

# Variational calculations on $H_4^{2+}$ using exponentially correlated Gaussian wave functions

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**Abstract:** The method of exponentially correlated Gaussian (ECG) wave functions is extended to the case of multicenter molecular systems with nuclei arranged in a 3-dimensional space. A particular case of a four-center two-electron system,  $H_4^{2+}$ , is studied by means of the variational approach. The energies reported in this work are the most accurate available to date.

**Key words:** exponentially correlated Gaussians (ECG), Gaussian geminals, variational optimization,  $H_4^{2+}$  ion

## 1. INTRODUCTION

Molecular systems built of protons and electrons, forming various clusters or rings, have been of interest for a long time now [1]. One reason for this interest is their strong analogy to the carbon rings. Another is the relative simplicity of their electronic structure which enables a theoretical treatment at a high level of accuracy. The questions raised in relation to such systems concern their thermochemical stability, pathways of dissociation and ways of stabilization of the unstable conformations. Another interesting issue is the relation of the stability to the topology of the nuclear centers held together by a given number of electrons. Glukhovtsev *et al.* studied theoretically the four-center two-electron (4c-2e) clusters of hydrogens and alkali metals and found that an incomplete description in terms of molecular orbitals may lead to an erroneous answer [2]. The 4c-2e bonding, although rare, can be found in various organic compounds. The  $H_4^{2+}$  system is the smallest species that might model this type of bonding. The stability of  $H_4^{2+}$  depends directly on the competition between the repulsive forces and the binding effect of the two electrons. Glukhovtsev *et al.* investigated a possible existence of the  $H_4^{2+}$  dication from the point of view of the quality of the one-electron basis set in the frames of the Hartree-Fock and MP2 methods [3]. They concluded that the standard value of the exponent in the  $p$  polarization function of the hydrogen atom, usually treated as satisfactory, leads to an incorrect description of the stationary point of the tetrahedral structure. Optimization of this exponent with respect to the energy led to qualitative changes in results and a conclusion that  $H_4^{2+}$  was unstable. They confirmed this assertion later on by increasing the level of theory to the coupled cluster with singles and doubles (CCSD) with a large basis set [4].

The unbound or weakly bound systems require particularly accurate theoretical description with the electron cor-

relation treated at a possibly high level. There are two explicitly correlated methods which for two electron systems are capable of supplying extremely accurate results. One method is based on the Kołos-Wolniewicz (KW) wave functions [5] and the other on the exponentially correlated Gaussian (ECG) wave functions [6]. The KW wave function is a generalization of the James-Coolidge function [7] and, being expressed in elliptic coordinates, it is particularly suited to two-center two-electron systems. The KW method supplied a large number of benchmark-quality results concerning mainly the hydrogen molecule (for a review see Chapter 2 in [6]). Unfortunately, this method has never been generalized to a multicenter case. In contrast, the ECG method is very well suited for description of multicenter systems and simultaneously it is as accurate as the KW method [8]. It is a well known feature of the Gaussian-type functions, usually referred to as the Gaussian Product Theorem, that the product of two Gaussian functions centered at two different points **A** and **B** in a 3-dimensional space gives a single Gaussian function centered at a point **P** lying somewhere on the line connecting the original centers:

$$e^{-\alpha_i r_{iA}^2} e^{-\alpha_j r_{jB}^2} = \exp\left(-\frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j} (\mathbf{A} - \mathbf{B})^2\right) e^{-(\alpha_i + \alpha_j) r_{iP}^2}, \quad (1)$$

where

$$\mathbf{P} = \frac{\alpha_i \mathbf{A} + \alpha_j \mathbf{B}}{\alpha_i + \alpha_j}. \quad (2)$$

This feature allows one to reduce significantly the number of Gaussian centers which, in turn, simplifies greatly an evaluation of molecular integrals. In more detail the ECG method will be described in the following sections. In particular, we shall report on an extension of the ECG programs to a multicenter 3-dimensional case and on accu-

rate variational estimates of the energies of the  $H_4^{2+}$  system in the most important conformations. We note that in the past the ECG methodology was applied to planar systems:  $H_3^+$  [9] and  $H_3$  [10]. There are also calculations by Cencek on nonplanar  $H_5^+$  cation cited in [11] as a ‘personal communication’.

## 2. THE METHOD OF THE EXPONENTIALLY CORRELATED GAUSSIAN FUNCTIONS (ECG)

The stationary Schrödinger equation  $\hat{H}\Psi = E\Psi$  to be solved involves the electronic clamped nuclei Hamiltonian (in atomic units)

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I=1}^N \sum_{i=1}^n \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I=1}^{N-1} \sum_{J=I+1}^N \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad (3)$$

where  $\mathbf{r}_i$  and  $\mathbf{R}_I$  are, respectively, the electronic and nuclear coordinates, and  $Z_I$  are the nuclear charges. In this work we shall be concerned with a specific case of systems built of 4 nuclei with  $Z = 1$  (protons) fixed in a 3-dimensional space and 2 spin-paired electrons. We are going to solve the Schrödinger equation variationally and our trial wave function,  $\Phi$ , is assumed in the form of a properly symmetrized  $K$ -term linear expansion in a 2-electron basis

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^K c_i \phi_i(\mathbf{r}_1, \mathbf{r}_2). \quad (4)$$

The basis functions employed are the Gaussian geminals

$$\phi_i(\mathbf{r}_1, \mathbf{r}_2) = [1 + (12)] \hat{P}_R \times \exp\left(-\alpha_{1i} |\mathbf{r}_1 - \mathbf{A}_i|^2 - \alpha_{2i} |\mathbf{r}_2 - \mathbf{B}_i|^2 - \beta_i |\mathbf{r}_1 - \mathbf{r}_2|^2\right), \quad (5)$$

each containing 5 nonlinear parameters  $\alpha_{1i}$ ,  $\alpha_{2i}$ ,  $\beta_i$ ,  $\mathbf{A}_i$ , and  $\mathbf{B}_i$  to be determined variationally. The projector  $1 + (12)$  ensures that the wave function fulfills the condition of electron undistinguishability, whereas the  $\hat{P}_R$  projector takes care of the spatial symmetry of the function. The spin part of the wave function was integrated out implicitly and the only trace it leaves is the + sign in the former operator.

The representation of the wave function in the Ritz form (4) allows the Schrödinger equation to be converted from its differential form to a more tractable matrix form of the general symmetric eigenvalue problem (GSEP)

$$Hc = \varepsilon Sc, \quad (6)$$

where the elements of the Hamiltonian and overlap matrices  $H$  and  $S$  are given by

$$h_{ij} = \int \phi_i \hat{H} \phi_j d\tau, \quad (7)$$

$$s_{ij} = \int \phi_i \phi_j d\tau. \quad (8)$$

Solving the GSEP gives the linear expansion parameters,  $c_i$ , and the eigenvalues of which the lowest,  $\varepsilon$ , is of our interest.

In the framework of the ECG method, most of the computational effort is spent on finding the optimal values of the nonlinear parameters. The variational principle ensures that for any set of the nonlinear parameters, constrained only by the requirement of the existence of integrals (7) and (8), the eigenvalue  $\varepsilon$  is never less than the exact solution of the Schrödinger equation,  $E$ . This fact gives a freedom in selecting an algorithm of optimization. On the other hand, there is no definite prescription on how to find a global minimum of the multivariable nonlinear functional,  $\varepsilon$ . In practice then, one has to be satisfied by locating one out of many low lying local minima. Taken a 100-term wave function of  $H_4^{2+}$  by way of example, the energy minimum is to be located in a 900-dimensional space of nonlinear parameters. In our approach, coded in a program GEMINI, we employed the Powell’s Conjugate Directions algorithm [12] combined with a random generation of the starting parameters. For the 2-electron systems, the optimization procedure [6, 10], although time consuming, is capable of giving the energy value accurate to a fraction of microhartree and, in particular cases, even of nanohartree [6, 9, 13, 14].

For the 100-term wave function mentioned above, the energy is evaluated ca.  $10^5$  times during the whole optimization process. For this reason, high efficiency of the energy evaluation is a central programming issue. One way to speed up the computation of this iterative process is through employing the so-called updating which relies on a partial utilization of the results computed in the previous iteration. More details on the updating algorithms applied to the evaluation of the energy can be found in Refs. [15–17]. Another way of speeding up the computations is their parallelization. For instance, the process of building the matrices  $H$  and  $S$ , because of the mutual independence of the matrix elements, is an ideal case for the parallel computation [18]. Likewise, the stage of solving the GSEP can be efficiently parallelized although this is not a trivial task [16, 19].

## 3. RESULTS AND DISCUSSION

We studied the following four highest symmetry conformations of the  $H_4^{2+}$  dication: tetrahedral, triangle, square, and linear (see Fig. 1). The explicit form of the  $\hat{P}_R$  projector applied for each configuration is shown in Table 1. The tetrahedral structure belongs to the  $T_d$  point symmetry group consisting of 24 symmetry elements. In this work we lowered the symmetry of the wave function to  $C_{3v}$  with the elements listed in the table.

Table 1. Explicit forms of the spatial symmetry projectors  $\hat{P}_R$  used for particular conformations

Structure	$R$	$\hat{P}_R$ projector
Tetrahedral	$C_{3v}$	$\hat{1} + \hat{P}_{+120} + \hat{P}_{-120} + \hat{P}_{\sigma_{12}} + \hat{P}_{\sigma_{13}} + \hat{P}_{\sigma_{23}}$
Triangle	$D_{3h}$	$\hat{1} + \hat{P}_{+120} + \hat{P}_{-120} + \hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23}$
Square	$D_{4h}$	$\hat{1} + \hat{P}_{+90} + \hat{P}_{+180} + \hat{P}_{+270} + \hat{P}_{13} + \hat{P}_{24} + \hat{P}_{12} + \hat{P}_{34}$
Linear	$D_{\infty h}$	$\hat{1} + \hat{i}$

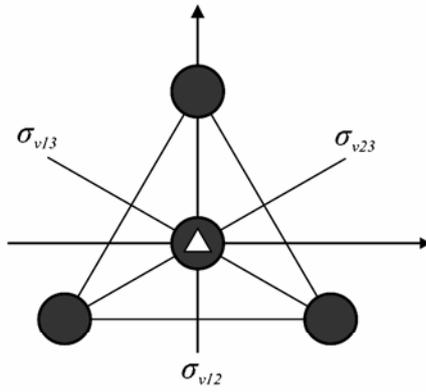
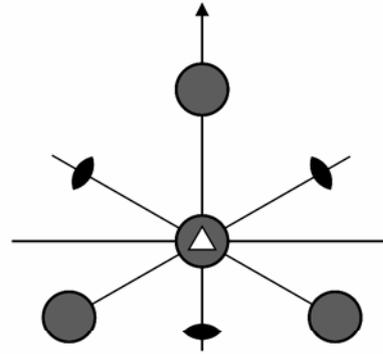
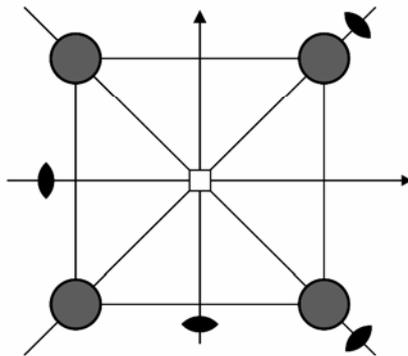
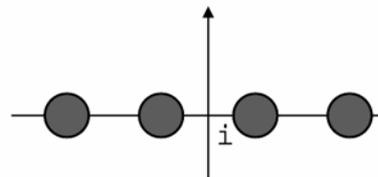
The operation  $\hat{P}_{\pm\omega}$  means a rotation around the main axis of symmetry by the angle of  $\pm\omega$  degrees,  $\hat{P}_{ij}$  – rotation around a twofold axis of symmetry going through the nuclei  $i$  and  $j$ ,  $\hat{P}_{\sigma_j}$  is a reflection in the plane of symmetry (see Fig. 1) perpendicular to the line connecting nuclei  $i$  and  $j$ , finally, the  $\hat{i}$  operator is responsible for an inversion with respect to the origin of the coordinate system. The presence of the projector  $\hat{P}_R$  permits not only the imposition of a correct spatial symmetry of the wave

function but also an implicit increase in the length of the expansion.

Formally, the projector  $\hat{P}_R$  acts on the electron coordinates  $(\mathbf{r}_1, \mathbf{r}_2)$ . Practically, this action can be carried into effect by multiplying the vectors of Gaussian centers  $\mathbf{A}_i$ , and  $\mathbf{B}_i$  by matrices representing particular operations of symmetry. For instance, a rotation of a center  $\mathbf{A}$  around a symmetry axis by an angle  $\omega$  can be written as  $\mathbf{A}' = \hat{P}_\omega \mathbf{A}$ . Assuming that the axis of rotation lies along the Z-axis of the Cartesian coordinate system we can write explicitly

$$\begin{bmatrix} A'_x \\ A'_y \\ A'_z \end{bmatrix} = \begin{bmatrix} \cos \omega & \sin \omega & 0 \\ -\sin \omega & \cos \omega & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} A_x \\ A_y \\ A_z \end{bmatrix}. \quad (9)$$

Analogously, we can represent the remaining symmetry operations listed in Table 1 as

 $C_{3v}$ ,  $R=2.338$  bohr $D_{3h}$ ,  $R=1.227$  bohr $D_{4h}$ ,  $R=2.254$  bohr $D_{\infty h}$ ,  $R=2.422$  bohrFig. 1. The four conformations of the nuclei in  $H_4^{2+}$ , their main elements of the symmetry, and the point group symbols

$$\hat{P}_{\sigma(xz)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \hat{i} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \quad (10)$$

In general, the projection changes only the Gaussian centers and retains the overall shape of a basis function, so that no new type of integrals is needed.

Although  $H_4^{2+}$  contains just two electrons, there are no accurate results on this system available in literature. As mentioned in the Introduction, there are computations of the energy of the  $H_4^{2+}$  system at the HF, MP2, CI, and CC levels of theory *i.e.* by methods of the chemical accuracy ( $\sim 1$  kcal/mol) [3, 4]. In our work we used the geometries described there as stationary points and obtained from CISD/6-311++G(2pd) optimization. Thanks to the symmetry of the considered conformations they can be characterized by just a single parameter, *e.g.* a distance  $R$  between the two nearest nuclei. Figure 1 shows the conformations and symmetry elements as well as the relevant values of  $R$ .

Table 2. The energies of the  $H_4^{2+}$  system in selected conformations computed by means of the ECG method compared with the best previous CCSD estimations [4]. Each geometry is unequivocally defined by  $R$  – the distance between the nearest protons

Conformation	R/bohr	Energy in hartree		Difference in millihartree
		ECG	CCSD	
Tetrahedral ( $T_d$ )	2.338	-1.0490415	-1.04678	2.26
Triangle ( $D_{3h}$ )	1.227	-1.0418037	-1.04013	1.67
Square ( $D_{4h}$ )	2.254	-1.0167223	-1.01379	2.93
Linear ( $D_{\infty h}$ )	2.422	-1.0057903	-1.00477 <sup>a</sup>	1.02

<sup>a</sup>This work, energy computed at the same level of theory as in [4]

This work is the first attempt to estimate variationally the energy of  $H_4^{2+}$  up to the microhartree accuracy. Based on our previous experience with the two-electron systems like  $H_2$ ,  $HeH^+$ , and  $H_3^+$  [6, 10, 13] we can safely assess that our 100-term wave functions yield an upper bound to the energy to an accuracy better than 20 microhartree that is 1-2 orders of magnitude higher than that known hitherto from literature. The ECG results are listed in Table 2 where, for comparison, the CCSD energies of Ref. [4] are also given. As shown in the last column of the table, the orbital-based computations yield energy with an error of the order of millihartree.

#### 4. CONCLUSIONS

We described an implementation of the symmetry projectors into the ECG methodology. Their presence increases significantly efficiency of the computations as it

implicitly increases the expansion length of the wave function. This observation can be illustrated by the fact that the number of the components of the projector  $\hat{P}_R$  (Table 1) correlates with the energy gain obtained with respect to the CCSD results given in the last column of Table 2.

We supply here the lowest variational energies for selected conformations of the test case system,  $H_4^{2+}$ . However, with the present capability of our software we are not able to characterize the location of the analyzed conformations on the potential energy hypersurface, which is an interesting issue from the chemical point of view, and we limit ourselves to the confirmation of the relative order of the conformers on the energy scale.

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