Correlated Atomic Pair Functions by the $e^{-\varrho}$-Method.
I. Ground State 1^1S and Lowest Excited States n^1S ($n > 1$) and n^3S of Helium

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Dedicated to Prof. Hans Kuhn, Switzerland, on the Occasion of his 80th Birthday

Some low n^1S and n^3S states of the helium atom are computed with the aid of the $e^{-\varrho}$ method which formulates the electronic wave function of the 2 electrons as $\Psi = e^{-\varrho}F$, where $\varrho = Z(r_1 + r_2) - \frac{1}{2}r_{12}$ and here $Z = 2$. Both the differential and the integral equation for F contain a pseudopotential $\tilde{V}$ instead of the true potential V that contrary to V is finite. For the ground state, $F = 1$ yields nearly the Hartree-Fock SCF accuracy, whereas a multinomial expansion in r_1, r_2, r_{12} yields a relative error of about 10^{-7}. All integrals can be computed analytically and are derived from one single "parent" integral.

Key words: Electron Correlation; Pair Function; S-states of Helium.

1. Introduction

More than 30 years ago, one of us (F. F. S.) formulated a method [1 - 6] that utilized the well-known cusp condition [7], [8] to replace the actual potential V, that varies between $-\infty$ at the nucleus-electron singularities and $+\infty$ at the electron-electron singularities, by a pseudo-potential $\tilde{V}$ that is finite though discontinuous at the former singularities. This was achieved by introducing an appropriately defined quantity ϱ and setting for the unknown wavefunction $\Psi = e^{-\varrho}F$, where F has to be determined either by solving a particular differential equation or by means of the variational principle that led to an integral equation. Although the expressions were relatively simple the practical treatment with numerical function F, numerical differentiation and integration was very unwieldy [9], particularly under the necessity to use 3-dimensional meshes with varying sizes. Thus this method was abandoned and completely different problems in theoretical chemistry pursued. On the other side the basic ideas and the exactness and at the same time simplicity of the underlying equations were challenging. Now quite recently it turned out

for some cases that F could be formulated in terms of analytical functions in the form of multinomials and that the relevant integrals could also be computed completely rigorously although the coordinates were not orthogonal.

In the case of the ground state of the helium atom one of us (G. A. B.) found by the way [10] that even the extremely simple and bold assumption $F = 1$ yielded an excellent approximation with an error slightly greater than that by a thorough Hartree-Fock-treatment so that we were encouraged to try a simple expansion. As a side effect results for the lowest singlet and triplet S-states were gained.

At this point it should be mentioned that the correlation function of He is a problem that was first treated by Hylleraas [11] in a nonlinear variational treatment and later by Pekeris [12] and Drake [13] in more sophisticated computations to a very high accuracy.

The aim of this paper is not to compete with these virtually exact solutions of the (nonrelativistic) Schrödinger equation of He nor to get more insight into this smallest nontrivial system as such, but to demonstrate the power of the simple $e^{-\varrho}$ method in the hope to expand the experience gained in this easy

to grasp example to more complicated molecules. E. g. it can be conjectured that – in the formulation of orbitals – 2 electrons in the same strongly localized orbital can be formulated as a correlated pair function, whereas the interaction of electrons in different pairs are treated in the frame of the conventional Hartree-Fock SCF theory.

2. Formulation of the Problem

On the way of getting accurate solutions of the Schrödinger equation by means of the $e^{-\varrho}$-method the simplest problem is that of the helium atom in its ground state. It is at the same time the most intensively investigated sample so that the accuracy of the method can be studied very well.

The Schrödinger equation for the spatial function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$, where $\boldsymbol{r}_1 = (x_1, y_1, z_1)$ and $\boldsymbol{r}_2 = (x_2, y_2, z_2)$ are the six spatial coordinates of the two electrons with respect to the nucleus of charge $+2e_0$ as the center of the coordinate system, is in atomic units for quantum state K

$$\mathcal{H}_K \Psi_K = E_K \Psi_K, \tag{1}$$

with

$$\mathcal{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad Z = 2, \tag{2}$$

where $\nabla_i^2 = \partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2$ $(i = 1; 2)$ and $r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$.

The $e^{-\varrho}$-method consists in formulating a quantity ϱ in such a way that the potential energy (here $-2/r_1 - 2/r_2 + 1/r_{12}$) is exactly represented by

$$V = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 \varrho, \quad (N = \text{number of electrons}) \tag{3}$$

which leads to $\varrho = \sum_i \sum_\alpha Z_\alpha r_{i\alpha} - \frac{1}{2}\sum_{i<j} r_{ij}$ in the general case and here to

$$\varrho = Z(r_1 + r_2) - \frac{1}{2}r_{12}. \tag{4}$$

Ψ is then formulated as

$$\Psi = e^{-\varrho}F \tag{5}$$

if we omit index K for the sake of simplicity, and obeys the cusp condition at the singularities of V at $r_1 \to 0$, $r_2 \to 0$ and $r_{12} \to 0$.

Insertion of (4) into (1) with (2) yields because of (3) after cancellation of $e^{-\varrho}$

$$-\frac{1}{2}\nabla_1^2 F - \frac{1}{2}\nabla_2^2 F + (\nabla_1 \varrho \cdot \nabla_1 F) + (\nabla_2 \varrho \cdot \nabla_2 F)$$
$$-\frac{1}{2}(\nabla_1 \varrho)^2 F - \frac{1}{2}(\nabla_2 \varrho)^2 F = EF. \tag{6}$$

This is the Schrödinger-like representation of our problem as a partial differential equation with the *finite* pseudopotential $\tilde{V} = -\frac{1}{2}(\nabla_1 \varrho)^2 - \frac{1}{2}(\nabla_2 \varrho)^2$ instead of the true potential $V = -\frac{1}{2}\nabla_1^2 \varrho - \frac{1}{2}\nabla_2^2 \varrho$ which varies between $-\infty$ and $+\infty$.

The integral representation of the problem which is directly suitable to the application of the variational principle is

$$E = \int e^{-2\varrho}\left[-\frac{1}{2}\nabla_1^2 F - \frac{1}{2}\nabla_2^2 F + (\nabla_1 \varrho \cdot \nabla_1 F)\right.$$
$$\left. + (\nabla_2 \varrho \cdot \nabla_2 F) - \frac{1}{2}(\nabla_1 \varrho)^2 F - \frac{1}{2}(\nabla_2 \varrho)^2 F\right] F dv$$
$$\Big/ \int e^{-2\varrho}F^2 dv, \tag{7}$$

and by means of partial integration

$$E = \int e^{-2\varrho}\left[\frac{1}{2}(\nabla_1 F)^2 + \frac{1}{2}(\nabla_2 F)^2 - \frac{1}{2}(\nabla_1 \varrho)^2 F^2\right.$$
$$\left. - \frac{1}{2}(\nabla_2 \varrho)^2 F^2\right] dv \Big/ \int e^{-2\varrho}F^2 dv. \tag{8}$$

This is the most convenient formulation which is derived from the Schrödinger equation *without any approximation!* (of course the Schrödinger equation itself is not "exact" in the strict sense, as it neglects some minute corrections like relativistic effects).

For comparison: The corresponding expression in terms of Ψ itself would be $E = \int \left(\frac{1}{2}(\nabla_1 \Psi)^2 + \frac{1}{2}(\nabla_2 \Psi)^2 - \frac{1}{2}(\nabla_1^2 \varrho)\Psi^2 - \frac{1}{2}(\nabla_2^2 \varrho)\Psi^2\right) dv / \int \Psi^2 dv$.

Now only r_1, r_2 and r_{12} enter the potential, and in the simplest case of the ground state as a ^1S-state the spatial wave function is only a function of these quantities which form a set of non-orthogonal coordinates. By the way some low excited ^1S-states and some ^3S-states are gained, too.

So $F(r_1, r_2, r_{12})$ and

$$\nabla_1 F = \frac{\partial F}{\partial r_1} \frac{\boldsymbol{r}_1}{r_1} + \frac{\partial F}{\partial r_{12}} \frac{\boldsymbol{r}_{12}}{r_{12}}, \tag{9}$$

$$\nabla_1 \varrho = Z \frac{\boldsymbol{r}_1}{r_1} - \frac{1}{2} \frac{\boldsymbol{r}_{12}}{r_{12}}, \tag{10}$$

$$(\nabla_1 F)^2 = \left(\frac{\partial F}{\partial r_1}\right)^2 + \left(\frac{\partial F}{\partial r_{12}}\right)^2 + 2\frac{\partial F}{\partial r_1} \frac{\partial F}{\partial r_{12}} \frac{(\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12})}{r_1 r_{12}}, \tag{11}$$

$$(\nabla_1 \varrho)^2 = Z^2 + \frac{1}{4} - Z\frac{(\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12})}{r_1 r_{12}} \tag{12}$$

$$\frac{(\boldsymbol{r}_1 \cdot \boldsymbol{r}_{12})}{r_1 r_{12}} = \cos\gamma_{012} = \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1 r_{12}}, \text{ etc.} \tag{13}$$

so that (8) is finally

$$E = \int e^{-4r_1 - 4r_2 + r_{12}} \Big[\frac{1}{2}\left(\frac{\partial F}{\partial r_1}\right)^2 + \frac{1}{2}\left(\frac{\partial F}{\partial r_{12}}\right)^2$$

$$+ \frac{\partial F}{\partial r_1} \cdot \frac{\partial F}{\partial r_{12}} \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1 r_{12}} - \frac{4Z^2 + 1}{8} F^2$$

$$+ \frac{Z}{2} \cdot \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1 r_{12}} F^2 + \frac{1}{2}\left(\frac{\partial F}{\partial r_2}\right)^2 + \frac{1}{2}\left(\frac{\partial F}{\partial r_{12}}\right)^2$$

$$+ \frac{\partial F}{\partial r_2} \frac{\partial F}{\partial r_{12}} \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2 r_{12}} - \frac{4Z^2 + 1}{8} F^2 \tag{14}$$

$$+ \frac{Z}{2} \cdot \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2 r_{12}} F^2 \Big] dv \Big/ \int e^{-4r_1 - 4r_2 + r_{12}} F^2 dv.$$

At this point it is necessary to make definite assumptions about how F depends on r_1, r_2 and r_{12}.

The simplest assumption is that F is a multinomial with coefficients c_k to be determined by the variational method

$$F(r_1, r_2, r_{12}) = \sum_k c_k r_1^{n_{1k}} r_2^{n_{2k}} r_{12}^{n_{12k}} \tag{15}$$

with certain symmetry constraints to be discussed later. Since there are divisions by r_1, r_2, r_{12} in (14), the volume element must contain r_1, r_2, r_{12} at least in the first degree each in order to get easily computable integrals, which is fulfilled as will be shown in the next section.

electron 1

electron 2

r_{12}

r_1

r_2

θ_2

nucleus
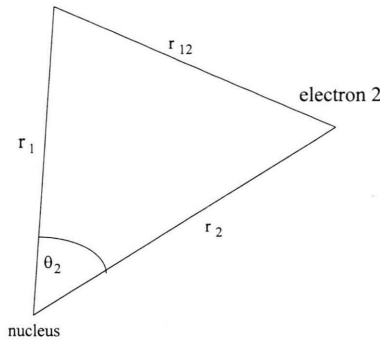
3. Derivation of the Volume Element and the Formulae of the Entering Integrals

Since the coordinates r_1, r_2, and r_{12} are not orthogonal to each other, the derivation of the volume element is not trivial though known, but here we want to develop another method which is much easier and will be helpful in later, more difficult cases. The usual derivation uses the functional determinant and leads to very complicated expressions which simplify finally. This can be done by means of existing strong computer algebra programs like MAPLE and MATHEMATICA e. g. We took MAPLE V, release 4.

We start from the volume element formulated in terms of undoubtedly orthogonal spherical coordinates

$$dv = r_1^2 \sin\theta_1 dr_1 d\theta_1 d\varphi_1 r_2^2 \sin\theta_2 dr_2 d\theta_2 d\varphi_2$$
$$= -r_1^2 \sin\theta_1 dr_1 d\theta_1 d\varphi_1 r_2^2 dr_2 d(\cos\theta_2) d\varphi_2, \tag{16}$$

where θ_1 and φ_1 are relative to a fixed (x_1, y_1, z_1)-system, whereas θ_2 and φ_2 are relative to the vector $\boldsymbol{r}_1$. Then

$$\cos\theta_2 = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2} \tag{17}$$

and

$$d(\cos\theta_2) = \frac{\partial(\cos\theta_2)}{\partial r_{12}} dr_{12}, \tag{18}$$

since θ_2 is independent of r_1 and r_2. As

$$\frac{\partial(\cos\theta_2)}{\partial r_{12}} = -\frac{r_{12}}{r_1 r_2}, \tag{19}$$

$$dv = r_1 r_2 r_{12} dr_1 dr_2 dr_{12} \sin\theta_1 d\theta_1 d\varphi_1 d\varphi_2. \tag{20}$$

In our case everything is dependent only on r_1, r_2 and r_{12} so that by integration over θ_1, φ_1 and φ_2

$$dv = 8\pi^2 r_1 r_2 r_{12} dr_1 dr_2 dr_{12}, \tag{21}$$

which is the known result from the functional determinant method.

The factors r_1, r_2, and r_{12} in (21) have the effect that in (8) together with (11), (12), (15) the lowest possible exponent of r_1, r_2, and r_{12} is 0, respectively.

There exists a basic integral containing these lowest powers,

$$\int e^{-2\varrho} \frac{dv}{r_1 r_2 r_{12}} = 8\pi^2 \int\limits_{r_1=0}^{\infty} \int\limits_{r_2=0}^{r_1} \int\limits_{r_{12}=r_1-r_2}^{r_1+r_2} e^{-2\varrho} dr_{12} dr_2 dr_1$$

$$+ 8\pi^2 \int\limits_{r_2=0}^{\infty} \int\limits_{r_1=0}^{r_2} \int\limits_{r_{12}=r_2-r_1}^{r_2+r_1} e^{-2\varrho} dr_{12} dr_1 dr_2, \tag{22}$$

from which all other integrals with higher powers can be derived. The splitting of the integral results from the property that

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2 \ , \ -1 \leq \cos\theta_2 \leq +1 \tag{23}$$

and thus with

$$|r_1 - r_2| \leq r_{12} \leq r_1 + r_2 \tag{24}$$

$|r_1 - r_2| = r_1 - r_2$ for $r_2 < r_1$, but $|r_1 - r_2| = r_2 - r_1$ for $r_2 > r_1$. So in a general formulation the basic integral is

$$I[0,0,0] = \int\limits_{r_1=0}^{\infty} \int\limits_{r_2=0}^{r_1} \int\limits_{r_{12}=r_1-r_2}^{r_1+r_2} e^{-(\alpha r_1 + \beta r_2 + \gamma r_{12})} dr_{12} dr_2 dr_1$$

$$+ \int\limits_{r_2=0}^{\infty} \int\limits_{r_1=0}^{r_2} \int\limits_{r_{12}=r_2-r_1}^{r_2+r_1} e^{-(\alpha r_1 + \beta r_2 + \gamma r_{12})} dr_{12} dr_1 dr_2$$

$$= \frac{2}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)}. \tag{25}$$

Partial differentiation yields in a somewhat simplified notation for the integral

$$\frac{\partial I[0,0,0]}{\partial \alpha} = -\int e^{-(\alpha r_1 + \beta r_2 + \gamma r_{12})} r_1 dr_1 dr_2 dr_{12}$$

$$= -I[1,0,0] \tag{26}$$

$$= -\frac{2}{(\alpha+\beta)^2(\alpha+\gamma)(\beta+\gamma)} - \frac{2}{(\alpha+\beta)(\alpha+\gamma)^2(\beta+\gamma)}.$$

With $\alpha = \beta = 4$ and $\gamma = -1$ to get $2\varrho = \alpha r_1 + \beta r_2 + \gamma r_{12}$:

$$I[0,0,0] = \frac{1}{36},$$

$$I[1,0,0] = I[0,1,0] = \frac{11}{864} \ ,$$

so that by successive partial differentiation whatever

$$I[n_1, n_2, n_{12}] = \int e^{-2\varrho} r_1^{n_1} r_2^{n_2} r_{12}^{n_{12}} dr_1 dr_2 dr_{12}$$

$$= (-1)^{n_1+n_2+n_{12}} \frac{\partial^{n_1+n_2+n_{12}} I[0,0,0]}{\partial\alpha^{n_1}\partial\beta^{n_2}\partial\gamma^{n_{12}}} \tag{27}$$

is needed can be gained. This again can be easily achieved by MAPLE.

Insertion of (15) into (14) leads together with the abbreviations

$$\begin{aligned}
n_{1kl} &= n_{1k} + n_{1l}, \\
n_{2kl} &= n_{2k} + n_{2l}, \\
n_{12kl} &= n_{12k} + n_{12l},
\end{aligned} \tag{28}$$

to the general variational problem to get the eigenvector matrix $\mathbf{C}$ and diagonal eigenvalue matrix $\mathbf{E}$ by the two step diagonalization (Löwdin orthogonalization) of

$$\mathbf{HC} = \mathbf{SCE} \tag{29}$$

with the matrix element S_{kl} of the overlap matrix as

$$S_{kl} = 8\pi^2 \int e^{-2\varrho} r_1^{n_{1k}+n_{1l}+1} r_2^{n_{2k}+n_{2l}+1} r_{12}^{n_{12k}+n_{12l}+1}$$

$$\cdot \, dr_1 dr_2 dr_{12}$$

$$= 8\pi^2 I[n_{1kl}+1, n_{2kl}+1, n_{12kl}+1] \tag{30}$$

and the matrix element H_{kl} of the energy matrix as

$$H_{kl} = 2\pi^2 \Big\{ 2n_{1k}n_{1l}I[n_{1kl}-1, n_{2kl}+1, n_{12kl}+1] + 2n_{2k}n_{2l}I[n_{1kl}+1, n_{2kl}-1, n_{12kl}+1]$$

$$+ 4n_{12k}n_{12l}I[n_{1kl}+1, n_{2kl}+1, n_{12kl}-1] + (n_{1k}n_{12l}+n_{1l}n_{12k})(I[n_{1kl}+1, n_{2kl}+1, n_{12kl}-1]$$

$$+ I[n_{1kl}-1, n_{2kl}+1, n_{12kl}+1] - I[n_{1kl}-1, n_{2kl}+3, n_{12kl}-1])$$

$$+ (n_{2k}n_{12l}+n_{2l}n_{12k})(I[n_{1kl}+1, n_{2kl}+1, n_{12kl}-1] + I[n_{1kl}+1, n_{2kl}-1, n_{12kl}+1] \qquad (31)$$

$$- I[n_{1kl}+3, n_{2kl}-1, n_{12kl}-1]) - 17I[n_{1kl}+1, n_{2kl}+1, n_{12kl}+1]$$

$$+ 2I[n_{1kl}+2, n_{2kl}+1, n_{12kl}] + 2I[n_{1kl}, n_{2kl}+1, n_{12kl}+2] - 2I[n_{1kl}, n_{2kl}+3, n_{12kl}]$$

$$+ 2I[n_{1kl}+1, n_{2kl}+2, n_{12kl}]) + 2I[n_{1kl}+1, n_{2kl}, n_{12kl}+2] - I[n_{1kl}+3, n_{2kl}, n_{12kl}] \Big\}$$

Note that whenever an integral $I[-1,$ anything, anything] seems to appear (this means that $n_{1kl} = 0$, $n_{1k} = n_l = 0$), a factor n_{1k} or n_{1l} equal to 0 cancels this term, and the same is true for $I[$anything, -1, anything] and $I[$anything, anything, $-1]$. So in (27) n_1, n_2, and n_{12} start with 0 and are truncated at some higher reasonably chosen value to be discussed later.

4. Numerical Results

It was mentioned in the introduction that already the extremely simple assumption $F = 1$ yielded excellent results for He. The matrices $\mathbf{S}$ and $\mathbf{H}$ reduce to scalars

$$S = 8\pi^2 I[1,1,1] \qquad (32)$$

and

$$H = 2\pi^2\big(-17I[1,1,1] + 2I[2,1,0] + 2I[0,1,2]$$
$$- 2I[0,3,0] + 2I[1,2,0] \qquad (33)$$
$$+ 2I[1,0,2] - 2I[3,0,0]\big).$$

Because of the equivalence of electrons 1 and 2 all

$$I[n_1, n_2, n_{12}] = I[n_2, n_1, n_{12}], \qquad (34)$$

so that

$$H = 2\pi^2(-17I[1,1,1] + 4I[2,1,0]$$
$$+ 4I[1,0,2] - 4I[3,0,0]) \qquad (35)$$

and

$$E = \frac{H}{S} = -\frac{17}{4} + \frac{I[2,1,0] + I[1,0,2] - I[3,0,0]}{I[1,1,1]}, \qquad (36)$$

and with

$$I[1,1,1] = -\left.\frac{\partial I[0,0,0]}{\partial\alpha\partial\beta\partial\gamma}\right|_{\substack{\alpha=\beta=4\\\gamma=-1}} = \frac{109}{64\cdot 243},$$

$$I[2,1,0] = -\left.\frac{\partial^3 I[0,0,0]}{\partial\alpha^2\partial\beta}\right|_{\substack{\alpha=\beta=4\\\gamma=-1}} = \frac{1193}{1024\cdot 243},$$

$$I[1,0,2] = -\left.\frac{\partial^3 I[0,0,0]}{\partial\alpha\partial\gamma^2}\right|_{\substack{\alpha=\beta=4\\\gamma=-1}} = \frac{19}{16\cdot 81}, \qquad (37)$$

$$I[3,0,0] = -\left.\frac{\partial^3 I[0,0,0]}{\partial\alpha^3}\right|_{\substack{\alpha=\beta=4\\\gamma=-1}} = \frac{803}{1024\cdot 81}$$

we get for 1^1S of He with $F = 1$

$$E = -\frac{17}{4} + \frac{152}{109} = -\frac{1245}{436} = -2.8555046. \qquad (38)$$

As can be seen from Table 1 this value compares favorably with both the exact corrected value and the Hartree-Fock value. Besides it can be shown that even the virial theorem is exactly fulfilled. So it can be expected that a reasonable power expansion should approach to the exact value with fast convergence.

As can be seen from (25), (26) and (27), all needed integrals belong to the same family of integrals derived from $I[0,0,0]$ by partial differentiation after α, β and γ and insertion of $\alpha = \beta = 4$, $\gamma = -1$. The series of singlet states n^1S and triplet states n^3S differ in their exchange symmetry: as in the case of 2-electron systems the total electronic wave function has to be antisymmetric with respect to electron exchange and is simply the product of a spin and a spatial function, and since futheron the spin function is antisymmetric $\big(\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))\big)$ for

Table 1. 1^1S ground state of He (all energies in atomic units).

Method	E
experimental after subtraction of relativistic effects [12]	-2.90372
Hartree-Fock SCF	-2.86168
quasi exact computation [13]	-2.903724377
$e^{-\varrho}$ with $F = 1$	-2.8555046
$e^{-\varrho}$ with multinomial expansion	-2.903723980

Table 2. $2^{1,3}S$ and $3^{1,3}S$ of He (all energies in atomic units).

2^1S	2^3S	3^1S	3^3S
a) Quasi exact computation [13]:			
-2.1459740	$-2,1752294$	-2.0612720	-2.0686891
b) $e^{-\varrho}$ with multinomial expansion:			
-2.1451772	-2.1750167	-2.0137441	-2.0363848

the singlet, but symmetric $\left(\alpha(1)\alpha(2), \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(2)), \beta(1)\beta(2)\right)$ for the triplet, the wanted spatial function is symmetric for n^1S and asymmetric for n^3S. F is expanced following (15), so the combinations $\frac{1}{\sqrt{2}}\left(r_1^{n_1k}r_2^{n_2k}r_{12}^{n_{12}k} + r_1^{n_2k}r_2^{n_1k}r_{12}^{n_{12}k}\right)$ and $r_1^{n_1k}r_2^{n_1k}r_{12}^{n_{12}k}$ form the set of symmetry-adopted basis functions for n^1S, and $\frac{1}{\sqrt{2}}\left(r_1^{n_1k}r_2^{n_2k}r_{12}^{n_{12}k} - r_1^{n_2k}r_2^{n_1k}r_{12}^{n_{12}k}\right)$ for n^3S. This corresponds to a simple transformation of the basis functions of (15) and a block diagonalization of the matrices **S** and **H**. That means smaller matrices, faster computation, and particularly smaller errors. Inspection of the magnitudes of the different integrals showed that the higher $I[n_1, n_2, n_{12}]$ are for great (> 10) n's many orders of magnitude greater than the lowest $I[0, 0, 0]$ which results in *ill-conditioned* matrices that can finally lead to near-singularities and thus overflows, etc. It turned out for a compromise between high accuracy and computationability to limit the sum of $n_1 + n_2 + n_{12}$ rather than each n singly.

The final result shown in Tables 1 and 2 was achieved by the following treatment: at first all necessary integrals were computed with the aid of MAPLE, which was the most time-consuming step because the necessary procedures cannot be compiled, but run under an interpreter. Then – under FORTRAN 77 to use packages like EISPACK for the eigenvalue procedures – matrices **S** and **H** were computed, symmetry transformed and diagonalized. It turned out to choose

as a maximum value for n_1, n_2 and n_{12} (v. (15)) $n_{max} = 6$, but max $(n_1 + n_2 + n_{12}) = 8$. As the integrals $I[n_1, n_2, n_{12}]$ go up to $n_{1k} + n_{1l} + 3$, e. g. (analogously for n_2 and n_{12}), the highest indices were 15. The variation method part of the computation needed on a PC with Pentium II, 300 MHz, a few seconds.

Since all integrals are over functions without nodes which overlap strongly, **S** is extremely far from being diagonal. In addition the values of its matrix elements extend over many orders of magnitude. This is quite unfavorable to the accuracy of the calculation. Nevertheless the accuracy of the ground state is very high, the relative error being only $1.4 \cdot 10^{-7}$. The higher states show a steep increase of the relative error to about 10^{-4} and 10^{-2}, respectively, but these states should not be very important.

Note that 2^3S and 3^3S are denominated this way for their correspondence to 2^1S and 3^1S, but are actually the lowest and second lowest triplet states!

5. Conclusions

The derivations and results given in the previous sections are specialized with various respects.

1. He is a 2-electron atom, so the wavefunction Ψ is the true wavefunction of the electronic state itself.

2. S-states are symmetric with respect to any spatial symmetry element (planes, rotations axes, point of inversion), so is F. But P, D-, ... states have several spatial antisymmetries, so if F remains symmetric and $e^{-\varrho}$ is always symmetric, some factors like $z_1 z_2$ have to be introduced. This is quite simple, the corresponding ϱ has to be adapted in a simple way, but the problem depends no more only on r_1, r_2, r_{12}. Especially the volume element is more complicated and therefore there are problems with the integrals. Similar considerations appear to complicate the treatment of a bond pair function like in H_2.

3. Real molecules with lone pairs at the atoms and bond pairs between atoms can be formulated as an antisymmetrized product of pair functions to obey the Pauli principle and the equivalence of all electrons, but again difficulties arise at the level of integration.

Finally it should be emphasized that this method is a linear variation problem with unknowns $\{c_k\}$ and E to be determined and with no adaption parameters that could be adjusted to empirical quantities to achieve good agreement with experiment!

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