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ON A SIMPLE CONFIGURATION INTERACTION METHOD USING NON-ORTHOGONAL BASIS FUNCTIONS*

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In the classical configuration interaction (CI) method [1] we write the approximate state fuction of an N-body problem as a linear combination of the configurations Φ_i

$$\Psi = \sum_i c_i \Phi_i , \tag{1}$$

The configurations Φ_i are built up from one-particle functions φ_i in such a way that the symmetry properties of the Hamiltonian and the state function are taken into account. We determine Ψ from the requirement

$$(\Psi|\mathscr{H}|\Psi) = \sum_{i,k} c_i^* c_k (\Phi_i|\mathscr{H}|\Phi_k) = \min \tag{2}$$

with the constraint

$$(\Psi|\Psi) = \sum_{i,k} c_i^* c_k (\Phi_i|\Phi_k) = 1 . \tag{3}$$

From requirement (2) we get a system of linear homogeneous equations and we determine the approximate energy E by solving the secular equation of the system.

In the CI method some mathematical difficulties have to be overcome. One of these is connected with the construction of the symmetry-adapted configurations. This construction is laborious if the number of particles is $N > 2$ [2]. Other complications are introduced if we use non-orthogonal orbitals [3]. In this paper we propose a method where these difficulties do not arise. In the proposed method we have to construct only one symmetry-adapted configuration and we can handle the non-orthogonal orbitals easily.

The main features of this method are as follows.

* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

1. We choose a state function Ψ_0 as a zeroth approximation and determine the energy E_0 in this approximation

$$E_0 = \frac{(\Psi_0|\mathscr{H}|\Psi_0)}{(\Psi_0|\Psi_0)} .$$

2. We define a derivative along the direction Ψ of the functional $E(\Psi)$ in the "point" Ψ_0 and we determine the state $\overline{\Psi}$ where the derivative is minimal.

3. From the states Ψ_0 and $\overline{\Psi}$ we determine the first approximation Ψ_1 and $E_1 < E_0$, etc.

Let us introduce the following notations:

$\mathscr{H}$ is the Hamiltonian of the N-particle system,

Λ is a constant of motion i.e. $[\Lambda, \mathscr{H}] = 0$,

$\varphi_1, \varphi_2, \ldots, \varphi_r$ is the one-particle basis,

$\Phi_1, \Phi_2, \ldots, \Phi_s$ is the N-particle basis constructed from the one-particle functions and

L_Φ is the subspace of the Hilbert space determined by N-particle basis.

We do not require the orthogonality of φ_i-s and Φ_i-s, and we do not assume that Φ_i-s are symmetry-adapted. But we require that φ_i-s and Φ_i-s have to form a basis, i.e. they have to be linear independent. We can formulate our problem in the following way: Find the minimum of the expectation value

$$E(\Psi) = \frac{(\Psi|\mathscr{H}|\Psi)}{(\Psi|\Psi)} \tag{4}$$

with the constraint*

$$\Lambda\Psi = \lambda\Psi , \quad \text{where} \quad \Psi \in L_\Phi .$$

As a zeroth approximation we construct a state function Ψ_0 with the properties

$$\begin{aligned} &(\Psi_0|\Psi_0) = 1 , \\ &\Lambda\Psi_0 = \lambda\Psi_0 , \\ &\Psi_0 \in L_\Phi . \end{aligned} \tag{5}$$

The last condition can be written as

$$\Psi_0 = \sum_i c_{0i} \Phi_i . \tag{6}$$

* We work here with one constant of motion but the generalization for the case of more constants of motion is trivial.

The energy in this approximation is

$$E_0 = (\Psi_0|\mathscr{H}|\Psi_0) .$$

Let us define the derivative along the direction Ψ of the functional $E(\Psi)$ in the "point" Ψ_0 as [4]

$$\frac{dE}{d\Psi} = \lim_{\alpha \to 0} \frac{E(\Psi_0 + \alpha\Psi) - E(\Psi_0)}{\alpha \|\Psi\|} . \tag{7}$$

Using (4) we get from (7)

$$\frac{dE}{d\Psi} = \frac{(\Psi|\mathscr{H} - E_0|\Psi_0) + (\Psi_0|\mathscr{H} - E_0|\Psi)}{\|\Psi\|} . \tag{8}$$

We can show easily that (8) is really a derivative. If α is a positive infinitesimal quantity we can write

$$\begin{aligned} E(\Psi_0 + \alpha\Psi) &= \frac{(\Psi_0 + \alpha\Psi|\mathscr{H}|\Psi_0 + \alpha\Psi)}{(\Psi_0 + \alpha\Psi|\Psi_0 + \alpha\Psi)} = \\ &= E_0 + \alpha \frac{(\Psi|\mathscr{H} - E_0|\Psi_0) + (\Psi_0|\mathscr{H} - E_0|\Psi)}{\|\Psi\|} , \end{aligned} \tag{9}$$

i.e. $dE/d\Psi$ is a derivative.

It can be seen from Equ.(9) that in the case $dE/d\Psi < 0$, $E(\Psi_0 + \alpha\Psi)$ decreases when α increases. We use this fact to construct the first approximation.

Note that the derivative $dE/d\Psi$ does not depend on $\|\Psi\|$; we can choose $\|\Psi\| = 1$.

We write $\Psi \in L_\Phi$ as a linear combination of the basis elements

$$\Psi = \sum_i x_i \Phi_i . \tag{10}$$

Let us introduce the following notations

$$\begin{aligned} (\Phi_i|\Phi_k) &= \mathscr{M}_{ik}, \\ (\Phi_i|\mathscr{H}|\Phi_k) &= \mathscr{H}_{ik} . \end{aligned} \tag{11}$$

Using (8), (10) and (11) we get

$$\frac{dE}{d\Psi} = \sum_{i,k} \left\{ x_i^* (\mathscr{H}_{ik} - E_0 \mathscr{M}_{ik}) c_{0k} + c_{0k}^* (\mathscr{H}_{ki} - E_0 \mathscr{M}_{ki}) x_i \right\} . \tag{12}$$

We are looking for the minimum value of $dE/d\Psi$ with the condition

$$(\Psi|\Psi) = \sum_{i,k} x_i^* \mathscr{M}_{ik} x_k = 1 . \tag{13}$$

The minimum is determined by the system of linear inhomogeneous equations

$$\sum_k \mathscr{M}_{ik} x_k = \frac{1}{\mu} \sum_k (\mathscr{H}_{ik} - E_0 \mathscr{M}_{ik}) c_{0k}, \tag{14}$$

where μ is the Lagrange multiplier determined by (13), or in matrix form

$$\boldsymbol{MX} = \frac{1}{\mu} (\boldsymbol{H} - E_0 \boldsymbol{M}) \boldsymbol{c}_0 . \tag{15}$$

The solution of (15) is

$$\boldsymbol{X} = \frac{1}{\mu} (\boldsymbol{M}^{-1}\boldsymbol{H} - E_0) \boldsymbol{c}_0$$

and from (13)

$$\mu = \pm \sqrt{\boldsymbol{c}_0^+ \boldsymbol{H}\boldsymbol{M}^{-1}\boldsymbol{H}\boldsymbol{c}_0 - E_0^2}. \tag{16}$$

We get the minimum value of (12) with the minus sign in (16)

$$\frac{dE}{d\Psi_{\min}} = -2\sqrt{\boldsymbol{c}_0^+ \boldsymbol{H}\boldsymbol{M}^{-1}\boldsymbol{H}\boldsymbol{c}_0 - E_0^2}. \tag{17}$$

It can easily be seen that

$$\boldsymbol{c}_0^+ \boldsymbol{H}\boldsymbol{M}^{-1}\boldsymbol{H}\boldsymbol{c}_0 - E_0^2 \geqslant 0 ,$$

where the equality is valid only if

$$\mathscr{H}\Psi_0 = E_0 \Psi_0$$

holds, i.e. Ψ_0 is an eigenfunction of $\mathscr{H}$. If the equality is valid we know the exact eigenfunction of $\mathscr{H}$. If that is not the case we determine the state

$$\overline{\Psi} = \sum_l x_l \Phi_l ,$$

which has the property that $E(\Psi_0 + \alpha\overline{\Psi})$ decreases when α increases from zero to α_0, where α_0 is the smallest positive root of the equation

$$\frac{d}{d\alpha} E(\Psi_0 + \alpha\overline{\Psi}) = 0 . \tag{18}$$

Let

$$\Psi_1 = \frac{\Psi_0 + \alpha_0 \overline{\Psi}}{\|\Psi_0 + \alpha_0 \overline{\Psi}\|}, \tag{19}$$

then

$$E_1 = (\Psi_1|\mathscr{H}|\Psi_1) < E_0 \tag{20}$$

iholds.

We take Ψ_1 as the first approximation, and from it we determine the second approximation in the same way, etc. In this way we get a set of energies $E_0, E_1, E_2, \ldots$ and

$$E_0 > E_1 > E_2 > \ldots \tag{21}$$

holds.

Now we examine the symmetry properties of the state functions Ψ_0, Ψ_1, etc.

Introducing the operator P projecting on the subspace L_Φ

$$P = \sum_{i,k} |\Phi_i) \mathscr{M}^{-1}_{ik} (\Phi_k| \tag{22}$$

the state $\overline{\Psi}$ can be written as

$$\overline{\Psi} = (P\mathscr{H} - E_0)\Psi_0. \tag{23}$$

Using the fact that Λ is a constant of motion and from Equ. (5)

if
$$\begin{aligned} \Lambda\overline{\Psi} &= \lambda\overline{\Psi} \\ P\Lambda - \Lambda P &= 0 \end{aligned} \tag{24}$$

is valid. If we choose the basis in such a way that

$$\Lambda\Phi_i = \sum_{k=1}^{s} c_{ik}\Phi_k \tag{25}$$

holds for every i, condition (24) is fulfilled and the symmetry remains in every approximation.

Applications based on this method will be published in a subsequent paper.

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REFERENCES

1. R. DAUDEL, R. LEFEBVRE and C. MOSER. Quantum Chemistry, Interscience Publishers, Inc. New York, 1959.
2. J. L. CALAIS, Uppsala preprint, No. 52. 1960.
3. H. SHULL and P. O. LÖWDIN, J. Chem. Phys., **23**, 1362, 1955; P. O. LÖWDIN and H. SHULL, Phys. Rev., **101**, 1730, 1956.
4. KANTOROWICH—AKILOW: Funktionalanalysis in normierten Räumen, Akademie Verlag, Berlin, 1964.