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Atomic Wave Functions by Rotational Projections of Floating Orbitals

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Floating orbitals and the rotational projector operators defined by Percus and Rotenberg, are used to obtain approximate wavefunctions for the ground states of He-like ions and for the first excited ^1P state of helium.

Mit Hilfe von "Floating Orbitals" und Rotationsprojektionsoperatoren, wie sie von Percus und Rotenberg definiert worden sind, werden näherungsweise Wellenfunktionen für die Grundzustände von He-ähnlichen Ionen und für den ersten angeregten He-Zustand ^1P erhalten.

The present paper reports the results obtained with a simple procedure based on the idea of different orbitals for different spins [1] together with the "floating gaussian" technique [2], which is able to take into account part of the correlation energy. Some preliminary results obtained with this procedure were already reported for He [3]. Here the procedure is described in a more detailed way and results for He-like systems in their ground states and an application to an excited state of He, $(1s\,2p)$ ^1P are given.

In the ground state of He-like atoms an easy way of introducing electron correlation, especially the angular correlation, is to displace the two space functions on opposite sides of the nucleus [3]. However this procedure involves two main difficulties: 1) a substantial loss in potential energy occurs as a result of taking away charge from the nucleus, and 2) the resulting wavefunction has no longer the required symmetry. As far as the first difficulty is concerned, a possible solution is to assume that the one-electron functions can be written as linear combination of the form

$$\varphi_i = \sum_k \lambda_k^i \varphi_k(\boldsymbol{r} - \boldsymbol{\delta}_k^i) \tag{1}$$

or more generally

$$\varphi_i = \int_0^\infty \lambda_i(\delta)\, \phi(\boldsymbol{r} - \boldsymbol{\delta})\, d\delta \tag{1a}$$

where $\phi_k(\boldsymbol{r}-\boldsymbol{\delta}_k^i)$ are orbitals centred at points, defined by the vectors $\boldsymbol{\delta}_k^i$, along an oriented line containing the nucleus and where λ_k^i and $|\delta_k^i|$ are taken as variational parameters. In the following we shall deal only with a discrete two-terms expansion, where one term is on the nucleus and the other at a distance δ_i:

$$\varphi_i(\boldsymbol{r})=\phi_{i0}(\boldsymbol{r})+\lambda_i\phi_{i1}(\boldsymbol{r}-\boldsymbol{\delta}_i) \tag{2}$$

As far as the lack the correct symmetry is concerned one can solve the difficulty by averaging the rotations of the impure state, with a suitable weight factor. This can be accomplished by the use of the formalism of rotational projectors introduced by Percus and Rotenberg [4] $\boldsymbol{O}_{JM}$, defined by the following equation:

$$\begin{aligned}\boldsymbol{O}_{JM}\Psi=\frac{2J+1}{8\pi^2}\iiint e^{iM(\phi+\chi)}\cos^{2M}(\Theta/2)\\ \cdot F[M-J,1+M+J,1;\sin^2(\Theta/2)]\,R_{\phi\theta\chi}S_{\phi\theta\chi}\,\Psi\sin\theta\,d\phi\,d\theta\,d\chi\end{aligned} \tag{3}$$

where Ψ is the impure state function and $\boldsymbol{O}_{JM}\Psi$ is the corresponding projected wavefunction of definite angular momentum J and its z component M. In Eq. (3) the integration variables ϕ, θ, χ are Eulerian angles and R, S are rotation operators in the ordinary and spin space respectively. The calculation of the expectation value of the hamiltonian with the projected wavefunction can be greatly simplified since: 1) the hamiltonian operator commutes with the projector $\boldsymbol{O}_{JM}$ [5]. The expectation value of the energy thus becomes

$$\langle H\rangle=\frac{\langle\boldsymbol{O}_{JM}\Psi|H|\,\boldsymbol{O}_{JM}\Psi\rangle}{\langle\boldsymbol{O}_{JM}\Psi|\boldsymbol{O}_{JM}\Psi|}=\frac{\langle\Psi|H|\,\boldsymbol{O}_{JM}\Psi\rangle}{\langle\Psi|\boldsymbol{O}_{JM}\Psi\rangle} \tag{4}$$

2) the spin factor for singlet states is left unchanged by the projection; 3) the order of the integrations in Eq. (4) may be interchanged and one can integrate first over the space coordinates and then over the Eulerian angles ϕ, θ and χ; 4) when states with $M=0$ are considered, a significant simplification in the expression of the projector $\boldsymbol{O}_{JM}$ is obtained. In this case, as it has been pointed out in the previous paper [3], a suitable choice of the reference system for the Eulerian angles makes the integrations over the variables φ and χ easily performed, resulting in a constant factor.

Ground State

In this section we describe the results obtained for some He-like systems in their ground state ^1S. According to Eq. (2) the orbitals φ_i are taken to be linear combinations of two STO – 1*s*, the first at the nucleus and the second at distance δ_i from it. Therefore we will write the total (unnormalized) wavefunction in the form:

$$\begin{aligned}\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)=\boldsymbol{O}_{00}\boldsymbol{A}[(e^{-\zeta_1 r_1}+\lambda_1 e^{-\zeta_1'|\boldsymbol{r}_1-\boldsymbol{\delta}_1|})(e^{-\zeta_2 r_2}+\lambda_2 e^{-\zeta_2'|\boldsymbol{r}_2-\boldsymbol{\delta}_2|})]\\ \cdot[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\end{aligned} \tag{5}$$

where O_{00} and A stand for rotational projector and antisymmetrizer respectively. If the ζ_i's, λ_i's and δ_i's are considered as adjustable parameters, function (5) contains as particular cases: 1) the uncorrelated single determinant for $\lambda_1 = \lambda_2 = 0$ and $\zeta_1 = \zeta_2$; 2) the conventional DODS approach of Hylleraas and Eckart [1] for $\lambda_1 = \lambda_2 = 0$ and $\zeta_1 \neq \zeta_2$. In our case the optimisation of variational parameters is performed after the projection, and when function (5) is optimized it corresponds to a restricted form of the Extended Hartree-Fock for He-like ions. Therefore one cannot expect to obtain from (5) the exact value of the energy, which requires, in that scheme, the use of hypercomplex spin orbitals [6]. It is easy to see that many centre integrals are needed for the computation of the energy in the present scheme. Therefore it was found convenient to expand each STO appearing in Eq. (5) as a linear combination of gaussian-type orbitals (GTO). A three term expansion according to McWeeny and Huzinaga [7] was considered adequate to approximate each STO for the present purposes. The optimisation of non-linear variational parameters was carried out by a simple modification of the procedure used by Roos *et al.* [8].

Table 1. Optimum values of variational parameters, computed total energy and correlation energy (a.u.) for H^-, He, Li^+

	H^-	He	Li^+
ζ_1	2.636	5.712	12.884
ζ'_1	0.372	2.086	3.290
δ_1	1.991	0.167	0.127
λ_1	21.831	11.348	20.187
ζ_2	3.768	3.547	6.831
ζ'_2	1.051	1.265	2.050
δ_2	− 0.550	− 0.601	− 0.201
λ_2	16.159	9.712	15.513
Total energy	− 0.51693	− 2.88780	− 7.26258
Correlat. energy	0.02910 (73%)	0.02613 (62%)	0.02618 (60%)
Exact energy [11]	− 0.52775	− 2.90372	− 7.27993
Radial limit [12]	− 0.51449	− 2.87903	− 7.25249
Best single ζ	− 0.4727	− 2.84765	− 7.22266
Conventional DODS [9]	− 0.5133	− 2.8757	− 7.2490

In Table 1 the computed total energies and correlation energies are reported together with optimum values of variational parameters. The comparison of total energies with the uncorrelated best-ζ single determinant and the DODS values of Shull and Löwdin [9], reported in the same Table 1, is satisfactory. The fraction of correlation energy here computed are beyond the limit of radial correlation. This means that, as expected, the procedure here proposed allows the introduction of a significant amount of angular correlation. In the case of

H^- the present results (-0.5169 a.u.) are better than the value (-0.5150 a.u.) computed by Banyard [10] by his configuration interaction-floating-orbital (CIFO) method. The wavefunction considered by this author is closely related to (5), buth with important differences. The CIFO function is a complete configuration interaction built from three 1s-STO, one of them centred on the nucleus, the other two being symmetrically placed at the two opposite sides of the nucleus itself. Thus the main differences between Banyard's and the present function can be summarized as follows: 1) function (5) has the correct spherical symmetry; 2) function (5) is equivalent to a restricted rather than to a complete CI; 3) the STO displaced from the nucleus are free to have different exponential factors and distances from the nucleus.

As far as the wavefunctions are concerned, qualitative information can be obtained by examining the shape of the two optimized orbitals for each system. In Fig. 1 are reported the sections of orbitals φ_1 and φ_2 for He in a plane containing the three centers of the STO's, together with the corresponding sections of the orbitals optimized by Shull and Löwdin in the conventional DODS scheme [9].

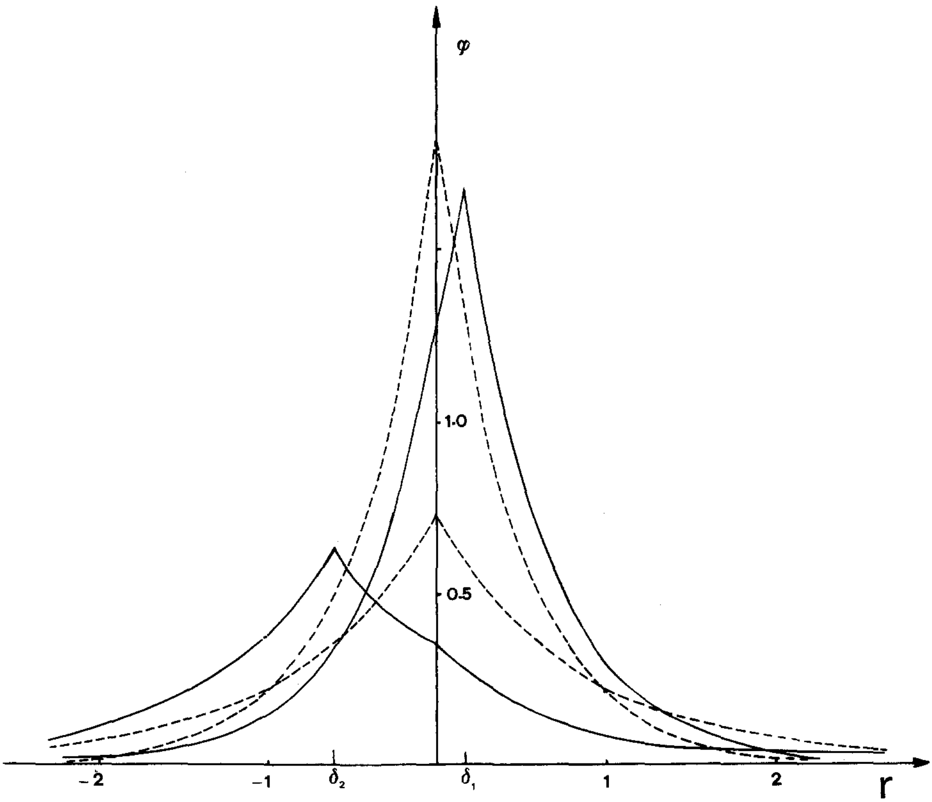

Fig. 1. Sections of the optimum orbitals in a plane containing the centers of the STO's, in case of He. Full lines refer to the orbitals described in this paper and dashed lines to the orbitals of Shull and Löwdin

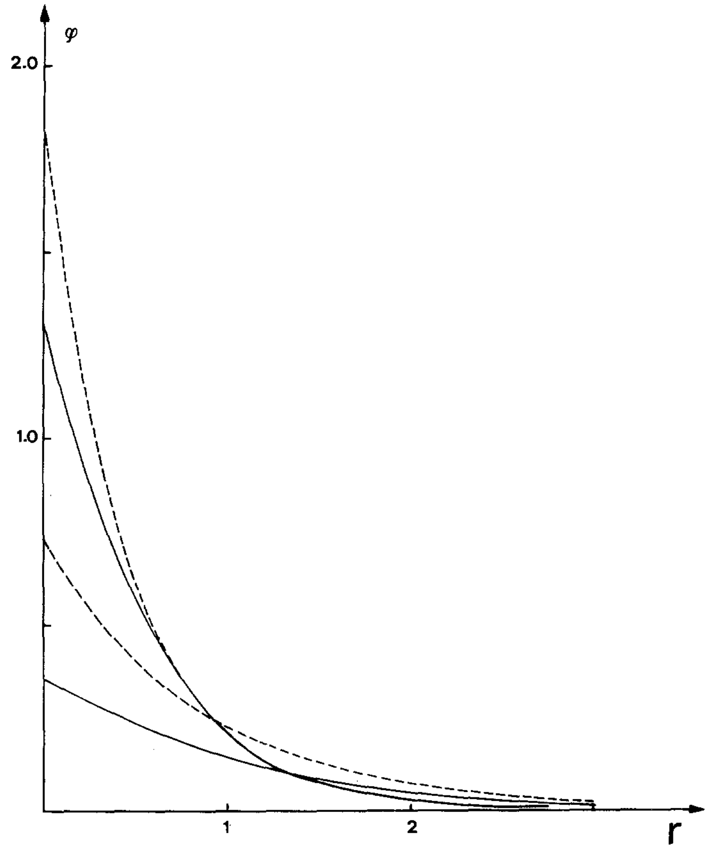

Fig. 2. Sections of the optimum orbitals in a plane perpendicular to that of Fig. 1. Full lines: this paper; dashed lines: Shull and Löwdin

One of the orbitals is more contracted and localized near to the nucleus, while the other is diffuse and has its maximum at large distance from nucleus. This is certainly related to the requirement of introducing radial correlation. In Fig. 2 are reported the sections of the same orbitals in the plane perpendicular to that of the previous figure and containing the nucleus. In this case the differences among the orbitals are less pronounced.

It should be pointed out that, relaxing the restriction that ϕ_0 and ϕ_1 in Eq. (2) are STO's, one can obtain better energies than those reported above. A simple example of such functions was obtained by arbitrarily putting in Eq. (2)

$$\begin{aligned} \varphi_1 &= \sum_{j=1}^{3} c_j \exp(-\alpha_j \eta_1 r^2) + \lambda_1 \sum_{j=4}^{5} c_j \exp[-\alpha_j \eta'_1 (r-\delta_1)^2] \\ \varphi_2 &= \sum_{j=1}^{2} c_j \exp(-\alpha_j \eta_2 r^2) + \lambda_2 \sum_{j=3}^{5} c_j \exp[-\alpha_j \eta'_2 (r-\delta_2)^2] \end{aligned} \tag{6}$$

where the coefficients c_j and α_j are chosen in such a way as to give, for $\eta_i = \eta'_i = \lambda_i = 1$ and $\delta_i = 0$, a five terms gaussian expansion of the two "different orbitals for different spins" of Shull and Löwdin [9]. The λ, η and δ parameters were optimized for He and the corresponding minimum energy was found to be -2.89170 a.u. corresponding to the 71% of the correlation energy, to be compared with 62% reported in Table 1. The function defined by orbitals (6) could certainly be improved or extended. Unfortunately this problem appears to be complicate and brute force optimisation of many non linear parameters seems to be unavoidable. For these reasons it was decided not to pursue this approach further.

Application to Excited States

It follows from the previous discussion that the present method, in principle, can be applied to states of symmetry different from that of the ground state as well. To test the applicability of the method, we have computed the total energy of the ^1P state of He atom. The trial function used is again of the type (5), with the projector replaced by the appropriate one for this state, $\boldsymbol{O}_{10}$. The 1*s* function centered on the nucleus has been approximated again by a three term gaussian expansion according to McWeeny [4] and Huzinaga [5], while the orbitals at the distance δ_i have been approximated by the following two-term expansion

$$\varphi_i = 0.82018 \exp[-0.131373(r-\delta_i)^2 \eta_i^2] + 0.274057 \exp[-0.852787(r-\delta_i)^2 \eta_i^2] \quad (7)$$

where η_i is a scaling parameter. This two-term expansion roughly simulates the radial part of a 2*p* Slater orbital. With this simple wave-function a total energy of -2.10768 a.u. has been obtained[1], which compares favourably with the experimental value of -2.12384 a.u. It must be underlined that the value computed here was obtained from an impure state function Ψ built on only with 1*s* Slater functions. Nevertheless the projected wavefunction $\boldsymbol{O}_{10}\Psi$ can be considered, on the basis of the energy value obtained, a reasonably accurate wavefunction for ^1P state of He. The energy value could certainly be improved, using in the wavefunction orbitals of *p* type together with orbitals of *s* type. Here we wanted only to show that the method can be satisfactorily applied to states of symmetry different from that of the ground state and we believe that the computation just described fulfills this purpose.

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[1] The optimum parameters are:

$\zeta_1 = 1.260$; $\zeta'_1 = 1.879$; $\delta_1 = 0.010$; $\lambda_1 = 0.968$

$\zeta_2 = 0.820$; $\zeta'_2 = 0.484$; $\delta_2 = 2.692$; $\lambda_2 = -1.134$

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