Theoret. chim. Acta (Berl.) 7, 1—3 (1967)

Commentationes

Modus Computandi Eigenvectores et Eigenaestimationes e Matrice Densitatis

T. K. LIM et M. A. WHITEHEAD

Universitas Collegii McGill Institutionis Regiae ad Doctrinam Propagandam, Monteregio 2, Quebec, Canada

Acceptum a. d. VI. Nonas Octobres, MCMLXVI

Modus McWEENY matrices densitatis extenditur, ut eigenaestimationes eigenvectoresque recta et confestim computari possint, si metricam matricem $S^{1/2} R_0 S^{1/2}$, in qua S est "overlap" matrix et R_0 est matrix densitatis, diagonalem facias. Via computandi quoque describitur.

McWEENY's density matrix method is extended so that the eigenvalues and eigenvectors can be calculated directly from the diagonalization of a metric matrix $S^{1/2} R_0 S^{1/2}$ where S is the overlap matrix and R_0 is the density matrix. The procedure of calculation is also described.

Es wird eine Methode angegeben, die es erlaubt, aus der nach McWEENY iterierten SCF-Dichtematrix R_0 und der Überlappungsmatrix S über eine Diagonalisierung der Matrix $S^{1/2} R_0 S^{1/2}$ die einzelnen Eigenwerte und Eigenvektoren direkt zu berechnen.

La méthode de McWEENY pour la matrice de densité est étendue de façon à ce que les valeurs propres et les vecteurs propres puissent être calculés directement par diagonalisation d'une matrice métrique $S^{1/2} R_0 S^{1/2}$ où S est la matrice de recouvrement et R_0 est la matrice de densité. Le procédé de calcul est décrit.

Exordium

McWEENY erat primus, qui modo matricis densitatis (sic nominatur) [*1—3*], in quo continua iteratio eigenaequationis $F C_0 = S C_0 E_0$ vitari potest, in quantum mechanica ratione usus est. In modo McWEENY matrix densitatis, quae mores systematis constituit sed tamen ad speciem singulorum orbitalium non advertit, declivissimi descensus modo iteratur. Est igitur difficile, vires singulorum orbitalium et orbitales moleculares, quae "unum-electron" nominatae sunt, recta confestimque computare. Itaque, orbitalibus atomicis quibus principiis utaris ignotis, hic modus ad moleculas computandum non idoneus est [*4*]. Hic autem libellus offert modum, quo vires singulorum orbitalium atque orbitales moleculares analogae e matrice densitatis computari possunt, ut omnino moleculae computari [*4*] possint, si matrix densitatis ex modo McWEENY iteratur.

Modus

In communi ratione ferme necesse est explicare eigenaequationem

$$F C = S C E , \tag{1}$$

in qua $\boldsymbol{C}$ est quadrata eigenmatrix, quae et in occupatis molecularibus orbitalibus $\boldsymbol{C}_o$ et in apertis molecularibus orbitalibus (re non verbo) $\boldsymbol{C}_u$ constitit. $\boldsymbol{C}_o$ viribus omnium eigenaestimationum in $\boldsymbol{E}$ digerendis ferme invenitur. Partiamur $\boldsymbol{C}$ in

$$\boldsymbol{C} = [\boldsymbol{C}_o \,|\, \boldsymbol{C}_u] \,. \tag{2}$$

Deinde facile est docere ex aequatione (1)

$$\left.\begin{aligned} \boldsymbol{F}\,\boldsymbol{C}_o &= \boldsymbol{S}\,\boldsymbol{C}_o\,\boldsymbol{E}_o \\ \boldsymbol{F}\,\boldsymbol{C}_u &= \boldsymbol{S}\,\boldsymbol{C}_u\,\boldsymbol{E}_u \end{aligned}\right\}, \tag{3}$$

in qua $\boldsymbol{E}_o$ et $\boldsymbol{E}_u$ sunt eigenvires occupatarum apertarumque molecularium orbitalium, in ordine.

Nunc, ex aequatione (2) et finitione densitatis matricis $\boldsymbol{R}_o = \boldsymbol{C}_o\boldsymbol{C}_o^\dagger$ habemus

$$\begin{aligned} \boldsymbol{C}^\dagger\,\boldsymbol{S}\,\boldsymbol{R}_o\,\boldsymbol{S}\,\boldsymbol{C} &= \left[\begin{array}{c} \boldsymbol{C}_o^\dagger \\ \hline \boldsymbol{C}_u^\dagger \end{array}\right] \boldsymbol{S}\,\boldsymbol{C}_o\,\boldsymbol{C}_o^\dagger\,\boldsymbol{S}\,[\boldsymbol{C}_o \,|\, \boldsymbol{C}_o] \\ &= \left[\begin{array}{c|c} \boldsymbol{C}_o^\dagger\boldsymbol{S}\,\boldsymbol{C}_o & \boldsymbol{C}_o^\dagger\boldsymbol{S}\,\boldsymbol{C}_o \\ \hline \boldsymbol{C}_u^\dagger\boldsymbol{S}\,\boldsymbol{C}_o & \boldsymbol{C}_u^\dagger\boldsymbol{S}\,\boldsymbol{C}_o \end{array}\right] = \left[\begin{array}{c|c} \boldsymbol{1} & \boldsymbol{0} \\ \hline \boldsymbol{0} & \boldsymbol{0} \end{array}\right] , \end{aligned} \tag{4}$$

in quibus admovemus condiciones orthonormalitatis exclusionisque:

$$\boldsymbol{1} = \boldsymbol{C}^\dagger\boldsymbol{S}\,\boldsymbol{C} = \left[\begin{array}{c} \boldsymbol{C}_o^\dagger \\ \hline \boldsymbol{C}_u^\dagger \end{array}\right] \boldsymbol{S}\,[\boldsymbol{C}_o \,|\, \boldsymbol{C}_u] = \left[\begin{array}{c|c} \boldsymbol{C}_o^\dagger\boldsymbol{S}\,\boldsymbol{C}_o & \boldsymbol{C}_o^\dagger\boldsymbol{S}\,\boldsymbol{C}_u \\ \hline \boldsymbol{C}_u^\dagger\boldsymbol{S}\,\boldsymbol{C}_o & \boldsymbol{C}_u^\dagger\boldsymbol{S}\,\boldsymbol{C}_u \end{array}\right] . \tag{5}$$

Aequatio (4) iterum scribi potest ut

$$\boldsymbol{X}^\dagger\,\boldsymbol{Q}\,\boldsymbol{X} = \boldsymbol{P} \,, \tag{4a}$$

in qua $\boldsymbol{X}$ est unitaria matrix, quae finitur a

$$\boldsymbol{X} = \boldsymbol{S}^{1/2}\,\boldsymbol{C} \,, \tag{6}$$

et $\boldsymbol{Q}$ $\boldsymbol{P}$que sunt

$$\left.\begin{aligned} \boldsymbol{Q} &= \boldsymbol{S}^{1/2}\,\boldsymbol{R}_o\,\boldsymbol{S}^{1/2} \\ \boldsymbol{P} &= \left[\begin{array}{c|c} \boldsymbol{1} & \boldsymbol{0} \\ \hline \boldsymbol{0} & \boldsymbol{0} \end{array}\right] \end{aligned}\right\} . \tag{7}$$

Ex aequatione (4a) videmus diagonalisationem matricis $\boldsymbol{Q}$ dare eigenmatricem $\boldsymbol{X}$ et eigenaestimationem $\boldsymbol{P}$. Hic, $\boldsymbol{X}$ quoque partiri potest in

$$\boldsymbol{X} = [\boldsymbol{X}_o \,|\, \boldsymbol{X}_u] \,, \tag{8}$$

in qua $\boldsymbol{X}_o$ convenit eigenaestimationi $\boldsymbol{1}$ et $\boldsymbol{X}_u$ convenit eigenaestimationi $\boldsymbol{0}$, in ordine, in $\boldsymbol{P}$. Cum $\boldsymbol{X}_o$ et $\boldsymbol{X}_u$ cognoscuntur, tum $\boldsymbol{C}_o$ inveniri possunt ex

$$\boldsymbol{C}_o = \boldsymbol{S}^{-1/2}\,\boldsymbol{X}_o \,. \tag{9}$$

Cum $\boldsymbol{C}_o$ invenitur, $\boldsymbol{E}_o$ computari potest multiplicatione a sinistra de $\boldsymbol{C}_o^\dagger$ in aequatione (3):

$$\boldsymbol{E}_o = \boldsymbol{C}_o^\dagger\,\boldsymbol{F}\,\boldsymbol{C}_o \,. \tag{10}$$

Itaque, eigenvectores $\boldsymbol{C}_o$ et eigenaestimationes $\boldsymbol{E}_o$ computari possunt, si matrix densitatis $\boldsymbol{R}_o$ ex modo McWeeny iteratur.

Via computandi breviter repeti potest sic:

(I) Computa $\boldsymbol{S}^{1/2}$ et $\boldsymbol{S}^{-1/2}$ ex

$$\boldsymbol{S}^{1/2} = \boldsymbol{Y}\,\boldsymbol{D}^{1/2}\boldsymbol{Y}^{\dagger}\,, \quad \boldsymbol{S}^{-1/2} = \boldsymbol{Y}\,\boldsymbol{D}^{-1/2}\,\boldsymbol{Y}^{\dagger}$$

in qua $\boldsymbol{Y}$ et $\boldsymbol{D}$ sunt eigenmatrix eigenaestimatioque de $\boldsymbol{S}$, in ordine; id est, $\boldsymbol{Y}^{\dagger}\,\boldsymbol{S}\,\boldsymbol{Y} = \boldsymbol{D}$.

(II) Computa $\boldsymbol{Q}$ ex aequatione (7) et deinde fac matricem diagonalem.

(III) Digere eigenaestimationes in $\boldsymbol{P}$ ut eigenmatrix analoga $\boldsymbol{X}$ partiri possit in $[\boldsymbol{X}_o \,\vdots\, \boldsymbol{X}_u]$.

(IV) $\boldsymbol{C}_o$ deinde inveniri potest ex aequatione (9).

(V) $\boldsymbol{E}_o$ inveniri potest ex aequatione (10).

Ad Quae Attinet

[1] McWeeny, R.: Proc. Roy. Soc. [London] **A235**, 496 (1956).
[2] — Physic. Rev. **114**, 1528 (1959).
[3] — Proc. Roy. Soc. [London] **A241**, 239 (1957).
[4] Lim, T. K., et M. A. Whitehead: Relatus ad J. chem. Physics.

Prof. M. A. Whitehead
Theoretical Chemistry Laboratory
Chemistry Department
McGill, University
Montréal 2, Québec, Canada