Two-Configuration, Self-Consistent Field Theory

By

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The Hartree-Fock pseudoeigenvalues equations have been derived for configuration interaction in the case of two atomic configurations ns2npN and npN+2. A special case of investigation is the interaction between the nearly-degenerate configurations 1s2s22pN and 1s2pN+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 ns2npN et npN+2. Le cas simple d’interaction entre les deux configurations presque dégénérées 1s2s22pN et 1s2pN+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 ns2npN und npN+2 abgeleitet. Ein Spezialfall, der untersucht wird, ist die Wechselwirkung zwischen den beinahe entarteten Konfigurationen 1s2s22dN und 1s2pN+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 ns2npN and npN+2.

I. General Orbital Theory

Our formalism is closely related to that used by ROOTHAN [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]:

\[
E = 2 \sum_{k} H_{k} + \sum_{k l} (2 J_{kl} - K_{kl}) + \int [2 \sum_{m} H_{m} + \int \sum_{m n} (2 aJ_{mn} - bK_{mn}) +
\]

\[
+ 2 \sum_{km} (2 J_{km} - K_{km})]
\]

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:

\[
\begin{align*}
A & \quad 1s^2 \ldots \ldots (n-1) p^6 \text{ or } d^{10} \quad ns^2 \quad np^N \quad (0 \leq N \leq 4) \\
& \quad \text{closed shell } C' \quad \text{open shell } O \\
B & \quad 1s^2 \ldots \ldots (n-1) p^6 \text{ or } d^{10} \quad np^{N+2} 
\end{align*}
\]

The two-configurations wave function is given as:

\[
\Phi = A \Psi \ldots \ldots ns^2 np^N + B \Psi \ldots \ldots np^{N+2}.
\]

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

\[
E = A^2 \left\{ \sum_k H_k + \sum_{kl} (2J_{kl} - K_{kl}) + 2 \sum_{k'} H_{k'} + \sum_{k'\nu} (2J_{k'\nu} - K_{k'\nu}) + \right. \\
\left. + 2 \sum_{k'} (2J_{kk'} - K_{kk'}) + \\
+ f_1 \left[ 2 \sum_m H_m + f_1 \sum_{mn} (2a_1 J_{mn} - b_1 K_{mn}) + 2 \sum_{km} (2J_{km} - K_{km}) + \\
\right. \\
\left. + 2 \sum_{k'\nu} (2J_{k'\nu} - K_{k'\nu}) \right] + \\
B^2 \left\{ \sum_k H_k + \sum_{kl} (2J_{kl} - K_{kl}) + f_2 \left[ 2 \sum_m H_m + f_2 \sum_{mn} (2a_2 J_{mn} - b_2 K_{mn}) + \\
\right. \\
\left. + 2 \sum_{km} (2J_{km} - K_{km}) \right] + 2 ABC \sum_{k'} \sum_m K_{k'm} \right. \\
\left. + B^2 \left( H + 2J_C - K_C + 2J_{O} - K_{O} \right) + B^2 \left( H + 2J_C - K_C + \\
+ 2J_{O} - K_{O} \right) \varphi_k = \sum \varphi_j \theta_{kj} = \sum \varphi_j \bar{\theta}_{kj} \right.
\]

The subscripts $k$ and $l/k'$ and $U/m$ 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 $c \sum_{k'} K_{k'm}$, 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 $1s^22s^22p^6$ and $1s^22s^2p^{N+2}$).

The orthonormalization conditions are:

\[
\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad (2)
\]

and:

\[
A^2 + B^2 = 1 \quad (3)
\]

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:

\[
[A^2 (H + 2J_C - K_C + 2J_{O} - K_{O}) + B^2 (H + 2J_C - K_C + \\
+ 2J_{O} - K_{O})] \varphi_k = \sum \varphi_j \theta_{kj} = \sum \varphi_j \bar{\theta}_{kj} \quad (4)
\]