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Mathematical aspects of the LCAO MO first order density function (3): A general localization procedure

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A general MO localization process based on Elementary Jacobi Rotations is described. The procedure is connected with Boys, Ruedenberg and Mezey MO localization algorithms.

KEY WORDS: MO theory, MO localization, One electron operators, MO unitary transformations, Elementary Jacobi rotations

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1. A Pipek–Mezey localization procedure variant

The present paper is the third part of a self-contained series [1, 2] dedicated to study several aspects of the quantum mechanical density function. Here, some details of the localization algorithms are analyzed.

Therefore, this work deals first with a simpler variant of a localization procedure proposed by Pipek and Mezey [3], which on the other hand can be considered as an Edminston and Ruedenberg [4] localization alternative. The present paper second part, which generalizes Pipek and Mezey proposal, perhaps can be considered as more related with a localization algorithm described by Boys [5], many years ago.

1.1. Setting up a localization functional

Suppose defined the projectors over atoms in a molecule: $\{P_A\}$, see for a recent application example of such an atomic projection set reference [6].

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Suppose some sum of them: $P_S = \sum_{A \in S} P_A$, which runs over the whole molecule or includes just some atomic subset,S ; for example: the set of backbone atoms, leaving the whole hydrogen molecular contribution not intervening in the projector description.

Construct, then, using the known MO set:[1] $\{|k\rangle\}$, the following positive definite functional, which will be thereafter called *localization functional*:

$$L(P_S) = \sum_k |\langle k| P_S |k\rangle|^2$$

an try to vary and optimize it by means of Elementary Jacobi Rotations (EJR) [7].

1.2. Localization algorithm and Jacobi diagonalization

For this purpose one can start performing a EJR over the MO pair:$\{|i\rangle ; |j\rangle\}$, by using the EJR cosine and sine $\{c; s\}$:

$$c^2 + s^2 = 1 : |i\rangle \to c|i\rangle - s|j\rangle \ \wedge \ |j\rangle \to s|i\rangle + c|j\rangle$$

and then the EJR transformed MO pair can be used within the localization functional.

To proceed further, first one can take into account that the localization functional can be written explicating the EJR rotated MO pair:

$$L(P_S) = \sum_{k \neq i,j} |\langle k| P_S |k\rangle|^2 + |\langle i| P_S |i\rangle|^2 + |\langle j| P_S |j\rangle|^2 ,$$

then, the EJR will produce the variations:

$$\begin{aligned} \langle i| P_S |i\rangle \to & (c\langle i| - s\langle j|) P_S (c|i\rangle - s|j\rangle) \\ & = c^2 \langle i| P_S |i\rangle + s^2 \langle j| P_S |j\rangle - 2sc\langle i| P_S |j\rangle \\ & = \langle i| P_S |i\rangle + s^2 (\langle j| P_S |j\rangle - \langle i| P_S |i\rangle) - 2sc\langle i| P_S |j\rangle \end{aligned}$$

and

$$\begin{aligned} \langle j| P_S |j\rangle \to & (s\langle i| + c\langle j|) P_S (s|i\rangle + c|j\rangle) \\ & = s^2 \langle i| P_S |i\rangle + c^2 \langle j| P_S |j\rangle + 2sc\langle i| P_S |j\rangle \\ & = \langle j| P_S |j\rangle + s^2 (\langle i| P_S |i\rangle - \langle j| P_S |j\rangle) + 2sc\langle i| S_B |j\rangle \end{aligned}$$

[1]It is not necessary to use all MO's, a chosen subset can be also equally employed. The algorithm will transform, by means of the localization procedure chosen, this MO subset only and the problem dimension will vary accordingly.

So, the variations of these terms can be compactly written as:

$$\delta \langle i| P_S |i\rangle = -\delta \langle j| P_S |j\rangle = s^2 (\langle j| P_S |j\rangle - \langle i| P_S |i\rangle) - 2sc \langle i| P_S |j\rangle .$$

Consequently, the variation of the localization functional is easily expressed as:

$$\begin{aligned}\delta L (P_S) &= 2 (\langle i| P_S |i\rangle \delta \langle i| P_S |i\rangle + \langle j| P_S |j\rangle \delta \langle j| P_S |j\rangle) \\ &= 2 (\langle i| P_S |i\rangle - \langle j| P_S |j\rangle) \delta \langle i| P_S |i\rangle \\ &= 2 (\langle i| S_B |i\rangle - \langle j| P_S |j\rangle) \left(s^2 (\langle j| P_S |j\rangle - \langle i| P_S |i\rangle) - 2sc \langle i| P_S |j\rangle\right)\end{aligned}$$

but the variation of the localization functional must be null, so this is the same as to write:

$$s^2 (\langle j| P_S |j\rangle - \langle i| P_S |i\rangle) - 2sc \langle i| P_S |j\rangle = 0$$

therefore, the optimal rotation angle α can be computed with the tangent:

$$t = \frac{s}{c} = \frac{2 \langle i| P_S |j\rangle}{(\langle j| P_S |j\rangle - \langle i| P_S |i\rangle)} \rightarrow \alpha = \arctan (t) .$$

However, this is exactly the same as to diagonalize, by employing EJR, a given matrix, whose elements can be expressed in general as: $\{\langle i| P_S |j\rangle\}$; because of this, the MO localization algorithm becomes equivalent to diagonalize by means of the well-known Jacobi diagonalization procedure [8], see for more information the set of references [9], the following matrix:

$$\mathbf{Z}_S = \left\{z_{S;ij} = \langle i| P_S |j\rangle\right\},$$

which is nothing else than the matrix representation of the operator P_S under the MO chosen (sub-)set.

2. General MO localization procedure involving any one-electron operator

On the other hand, a quick glance at the reasoning previously put forward, shows that this previous result is somehow independent of the operator used. Accordingly, in principle any Hermitian one-electron operator Ω can be employed into the MO localization functional for this purpose.

Then, the general localization functional, which can be employed, becomes:

$$L (\Omega) = \sum_k |\langle k| \Omega |k\rangle|^2$$

and after varying it by EJR, the net result appears to be the same as to diagonalize the matrix representation of the operator Ω under the MO basis set:

$$\mathbf{Z}_\Omega = \left\{ z_{\Omega;ij} = \langle i | \, \Omega \, | j \rangle \right\}.$$

In any case, the matrix $\mathbf{Z}_\Omega$ will furnish upon diagonalization a unique unitary transformation: $\mathbf{U}$, say, attached to its eigenvectors, that is:

$$\mathbf{Z}_\Omega \mathbf{U} = \mathbf{U}\Theta \rightarrow \Theta = Diag\left(\theta_k\right) \wedge \mathbf{U}^+\mathbf{U} = \mathbf{U}\mathbf{U}^+ = \mathbf{I}.$$

Such a unitary matrix will act over the MO basis set, transforming their elements in the way shown below:

$$\Omega \, | p \rangle = \sum_k u_{kp} \, | k \rangle.$$

In order to see how the MO coordinates with respect to some AO basis set are transformed, suppose known an AO basis set:

$$\left\{ \chi_\mu \equiv | \mu \rangle \right\},$$

then the MO can be expressed by the linear combinations:

$$| k \rangle = \sum_\mu c_{\mu k} \, | \mu \rangle$$

where: $\mathbf{C} = \left\{ c_{\mu k} \right\}$ are the MO coordinates ordered as matrix elements and thus it can be written:

$$\Omega \, | p \rangle = \sum_k u_{kp} | k \rangle = \sum_k u_{kp} \sum_\mu c_{\mu k} | \mu \rangle = \sum_\mu \sum_k \left(c_{\mu k} u_{kp} \right) | \mu \rangle .$$

Therefore, this is the same as to transform the MO coordinates with respect to the AO basis set, while preserving the attachment of the AO basis set functions to some centers, as the new transformed localized coordinates: $\mathbf{C}_L = \left\{ c_{L;\mu p} \right\}$ can be easily defined as:

$$c_{L;\mu p} = \sum_k \left(c_{\mu k} u_{kp} \right) \rightarrow \mathbf{C}_L = \mathbf{C}\mathbf{U}.$$

3. Value of the localization functional after optimization

In the proposed procedure, the matrix $\mathbf{Z}_\Omega$ is diagonal when expressed in the localized MO set. Thus, at the optimal setting of the localization functional it can be written:

$$L^* (\Omega) = \sum_k |\theta_k|^2.$$

This result indicates that the optimal functional value is coincident with the trace of the squared matrix representation of the chosen operator:

$$L^* (\Omega) = Tr \left| \mathbf{Z}_\Omega^2 \right|.$$

4. The density matrix in the new localized MO basis set

4.1. General case

If the first order density matrix is written in terms of the MO as, see for more details references [1, 2]:

$$\rho (\mathbf{r}) = \sum_p \nu_p \, |p\rangle \, \langle p| \,,$$

where the set of non-negative definite real numbers $\{\nu_p\}$ represent the MO occupations, then it will be obtained the following relationship between the original and the new transformed MO:

$$\rho_\Omega (\mathbf{r}) = \sum_p \nu_p \, |\Omega| \, p\rangle \, \langle p \, |\Omega| = \sum_p \nu_p \sum_k \sum_l u_{kp} u_{pl}^* \, |k\rangle \, \langle l|$$

$$= \sum_k \sum_l \left(\sum_p \nu_p u_{kp} u_{pl}^* \right) |k\rangle \, \langle l|$$

in that case, one can construct the diagonal matrix:

$$\mathbf{N} = Diag \left(\nu_p \right);$$

therefore, a new non-diagonal occupation number matrix can be defined as:

$$\mathbf{M} = \mathbf{UNU}^+ = \{m_{kl}\}$$

and the new density function can be written:

$$\rho_\Omega (\mathbf{r}) = \sum_k \sum_l m_{kl} \, |k\rangle \, \langle l|.$$

4.2. Monodeterminantal closed shell particular case

In the monodeterminantal closed shell case, when the transformed MO are the occupied ones, the particular situation:

$$\mathbf{N} = 2\mathbf{I}$$

is encountered, so it can be written:

$$\mathbf{M} = 2\mathbf{U}\mathbf{U}^{+} = 2\mathbf{I}$$

and thus the density function in the localized MO frame becomes:

$$\rho_{\Omega}(\mathbf{r}) = 2\sum_{k}\sum_{l}\delta_{kl}|k\rangle\langle l| = 2\sum_{k}|k\rangle\langle k| = \rho(\mathbf{r});$$

that is, a well-known result is found, meaning that the old and the unitary transformed density functions are the same.

5. Conclusions

Starting from a simpler variant of a Pipek–Mezey MO procedure, a general MO localization algorithm is proposed. The new proposed process consisting to use for MO localization purposes the unitary eigenvector matrix attached to the matrix associated to any one-electron Hermitian operator. Numerical tests have been performed with adequate localization results, at least for the projection operators similar to Pipek–Mezey localization procedure. As the square of a Hermitian operator is used, the diagonalization procedure for real matrix representations will furnish non-negative eigenvalue sets, assuring that the MO localization functional acquires a maximal value when optimal. A final remark can be also indicated here: as in the present algorithm, there is only need of a Hermitian operator matrix representation and a diagonalization routine, besides of the MO to be localized, the proposed set of procedures can be straightforwardly implemented within any currently available MO calculation program.

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