IBM San Jose Research Laboratory, San Jose, California

Two-Configuration, Self-Consistent Field Theory

By

A. Veillard*

The Hartree-Fock pseudoeigenvalues equations have been derived for configuration interaction in the case of two atomic configurations ns^2np^N and np^{N+2}. A special case of investigation is the interaction between the nearly-degenerate configurations $1s^22s^22p^N$ and $1s^22p^{N+2}$. The LCAO form of the equations has also been established.

On établit les équations de Hartree-Fock correspondant à une interaction de configuration entre deux configurations atomiques ns^2np^N et np^{N+2}. Le cas simple d'interaction entre les deux configurations presque dégénérées $1s^22s^22p^N$ et $1s^22p^{N+2}$ a été plus particulièrement étudié. Les équations sont également présentées sous leur forme L.C.A.O.

Hartree-Fock Pseudoeigenwertgleichungen werden für die Konfigurationswechselwirkung im Fall der zwei Atomkonfigurationen ns^2np^N und np^{N+2} abgeleitet. Ein Spezialfall, der untersucht wird, ist die Wechselwirkung zwischen den beinahe entarteten Konfigurationen $1s^22s^22d^N$ und $1s^22p^{N+2}$. Die Gleichungen werden auch in ihrer LCAO Form angegeben.

Introduction

The process of configuration interaction is generally carried out by minimizing separately the energy expressions for the different configurations, which allows the determination of the wavefunctions for these different configurations; it is only in a second step that configuration interaction is introduced, taking into account the interaction between the previous defined configurations. The rigorous scheme (see for instance ref. [3] and [7]) would consist of introducing configuration interaction at the first step when writing the expression of the energy, then applying the variational principle to this expression in order to derive the equations for the orbitals. We establish, in the following pages, the corresponding Hartree-Fock type equations in the case of two atomic configurations ns^2np^N and np^{N+2}.

I. General Orbital Theory

Our formalism is closely related to that used by Roothaan [5] and we shall define only original notations.

The following limitations will be introduced:

— the interaction involves only two configurations;

— the expectation value of the energy is given, for each configuration, by [5]:

$$E = 2 \sum_k H_k + \sum_{kl} (2 J_{kl} - K_{kl}) + f [2 \sum_m H_m + f \sum_{mn} (2 a J_{mn} - b K_{mn}) + 2 \sum_{km} (2 J_{km} - K_{km})]$$

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* Presently at Laboratoire de Chimie de l'Ecole Normale Supérieure, 24 rue Lhomond, Paris 5ème France.

— the two configurations A and B are built from the following shells:

— a common closed shell C;

— a closed shell C' which appears only in A;

— a common open shell O with different occupation numbers in A and B.

Finally we shall restrict this study to the case where C' includes only one closed shell s^2, and where O is an open or closed shell p; the two configurations involved are then:

$$A \quad \underbrace{1s^2\ldots\ldots(n-1)\,p^6 \text{ or } d^{10}}_{\text{closed shell } C} \quad \underbrace{ns^2}_{\text{closed shell } C'} \quad \underbrace{np^N}_{\text{open shell } O} \quad (0 \le N \le 4)$$

$$B \quad \underbrace{1s^2 \qquad (n-1)\,p^6 \text{ or } d^{10}} \qquad\qquad\qquad \underbrace{np^{N+2}}\,.$$

The two-configurations wave function is given as:

$$\Phi = A\,\Psi\,(\ldots\,ns^2\,np^N) + B\,\Psi\,(\ldots\,np^{N+2})\,.$$

We assume that the expectation value of the energy is given by

$$
\begin{aligned}
E = A^2 \Big\{ &2\sum_k H_k + \sum_{kl}(2J_{kl} - K_{kl}) + 2\sum_{k'}H_{k'} + \sum_{k'l'}(2J_{k'l'} - K_{k'l'}) + \\
&+ 2\sum_{kk'}(2J_{kk'} - K_{kk'}) + \\
&+ f_1\,[2\sum_m H_m + f_1\sum_{mn}(2\,a_1\,J_{mn} - b_1\,K_{mn}) + 2\sum_{km}(2J_{km} - K_{km}) + \\
&+ 2\sum_{k'm}(2J_{k'm} - K_{k'm})]\Big\} + \\
&+ B^2\Big\{2\sum_k H_k + \sum_{kl}(2J_{kl} - K_{kl}) + f_2\,[2\sum_m H_m + f_2\sum_{mn}(2\,a_2\,J_{mn} - b_2\,K_{mn}) + \\
&+ 2\sum_{km}(2J_{km} - K_{km})]\Big\} + 2\,ABc\sum_{k'}\sum_m K_{k'm}\,.
\end{aligned}
\tag{1}
$$

The subscripts k and l/k' and l'/m and n refer to orbitals of the closed shell C/closed shell C'/open shell O. f_1 and f_2 are the fractional occupation of the open shell O in the two configurations.

Eq. (1) implies that the interaction energy term between the two configurations is given by $c\sum_{k'}\sum_m K_{k'm}$, where c means a real number. That is, we assume that for atoms this term can be expressed by means of Slater-Condon integrals G^k (see Appendix for the interaction term in the special case of the two configurations $1s^2 2s^2 2p^N$ and $1s^2 2p^{N+2}$).

The orthonormalization conditions are:

$$\langle \varphi_i \mid \varphi_j \rangle = \delta_{ij} \tag{2}$$

and:

$$A^2 + B^2 = 1\,. \tag{3}$$

We minimize the energy (1) with respect to the orbitals and the parameters A and B, taking into account the constraints (2) and (3). The resulting equations for the two closed shells C and C' and for the open shell O are:

$$
\begin{aligned}
[A^2\,(H + 2\,J_C - K_C + 2\,J_{C'} - K_{C'} + 2\,J_O^1 - K_O^1) + B^2\,(H + 2\,J_C - K_C + \\
+ 2\,J_O^2 - K_O^2]\,\varphi_k = \sum \varphi_j\,\theta_{jk} = \sum \varphi_j\,\overline{\theta}_{kj}
\end{aligned}
\tag{4}
$$

$$[A^2 (H + 2 J_C - K_C + 2 J_{C'} - K_{C'} + 2 J_O^1 - K_O^1) + A Bc \sum_m K_m] \varphi_{k'}$$

$$= \sum_j \varphi_j \theta_{jk'} = \sum_j \varphi_j \overline{\theta}_{k'j} \tag{5}$$

$$[A^2 f_1 (H + 2 J_C - K_C + 2 J_{C'} - K_{C'} + 2 a_1 J_O^1 - b_1 K_O^1) + B^2 f_2 (H + 2 J_C -$$

$$- K_C + 2 a_2 J_O^2 - b_2 K_O^2) + A Bc \, K_{C'}] \varphi_m = \sum_j \varphi_j \theta_{jm} = \sum_j \varphi_j \overline{\theta}_{mj} . \tag{6}$$

The parameters A and B are defined by:

$$A H_A + Bc \sum_{k'} \sum_m K_{k'm} - \lambda A = 0 \tag{7}$$

$$B H_B + Ac \sum_{k'} \sum_m K_{k'm} - \lambda B = 0 . \tag{8}$$

We used the notations:

$$J_O^1 = f_1 \sum_m J_m \qquad K_O^1 = f_1 \sum_m K_m \qquad J_O^2 = f_2 \sum_m J_m \qquad K_O^2 = f_2 \sum_m K_m \tag{9}$$

$$H_A = 2 \sum_k H_k + \sum_{kl} (2 J_{kl} - K_{kl}) + 2 \sum_{k'} H_{k'} + \sum_{k'l'} (2 J_{k'l'} - K_{k'l'}) +$$

$$+ 2 \sum_{kk'} (2 J_{kk'} - K_{kk'}) +$$

$$+ f_1 [2 \sum_m H_m + f_1 \sum_{mn} (2 a_1 J_{mn} - b_1 K_{mn}) + 2 \sum_{km} (2 J_{km} - K_{km}) + \tag{10}$$

$$+ 2 \sum_{k'm} (2 J_{k'm} - K_{k'm})]$$

$$H_B = 2 \sum_k H_k + \sum_{kl} (2 J_{kl} - K_{kl}) + f_2 [2 \sum_m H_m + f_2 \sum_{mn} (2 a_2 J_{mn} - b_2 K_{mn}) +$$

$$+ 2 \sum_{km} (2 J_{km} - K_{km})] . \tag{11}$$

From (7) and (8) we can derive:

$$\lambda = E = A^2 H_A + B^2 H_B + 2 A Bc \sum_{k'} \sum_m K_{k'm} . \tag{12}$$

We notice that the Lagrangian multipliers constitute a Hermitian matrix:

$$\theta_{ij} = \overline{\theta}_{ji} . \tag{13}$$

All the operators which appear in Eqs. (4), (5) and (6) are invariant under the transformations:

$$\varphi'_C = \varphi_C \, U_C \qquad \varphi'_{C'} = \varphi_{C'} \, U_{C'} \qquad \varphi'_O = \varphi_O \, U_O \tag{14}$$

but such transformations cannot eliminate the off-diagonal multipliers $\theta_{kk'}$, θ_{km}, $\theta_{k'm}$ in order to reduce Eqs. (4), (5) and (6) to pseudoeigenvalue equations. So we are faced with the problem of eliminating these off-diagonal multipliers by absorbing them into the left-hand side of Eqs. (4), (5) and (6) [5].

It can be seen easily that, in the case where C' is an s^2 closed-shell and O is a p open-shell:

$$\theta_{mk'} \equiv 0 .$$

Further, if we limit the scope of this study to the case where C is a closed shell $1s^2$ (that is, to the first row atoms and isoelectronic ions):

$$\theta_{mk} \equiv 0 .$$

The only problem is then to eliminate $\theta_{k'k} = \theta_{2s,\,1s}$. This is done in Part II,

where the straightforward Hartree-Fock pseudoeigenvalue equations are also deduced.

In the general case, we can drop the restriction:

$$\theta_{mk'} = 0$$

this may be useful for subsequent generalizations. We rewrite Eqs. (4), (5) and (6) in the form:

$$F_C \, \varphi_k = \sum_l \varphi_l \, \theta_{lk} + \sum_{l'} \varphi_{l'} \, \theta_{l'k} + \sum_n \varphi_n \, \theta_{nk}$$

$$F_{C'} \, \varphi_{k'} = \sum_l \varphi_l \, \theta_{lk'} + \sum_{l'} \varphi_{l'} \, \theta_{l'k'} + \sum_n \varphi_n \, \theta_{nk'} \qquad (15)$$

$$F_O \, \varphi_m = \sum_l \varphi_l \, \theta_{lm} + \sum_{l'} \varphi_{l'} \, \theta_{l'm} + \sum_n \varphi_n \, \theta_{nm} \, .$$

Using the hermiticity of the off-diagonal multipliers, we can express the off-diagonal multipliers between orbitals of C, C', and O in the following manner [4]:

$$\theta_{l'k} = \langle \varphi_{l'} \mid \Theta_{C'}^C \mid \varphi_k \rangle \qquad\qquad \theta_{lk'} = \langle \varphi_l \mid \Theta_C^{C'} \mid \varphi_{k'} \rangle$$

$$\theta_{nk} = \langle \varphi_n \mid \Theta_O^C \mid \varphi_k \rangle \qquad\qquad \theta_{lm} = \langle \varphi_l \mid \Theta_C^O \mid \varphi_m \rangle \qquad (16)$$

$$\theta_{nk'} = \langle \varphi_{n'} \mid \Theta_O^{C'} \mid \varphi_{k'} \rangle \qquad\qquad \theta_{l'm} = \langle \varphi_{l'} \mid \Theta_{C'}^O \mid \varphi_m \rangle$$

with

$$\Theta_X^Y = \lambda_X^Y \, F_Y + (1 - \lambda_X^Y) \, F_X \, . \qquad (17)$$

where λ_X^Y is an arbitrary real number.
We choose:

$$\Theta_{C'}^C = \Theta_C^{C'} = A^2 \, (2 \, J_{C'} - K_{C'} + 2 \, J_O^1 - K_O^1 - 2 \, J_O^2 + K_O^2) + \frac{A \, B c}{1 - A^2} \sum_m K_m = \Theta_{CC'} \qquad (18)$$

$$\Theta_O^C = \Theta_C^O = \frac{1}{A^2 f_1 + B^2 f_2 - 1} \{ A^2 \, B^2 \, (f_2 - f_1) \, (2 \, J_{C'} - K_{C'}) + A^2 \, [(A^2 - a_1) \, f_1 +$$
$$+ \, B^2 \, f_2] \, 2 \, J_{O_1} - A^2 \, [(A^2 - b_1) \, f_1 + B^2 \, f_2] \, K_O^1 + B^2 \, [A^2 \, f_1 +$$
$$+ \, (B^2 - a_2) \, f_2] \, 2 \, J_O^2 - B^2 \, [A^2 \, f_1 + (B^2 - b_2) \, f_2] \, K_O^2 - A \, B c \, K_{C'} \} = \Theta_{CO} \qquad (19)$$

$$\Theta_O^{C'} = \Theta_{C'}^O = \frac{1}{A^2 f_1 + B^2 f_2 - A^2} \{ A^2 \, B^2 \, f_2 \, (2 \, J_{C'} - K_{C'}) + A^2 \, [A^2 \, f_1 \, (1 - a_1) +$$
$$+ \, B^2 \, f_2] \, 2 \, J_O^1 - A^2 \, [A^2 \, f_1 \, (1 - b_1) + B^2 \, f_2] \, K_O^1 - A^2 \, B^2 \, f_2 \, a_2 \cdot 2 \, J_O^2 +$$
$$A^2 \, B^2 \, f_2 \, b_2 \, K_O^2 + (A^2 \, f_1 + B^2 \, f_2) \, A \, B c \sum_m K_m - A^2 \, A \, B c \, K_{C'} \} = \Theta_{C'O} \, . \qquad (20)$$

Defining the coupling operators:

$$R_{C'}^C = - \, [\sum_{l'} \varphi_{l'} \, \langle \varphi_{l'} \mid \Theta_{CC'}) + (\Theta_{CC'} \mid \varphi_{l'} \rangle \varphi_{l'}]$$

$$R_O^C = - \, [\sum_n \varphi_n \, \langle \varphi_n \mid \Theta_{CO}) + (\Theta_{CO} \mid \varphi_n \rangle \varphi_n]$$

$$R_C^{C'} = - \, [\sum_l \varphi_l \, \langle \varphi_l \mid \Theta_{CC'}) + (\Theta_{CC'} \mid \varphi_l \rangle \varphi_l] \qquad (21)$$

$$R_O^{C'} = - \, [\sum_n \varphi_n \, \langle \varphi_n \mid \Theta_{C'O}) + (\Theta_{C'O} \mid \varphi_n \rangle \varphi_n]$$

$$R_C^O = - \, [\sum_l \varphi_l \, \langle \varphi_{l'} \mid \Theta_{CO}) + (\Theta_{CO} \mid \varphi_{l'} \rangle \varphi_l]$$

$$R_{C'}^O = - \, [\sum_{l''} \varphi_{l'} \, \langle \varphi_{l'} \mid \Theta_{C'o}) + (\Theta_{C'o} \mid \varphi_{l'} \rangle \varphi_{l'}] \, .$$

Eqs. (15) can be written in new forms which constitute the Hartree-Fock pseudo-eigenvalue equations:

$$(F_C + R_{C'}^C + R_O^C)\, \varphi_k = \sum_l \varphi_l\, \theta_{lk}$$

$$(F_{C'} + R_C^{C'} + R_O^{C'})\, \varphi_k = \sum_{l'} \varphi_{l'}\, \theta_{l'k'} \tag{22}$$

$$(F_O + R_C^O + R_{C'}^O)\, \varphi_m = \sum_n \varphi_n\, \theta_{nk}.$$

The explicit forms of the operators R_Y^X have been given elsewhere [6] and for the sake of briefness we shall not report them.

II. Special Case of the Configurations $1s^2\, 2s^2\, 2p^N - 1s^2\, 2p^{N+2}$

In the simple case of configuration interaction between two configurations $1s^2 2s^2 2p^N$ and $1s^2 2p^{N+2}$, Eqs. (4), (5), and (6) become:

$$F_{1s}\, \varphi_{1s} = [H + 2\, J_{1s} - K_{1s} + A^2\, (2\, J_{2s} - K_{2s} + 2\, J_O^1 - K_O^1) + B^2\, (2\, J_O^2 -$$
$$- K_O^2)]\, \varphi_{1s} = \varphi_{1s}\, \theta_{1s} + \varphi_{2s}\, \theta_{2s,\, 1s} \tag{23}$$

$$F_{2s}\, \varphi_{2s} = [A^2\, (H + 2\, J_{1s} - K_{1s} + 2\, J_{2s} - K_{2s} + 2\, J_O^1 - K_O^1) + A Bc \sum_m K_m]\, \varphi_{2s}$$
$$= \varphi_{1s}\, \theta_{1s,\, 2s} + \varphi_{2s}\, \theta_{2s} \tag{24}$$

$$F_O\, \varphi_m = [A^2 f_1\, (H + 2\, J_{1s} - K_{1s} + 2\, J_{2s} - K_{2s} + 2\, a_1\, J_O^1 - b_1\, K_O^1) +$$
$$+ B^2 f_2\, (H + 2\, J_{1s} - K_{1s} + 2\, a_2\, J_O^2 - b_2\, K_O^2) +$$
$$+ A Bc\, K_{2s}]\, \varphi_m = \sum_n \varphi_n\, \theta_{nm}. \tag{25}$$

In our attempt to eliminate the off-diagonal multipliers $\theta_{2s,\, 1s}$ and $\theta_{1s,\, 2s}$, we choose $\lambda = -\dfrac{A^2}{B^2}$ $\quad 1 - \lambda = \dfrac{1}{1 - A^2}$ in Eq. (17) so that:

$$\Theta = A^2\, (2\, J_{2s} - K_{2s} + 2\, J_O^1 - K_O^1 - 2\, J_O^2 + K_O^2) + \frac{A Bc}{1 - A^2} \sum_m K_m \tag{26}$$

and we define the coupling operators:

$$R_{2s} = -\, [\varphi_{2s}\, \langle \varphi_{2s} \mid \Theta) + (\Theta \mid \varphi_{2s}\rangle\, \langle \varphi_{2s} \mid] \tag{27}$$
$$R_{1s} = -\, [\varphi_{1s}\, \langle \varphi_{1s} \mid \Theta) + (\Theta \mid \varphi_{1s}\rangle\, \langle \varphi_{1s} \mid].$$

Using Eq. (27), Eqs. (23) and (24) become:

$$(F_{1s} + R_{2s})\, \varphi_{1s} = \varphi_{1s}\, \theta_{1s} \tag{28}$$
$$(F_{2s} + R_{1s})\, \varphi_{2s} = \varphi_{2s}\, \theta_{2s}.$$

Eqs. (28) and (25) are the pseudoeigenvalue Hartree-Fock equations. A formulation in which the $1s$ and $2s$ orbitals are solutions of the same eigenvalue equation has been reported elsewhere [6]. We must join the Eqs. (7), (8) and (12) with, in this case:

$$H_A = 2\, H_{1s} + J_{1s,\, 1s} + 2\, H_{2s} + J_{2s,\, 2s} + 2\, (2\, J_{1s,\, 2s} - K_{1s,\, 2s}) + f_1\, [2 \sum_m H_m$$
$$+ f_1 \sum_{mn} (2\, a_1\, J_{mn} - b_1\, K_{mn}) + 2 \sum_m (2\, J_{1s,\, m} - K_{1s,\, m}) +$$
$$+ 2 \sum_m (2\, J_{2s,\, m} - K_{2s,\, m})] \tag{29}$$

$$H_B = 2\, H_{1s} + J_{1s,\, 1s} + f_2\, [2 \sum_m H_m + f_2 \sum_{mn} (2\, a_2\, J_{mn} - b_2\, K_{mn}) +$$
$$+ 2 \sum_m (2\, J_{1s,\, m} - K_{1s,\, m})]$$

III. LCAO Form for the Configurations $1s^2\, 2s^2\, 2p^N - 1s^2\, 2p^{N+2}$

If the orbitals are expanded in terms of basis functions according to [5]:

$$\varphi_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha}\, C_{i\lambda p}$$

the energy expression for each configuration can be written in a form similar to that given in Ref. [1].

The interaction energy term H_{AB} can be written in the form (see Appendix):

$$H_{AB} = \sum_{pqrs} N_{2S}\, C_{2Sp}\, C_{2Sq}\, Q_{Spq,\,Prs}\, (\alpha\, N_{1P}^1\, C_{1Pr}\, C_{1Ps} + \beta\, N_{1P}^2\, C_{1Pr}\, C_{1Ps}) \qquad (30)$$

Minimizing the corresponding total expression in respect with the coefficients C, we derive the following equations:

$$\sum_q \{ A^2\, [H_{Spq} + \sum_{rs} P_{Spq,\,Srs}\, D_{T,\,Srs}^1 + \sum_{rs} P_{Spq,\,Prs}\, D_{T,\,Prs}^1] + B^2\, [H_{S,\,pq} +$$
$$+ \sum_{rs} P_{Spq,\,Srs}\, D_{T,\,Srs}^2 + \sum_{rs} P_{Spq,\,Prs}\, D_{T,\,Prs}^2] \}\, C_{1Sq} = \sum_q S_{Spq}\, C_{1Sq}\, \frac{\theta_{s\,11}}{N_{1s}} + \qquad (31)$$
$$+ \sum_q S_{Spq}\, C_{2Sq}\, \frac{\theta_{s\,21}}{N_{1s}}$$

$$\sum_q \{ A^2\, [H_{Spq} + \sum_{rs} P_{Spq,\,Srs}\, D_{T,\,Srs}^1 + \sum_{rs} P_{Spq,\,Prs}\, D_{T,\,Prs}^1] +$$
$$+ AB \sum_{rs} Q_{Spq,\,Prs}\, (\alpha D_{T,\,Prs}^1 + \beta D_{T,\,Prs}^2) \}\, C_{2Sq} = \sum_q S_{Spq}\, C_{1Sq}\, \frac{\theta_{s\,12}}{N_{2s}} +$$
$$+ \sum_q S_{Spq}\, C_{2Sq}\, \frac{\theta_{s\,22}}{N_{2s}} \qquad (32)$$

$$\sum_q \{ N_{1P}^1\, A^2\, [H_{Ppq} + \sum_{rs} P_{Spq,\,Prs}\, D_{T,\,Srs}^1 + \sum_{rs} P_{Ppq,\,Prs}\, D_{T,\,Prs}^1 -$$
$$- \sum_{rs} Q_{Ppq,\,Prs}^1\, D_{O,\,Prs}^1] + N_{1P}^2\, B^2\, [H_{Ppq} + \sum_{rs} P_{Spq,\,Prs}\, D_{T,\,Srs}^2 +$$
$$+ \sum_{rs} P_{Ppq,\,Prs}\, D_{T,\,Prs}^2 - \sum_{rs} Q_{Ppq,\,Prs}^2\, D_{O,\,Prs}^2] + \qquad (33)$$
$$+ (\alpha N_{1P}^1 + \beta N_{1P}^2)\, AB \sum_{rs} Q_{Ppq,\,Srs}\, D_{2S,\,rs} \}\, C_{1Pq} = \sum_q S_{Ppq}\, C_{1Pq}\, \theta_{P11}$$

by defining:

$$D_{T,\,Srs}^1 = \sum_{rs} (N_{1S}\, C_{1Sr}\, C_{1Ss} + N_{2S}\, C_{2Sr}\, C_{2Ss}) = D_{1S,\,rs} + D_{2S,\,rs}$$

$$D_{T,\,Srs}^2 = \sum_{rs} N_{1S}\, C_{1Sr}\, C_{1Ss} \qquad\qquad = D_{1S,\,rs}$$

$$D_{T,\,Prs}^1 = \sum_{rs} N_{1P}^1\, C_{1Pr}\, C_{1Ps} \qquad\qquad = D_{1P,\,rs}^1 = D_{OP,\,rs}^1$$

$$D_{T,\,Prs}^2 = \sum_{rs} N_{1P}^2\, C_{1Pr}\, C_{1Ps} \qquad\qquad = D_{1P,\,rs}^2 = D_{OP,\,rs}^2$$

$$D_{2S,\,rs} = D_{C',\,rs} = \sum_{rs} N_{2S}\, C_{2Sr}\, C_{2Ss}\,.$$

We rewrite Eqs. (31) and (32) in the form:

$$\sum_q F_{1S,\,pq}\, C_{1Sq} = \sum_q S_{Spq}\, C_{1Sq}\, \frac{\theta_{s\,11}}{N_{1s}} + \sum_q S_{Spq}\, C_{2Sq}\, \frac{\theta_{s\,21}}{N_{1s}} \qquad (34)$$

$$\sum_q F_{2S,\,pq}\, C_{2Sq} = \sum_q S_{Spq}\, C_{1Sq}\, \frac{\theta_{s\,12}}{N_{2s}} + \sum_q S_{Spq}\, C_{2Sq}\, \frac{\theta_{s\,22}}{N_{2s}}\,. \qquad (35)$$

We define:

$$N_{1S}\, G_{S,\,pq} = N_{2S}\, G_{S,\,pq} = \lambda N_{1S}\, F_{1S,\,pq} + (1-\lambda)\, N_{2S}\, F_{2S,\,pq}$$
$$R_{2S,\,pq} = -\sum_{uw} (S_{Spu}\, C_{2Su}\, G_{Swq}\, C_{2Sw} + G_{Spu}\, C_{2Su}\, S_{Swq}\, C_{2Sw})\,.$$

After some straightforward algebra Eqs. (34) can be written in the new form:

$$\sum_q (F_{1S,\ pq} + R_{2S,\ pq}) C_{1Sq} = \sum_q S_{Spq} C_{1Sq} \frac{\theta_{S\,11}}{N_{1s}}. \tag{36}$$

In a similar manner, defining:

$$R_{1S,\ pq} = -\left[\sum_{uw} S_{Spu} C_{1Su} G_{S,\ wq} C_{1Sw} + \sum_{uw} G_{Spu} C_{1Su} S_{Swq} C_{1Sw} \right]$$

it can be shown easily that Eq. (35) can be written:

$$\sum_q (F_{2S,\ pq} + R_{1S,\ pq}) C_{2Sq} = \sum_q S_{Spq} C_{2Sq} \frac{\theta_{S\,22}}{N_{2s}}. \tag{37}$$

Eqs. (36) (37) and (33) are the three eigenvalue equations. We must join again the two equations defining A and B:

$$AH_A + BH_{AB} - \lambda A = 0 \tag{7}$$

$$AH_{AB} + BH_B - \lambda B = 0 \tag{8}$$

with:

$$H_A = \sum_{pq} (H_{Spq} D^1_{T,Spq} + H_{Ppq} D^1_{T,Ppq}) + \tfrac{1}{2} \sum_{pqrs} (D^1_{T,Spq} P_{Spq,\ srs} D^1_{T,Srs} +$$
$$+ 2 D^1_{T,Spq} P_{Spq,\ Prs} D^1_{T,Prs} + D^1_{T,Ppq} P_{Ppq,\ Prs} D^1_{T,Prs} -$$
$$- D^1_{T,Ppq} Q^1_{Ppq,Prs} D^1_{T,Prs}) \tag{38}$$

$$H_B = \sum_{pq} (H_{Spq} D^2_{T,Spq} + H_{Ppq} D^2_{T,Ppq}) + \tfrac{1}{2} \sum_{pqrs} (D^2_{T,Spq} P_{Spq,\ srs} D^2_{T,Srs} +$$
$$+ 2 D^2_{T,Spq} P_{Spq,\ Prs} D^2_{T,Prs} + D^2_{T,Ppq} P_{Ppq,\ Prs} D^2_{T,Prs} -$$
$$- D^2_{T,Ppq} Q^2_{Ppq,Prs} D^2_{T,Prs}) \tag{39}$$

$$H_{AB} = \sum_{pqrs} D_{2S,\ pq} Q_{Spq,\ Prs} (\alpha D^1_{T,\ Prs} + \beta D^2_{T,\ Prs}) \tag{40}$$

Results for the first row atoms and isoelectronic ions and their discussion in respect with correlation energy will be given in a subsequent paper [2].

Appendix

Interaction Term H_{AB} for the Two Configurations $1s^2\,2s^2\,2p^N$ and $1s^2\,2\,p^{N+2}$

For the two configurations $1s^2 2s^2 2p^N$ and $1s^2 2p^{N+2}$ the interaction term H_{AB} is given by:

$$H_{AB} = CG^1\,(2s,\ 2p)\,.$$

The values of C are reported in the table for each spectroscopic state of interest:

Table

		C	K_{SP1}
$N = 0$	^1S	$\dfrac{\sqrt{3}}{3}$	$-\dfrac{\sqrt{3}}{6}$
$= 1$	^2P	$\dfrac{\sqrt{2}}{3}$	$-\dfrac{\sqrt{2}}{9}$
$= 2$	^3P	$\dfrac{1}{3}$	$-\dfrac{1}{12}$
$= 3$	^2P	$\dfrac{\sqrt{2}}{3}$	$-\dfrac{\sqrt{2}}{15}$
$= 4$	^1S	$\dfrac{\sqrt{3}}{3}$	$-\dfrac{\sqrt{3}}{18}$

In the LCAO equation, Eq. (40), we wrote this term:

$$H_{AB} = \sum_{pqrs} D_{2S, pq} Q_{Spq, Prs} \left(\alpha\, D_{T, Prs}^{1} + \beta\, D_{T, Prs}^{2}\right)$$

with:

$$Q_{Spq, Prs} = \sum_{\nu=0}^{2(\lambda,\mu)\,<} \mathscr{G}_{\lambda\mu\nu}^{\nu}\, G_{\lambda pq, \mu rs}^{\nu} - \frac{1}{2} \sum_{\nu=|\lambda-\mu|}^{|\lambda+\mu|} K_{\lambda\mu\nu}\, \mathscr{K}_{\lambda pq, \mu rs}^{\nu}$$

$$= J_{SPO}\, \mathscr{G}_{Spq, Prs}^{0} - \frac{1}{2} K_{SP1}\, \mathscr{K}_{Spq, Prs}^{1}$$

The identification is straightforward:

$$J_{SPO} = 0$$

$$K_{SP1} = -\frac{2\,C}{N_{2s}\,N_{1p}^{2}} = -\frac{C}{N_{1P}^{2}} \quad \text{if we put } \alpha = 0 \qquad \beta = 1 \, .$$

We report K_{SP1} in the table.

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