AN ALGORITHM FOR SELF-CONSISTENT FIELD MO LCAO COMPUTATIONS ON CONJUGATED SYSTEMS WITH ALLOWANCE FOR CONFIGURATION INTERACTION


The Pariser-Parr-Pople method is described briefly. An algorithm is presented for quantum-mechanical computation of molecular structures. A program for the BESM-2M computer is presented.

The semiempirical Pariser-Parr-Pople (PPP) method is the best of the quantum-mechanical methods of deriving the electronic spectra of polyatomic molecules [1, 2]. Algorithms for use with Russian computers have been published, but all of them either assume previous computation of the main semiempirical quantities, or use formulas for these [3, 4] or give only the minimum of useful information [5, 6].

The present algorithm demands only the minimum of input data but yields the energies of the MO, the coefficients in the expansion of the MO with respect to the AO, the charges, and the bond orders for the ground and first excited states, the transition energies and oscillator strengths for the transitions from the ground state to the excited states, and also certain other quantities. The method involves the computation of the molecular parameters and the elements of the matrix for the Coulomb repulsion integrals; allowance is also made for the penetration integrals.

The energies of the excited states are derived by the method of configuration interaction, which gives an improvement on the results from the MO calculation.

THE PARISER-PARR-POPLE METHOD

In the PPP method it is assumed that the \( \pi \) electrons of an unsaturated molecule move in the field of the ionized residue of the molecule, which consists of the \( \sigma \) electrons and of the nuclei screened by the inner shells.

A Slater determinant is used for the wave function of the ground state of a system containing 2m electrons:

\[
\psi_0 = \frac{1}{\sqrt{m!}} \det \{ \Phi_1(1) \Phi_1(2) \ldots \Phi_m(2m-1) \Phi_m(2m) \}.
\]

The energy of this state is \( E = \int V_0 \hat{H}_0 \psi_0 d\tau \) and has the electron hamiltonian

\[
\hat{H}_0 = \sum_{\mu} H^{\pi}_{\mu}(\mu) + \frac{1}{2} \sum_{\mu,\nu} \frac{e^2}{r_{\mu\nu}}.
\]

Here \( H^{\pi}_{\mu}(\mu) = T(\mu) + U^{\pi}(\mu) \) is the one-electron hamiltonian of electron \( \mu \) in the field of the residue; \( e^2/r_{\mu\nu} \) is the potential energy due to the Coulomb interaction of electrons distance \( r_{\mu\nu} \) apart; and \( \Phi_\mu(\mu) = \psi_\mu(\mu) \alpha; \Phi_\mu(\mu) = \psi_\mu(\mu) \beta \) are the molecular spin orbitals.

Then (1) gives the total \( \pi \)-electron energy as

\[
E = 2 \sum_i I_{ii} + \sum_{i \neq j} (2J_{ij} - K_{ij}).
\]

in which the \( f \) denotes summation over all filled MO of the ground state; (2) contains \( I_{ii} \) (orbital energies in the nuclear field), \( J_{ij} \) (Coulomb integrals), and \( K_{ij} \) (exchange integrals), all of which are defined by

\[
I_{ii} = \int \Phi'_i(\mu) \Phi_i(\mu) d\tau(\mu),
\]

\[
J_{ii} = \int \int \Phi'_i(\mu) \Phi'_j(\nu) \psi^2(\eta) \frac{e^2}{r_{\mu\nu}} \Phi_i(\mu) \Phi_j(\nu) d\tau(\mu) d\tau(\nu),
\]

\[
K_{ij} = \int \int \Phi'_i(\mu) \Phi'_j(\nu) \psi^2(\eta) \Phi_i(\mu) \Phi_j(\nu) d\tau(\mu) d\tau(\nu),
\]

but which are virtually impossible to calculate. The problem is much simplified if the MO are put as linear combinations of the AO (LCAO approximation); a one-electron MO becomes

\[
\psi_\mu = \sum_p C_{\mu p} \chi_p
\]

in which \( \chi_p \) is the basis group of AO (p = 1 to n) centered on the atoms in the \( \pi \)-electron system; \( C_{\mu p} \) is the coefficient of AO \( p \) in MO \( \mu \) and represents a solution of the equation [7]

\[
\sum_p C_{\mu p} (H^C_{pq} - \epsilon_p S_{pq}) = 0 \quad (i = 1, n; \quad p, q = 1, n),
\]

in which the matrix elements of the self-consistent hamiltonian \( H^C \) are defined as

\[
H^C_{pq} = H^T_{pq} + \sum_{i} \sum_{r,s} C_{pi} C_{qj} (2(pq | rs) - (pr | sq)),
\]

and the \( S_{pq} = \int \chi_p(\mu) \chi_q(\mu) d\tau(\mu) \) are the overlap integrals for AO \( \chi_p \) and \( \chi_q \). The notation used in (4) and (5) is as follows: \( H^T_{pq} = \int \chi_p H^T(\mu) \chi_q(\mu) d\tau(\mu) \) are the matrix elements of the hamiltonian for the residue that corresponds to the wave functions \( \chi_p \) and \( \chi_q \); and \( (pq | rs) = \int \chi_p(\mu) \chi_q(\mu) \psi^2(\eta) \psi_r(\nu) \chi_s(\nu) d\tau(\mu) d\tau(\nu) \) are the integrals for the electron interaction.

System (4) has a nonzero solution if

\[
\det | H^C_{pq} | = 0.
\]
The Cip and MO energies \( \varepsilon_i \) in the zero differential overlap approximation \( S_{pq} = \delta_{pq} = \begin{cases} 1, & p = q \\ 0, & p \neq q \end{cases} \) become the eigenvectors and eigenvalues of the matrix for the Hartree-Fock Hamiltonian. The matrix elements themselves are functions of the Cip [see (9)], so the Cip and \( \varepsilon_i \) are determined by successive approximation.

The notation of quantum chemistry is

\[
\langle \rho \rangle = \sum_{pq} \rho_{pq} = \sum_{pq} \langle \rho \rangle_{pq}
\]

with which we use the approximation of [8] for certain integrals of the residue, the detailed formulas for the matrix elements of \( H_C \) then becoming

\[
H_{pq}^C = \rho_{pq} \left( \begin{array}{c}
\rho_{pq} = \frac{1}{2} P_{pq} y_{pq} \\
(p \neq q)
\end{array} \right)
\]

Hence \( W_p \) is the energy of a \( \pi \) electron of atom \( p \) in the appropriate valency state, \( D_p \) is the number of electrons supplied by atom \( p \), \( \langle \rho | \rho \rangle = \sum_{pq} \rho_{pq} \) are the penetration integrals, and \( P_{pq} \) are the elements of the charge and bond-order matrix, which are defined as

\[
P_{pq} = \sum_i g_i C_{ip} C_{iq}
\]

in which \( g_i = 0, 1, 2 \) are the filling numbers.

ALLOWANCE FOR CONFIGURATION INTERACTION

The wave functions of excited states are here represented as linear combinations of the determinant wave functions corresponding to different (e.g., singly) excited configurations:

\[
| \psi \rangle = \sum_{i>1} A_{i} | \psi_i \rangle
\]

in which \( \alpha \) is the number of the excited state and \( V_{i>1} \) is the determinant wave function of the state obtained by a single excitation of an electron from a MO \( i > 1 \) filled in the ground state to a vacant one \( \psi_i \):

\[
| \psi_i \rangle = \frac{1}{V} \left[ | \Phi_i \delta_1 \cdots \Phi_i \delta_{i-1} \delta_i \delta_{i+1} \cdots | + | \Phi_i \delta_1 \cdots \Phi_i \delta_{i-1} \delta_{i+1} \cdots \delta_i | \right]
\]

(The - and + signs correspond respectively to the singlet \( V_{i>1} \) and triplet \( V_{i>1} \) configurations).

We obtain a system of equations and a secular equation analogous to (4) and (6) by using variational principles to get a set of \( A_{i>1} \) that minimize the corresponding energy; these are now in terms of the determinant wave functions:

\[
\sum_{i>1} A_{i} \{ 1 \} H_{i>1} - E_o S_{i>1} = 0.
\]

Here \( H_{i>1} = \langle \psi_i | H_1 | \psi_i \rangle \) are the elements of the configuration-interaction matrix (CIM).

The determinant wave functions corresponding to different sets of filled MO are orthonormalized,

\[
\langle V_{i>1} | V_{j>1} \rangle = \delta_{ij} E_o = \delta_{ij} H_{i>1} - \delta_{ij} H_{i>1} - (i, j, k),
\]

in which

\[
H_{i>1} = H_{i>1} + \sum_i \{ 2 (i | i) - (i | j) \}
\]

and

\[
\langle i | j | k \rangle = \int \psi_i^* (\mu) \psi_j (\nu) d\mu d\nu.
\]

COMPUTER ALGORITHM

A distinctive feature of the PPP method is that the matrix elements of the Hartree-Fock Hamiltonian are used in the form of (7) and (8), which allows us to introduce quantities found by experiment in place of direct computation of integrals of the type \( \alpha_{pq} \), \( \beta_{pq} \), and \( \gamma_{pq} \). These semiempirical parameters are calculated via \( Z_p \), the effective nuclear charge for the given AO. We use Leroy's approach [10, 11] to allow for the mobile charge effect and assume the relation of effective charge to electron population on the atom to be of the form

\[
Z_p^{(\xi+1)} = Z_p [1 + \xi \beta_p (D_p - P_{pq})].
\]

Here \( Z_p \) is the effective charge of AO \( p \) as calculated from Slater's rule, \( \beta_p \) is an atomic constant equal to \( (1 - Z_p/Z_p') \), and \( \xi \) is the number of the iteration, thus characterizing the variation in the quantities during derivation of the self-consistent solution.

The following formulas are used to find \( \gamma_{pp} \) and \( W_p \) in relation to the \( \pi \)-electron charges on the atoms:

\[
\gamma_{pp} = k_p Z_p^2,
\]

\[
W_p = m_p Z_p^2
\]

Leroy [10] considered this method of estimating the parameters and described the computation of the atomic constants \( k_p \) and \( m_p \).

It is usual [1] to consider two cases in deriving the \( \gamma_{pq} \) as functions of \( \pi_{pq} \); for \( \pi_{pq} \geq 2.8 \) the \( \gamma_{pq} \) are