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Commentationes

Four-Particle Perimetric Coordinates*

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An attempt was made to find perimetric coordinates for a 4-particle system. It is conjectured that such coordinates do not exist.

Es wurde ein Versuch gemacht, Perimeter-Koordinaten für ein 4-Teilchen-System zu finden. Es wird vermutet, daß solche Koordinaten nicht existieren.

On a fait une tentative pour trouver des coordonnées périmétriques d'un système a 4 particules. On pense que de telles coordonnées n'existent pas.

Introduction

As is well known, the independent particle model of many-electron atoms and molecules is inadequate for the detailed description of the relative motion of the individual electrons. It has been shown by many workers [*1*] that the simple (but tedious) approach of superimposing configurations leads to a rather slowly converging process.

On the other hand, the introduction of interelectronic distances into the wave function as independent variables, while giving lots of "mileage" in terms of configuration interaction, as shown by the results of HYLLERAAS [*2*] on helium and JAMES and COOLIDGE [*3*] on lithium, also leads to difficult integrals, encountered in the calculation of the Hamiltonian matrix elements [*4*]. The difficulty of computing these integrals depends, in general, on the way in which the interelectronic distances appear in the wave function. In fact, PEKERIS [*5*] by-passed integral computation by a coordinate transformation into *perimetric* coordinates [*6*] for the helium atom.

The Ground State of Helium

PEKERIS [*5*] has calculated one of the most [*6*] accurate wave functions for the ground state of helium by a modification of the Hylleraas technique, which included interelectronic distances. The essence of the method, for a 2-electron system in an s-state is as follows.

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Assume the wave function to have the form

$$\psi = N\, e^{-\frac{ks}{2}} \sum_{l,\,m,\,n=0}^{\infty} c_{l,\,m,\,n}\, k^{l+m+n}\, s^l\, t^m\, u^n \tag{1}$$

where

$$s = r_1 + r_2, \qquad t = r_1 - r_2, \qquad u = r_{12}$$

are the Hylleraas coordinates, and the Hamiltonian after extraction of Euler angles depends only on the three distance coordinates:

$$\begin{aligned} H = {} & \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + 2\,\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_1}\,\frac{\partial}{\partial r_1} + \frac{2}{r_2}\,\frac{\partial}{\partial r_2} + \frac{4}{r_{12}}\,\frac{\partial}{\partial r_{12}} + \\ & + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1\, r_{12}}\,\frac{\partial^2}{\partial r_1\, \partial r_{12}} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2\, r_{12}}\,\frac{\partial^2}{\partial r_2\, \partial r_{12}} + \\ & + 2\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{r_{12}}\right). \end{aligned} \tag{2}$$

Usually k is chosen as a variational parameter, but in order to require the correct asymptotic behavior of ψ when $s \to \infty$ and to reduce the calculations PEKERIS set

$$k = 2\sqrt{-E} \equiv 2\,\varepsilon \tag{3}$$

where E is the electronic energy.

Since the Hylleraas coordinates are not independent, due to the triangular conditions, they are replaced by a set of variables which are independent:

$$\begin{aligned} 2\,u_1 &= (-r_1 + r_2 + r_{12})\,k \\ 2\,u_2 &= (r_1 - r_2 + r_{12})\,k \\ u_3 &= (r_1 + r_2 - r_{12})\,k \end{aligned} \tag{4}$$

or

$$\boldsymbol{U} = \boldsymbol{A}\boldsymbol{R}\,. \tag{5}$$

The variables $\{u_i\}$ are independent, and can take any arbitrary positive value. The factor of 2 is introduced for the convenience of having

$$k \sum r_i = \sum u_i = ks\,.$$

The $\{u_i\}$ are called perimetric coordinates [6]. The volume element is given by

$$d\tau = \left(\frac{\pi^2}{16\,k^2}\right)(u_1 + u_2)\,(2\,u_1 + u_3)\,(2\,u_2 + u_3)\,du_1\,du_2\,du_3 \tag{6}$$

and a transformation of H into perimetric coordinates is straightforward.

We now transform Eq. (1) into

$$\psi = Ne^{-\frac{1}{2}(u_1+u_2+u_3)}\,F\,(u_1\,u_2\,u_3) \tag{7}$$

and assume F to have the form

$$F = \sum_{l,m,n} A_{l,m,n}\,L_l\,(u_1)\,L_m\,(u_2)\,L_n\,(u_3) \tag{8}$$

where $L_p\,(x)$ denotes the normalized Laguerre polynomial of order p which are appropriate for the region zero to infinity with an exponential weight factor. By substitution of Eq. (7) into the wave equation, and use of the recursion relations:

$$x L_n''(x) = (x-1) L_n'(x) - n L_n(x)$$
$$x L_n'(x) = n L_n(x) - n L_{n-1}(x) \tag{9}$$
$$x L_n(x) = -(n+1) L_{n+1}(x) + (2n+1) L_n(x) - n L_{n-1}(x) .$$

One gets a recursion relation between the $A_{l,m,n}$ which is long, but not unmanageable. This recursion relation has the form

$$\sum_{\alpha,\beta,\gamma=-2}^{+2} C_{\alpha,\beta,\gamma}(l, m, n; k) A(l+\alpha, m+\beta, n+\gamma; k) = 0 . \tag{10}$$

Symmetry conditions may simplify Eq. (10); thus, if ψ is symmetric,

$$A_{l,m,n} = A_{m,l,n} \qquad \text{(para)}$$

and if ψ is antisymmetric

$$A_{l,m,n} = -A_{m,l,n} \qquad \text{(ortho)} .$$

The important point is, that due to the particular choice of the $L_m(x)$ in the expansion of F, the matrix associated with the set of homogeneous linear Eq. (10) is Hermitian [7]. Since we have a linear equation for each choice of (l, m, n), we now have an infinite secular equation, which can be truncated when the determinant of the coefficient is symmetric. The vanishing of the determinant will then yield a value of k, and consequently E. Actually, the method is completely equivalent to the variation method. However, all the elements of the secular determinant are integers, and no integrals are computed. Also, the determinant is sparse, non zero elements are concentrated in a band along the diagonal. PEKERIS actually used a 1071-order determinant and achieved not only accurate energy but also other 1- and 2-electron expectation values.

The Four-Particle System

We attempted to find a corresponding transformation which would yield perimetric coordinates for a four-particle system. It is more convenient to search for $\boldsymbol{A}^{-1}$ than for $\boldsymbol{A}$ itself.

$$\boldsymbol{R} = \boldsymbol{A}^{-1}\boldsymbol{U}, \qquad \boldsymbol{U} = \boldsymbol{A}\boldsymbol{R} \tag{1}$$

where

$$\boldsymbol{R} = \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_{12} \\ r_{13} \\ r_{23} \end{pmatrix} \qquad \boldsymbol{U} = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{pmatrix} .$$

The demand that the $\{u_i\}$ range independently from zero to infinity means that there should be a one-to-one correspondence between all sets of 6 positive numbers $\{u_i\}$ and all tetrahedrons (within a parity transformation). At this point it is clear that since $r_i, r_{ij} \geq 0$, every element in $\boldsymbol{A}^{-1}$ is positive or zero; in the latter case the tetrahedron may degenerate into a triangle.

The correspondence $\{u_i\} \rightarrow$ tetrahedron is met if the relevant triangular conditions on the r_i, r_{ij} are satisfied. There are twelve of these, three for each of the four triangles which form the tetrahedron faces.

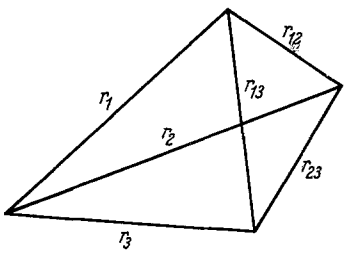

Fig. 1

All the distances in the diagram can be fixed arbitrarily, within the triangular conditions, to determine the size and shape of a unique tetrahedron, within a parity transformation. The disymmetry of the tetrahedron can be taken into account by a weight factor of 2 for each configuration.

The triangular conditions which must be obeyed are:

$$\begin{aligned} r_1 + r_2 - r_{12} &\geq 0 \qquad & r_1 + r_3 - r_{13} &\geq 0 \\ r_1 - r_2 + r_{12} &\geq 0 \qquad & r_1 - r_3 + r_{13} &\geq 0 \\ -r_1 + r_2 + r_{12} &\geq 0 \qquad & \text{etc.} & \end{aligned} \tag{2}$$

Letting $\boldsymbol{A}^{-1} = \boldsymbol{B}$, we get for example:

$$\begin{aligned} r_1 + r_2 - r_{12} = \quad & b_{11}\, u_1 + b_{12}\, u_2 + b_{13}\, u_3 + \ldots \\ & b_{21}\, u_1 + b_{22}\, u_2 + b_{23}\, u_3 + \ldots \\ & - b_{41}\, u_1 - b_{42}\, u_2 - b_{43}\, u_3 - \ldots \end{aligned}$$

Therefore, if this triangular condition is to be satisfied for arbitrary values of the u_i's we must require that

$$\begin{aligned} b_{11} + b_{21} - b_{41} &\geq 0 \\ b_{12} + b_{22} - b_{42} &\geq 0\,. \\ \text{etc.} & \end{aligned}$$

Following through with this we get triangular conditions between certain elements in each column of the matrix $\boldsymbol{B}$. Writing

$$\boldsymbol{A}^{-1} = \boldsymbol{B} = \begin{pmatrix} a & . & . & . & . & . \\ b & . & . & . & . & . \\ c & . & . & . & . & . \\ d & . & . & . & . & . \\ e & . & . & . & . & . \\ f & . & . & . & . & . \end{pmatrix}$$

the triangular conditions are

$$\begin{aligned} &\Delta(a\ b\ d)\\ &\Delta(a\ c\ e)\\ &\Delta(b\ c\ f)\\ &\Delta(d\ e\ f) \end{aligned} \tag{3}$$

where $\Delta\ (a\ b\ d)$ means that the numbers a, b and d form a triangle. This set of conditions must hold in each column. It is easy to pick positive matrix elements of $\boldsymbol{B}$ such that these conditions are satisfied in each column and thus every set of positive u_i's does form a tetrahedron. However, if the matrix is constructed in this manner with no further considerations, not all possible tetrahedrons will be "reached" by the transformation. There will be imposed superfluous triangular conditions of the form of Eq. (2) that will be satisfied which are not true for an arbitrary tetrahedron. For example, one may find that

$$r_1 + r_3 - r_{23} = a\,u_1 + b\,u_2 \geq 0$$

where a and b are positive numbers formed by the sum and difference of some of the elements of $\boldsymbol{B}$. Now there are

$$\frac{6 \cdot 5 \cdot 4}{2} = 60$$

conditions of the form of Eq. (2) and out of these 12 of them must be positive in order to assurre that any set of u_i's does form a tetrahedron. The remaining 48 combinations must be unrestricted so there be no limitation on the tetrahedron imposed by the transformation. Thus we want something like

$$r_1 + r_3 - r_{23} = a\,u_1 + b\,u_2 \tag{4}$$

where $a > 0$ and $b < 0$ for each of the 48 combinations of $r_1\ r_2\ r_3\ r_{12}\ r_{13}\ r_{23}$. There is no difficulty in getting the $a > 0$. The problem is to get a coefficient $b < 0$. Thus the "difficult" conditions which the Matrix $\boldsymbol{B}$ must meet are:

(α) all elements of $\boldsymbol{B}$ are ≥ 0.

(β) The 12 triangular conditions (3) must be satisfied between the elements of each column.

(γ) Take any two elements minus a third, all from the same column. If this combination is not one of the 12 conditions from (3), the combination must be negative definite in at least one of the six columns.

The other conditions which $\boldsymbol{B}$ must satisfy are, in general, easily met. For example, the combination mentioned in step (γ) above must also be positive definite in at least one column. But this is easily achieved. Also we do not want to form a matrix that is singular.

The difficulty is producing the 48 negative definite numbers in step (γ). Our best attempt at this is:

$$\boldsymbol{B} = \begin{pmatrix} 1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 & 0 & 1 \\ 1 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 1 & 1 \\ 0 & 1 & 1 & 0 & 1 & 0 \end{pmatrix} . \tag{5}$$

In each of the first four columns nine different negative numbers are obtained out of the 48. This is a good average since if distributed evenly we would need to get eight per column. However, in the last two columns only four negative numbers are obtained per column. This all adds up to 44, four short of the 48, giving four unnecessary limitations on the shape of possible tetrahedrons described by the $\boldsymbol{U}$ variables when the u's are defined by $\boldsymbol{U} = \boldsymbol{B}^{-1}\,\boldsymbol{R}$. ($\boldsymbol{B}^{-1}$ does exist in this case).

It is very difficult to see how to improve on the $\boldsymbol{B}$ given in Eq. (5). Any scheme other than the first four columns does not yield enough negative numbers per column to add use to 48. (For example, if matrix elements other than zero or one are used, we could not even construct a single column that would yield the minimum of eight negative numbers.) And we can not seem to find two remaining columns that give the required 12 more negative numbers. We observe that we have, in fact, exhausted all possible matrices composed of elements which are either zero or one, and since these most successful matrix elements do not actually yield perimetric coordinates, we are led to the following conjecture:

Perimetric coordinates, in the sense discussed here, do not exist for the four particle system. (One might also ask for perimetric coordinates associated with orthogonal polynomials other than Laguerre.)

Unit Tetrahedrons

Since the above discussion of an attempt to find the four particle perimetrics coordinates seems to raise the question of their existance, it might be advantageous to try to state the problem more formally so that one could work toward an existance proof of some kind. This might proceed along the following lines.

Writing out $\boldsymbol{R} = \boldsymbol{B}\,\boldsymbol{U}$:

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_{12} \\ r_{13} \\ r_{23} \end{pmatrix} = \begin{pmatrix} b_{11}\,u_1 + b_{12}\,u_2 + b_{13}\,u_3 + \dots \\ b_{21}\,u_1 + b_{22}\,u_2 + b_{23}\,u_3 + \dots \\ b_{31}\,u_1 + b_{32}\,u_2 + b_{33}\,u_3 + \dots \\ \cdot \quad\quad \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \quad\quad \cdot \end{pmatrix}$$

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_{12} \\ r_{13} \\ r_{23} \end{pmatrix} = u_1 \begin{pmatrix} b_{11} \\ b_{21} \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} + u_2 \begin{pmatrix} b_{12} \\ b_{22} \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} + u_3 \begin{pmatrix} b_{13} \\ b_{23} \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} + \dots \tag{6}$$

or

$$\boldsymbol{R} = u_1\,\boldsymbol{T}_1 + u_2\,\boldsymbol{T}_2 + u_3\,\boldsymbol{T}_3 + \dots \tag{7}$$

where $\boldsymbol{T}_i$ are the columns of the matrix $\boldsymbol{B}$. Motivated by Eq. (5) we call these $\boldsymbol{T}$'s "unit tetrahedrons" because the columns of $\boldsymbol{B}$ in Eq. (5) are degenerate tetrahedrons reminding us of, say, the matrices

$$\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}, \quad \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}, \quad \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}, \quad \begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}$$

which are "unit matrices" spanning the space of all 2×2 matrices.

The unit tetrahedrons are defined by the triangular conditions among its elements given in Eq. (3). As mathematical entities, unit tetrahedrons seem to be something new. They fall short on only one count of about ten requirements for being abstract vectors. This one unfilfilled condition is the existence of a $\overline{\boldsymbol{T}}$ for a given $\boldsymbol{T}$ such that $\boldsymbol{T} + \overline{\boldsymbol{T}} = 0$, where addition is defined as indicated in Eq. (6).

Now the following question can be formulated from considering Eq. (7): Is the space of all possible tetrahedrons spanned by six unit tetrahedrons? Perhaps in this fashion the problem may be put on a rigorous mathematical basis.

„Almost" Perimetric Coordinates in the Case of H_2

The above unsuccessful attempt at finding perimetric coordinates leads to a transformation which does not permit all possible tetrahedrons. Thus a wave function in terms of these variables would be restricted in some way and might correspond to a trial function in a variational calculation. Therefore, it is of interest to examine the restrictions imposed by "almost" perimetric coordinates.

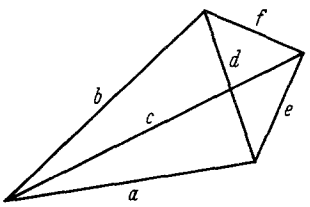

Fig. 2

The four restrictions on the configuration of particles imposed by the transformation $\boldsymbol{B}$ in Eq. (5) are:

$$\begin{aligned} a + f &\geq b \\ a + f &\geq c \\ a + f &\geq d \\ a + f &\geq e\,. \end{aligned} \tag{8}$$

Now, as an example, consider the H_2 molecule with the internuclear distance equal to the "a" above. The interelection distance would be "f". The conditions (8) then say that if the electrons are close together they are near the nuclei and if close enough together, the electrons will be between the nuclei. This seems like a reasonable approximation for H_2. In this approximation PEKERIS's series solution could be carried out for the H_2 example. The attempt to show that this approximation corresponds to a variational principle was unsuccessful.

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