RAPID COMMUNICATIONS

PHYSICAL REVIEW A, VOLUME 63, 040502(R)

Configuration-interaction approach for high-lying singly and doubly excited states of two-electron systems

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(Received 8 December 2000; published 21 March 2001)

We introduce a configuration-interaction expansion in terms of Sturmian functions, which provides very accurate nonrelativistic energies for the high-lying singly and doubly excited states of a two-electron system. The approach, which requires a substantially smaller basis size by contrast to the standard configuration interaction methods, provides accurate results even for large total angular momenta. Key features are the use of different numbers of Sturmian functions for each electron, the inclusion of many different pairs of nonlinear parameters in the expansion, as well as complex scaling. The accuracy and convergence of the method, applied to helium, increases with the degree of excitation of one of the two electrons.

DOI: 10.1103/PhysRevA.63.040502 PACS number(s): 31.15.Ar, 31.25.Jf, 31.50.Df

The configuration-interaction (CI) method is based on the wave-function expansion in terms of an antisymmetrized product of functions of the electron radial coordinates r_i, and spherical harmonics $Y_{\ell_i,m_i}(\hat{r}_i)$ coupled for a total angular momentum L. This is one of the simplest and most flexible techniques for *ab initio* calculations in two (or more) electron systems. However, CI calculations are known to have poor energy convergence and to require very large expansions for reliable results [1,2], so that perimetric coordinate [3] or Hylleraas-like [4–6] expansions are usually preferred. Convergence is particularly slow for the ground state due to a cusp [7] in the two-electron wave function, which is a consequence of the singularity of the Coulomb repulsion operator $1/r_{12}$ at $r_{12}=0$. Schwartz [8] suggested that convergence may be improved by using $r_<=\min(r_1,r_2)$ and $r_>=\max(r_1,r_2)$, instead of r_i in the CI expansion. This approach has been extended [9], and the resulting modified CI significantly improves the accuracy and convergence of the ground-state energy of He. For high asymmetrically excited states (HAESs), where one electron is in a highly excited level and the other in the ground state or in a much lower excited level, there is little overlap between the two electron clouds and therefore the cusp is less relevant. This work shows that the standard CI may be the best *ab initio* approach for dealing with such states.

Obtaining accurate energies for HAESs in helium has been a long standing problem in theoretical atomic structure physics. Variational calculations have yielded very accurate energies for low-lying states in He [3,5], but the accuracy of the results for excited states deteriorates rapidly with increasing principal quantum number n. Improvements in variational techniques [6,10] and in CI expansions [11] have made possible the extension of variational calculations to the intermediate n and L range (n up to 18 for $L=0$ in Refs. [10,11], and n up to 10 for $L=2-7$ in Refs. [6,12]). However, the loss of accuracy in these variational approaches subsists when the degree of excitation of the outer electron is increased (see e.g., Ref. [13]). Until now, this loss of accuracy have prevented direct application of variational calculations to higher Rydberg states. For higher-L bound states, asymptotic expansions based on a core polarization model [14] have been considered as the only reliable approach, due to difficulties encountered by *ab initio* variational calculations [6,12]. In this work, we propose an adequate CI expansion that allows one to accurately describe high singly and doubly excited states in heliumlike atoms for almost arbitrary n and L, in the nonrelativistic case with an infinitely massive point nucleus. In addition, our approach permits one to simultaneously obtain a large set of atomic state energies accurately by means of a single diagonalization, while requiring a substantially smaller basis size.

The Hamiltonian of the two-electron system is written as

$$H=-\tfrac{1}{2}\nabla_{r_1}^2-\tfrac{1}{2}\nabla_{r_2}^2-(Z/r_1)-(Z/r_2)+(1/r_{12}), \quad (1)$$

where Z denotes the nucleus charge and

$$\frac{1}{r_{12}}=\sum_{q=0}^{\infty}\frac{4\pi}{2q+1}\frac{r_<^q}{r_>^{q+1}}\sum_{p=-q}^{q}Y_{q,p}^{*}(\hat{r}_<)Y_{q,p}(\hat{r}_>). \quad (2)$$

For a given L and its projection M, we expand the solution of the Schrödinger equation $H\Psi=E\Psi$ as

$$\Psi_{L,M}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\lambda,\ell}\sum_{s}\sum_{\nu n}\psi_{\kappa_s k_s \nu n}^{\lambda\ell LM}\mathcal{A}\times\frac{S_{\nu\lambda}^{\kappa_s}(r_1)}{r_1}\frac{S_{n\ell}^{k_s}(r_2)}{r_2}\Lambda_{\lambda\ell}^{LM}(\hat{r}_1,\hat{r}_2), \quad (3)$$

where $\psi_{\kappa_s k_s \nu n}^{\lambda\ell LM}$ is the expansion coefficient and $\mathcal{A}$ the symmetrization operator. The Sturmian functions [15] are given by $S_{n\ell}^{\kappa}(r)=N_{n\ell}^{\kappa}r^{\ell+1}e^{-\kappa r}L_{n-\ell-1}^{2\ell+1}(2\kappa r)$, where κ is the nonlinear parameter, $L_{n-\ell-1}^{2\ell+1}(2\kappa r)$ a Laguerre polynomial, and $N_{n\ell}^{\kappa}$ a normalization factor. The index n of the Sturmian functions (SFs) takes the values $\ell+1,\ \ell+2,\ \ell+3,\ \ldots.$ To avoid clumsy subscripts, we denote for the first electron

1050-2947/2001/63(4)/040502(4)/$20.00

TABLE I. Energy convergence for $4\ ^1F$ and $8\ ^1K$ states of He. Reference data in bold characters are from Ref. [6].

$4\ ^1F$			$8\ ^1K$		
(λ,ℓ)	Size	$-E$ (a.u.)	(λ,ℓ)	Size	$-E$ (a.u.)
(0,3)	24	2.031249981	(0,7)	24	2.00781249999999
(1,2)	48	2.031252264	(1,6)	48	2.00781250587709
(1,4)	72	2.031255076	(1,8)	72	2.00781251256537
(2,3)	96	2.031255095	(2,5)	96	2.00781251256693
(2,5)	120	2.031255122	(2,7)	120	2.00781251256816
(3,4)	144	2.031255123	(2,9)	144	2.00781251257019
(3,6)	168	2.031255124	(3,4)	168	2.00781251257020
−2.03125514438175			**−2.00781251257023**		

by Greek letters the nonlinear parameter κ and the radial, orbital, and magnetic quantum numbers ν, λ, and μ, while Roman letters k, n, ℓ, and m are used for electron 2. $\Lambda^{LM}_{\lambda\ell}$ denotes the bipolar spherical harmonics [16]. Atomic units are used throughout this work.

The difficulty in describing HAESs arises from the fact that two distinct regions of space are associated with the electron clouds: a region close to the nucleus for the inner electron cloud, and a region at large distance from the nucleus for the outer electron cloud. An efficient expansion for the wave function should contain both distance scales and span the two regions simultaneously. SFs are suitable for this purpose because (i) they form a complete basis set; (ii) they are exact solutions of the Schrödinger equation for a single electron in the field of the nucleus; (iii) they depend on a nonlinear parameter κ and an index n, which both act like spatial dilation factors. Indeed, for n and ℓ fixed, decreasing κ increases the radial spread of the SF $S^{\kappa}_{n\ell}(r)$, and similarly when n increases with κ and ℓ being fixed. Therefore, nonlinear parameters and radial indices of SFs could be adjusted in the basis in order to span the two regions mentioned earlier. This requires the basis to be built in such a way that the nonlinear parameter and the number of SF, attributed to one electron could be different from those attributed to the other [17].

In practice, we introduce a *set of Sturmian functions* (SSFs), i.e., a combination $[\kappa_s,\nu_>;k_s,n_>]$ involving the SF $S^{\kappa_s}_{\nu,\lambda}(r_1)$ with index $\nu=\lambda+1,\ \lambda+2,\dots,\lambda+\nu_>$ associated with electron 1, and $S^{k_s}_{n,\ell}(r_2)$ with index $n=\ell+1,\ \ell+2,\dots,\ell+n_>$ associated with electron 2. The pairs $(\nu_>,\kappa_s)$ and $(n_>,k_s)$ are to be adjusted for each electron in order to increase the density of SFs in the two regions mentioned above for a HAES. Note that limitations of previous CI Sturmian expansions [18] are due to the use of only one SSF with $\kappa_s=k_s$ and $\nu_>=n_>$. Correlations are included in the basis by mixing different (λ,ℓ) pairs (angular configurations) in the infinite sum in Eq. (2). For each (λ,ℓ) selected in the basis, one or many SSFs [labeled in Eq. (3) by the index s] may be selected. Using many SSFs allows one to span a larger region, and thus permits a simultaneous description of many eigenstates. As the degree of excitation of one electron increases, only $n_>$ or $\nu_>$ (not both) should be increased, and the corresponding nonlinear parameter decreased in the basis. On the other hand, as this degree of excitation increases, correlations between the two electrons decrease and therefore fewer angular configurations are necessary for accurate results, so that the overall basis size can be kept within minimal limits.

TABLE II. Energy absolute values for $n\ ^3S$ states of He, obtained with one and with five SSFs. Reference data are from Ref. [10], except the last three entries, which are taken from Ref. [11].

n	One SSF	Five SSF	Ref. data [10,11]
2	2.1749379	2.1752283	2.175229378237
3	2.0686388	2.0686888	2.068689067472
4	2.0364951	2.03651198	2.036512083098
5	2.0226110	2.022618816	2.02261887230
6	2.0153731	2.015377421	2.01537745299
7	2.0111273	2.011129900	2.01112991951
8	2.0084254	2.008427109	2.00842712199
9	2.0066003	2.0066015077	2.00660151645
10	2.0053099	2.0053107884	2.0053107941
11	2.0043641	2.00436469602	2.004364698
12	2.0036501	2.00365062305	2.003650618
13	2.0030981	2.00309846491	2.003098445
14	2.0026626	2.00266272632	2.00266266
15	2.0023126	2.00231283777	2.00231267
16	2.0020267	2.00202764274	2.00202763
17	2.0017677	2.00179212209	2.00179211
18	2.0014276	2.00159537519	2.00159535
19	2.0009003	2.00142933541	
20	2.0000458	2.00128792977	
21	1.9986305	2.00116651566	
22		2.00106149479	
23		2.00097004347	
24		2.00088992080	
25		2.00081933006	
26		2.00075681712	
27		2.00070119491	
28		2.00065148669	
29		2.00060688281	
30		2.00056670762	

The stationary Schrödinger equation leads to a generalized eigenvalue problem that is solved through diagonalization. To describe doubly excited states, we use the complex rotation technique [19], which consists in performing the transformation $r_j\rightarrow e^{i\theta}r_j$ $(0\leqslant\theta\leqslant\pi/2,\ j=1,2)$ on the Hamiltonian. With this technique, both energies and widths of doubly excited states are simultaneously obtained. Note that the inclusion of many SSFs in the expansion causes near linear dependency problems in the basis that are adequately solved. A full account of this work will be presented in a future publication.

Table I illustrates the energy convergence with respect to (λ,ℓ), for the $4\ ^1F$ and $8\ ^1K$ states of He, using the SSFs [2.0,2;0.39,12] and [2.0,2;0.17,12], respectively. The rate of convergence and the accuracy of the results improve as the asymmetry of the states increases from $4\ ^1F$ to $8\ ^1K$. Indeed, with an expansion of only 144 terms, we obtain energies for

TABLE III. Energies (in a.u.) for the 10 lowest singly excited singlet states in He for $L=7$, $L=10$, and $L=11$. Reference data in bold characters are from Ref. [12].

$L=7$			
n	$-E$ (a.u.)	n	$-E$ (a.u.)
8	2.007812512570227	8	**2.0078125125702293**
9	2.006172849096329	9	**2.0061728490963298**
10	2.005000007388375	10	**2.0050000073883759**
11	2.004132237176717		
12	2.003472226797281		
13	2.002958583559211		
14	2.002551023402907		
15	2.002222224690043		
16	2.001953127055667		
17	2.001730105535418		

$L=10$		$L=11$	
n	$-E$ (a.u.)	n	$-E$ (a.u.)
11	2.004132231822048	12	2.003472222425807
12	2.003472222565847	13	2.002958580052222
13	2.002958580165612	14	2.002551020551360
14	2.002551020644217	15	2.002222222342998
15	2.002222222419846	16	2.001953125102446
16	2.001953125166681	17	2.001730103893669
17	2.001730103947851	18	2.001543209951633
18	2.001543209997729	19	2.001385041616127
19	2.001385041655637	20	2.001250000056391
20	2.001250000090496	21	2.001133786897338

TABLE IV. Energies (E) and widths (Γ) of the $(N,\mathbf{K})=(2,1)$ Rydberg series in He.

	Burgers *et al.* [10]		This work	
n	$-E$ (a.u.)	$-\Gamma/2$ (a.u.)	$-E$ (a.u.)	$-\Gamma/2$ (a.u.)
2	0.777867636	0.002270653	0.777870717	0.002262839
3	0.589894682	0.000681239	0.589890735	0.000686687
4	0.544881618	0.000246030	0.544878876	0.000247469
5	0.526686857	0.000109335	0.526685308	0.000109743
6	0.517641112	0.000056795	0.517640185	0.000056913
7	0.512513488	0.000032992	0.512512896	0.000033021
8	0.509332686	0.000020795	0.509332287	0.000020796
9	0.507225835	0.000013936	0.507225555	0.000013927
10	0.505759104	0.000009790	0.505758903	0.000009779
11			0.504697187	0.000007131
12			0.503904047	0.000005360
13			0.503296011	0.000004131
14			0.502819669	0.000003239
15			0.502439599	0.000002689
16			0.502131536	0.000002091
17			0.501878202	0.000001682
18			0.501667500	0.000001452
19			0.501490409	0.000001275
20			0.501340120	0.000001108

the $4\,^1F$ and $8\,^1K$ states within uncertainties of about 10^{-8} and 10^{-13}, respectively. Note that the SSFs used for these states require very few SFs with larger nonlinear parameters (only two of these are used here), which are mainly involved in describing the inner electron. Also, the use of a SSF with different nonlinear parameters appears to be crucial, because such accuracy and convergence could not be achieved with a SSF having identical nonlinear parameters.

The interest in using many SSFs simultaneously in the expansion is illustrated in Table II. The second column contains results obtained with only one SSF (namely, the set [2.0,2;0.09,25]) used in four angular configurations, leading to 196 basis functions. Since the nonlinear parameter $k=0.09$ associated with the larger number of SFs $n_{>}=25$ is not large, only moderately high Rydberg states ($n=10-15$) are accurate to the order 10^{-7}, which is already comparable with results from available high precision variational calculations for $n=14$ and $n=15$. Energies become less accurate for $n\geqslant 16$ and for $n\leqslant 10$. Results in the third column are obtained with five SSFs adequately chosen to give about 700 basis terms and to span a larger region where electrons are expected. The accuracy of energies is significantly improved compared to the case with only one SSF. Almost all n^3S state energies, with n ranging from 2 to 30, are well converged, with an accuracy ranging from 10^{-6} for low-lying states to at least 10^{-10} for higher Rydberg states. Note that all these energies are obtained simultaneously, with a single basis expansion. Comparing with reference data, it appears that the accuracy of our results increases with n, and that for $n\geqslant 12$ our results turn out to be lower (i.e., more accurate according to the variational principle) than reference data. This is impressive, comparing the basis size used here with the expansion in perimetric coordinates of Ref. [10], where 24 497 terms were used and optimization was performed for each eigenstate separately.

An adequate SSF for describing a given atomic state is consistently obtained by exploiting the fact that $S^{k}_{n,\ell}(r)$ describes an electron of energy $\mathcal{E}=-k^2/2=-Z^2/2n^2$, in the field of a nucleus of charge Z [15]. Indeed, consider, for example, a bound state of He, with electron 1 in the 1s state, and electron 2 in an excited state with principal quantum number n_2. These electrons experience effective charges 2 and $Z-\sigma$, respectively, where σ $(0<\sigma\leqslant 1)$ results from screening by the inner electron. Such a state is accurately described by including in the basis expansion, a SSF involving $S^{\kappa_s}_{\nu,\lambda}(r_1)$ with $\kappa_s=2$, and $S^{k_s}_{n,\ell}(r_2)$ with $k_s=(Z-\sigma)/n_2$ [i.e., $(Z-1)/n_2\leqslant k_s\leqslant Z/n_2$]. For doubly excited states, adequate SSFs are determined similarly.

An optimization of nonlinear parameters for each eigenstate, as in standard variational calculations, may give energies with the same accuracy as in Table II, with a smaller basis size. However, this optimization leads to a loss of precision for high Rydberg states [12]. Therefore, instead of such a procedure, we use several SSFs with nonlinear parameters covering a range of suitable values. As it appears from a comparison of the second and third columns in Table II, this gives high precision for many states in a single calculation, with no significant gains by optimization. The price to pay is an increase of the basis size. This way, we have been able to perform calculations with n as high as 70 and L as high as 15.

Energies obtained for the first ten singlet bound states for $L=7$, $L=10$, and $L=11$ are presented in Table III. For given L, energies have all been obtained simultaneously using a single basis expansion. The purpose here is to illustrate the efficiency of our method for large L $(L\geqslant 8)$, where no *ab initio* calculations have been performed. A comparison of our results with high precision variational calculations of Ref. [12] shows an agreement within 10^{-15} for $L=7$, and also indicates that the accuracy of our results increases with increasing L and n.

We now show that our method applies equally well to high-lying doubly excited states. Results obtained for $\theta=0.2$ are presented in Table IV in comparison with data from Ref. [10] for a doubly excited Rydberg series below the $2s$ threshold. We use the $(N,\mathbf{K},n)$ nomenclature [20], where N and n respectively denote the principal quantum numbers for the inner and outer electrons, and $\mathbf{K}$ is related to the angle between the two electrons. For small n, where the cusp influence is important, our results (energies and widths) agree with reference data within 10^{-5} a.u. As n increases, this agreement improves, and for $n>8$ the accuracy of our results is better than 10^{-7}. Here again, a single basis expansion has been used to simultaneously obtain all results presented in Table IV.

In conclusion, we have shown that although CI fails to accurately describe atomic states where the cusp effect is important, it may be the best approach when dealing with HAESs, provided that it is implemented in a way that accounts for the asymmetry of the two electrons. This work provides an *ab initio* CI approach for obtaining accurate nonrelativistic energies for high singly and doubly excited states in heliumlike atoms. The method is fast, requires smaller basis sizes than standard CI methods, and contrary to traditional variational techniques, becomes increasingly accurate as the degree of excitation of one of the electrons increases. Our calculations also extend *ab initio* techniques to the domain of large L $(L\geqslant 8)$, where asymptotic expansions have been considered as the only reliable approach. The extension of this work to account for mass-polarization, relativistic, and QED effects is straightforward. In addition, its extension to three (or more) electron systems would not involve significant difficulties compared to standard CI.

G.L.K is grateful for the hospitality enjoyed at Université Catholique de Louvain and acknowledges partial support from the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant No. DE-FG03-96ER14646.

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