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Helium States

I. Novel Wave Functions for Singly Excited ^1S States

DAVID M. SCHRADER

Chemistry Department, University of Iowa, Iowa City, Iowa 52240

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Wave functions for the 2^1S, 3^1S, and 4^1S states of helium are calculated using as trial wave functions screened hydrogenic orbitals which have the coordinates $r_<$ and $r_>$ as arguments. Direct minimization of the energy expression for each state, without assuming orthogonality to any lower state, gives quite reasonable results. In the case of the 2^1S state and no other, the energy as a function of the variational parameters exhibits two minima, the deeper of which is shown by overlap considerations to correspond to the ground state. Our results are compared to those obtained with the Eckart-type screened hydrogenic wave functions.

2^1S, 3^1S, 4^1S-Zustände von He werden mit Variationsfunktionen berechnet, die aus wasserstoffähnlichen Orbitalen aufgebaut sind, welche als Argumente $r_<$ und $r_>$ enthalten. Die Energieminimisierung wird vorgenommen, ohne Orthogonalität auf den tieferen Zuständen zu berücksichtigen. Nur im Falle der 2^1S-Funktion treten zwei relative Energieminima auf, von denen das tiefere dem Grundzustand entspricht.

Les fonctions d'ondes des états 2^1S, 3^1S et 4^1S de l'hélium sont calculées en utilisant comme fonctions variationnelles des orbitales hydrogénoïdes à constante d'écran ayant les coordonnées $r_<$ et $r_>$ comme arguments. Une minimisation directe de l'énergie pour chaque état, sans aucune contrainte d'orthogonalité à des états d'énergie inférieure, donne des résultats raisonnables. Dans le cas de 2^1S seulement, l'énergie présente deux minima en fonction des paramètres variationnels; le plus bas des deux correspond, d'après des considérations de recouvrement, à l'état fondamental. Nos résultats sont comparés à ceux obtenus avec des fonctions d'onde hydrogénoides du type d'Eckart.

Introduction

One of the principal activities of quantum chemists in recent years has been to seek simplifications in methods of calculating wave functions. Much of this effort has been directed at the ground state of the helium atom, where the problem is somehow to account for the correlated motions of the two electrons without introducing prohibitive quantities of additional calculation. One of the more ingenious suggestions, due to SKVORTSOVA, SHUGUROV, and ERINGIS [1] is to express a trial ground state wave function as

$$\Psi(\mathfrak{r}_1, \mathfrak{r}_2) = \varphi(r_<)\,\psi(r_>)\,, \tag{1}$$

where $r_>$ and $r_<$ are the lesser and greater, respectively, of r_1 and r_2. Such a function will introduce radial correlation by allowing the inside electron to have a different distribution than the outside electron. The idea was first used in a calculation by SNYDER and PARR [2], who approximated the functions φ and ψ as screened exponentials:

$$\varphi = e^{-ar_<}$$
$$\psi = e^{-br_>} \,. \qquad (2)$$

The variationally determined parameters are $a = 1.8465$ and $b = 1.5103$, which give an energy of -2.8727 au, results which were later confirmed by SCHWARTZ [3]. This energy is considerably more accurate than that obtained with a screened exponential without correlation,

$$\Psi = e^{-a\,(r_1 + r_2)}$$

($a = 1.6875$, $E = -2.8476$) and is somewhat more accurate even than the Hartree-Fock result, -2.8617. It is practically as good as the energy obtained by ECKART [4] who used a screened exponential wave function with radial correlation:

$$\Psi = e^{-ar_1 - br_2} + e^{-br_1 - ar_2}$$

($a = 1.1885$, $b = 2.1832$, $E = -2.8757$). The exact nonrelativistic energy of the ground state is -2.9037 au.

Our interest here is in some of the helium excited states which belong to the same symmetry classification as the ground state. The problem in calculating the energies of such states is to assure the existence of a variational principle which guarantees lower bounds on calculated energies appropriate to the states of interest. If one does not have such a bound, one's calculated energy might be seriously in error, and one's wave function might bear no resemblance to the (unknown) exact wave function. HYLLERAAS [5] observed a long time ago that the n^{th} lowest root of the secular equation is an upper bound to the energy of the n^{th} lowest state. ECKART [4] and VINTI [6] orthogonalized excited state wave functions to approximate lower state wave functions, thus assuring a proper variational principle, but at the same time, adding the inaccuracies of the ground state wave function to those of the excited state. Various aspects of the problem are still under investigation [7—9].

Our own approach is rather direct and springs from our desire to find reliable yet simple theoretical methods which do not entail extensive and expensive calculations. We use wave functions of the form (1), in which we make φ a screened $1s$ orbital, and ψ a screened hydrogenic ns orbital, and minimize the energy *without* regard to lower states of the same symmetry.

In starting this calculation our thought was that the function (1) is particularly suitable for excited states since the outer orbital always contains the outer electron regardless of its identity; one never finds the excited electron inside the unexcited electron; and this peculiar physical aptness of (1) *might* reflect itself mathematically by providing an accurate minimum in the energy corresponding to the $(1sns)^1S$ state. Our expectations were confirmed, as we show below. The minimum for the 2^1S State turned out to be a relative minimum. For the 3^1S and 4^1S states absolute minima were found.

Minimizing the energy in the neighborhood of a relative rather than an absolute minimum is not a new idea with us. HORAK [10] has studied the 2^1S state of helium and the K-state of neon by means of relative minimization, and recently BAGUS [11] has reported extensive Hartree-Fock calculations on the X-ray states of noble gas atoms.

Calculations and Results

Our orbitals are:

$$\begin{aligned}
\varphi(r) &= e^{-r} \\
\psi_2(r) &= (2 - r)\, e^{-r/2} \\
\psi_3(r) &= \left(3 - 2r + \frac{2}{9} r^2\right) e^{-r/3} \\
\psi_4(r) &= \left(4 - 3r + \frac{1}{2} r^2 - \frac{1}{48} r^3\right) e^{-r/4}
\end{aligned} \tag{3}$$

and the wave function for the $(1sns)^1S$ state is

$$\Psi = \varphi(akr_<)\, \psi_n(kr_>)\,. \tag{4}$$

Since our wave function has a discontinuous first derivative at $r_1 = r_2$, we calculate the kinetic energy as

$$T(k, a) = \tfrac{1}{2} \iint d\mathfrak{r}_1\, d\mathfrak{r}_2\, [(\nabla_< \varphi)^2 \psi_n^2 + \varphi^2 (\nabla_> \psi_n)^2]/N \tag{5a}$$

where

$$N = \iint d\mathfrak{r}_1\, d\mathfrak{r}_2\, \varphi^2 \psi_n^2\,. \tag{5b}$$

This avoids the problem of the domain boundary discussed by HIRSCHFELDER and NAZAROFF [12]. The potential energy is

$$\begin{aligned}
V(k, a) &= \iint d\mathfrak{r}_1\, d\mathfrak{r}_2\, \varphi^2 \psi_n^2 \left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right) / N \\
&= \int_0^\infty r_1^2\, dr_1 \int_0^\infty r_2^2\, dr_2\, \varphi^2 \psi_n^2 \left(-\frac{Z}{r_<} - \frac{Z}{r_>} + \frac{1}{r_>}\right) / N\,.
\end{aligned} \tag{6}$$

We assumed the validity of the virial theorem, since one can apparently lower (or at least one will fail to raise) a root of a secular equation by scaling the coordinates of a trial wave function. We have accomplished this by minimizing $-V^2(1,a)/4T(1,a)$ with respect to a. The optimum value of k is, of course, $-V(1,a)/2T(1,a)$. The results for the 2^1S, 3^1S, and 4^1S states are given in Fig. 1, 2, and 3 and Tab. 1.

The most striking feature of Fig. 1 is the deep minimum at $a = 0.3175$. The corresponding energy is -2.2398 au, which is about 15% of the way down from the 2^1S energy to the ground state energy. We performed an auxiliary calculation which identifies this absolute minimum as a poor approximation of the ground state.

We calculated the overlap of our 2^1S function with HYLLERAAS' 6-term ground state function [13] and PERKINS' 11-term 2^1S function [14], which he obtained by minimizing the second root of the secular equation. The overlap of HYLLERAAS' 1^1S function with our 2^1S function is 0.9267 at $a = 0.3175$, and -0.0244 at $a = 1.7250$. The overlap of PERKINS' 2^1S with our 2^1S function is 0.0172 at $a = 0.3175$ and 0.9979 at 1.7250. The extrema and nodes of the overlaps of the HYLLERAAS' and PERKINS' functions with our 2^1S function are given in Tab. 2.

The values of the scaled parameters for the relative minimum are $ka = 1.9997$ and $k = 1.1593$, which are reasonable values for the 2^1S state. On the other hand, the absolute minimum occurs for the rather unphysical values $ka = 1.6282$ and

$k = 5.1284$. These results clearly identify the absolute minimum of curve A in Fig. 1 as corresponding to a poor approximation of the ground state, and the relative minimum as a good approximation of the 2^1S state.

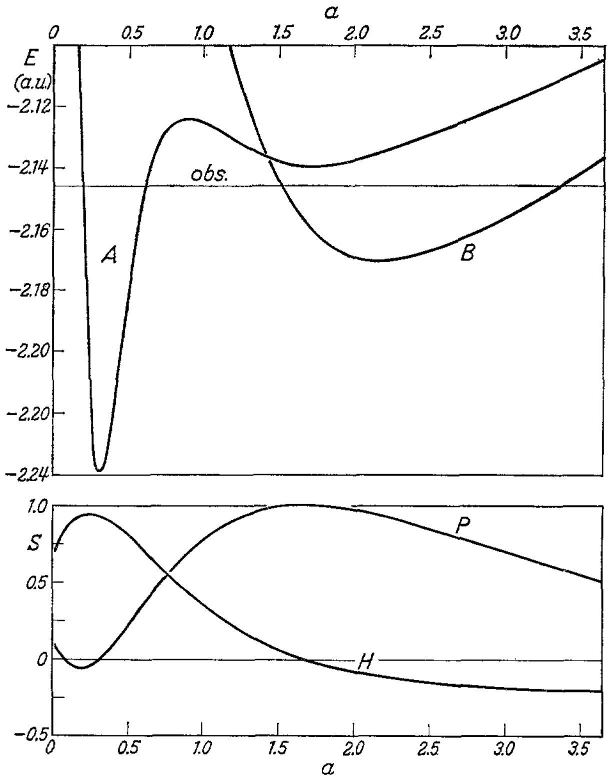

Fig. 1. Energy and overlap results for 2^1S state. Curve A is the energy for our wave function, B that for the Eckart-type wave function, Eq. (7). The observed energy of the state is indicated. Curves H and P are the overlaps between our 2^1S function with the ground-state Hylleraas function and Perkins' 2^1S function, respectively

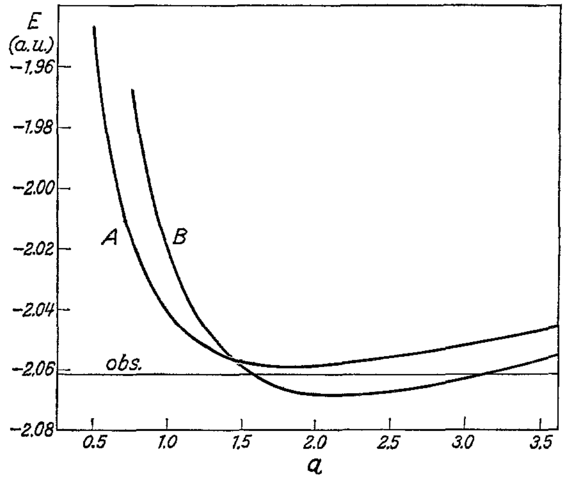

Fig. 2. Energy of the 3^1S state resulting from our function (curve A) and from the Eckart-type function (curve B)

We ascribe no physical significance to the maximum in the curve.

Also in Fig. 1 is the energy one obtains from an Eckart-type function:

$$\Psi = \varphi(akr_1)\,\psi_2(kr_2) + \psi_2(akr_1)\,\varphi(kr_2)\,. \tag{7}$$

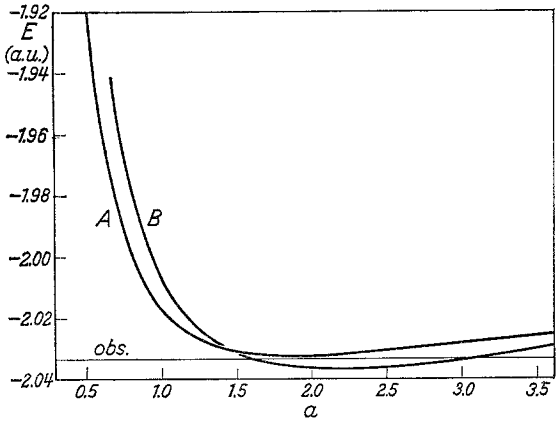

Fig. 3. Energy of the 4^1S state resulting from our function (curve A) and from the Eckart-type function (curve B)

Table 1. *Energies[a] and parameters of 2^1S, 3^1S, and 4^1S states*

State		Parameter Values			Energy[a]	
		a	ka	k	Calculated[b]	Observed
2^1S	Eckart-type [Eq. (7)]	2.189	2.0147	0.920	−2.1707 (−0.0247)	−2.14600
	This Work [Eq. (4)]	1.7250	1.9997	1.1593	−2.139320 (+0.00668)	
3^1S	Eckart-type [Eq. (7)]	2.188	2.004	0.916	−2.0686 (−0.0073)	−2.06130
	This Work [Eq. (4)]	1.8367	2.0005	1.0892	−2.059102 (+0.00220)	
4^1S	Eckart-type [Eq. (7)]	2.150	2.002	0.931	−2.0366 (−0.0030)	−2.03361
	This Work [Eq. (4)]	1.8788	2.0004	1.0647	−2.032653 (+0.00096)	

[a] In atomic units.

[b] Figure in parentheses is the error.

Table 2. *Some of the points in the overlap curves of Fig. 1*

a	Overlap with Hylleraas' function	Overlap with Perkins' function
0.2515	0.9368 (maximum)	
0.2978		0.0000
0.3175	0.9267	0.0172
1.6512	0.0000	
1.7250	−0.0244	0.9979
1.7333		0.9980 (maximum)

It is seen that the energy curve actually goes below the observed value by about 0.0247 au at its minimum.

Figs. 2 and 3 show the results for the 3^1S and 4^1S calculations. These states exhibited no multiple minima. Results are summarized in Tab. 1.

Conclusions

Relative minimization of the energy without benefit of a valid variational principle may be made to yield reasonable results providing the trial wave function is sufficiently suited to the structure of the atom in a given state. Caution in the use of this idea is advisable, however, since the indiscriminate addition of further terms to the trial wave function may serve to destroy its suitability.

Appendix

All the integrals encountered in this work are of the form

$$I(a,b,c,d;i,j,k,l,m) = \iint d\mathfrak{r}_1\, d\mathfrak{r}_2\, e^{-ar_< - br_> - cr_1 - dr_2}\, r_<^i\, r_>^j\, r_1^k\, r_2^l\, r_{12}^m$$

$$= \frac{16\pi^2}{m+2} \sum_{\substack{p=1\\(2)}}^{m+2} \binom{m+2}{p} \left\{ \frac{(i+l+p+1)!}{(a+d)^{i+l+p+2}} \left[\frac{(j+k+m+3-p)!}{(b+c)^{j+k+m+4-p}} - \right.\right.$$

$$\left. - \sum_{q=0}^{j+l+p+1} \frac{(a+d)^q}{q!} \frac{(j+k+m+3-p+q)!}{(a+b+c+d)^{j+k+m+4-p+q}} \right] +$$

$$\left. + \frac{(j+l+m+3-p)!}{(b+d)^{j+l+m+4-p}} \sum_{q=0}^{j+l+m+3-p} \frac{(b+d)^q}{q!} \frac{(i+k+1+p+q)!}{(a+b+c+d)^{i+k+2+p+q}} \right\} \qquad (8)$$

where the (2) beneath the sum over p means p is increased by two in successive terms.

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Prof. D. M. SCHRADER
Chemistry Department
The University of Iowa
Iowa City, Iowa 52240 (USA)