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Non-Relativistic Self-Consistent-Field Theory. II. *

By

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The condition to be satisfied by the orbitals which minimize the orbital energies is determined. This condition provides a link with the Thomas-Fermi approximation.

Es wird eine Bedingung bestimmt, die von den Orbitalen, die die Orbital-Energien auf ein Minimum herabsetzen, erfüllt wird. Diese Bedingung bringt eine Verbindung zu der Thomas-Fermi-Methode.

On a déterminé la condition qui doit être satisfaite par les orbitales qui produisent un minimum pour les énergies des orbitales. Cette condition permet d'établir un rapport avec la théorie de Thomas-Fermi.

Introduction

In a preceding paper of this series**, hereafter designated as I [*3*], a reformulation of the SCF formalism has led to simplified SCF pseudoeigenvalue equations, which must be satisfied by those orbitals which minimize the total electronic energy.

In this paper the condition which must be satisfied by those orbitals which minimize the orbital energies is determined, using the preceding SCF scheme. Unfortunately it is seen that the SCF orbitals cannot minimize the orbital energies.

On the other hand, inspection of this condition shows that it is possible to find a link to the Thomas-Fermi theory.

Mathematical Formulation

The minimization of the parameters $\theta_{ii}^{\lambda\alpha}$, defined by

$$\theta_{ii}^{\lambda\alpha} = \langle \varphi_i^{\lambda\alpha} | F_i^{\lambda\alpha} | \varphi_i^{\lambda\alpha} \rangle = \langle \varphi_i^{\lambda\alpha} | G^{\lambda\alpha} | \varphi_i^{\lambda\alpha} \rangle \ ,$$

can be carried out in the standard fashion, using only the normalization conditions as constraints.

Defining a new set of Lagrangian multipliers $\xi_{mm}^{\mu\beta}$, the new function which must be varied, free of constraints, is

$$(\theta_{ii}^{\lambda\alpha})' = \theta_{ii}^{\lambda\alpha} - \sum_m \sum_\mu \sum_\beta S_{mm}^{\mu\beta} \, \xi_{mm}^{\mu\beta} \ , \tag{1}$$

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** For more details on the notation and definitions see Ref. [*3*].

which can be rewritten as

$$\begin{aligned}(\theta_{ii}^{\lambda\alpha})' &= f_i^{\lambda} \langle \varphi_i^{\lambda\alpha} \,|\, H \,|\, \varphi_i^{\lambda\alpha} \rangle \\ &+ \sum_m \sum_\mu \sum_\beta f_i^{\lambda} f_m^{\mu} \langle \varphi_i^{\lambda\alpha} \,|\, I_{m\,(i)}^{\mu\beta\,(\lambda\alpha)} \,|\, \varphi_i^{\lambda\alpha} \rangle \\ &- \sum_m \sum_\mu \sum_\beta \langle \varphi_m^{\mu\beta} \,|\, \varphi_m^{\mu\beta} \rangle \, \xi_{mm}^{\mu\beta} \ .\end{aligned}$$

Giving an infinitesimal variation to the orbitals (independently for each symmetry designation) one obtains the SCF equations

$$\mathscr{F}_{m\,(i)}^{\mu\beta\,(\lambda\alpha)} \, \varphi_m^{\mu\beta} = \varphi_m^{\mu\beta} \, \xi_{mm}^{\mu\beta} \ , \tag{2}$$

with

$$\begin{aligned}\mathscr{F}_{i\,(i)}^{\lambda\alpha\,(\lambda\alpha)} &= f_i^{\lambda} [H + f_i^{\lambda} I_{i\,(i)}^{\lambda\alpha\,(\lambda\alpha)} + \sum_m \sum_\mu \sum_\beta f_m^{\mu} I_{m\,(i)}^{\mu\beta\,(\lambda\alpha)}] \ , && (\text{for } \varphi_i^{\lambda\alpha}) \\ \mathscr{F}_{j\,(i)}^{\lambda\alpha\,(\lambda\alpha)} &= f_i^{\lambda} f_j^{\lambda} \; I_{i\,(j)}^{\lambda\alpha\,(\lambda\alpha)} \ , && (\text{for } \varphi_j^{\lambda\alpha} \neq \varphi_i^{\lambda\alpha}) \\ \mathscr{F}_{m\,(i)}^{\mu\beta\,(\lambda\alpha)} &= f_i^{\lambda} f_m^{\mu} I_{i\,(m)}^{\lambda a\,(\mu\beta)} \ , && (\text{for every } \mu\beta \neq \lambda\alpha)\end{aligned}$$

where the subscript (i) and the superscript $(\lambda\alpha)$ indicate that these basic operators were obtained in the minimization of $\theta_{ii}^{\lambda\alpha}$.

Summing all the equations obtained (in the minimization of the $\theta_{mm}^{\mu\beta}$ corresponding to all the occupied orbitals), e. g., for $\varphi_i^{\lambda\alpha}$, one obtains, t being the total number of occupied orbitals of all symmetries,

$$\mathscr{F}_i^{\lambda\alpha} \, \varphi_i^{\lambda\alpha} = \varphi_i^{\lambda\alpha} \, \tau_{ii}^{\lambda\alpha} \ , \tag{3}$$

with

$$\mathscr{F}_i^{\lambda\alpha} = \sum_n \sum_\nu \sum_\gamma \mathscr{F}_{i\,(n)}^{\lambda\alpha\,(\nu\gamma)} = f_i^{\lambda} [H + 2 \sum_m \sum_\mu \sum_\beta f_m^{\mu} I_{m\,(i)}^{\mu\beta\,(\lambda\alpha)}] \ ,$$

$$\tau_{ii}^{\lambda\alpha} = t \, \xi_{ii}^{\lambda\alpha} \ .$$

A general coupling operator for every symmetry designation can be defined now; e. g., for symmetry designation $\lambda\alpha$ it is

$$\mathscr{G}^{\lambda\alpha} = \sum_k |\, \varphi_k^{\lambda\alpha} \rangle \langle \varphi_k^{\lambda\alpha} \,|\, \mathscr{F}_k^{\lambda\alpha} \,|\, \varphi_k^{\lambda\alpha} \rangle \langle \varphi_k^{\lambda\alpha} \,| \ ,$$

in which case all the equations represented by Eq. (3) can be written as

$$\mathscr{G}^{\lambda\alpha} \, \varphi_i^{\lambda\alpha} = \varphi_i^{\lambda\alpha} \, \tau_{ii}^{\lambda\alpha} \ . \tag{4}$$

Could the eigenvectors obtained at self-consistency from this equation be also eigenvectors of the general coupling operators $R^{\lambda\alpha}$ and $G^{\lambda\alpha}$? From the definitions of these operators it can be seen that the only possible set of eigenvectors which will simultaneously diagonalize the three matrices $\mathbf{R}^{\lambda\alpha}$, $\mathbf{G}^{\lambda\alpha}$, and $\mathscr{G}^{\lambda\alpha}$ (constructed from the same basis set) will be that for which the condition

$$\sum_m \sum_\mu \sum_\beta f_i^{\lambda} f_m^{\mu} \langle \varphi_i^{\lambda\alpha} \,|\, I_{m\,(i)}^{\mu\beta\,(\lambda\alpha)} \,|\, \varphi_i^{\lambda\alpha} \rangle = 0 \tag{5}$$

is satisfied for every occupied orbital.

Taking into account the definition of $\theta_{ii}^{\lambda\alpha}$, the above conditions imply that the SCF orbitals should be solutions of the one-electron operator H, which can be considered to be an absurd result.

It is now interesting to consider a special set of orthonormal orbitals; that is, the set for which the condition

$$\sum_{i}\sum_{\lambda}\sum_{\alpha}\tau_{ii}^{\lambda\alpha}=0 \tag{6}$$

is satisfied. This condition includes the case when the individual $\tau_{ii}^{\lambda\alpha}$ are identically zero, but it must be pointed out that the question of which is the actual case is of no concern to the present derivation.

Taking into account that the total electronic energy can be written [*1*] as

$$\boldsymbol{E}=\sum_{i}\sum_{\lambda}\sum_{\alpha}[2\,f_i^{\lambda}\,\mathrm{H}_{ii}^{\lambda\alpha}+\sum_{m}\sum_{\mu}\sum_{\beta}f_i^{\lambda}\,f_m^{\mu}\,\mathrm{I}_{im}^{\lambda\alpha,\,\mu\beta}]\ , \tag{7}$$

and using the notation

$$\begin{aligned}\boldsymbol{H}&=\sum_{i}\sum_{\lambda}\sum_{\alpha}f_i^{\lambda}\,\mathrm{H}_{ii}^{\lambda\alpha}\\&=\sum_{i}\sum_{\lambda}\sum_{\alpha}f_i^{\lambda}\,\langle\varphi_i^{\lambda\alpha}\,|\,H\,|\,\varphi_i^{\lambda\alpha}\rangle\ ,\end{aligned} \tag{8a}$$

$$\begin{aligned}\boldsymbol{I}&=\sum_{i}\sum_{\lambda}\sum_{\alpha}\sum_{m}\sum_{\mu}\sum_{\beta}f_i^{\lambda}\,f_m^{\mu}\,\mathrm{I}_{im}^{\lambda\alpha,\,\mu\beta}\\&=\sum_{i}\sum_{\lambda}\sum_{\alpha}\sum_{m}\sum_{\mu}\sum_{\beta}f_i^{\lambda}\,f_m^{\mu}\,\langle\varphi_i^{\lambda\alpha}\,|\,I_{m\,(i)}^{\mu\beta\,(\lambda\alpha)}\,|\,\varphi_i^{\lambda\alpha}\rangle\ ,\end{aligned} \tag{8b}$$

it is possible to rewrite Eqs. (6) and (7) as

$$\boldsymbol{H}+2\,\boldsymbol{I}=0\ ,$$

$$\boldsymbol{E}=2\,\boldsymbol{H}+\boldsymbol{I}\ ,$$

which lead to the conditions

$$\boldsymbol{H}=-2\,\boldsymbol{I}\ , \tag{9a}$$

$$\boldsymbol{E}=\frac{3}{2}\boldsymbol{H}\ , \tag{9b}$$

$$\boldsymbol{E}=-3\,\boldsymbol{I}\ . \tag{9c}$$

It is also possible to relate* these conditions to the virial theorem. Representing the total kinetic energy by $\boldsymbol{T}$ and the total nuclear attraction energy by $\boldsymbol{N}$, it is possible to write

$$\boldsymbol{T}=-\boldsymbol{E}\ ,$$

$$\boldsymbol{H}=\frac{1}{2}(\boldsymbol{T}+\boldsymbol{N})\ ,$$

which lead to the conditions

$$\boldsymbol{N}=\frac{7}{2}\boldsymbol{H}\ , \tag{9d}$$

$$\boldsymbol{N}=-7\,\boldsymbol{I}\ . \tag{9e}$$

Furthermore it is possible to couple those conditions with the Hellmann-Feynman theorem**. One can write (for atoms)

$$\boldsymbol{N}+\boldsymbol{I}=2\,\boldsymbol{E},$$

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$$\boldsymbol{N} = Z \frac{\partial \boldsymbol{E}}{\partial Z} ,$$

where Z is the atomic number of the atom under consideration. Taking now into account the original conditions one obtains

$$Z \frac{\partial \boldsymbol{E}}{\partial Z} = \frac{7}{3} \boldsymbol{E} ,$$

and therefore

$$\boldsymbol{E} = k Z^{7/3} ,$$

expression similar to that obtained in the Thomas-Fermi approximation.

Table 1

Calculated values for $\boldsymbol{H}/\boldsymbol{E}$*,* $\boldsymbol{N}/\boldsymbol{H}$*, and* $-\boldsymbol{H}/\boldsymbol{I}$ *for ground and excited states of neutral atoms**

	H/E	N/H	$-H/I$		H/E	N/H	$-H/I$
He ^1S	0.68	3.47	1.89	Cl ^2P	0.69	3.45	1.81
Li ^2S	0.65	3.53	2.13	Ar ^1S	0.69	3.45	1.81
Be ^1S	0.65	3.53	2.12	K ^2S	0.69	3.45	1.83
B ^2P	0.66	3.52	2.06	Ca ^1S	0.68	3.46	1.86
C ^3P	0.67	3.49	1.98	Sc ^2D	0.68	3.46	1.85
C ^1D	0.67	3.49	1.99	Ti ^3F	0.69	3.46	1.85
C ^1S	0.67	3.50	1.98	Va ^4F	0.69	3.46	1.84
N ^4S	0.68	3.47	1.89	Cr ^5D	0.69	3.45	1.83
N ^2D	0.68	3.47	1.89	Mn ^6S	0.69	3.45	1.82
N ^2P	0.68	3.47	1.89	Fe ^5D	0.69	3.45	1.81
O ^3P	0.69	3.45	1.81	Co ^4F	0.69	3.44	1.80
O ^1D	0.69	3.45	1.81	Ni ^3F	0.69	3.44	1.78
O ^1S	0.69	3.45	1.81	Cu ^2S	0.70	3.43	1.76
F ^2P	0.70	3.43	1.75	Cu ^2D	0.70	3.44	1.77
Ne ^1S	0.71	3.41	1.69	Zn ^1S	0.70	3.43	1.76
Na ^2S	0.70	3.42	1.73	Ga ^2P	0.70	3.43	1.76
Mg ^1S	0.70	3.43	1.75	Ge ^3P	0.70	3.43	1.77
Al ^2P	0.70	3.44	1.78	Ge ^1D	0.70	3.43	1.77
Si ^3P	0.69	3.44	1.79	As ^4S	0.70	3.43	1.77
Si ^1D	0.69	3.44	1.79	As ^2D	0.69	3.44	1.78
Si ^1S	0.69	3.44	1.80	As ^2P	0.70	3.43	1.77
P ^4S	0.69	3.45	1.80	Se ^3P	0.70	3.44	1.77
P ^2D	0.69	3.45	1.80	Se ^1D	0.70	3.44	1.77
P ^2P	0.69	3.45	1.80	Se ^1S	0.70	3.44	1.77
S ^3P	0.69	3.45	1.81	Br ^2P	0.70	3.44	1.77
S ^1D	0.69	3.45	1.81	Kr ^1S	0.70	3.44	1.77
S ^1S	0.69	3.45	1.81				

The conditions represented by Eqs. (9) would apply as well for molecules if the nuclear repulsion energy is included in $\boldsymbol{N}$. It is interesting to point out that those conditions are almost satisfied by exact SCF functions of neutral systems or their negative ions, but not by the functions of positive ions. Numerical calculations have been carried out using the exact SCF functions determined by CLEMENTI [2]

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* Using functions (unpublished) determined by Dr. E. CLEMENTI (IBM Research Laboratory, San Jose, Cal.).

for neutral atoms and their negative ions*. The corresponding results are presented in Tab. 1 and 2.

Table 2. *Calculated values for* H/E *and* $-H/I$ *for ground and excited states of negative* ions**

	H/E	$-H/I$		H/E	$-H/I$
Li ${}^1S$	0.69	1.85	S ${}^2P$	0.70	1.77
B ${}^3P$	0.69	1.84	Cl ${}^1S$	0.70	1.77
B ${}^1D$	0.68	1.86	K ${}^1S$	0.69	1.82
B ${}^1S$	0.68	1.87	Sc ${}^3F$	0.69	1.83
C ${}^4S$	0.70	1.77	Ti ${}^4F$	0.69	1.82
C ${}^2D$	0.70	1.78	Va ${}^5D$	0.69	1.81
C ${}^2P$	0.69	1.79	Cr ${}^6S$	0.69	1.80
N ${}^3P$	0.71	1.72	Mn ${}^5D$	0.69	1.79
N ${}^1D$	0.70	1.72	Fe ${}^4F$	0.69	1.78
N ${}^1S$	0.70	1.73	Co ${}^3F$	0.70	1.77
O ${}^2P$	0.71	1.66	Ni ${}^2S$	0.70	1.76
F ${}^1S$	0.72	1.62	Cu ${}^1S$	0.70	1.74
Na ${}^1S$	0.71	1.70	Ga ${}^3P$	0.70	1.75
Al ${}^3P$	0.70	1.74	Ga ${}^1D$	0.70	1.75
Al ${}^1D$	0.70	1.75	Ge ${}^4S$	0.70	1.75
Al ${}^1S$	0.70	1.76	Ge ${}^2D$	0.70	1.75
Si ${}^4S$	0.70	1.75	Ge ${}^2P$	0.70	1.76
Si ${}^2D$	0.70	1.76	As ${}^3P$	0.70	1.76
Si ${}^2P$	0.70	1.76	As ${}^1D$	0.70	1.76
P ${}^3P$	0.70	1.76	As ${}^1S$	0.70	1.76
P ${}^1D$	0.70	1.76	Se ${}^2P$	0.70	1.73
P ${}^1S$	0.70	1.77	Br ${}^1S$	0.70	1.76

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** Using functions (unpublished) determined by Dr. E. Clementi (IBM Research Laboratory, San Jose, Cal.).

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