[1s3s]+\ldots$	−2.14583

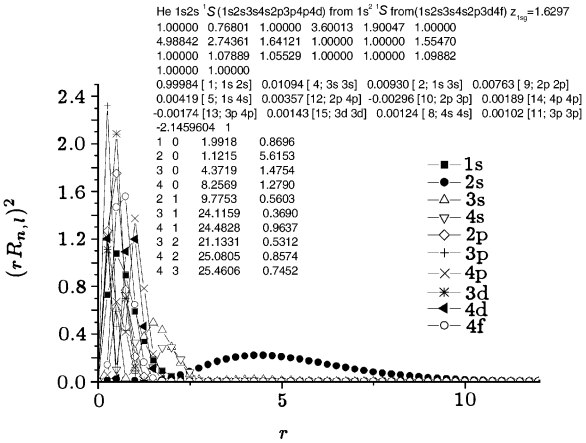


Fig.3. Our He 1s2s ^1S orbitals for full CI up to 4f.

In a similar way, we calculate the 1s2s ^1S isoelectronic sequence from helium to neon. Our calculation energy and compared with other calculations are given in Table 3. One can see our energies are comparable with Fischer's NMCHF (seven-configure) values.[5]

Table 3. Our CI calculation results for 1s2s ^1S isoelectric sequence from helium to neon compared with other calculations (in a.u.).

	Our results (CI)	Exact[10]	MCHF[6] (seven-config.)	Z_{1sg}
He I	2.1459604	2.14597	2.14563	1.6297
Li II	5.0408709	5.04087	5.04028	2.4353
Be III	9.1846874	9.18487	9.18413	3.6849
B IV	14.5782512	14.57853	14.57769	4.6840
C V	21.2202763	21.22202	21.22111	5.6868
N VI	29.1138171	29.11542	29.11445	6.4736
O VII	38.2584099	38.25876	38.25775	7.4671
F VII	48.6520624	48.65206	48.65102	8.4689
Ne IX	60.2953450	60.29534	60.29428	9.4527

Furthermore, we compare our calculation value −2.1459604 (a.u.) for 1s2s ^1S of helium with the latest NMCHF calculation performed by Fischer up to 6h[9] −2.1459531 (a.u). It seems our method converges faster than her method in orbitals space. The reason probably is because we implement the Eckart upper bound theorem,[7] that we vary the lowest root in CI space whereas she implements the Hylleraas–Undheim–MacDonald theorem,[20] so that she essentially varies the second lowest root in CI space. Actually optimizing the second lowest root with our analytic 1s, 1s', 2s orbitals, we got −2.1440709 (a.u) whereas her value is −2.1434743 (a.u.)[9] with 1s, 2s numerical orbitals.

4. Conclusion

In summary, the atomic CI variational calculation method has been successfully developed based on the new internally orthogonalized through the g-functions modified Laguerre orbitals. Like the standard CI calculation methods, it can be used for many-electron atoms with necessary configurations. It is shown that our method is more accurate and more intuitive understandable for 1s2s ^1S isoelectronic sequence from helium to neon since it can simply implement the Eckart upper bound theorem. The NMCHF orbitals can be simulated very well by our new analytic orbitals. Furthermore, our CI variational method is more stable then HF method because variational col-

lapse is avoided. Our analytic orbitals are being used to study highly excited states, applied to computation of recently measured VUV spectra of He states near the second ionization threshold. The activity in this field is rapidly growing.[21]

Appendix

By simultaneously solving $\langle 1s|2s\rangle = 0, \langle 1s|3s\rangle = 0$ and $\langle 2s|3s\rangle = 0$, we obtain Eq.(6) and

$$g(3,s,0) = \frac{4z_{3s}^2[-60z_{1s}^2 + z_{2s}(3z_{2s} - 8z_{3s}) + 4z_{1s}(3z_{2s} + 2z_{3s})]}{(3z_{1s} + z_{3s})(3z_{2s} + 2z_{3s})(-12z_{1s}^2 + 3z_{1s}z_{2s} + 2z_{1s}z_{3s} - 2z_{2s}z_{3s})},$$

$$g(3,s,1) = \frac{8}{3} - \frac{4z_{1s}}{3z_{1s} + z_{3s}} - \frac{5z_{2s}}{3z_{2s} + 2z_{3s}} + \frac{z_{1s}(4z_{1s} - z_{2s})}{12z_{1s}^2 - 3z_{1s}z_{2s} - 2z_{1s}z_{3s} + 2z_{2s}z_{3s}},$$

$$g(3,s,2) = 1.$$

Similarly,

$$g(3,p,0) = \frac{5z_{3p}}{3z_{2p} + 2z_{3p}},$$

$$g(3,p,1) = 1,$$

$$g(3,d,1) = 1.$$

In the same way, we calculated the g-factors for n=4, but displaying the formulas would take several pages because the number of the terms involved increases factorially.

Acknowledgements

Xiong Zhuang acknowledges the Greek State Scholarship Foundation (I.K.Y.) and the National Hellenic Research Foundation Scholarship that partially supported this work.

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