A Modification of the Free-Electron Model for Cyclic Polyenes

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In the free-electron model (FE) of cyclic polyenes the π-electrons are allowed to move freely in a ring. A modification of the FE-model (the MFE-model) is discussed in which the N-fold symmetry due to the N C-atoms of the ring is taken into account by an appropriate potential. The results of the MFE-model are compared with HMO-theory. The sequence of degenerate and non-degenerate levels which determines the chemical properties (aromaticity and anti-aromaticity) of the annulenes is the same for both models.

Key words: HMO-theory, Free-electron model, Annulenes, Perturbation theory, Variation theory.

1. Introduction

A theory of conjugated π-systems must be able to explain Hückel's rule [1] on aromaticity according to which ring systems with $(4n+2)$ π-electrons are stabilized (aromatic), whereas ring systems with $4n$ π-electrons are destabilized (anti-aromatic). A cyclic conjugated polyene with N C-atoms is called [N]-annulene. There are two simple theories of π-systems taking into account the π-electrons only, the Hückel molecular orbital (HMO) theory and the free electron (FE) model. In both models the mutual electrostatic repulsion of the electrons is neglected.

The sequence of degeneracy of the occupied levels in the ground state of the molecule is the same for both theories. The lowest level is non-degenerate, whereas the other levels up to the HOMO (highest occupied molecular orbital) are doubly degenerate. If those levels are occupied by electrons obeying Pauli's principle and Hund's rule, each HOMO of the ground state of a $(4n+2)$-system is occupied by two electrons of opposite spin giving a stable singlett state, whereas the HOMOs of the ground state of a $4n$-system are each occupied by one electron of parallel spin forming an unstable diradical.

The alternation of aromaticity and anti-aromaticity of the annulenes with increasing number of π-electrons can be explained by any model which gives the above mentioned scheme of degeneracy. In this paper the results of the HMO- and FE-model of annulenes will be compared briefly, and a modification of the FE-model will be suggested.

2. The HMO Model

The HMO-theory has been reviewed in various articles and books, e.g. [2–5]. The HMO-energies of an [N]-annulene have been given in a closed form by Coulson [6]

$$E_J = \alpha + 2\beta \cos\left[\frac{2\pi}{N} J\right], \quad J = 0, 1, \ldots, N-1\,, \qquad (1)$$

where α is the Coulomb integral and β is the resonance integral. Recently Razi Naqvi [7] has given an alternative derivation of (1). A simple mnemonic scheme for the energy formula has been given by Frost and Musilin [8]. It can be seen from (1) that the lowest and the highest level of [$2N$]-annulenes are nondegenerate, whereas for rings with an odd number of C-atoms only the lowest level is nondegenerate. All other levels are doubly degenerate. The sequence of degeneracy of the levels calculated from the HMO-model allows to predict Hückel's rule.

3. The Simple FE-Model

In the FE-model the π-electrons of a cyclic polyene are allowed to move freely in a ring of constant potential, but they cannot leave the ring. The problem is discussed in most books on quantum mechanics [9]; here we follow the notation used by Lowe [2]. The energies and wave functions can be obtained by solv-

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ing the Schröder-equation.

$$-\frac{\hbar^2}{2m}\,\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\,\psi(x), \qquad 0 \le x < L\,. \tag{2}$$

The cyclic domain in which the particle can move is taken into account by the boundary conditions on the wave function ψ and its derivative ψ'.

$$\psi(0) = \psi(L), \qquad \psi'(0) = \psi'(L)\,. \tag{3}$$

Using the angle ϕ as the independent variable, the eigenfunctions can be written in the complex form [2]

$$\psi_k = \frac{1}{\sqrt{2\pi}} \exp(i k \phi), \quad k = 0, \pm 1, \pm 2, \ldots, \quad \phi \in [0, 2\pi]\,. \tag{4}$$

The energies are

$$E_k = \frac{\hbar^2 k^2}{2 m r^2}, \tag{5}$$

where m is the mass of the particle and r is the radius of the ring. All levels with $k \neq 0$ are doubly degenerate. Hence, wave functions with the same absolute value $|k|$ can be mixed arbitrarily. The form of ψ given in (4) will turn out to be well suited for most of the subsequent discussion. Due to the degeneracy of all levels except the lowest, the same arguments as for the HMO model can be applied to explain the alternation of aromatic and antiaromatic rings with increasing (even) number of π electrons.

4. Modification of the FE-Model

The simple FE-model outlined in the last section makes rather drastic approximations. Assuming that the circumference of the ring is proportional to the number N of C-atoms in it, the radius of the ring is the only parameter depending on N which influences the energies. Let us assume that the ring has the form of an ideal circle. Then the particle moving in a ring with a constant potential $V = 0$ is influenced by a potential with a C_∞-axis. In a realistic model of a cyclic compound with N C-atoms placed equidistant on the ring the symmetry of the potential should be C_N instead of C_∞. Thus the FE-model can be improved by introducing an N-fold symmetry into the potential. Without doing further calculations, Platt has pointed out that the introduction of a periodic potential will improve the results of the FE-model [10].

Decreasing the symmetry of a problem can remove degeneracy. As pointed out in the former sections, degeneracy is necessary to explain Hückel's rule. Therefore the influence of a C_N-axis on the levels which are degenerate in the simple FE-model has to be investigated.

A potential with an N-fold axis can be expanded as a Fourier-series

$$\tilde{V}'(\phi) = \sum_{n=0}^{\infty} \tilde{a}_n \cos(n N \phi) + \sum_{n=1}^{\infty} \tilde{b}_n \sin(n N \phi)\,. \tag{6}$$

Putting the atoms into the appropriate positions, all the sine-terms can be omitted. The cosine-term with $n = 0$ gives only a constant shift of the energy eigenvalues. The remaining potential is

$$V'(\phi) = \sum_{n=1}^{\infty} 2 a_n \cos(n N \phi)\,. \tag{7}$$

The factor two is introduced for convenience of the further calculation. The coefficient a_1 does not vanish, because a Fourier-series beginning from a_2 is not a model of an N-ring but of a $(2N)$-ring. No further restriction on the coefficients a_n is made.

The energies of the modified FE-model (MFE-model) will be calculated using two different approximation methods. In both cases the simple FE-method will be used as the unperturbed problem. As the eigenfunctions of the "particle in a ring" have a very simple structure, the evaluation of the matrix elements is straightforward. A qualitative insight into the structure of the solutions of the MFE-model can be obtained by perturbation theory, which will be worked out up to the second order. Using direct diagonalization of the matrix of the Hamiltonian, pairs of levels can be found, from which degeneracy cannot be removed by any perturbation of the form of $V'(\phi)$ (7).

5. Perturbation Theory

5.1. Calculation of the Matrix Elements

The matrix elements V'_{ij}

$$V'_{ij} = \langle \psi_i | \hat{V}' | \psi_j \rangle = \int_0^{2\pi} \psi_i^*(\phi)\, V'(\phi)\, \psi_j(\phi)\, \mathrm{d}\phi \tag{8}$$

can be written as a sum of matrix elements $V'^{(n)}_{ij}$ which are due to the terms $[2 a_n \cos(n N \phi)]$ in $V'(\phi)$,

$$V'^{(n)}_{ij} = \langle \psi_i | 2 a_n \cos(n N \phi) | \psi_j \rangle\,. \tag{9}$$

It can be easily seen that

$$V'^{(n)}_{k,(k+l)} = \begin{cases} 0 & \text{if} \quad |l| \neq n N \\ a_n & \text{if} \quad l = \pm n N \end{cases}. \tag{10}$$

Thus only levels with quantum numbers k differing by a multiple of N can be connected through the potential $V'(\phi)$.

5.2. *First Order Perturbation Theory*

In first order perturbation theory, levels can be shifted only due to matrix-elements connecting levels of same energy, viz. diagonal matrix-elements or matrix-elements connecting degenerate levels. As was concluded from (10), there are no diagonal matrix-elements $V'^{(n)}_{k,k}$. However, matrix elements connecting degenerate levels $V'^{(n)}_{-k,k}$ are non-zero if $k = \pm nN/2$. The energies $E^{(1)}_{\pm|k|}$ up to the first order are obtained from a (2×2) secular equation

$$E^{(1)}_{\pm|k|} = E^{(0)}_{|k|} \pm a_n , \quad E^{(0)}_{|k|} = \frac{\hbar^2 k^2}{2mr^2} , \quad |k| = \frac{nN}{2} . \tag{11}$$

For an odd-numbered N-ring a splitting of degenerate levels can occur for $k = \pm N, \pm 2N, \pm 3N, \dots$. The number of levels which have to be compared with the HMO-model is N, corresponding to the quantum numbers $k = 0, \pm 1, \pm 2, \dots, \pm(N-1)/2$ in the FE-model. Thus in first order perturbation theory, the degeneracy is not removed from those lowest levels of the MFE-model which are relevant for the comparison with the HMO-model.

For an even-numbered N-ring, degeneracy can be removed for $k = \pm 1/2N, \pm 2/2N, \pm 3/2N, \dots$. In the HMO-model all levels except the lowest and the highest one are doubly degenerate. The lowest levels affected by the perturbation $V'(\phi)$ are $\psi_{\pm N/2}$. Thus also in the MFE-model the N-th level is nondegenerate due to the linear splitting $\propto a_1$ in first order perturbation theory. This splitting does not vanish, because the coefficient a_1 is the only one in the Fourier-series (7) which is certainly non-zero.

In first order perturbation theory the sequence of degenerate and non-degenerate levels in the MFE-model is the same as in the HMO-model for both even- and odd-numbered rings.

5.3. *Second Order Perturbation Theory*

As the levels with $k = \pm nN/2$ are mixed completely in first order perturbation theory (PT) giving new zero order wave functions $\psi_{\pm|k|}$ (11), it seems useful to change the whole basis set in the same manner. With the wave functions

$$\psi_{+|0|} = \frac{1}{\sqrt{2\pi}} , \tag{12}$$

$$\psi_{+|k|} = \frac{1}{\sqrt{\pi}} \cos(k\phi), \quad \psi_{-|k|} = \frac{\iota}{\sqrt{\pi}} \sin(k\phi) , \quad k \in \mathbb{N}$$

the matrix elements in the new basis are

$$\langle \psi_{\pm|k|} | \hat{V}'^{(n)} | \psi_{\pm|m|} \rangle = a_n (\delta_{|k-m|, nN} \pm \delta_{k+m, nN}) , \quad k, m \in \mathbb{N} , \tag{13}$$

$$\langle \psi_{+|0|} | \hat{V}'^{(n)} | \psi_{+|k|} \rangle = \sqrt{2}\, a_n \, \delta_{k, nN} , \quad \delta_{ij}\text{: Kronecker symbol,} \tag{14}$$

$$\langle \psi_{\pm|k|} | \hat{V}'^{(n)} | \psi_{\mp|m|} \rangle = 0 , \quad k, m \in \mathbb{N}_0 . \tag{15}$$

In the new basis the perturbation in first order is diagonal,

$$E^{(1)}_{\pm|nN/2|} = E^{(0)}_{|nN/2|} \pm a_n, \quad (nN) \text{ even} . \tag{16}$$

As there is no coupling between the ψ_+ and the ψ_-, the usual formula for second order PT for nondegenerate states can be used. For those levels which are not split in second order the contribution $\Delta E^{(2)}$ is

$$\Delta E^{(2)}_{+|0|} = -\frac{2}{\alpha N^2} \sum_{n=1}^{\infty} \left(\frac{a_n}{n} \right)^2 , \tag{17}$$

$$\Delta E^{(2)}_{\pm|k|} = \frac{2}{\alpha} \sum_{n=1}^{\infty} \frac{a_n^2}{(2k)^2 - (nN)^2} , \quad k \neq \frac{mN}{2} , \quad m \in \mathbb{N} , \tag{18}$$

$$\Delta E^{(2)}_{\pm|mN/2|} = -\frac{a_m^2}{2\alpha(mN)^2} + \frac{1}{\alpha N^2} \sum_{\substack{n=1 \\ n \neq m}}^{\infty} \frac{a_n^2}{m^2 - n^2} , \quad N \text{ even, } m \text{ odd,} \tag{19}$$

where $\alpha = \hbar^2/(2mr^2)$. The levels $\psi_{+|mN|}$ and $\psi_{-|mN|}$ are influenced differently:

$$\Delta E^{(2)}_{-|mN|} = \frac{2}{\alpha N^2} \sum_{\substack{n=1 \\ n \neq m \\ n \neq 2m}}^{\infty} \frac{a_n^2}{4m^2 - n^2} - \frac{1}{\alpha(mN)^2} \left(\frac{a_m^2}{3} + \frac{a_{2m}^2}{8} \right) , \tag{20}$$

$$\Delta E^{(2)}_{+|mN|} = \Delta E^{(2)}_{-|mN|} + \frac{2a_m^2}{\alpha(mN)^2} , \tag{21}$$

thus giving a net splitting of $\Delta^{(2)}_{(mN)}$ in second order PT

$$\Delta^{(2)}_{(mN)} = \frac{2a_m^2}{\alpha(mN)^2} . \tag{22}$$

The additional term $\propto a_m^2$ in (21), which causes the splitting $\Delta^{(2)}_{(mN)}$, is due to the coupling between $\psi_{+|mN|}$ and $\psi_{+|0|}$. This interaction due to the term

$[2a_m\cos(mN\phi)]$ of the potential $V'(\phi)$ cannot shift $\psi_{-|mN|}$ because a level $\psi_{-|0|}$ does not exist.

For an odd-numbered ring the lowest pair of levels from which degeneracy is removed is $\psi^{(0)}_{\pm|nN|}$. It is worth noting that in first order PT those levels are not splitted linearly in a_1, the only contribution in first order is $\propto a_2$. Only a second order splitting $\propto a_1^2$ can be observed.

In conclusion, it has been shown that no pairs of levels relevant for the comparison of HMO- and MFE-model are splitted in second order PT.

6. Variational Approach

In this section the eigenvalues of the MFE-method will be calculated to, in principle, arbitrary accuracy. This can be done using a variational approach in the orthogonal basis of the unperturbed FE-model. As an important by-product, pairs of levels will be found from which degeneracy cannot be removed by any potential of the form (7).

The most appropriate basis for setting up the matrix $\mathbf{H}$ of $\hat{H} = \hat{H}^{(0)} + \hat{V}'(\phi)$, where $\hat{H}^{(0)}$ is the Hamiltonian for the particle in a ring, are the complex functions $\psi_k^{(0)}$ (4). For a special matrix $\mathbf{H}_{\tilde{n}}$ we include all $\psi_k^{(0)}$ with $-(\tilde{n}N) \le k \le (\tilde{n}N)$.

The matrix $\mathbf{H}_{\tilde{2}}$ of [3]-annulene is given as an instructive example.

$$\mathbf{H}_{\tilde{2}} = \begin{pmatrix}
\bar{6}^2 & 0 & 0 & b_1 & 0 & 0 & b_2 & 0 & 0 & b_3 & 0 & 0 & b_4 \\
0 & \bar{5}^2 & 0 & 0 & b_1 & 0 & 0 & b_2 & 0 & 0 & b_3 & 0 & 0 \\
0 & 0 & \bar{4}^2 & 0 & 0 & b_1 & 0 & 0 & b_2 & 0 & 0 & b_3 & 0 \\
b_1 & 0 & 0 & \bar{3}^2 & 0 & 0 & b_1 & 0 & 0 & b_2 & 0 & 0 & b_3 \\
0 & b_1 & 0 & 0 & \bar{2}^2 & 0 & 0 & b_1 & 0 & 0 & b_2 & 0 & 0 \\
0 & 0 & b_1 & 0 & 0 & \bar{1}^2 & 0 & 0 & b_1 & 0 & 0 & b_2 & 0 \\
b_2 & 0 & 0 & b_1 & 0 & 0 & 0^2 & 0 & 0 & b_1 & 0 & 0 & b_2 \\
0 & b_2 & 0 & 0 & b_1 & 0 & 0 & 1^2 & 0 & 0 & b_1 & 0 & 0 \\
0 & 0 & b_2 & 0 & 0 & b_1 & 0 & 0 & 2^2 & 0 & 0 & b_1 & 0 \\
b_3 & 0 & 0 & b_2 & 0 & 0 & b_1 & 0 & 0 & 3^2 & 0 & 0 & b_1 \\
0 & b_3 & 0 & 0 & b_2 & 0 & 0 & b_1 & 0 & 0 & 4^2 & 0 & 0 \\
0 & 0 & b_3 & 0 & 0 & b_2 & 0 & 0 & b_1 & 0 & 0 & 5^2 & 0 \\
b_4 & 0 & 0 & b_3 & 0 & 0 & b_2 & 0 & 0 & b_1 & 0 & 0 & 6^2
\end{pmatrix}. \quad (23)$$

The matrix-elements are given in units of α; squares of negative numbers are indicated as $\bar{n}^2 = (-n)^2$; the off-diagonal elements are abbreviated as $b_j = a_j/\alpha$. Collecting rows and columns which are connected by non-zero matrix-elements (e.g. No. 1, 4, 7, 10, and 13 with the diagonal elements $\bar{6}^2$, $\bar{3}^2$, 0^2, 3^2, and 6^2), it can easily be seen from (23) that the eigenvalue-equation of $\mathbf{H}_{\tilde{2}}$ can be block-factorized. For the matrix shown above, the following three submatrices $\mathbf{M}_0$, $\mathbf{M}_{+1}$, and $\mathbf{M}_{-1}$ exist:

$$\mathbf{M}_0 = \begin{pmatrix}
\bar{6}^2 & b_1 & b_2 & b_3 & b_4 \\
b_1 & \bar{3}^2 & b_1 & b_2 & b_3 \\
b_2 & b_1 & 0^2 & b_1 & b_2 \\
b_3 & b_2 & b_1 & 3^3 & b_1 \\
b_4 & b_3 & b_2 & b_1 & 6^2
\end{pmatrix}, \quad (24)$$

$$\mathbf{M}_{+1} = \begin{pmatrix}
\bar{5}^2 & b_1 & b_2 & b_3 \\
b_1 & \bar{2}^2 & b_1 & b_2 \\
b_2 & b_1 & 1^2 & b_1 \\
b_3 & b_2 & b_1 & 4^2
\end{pmatrix}, \quad \mathbf{H}_{-1} = \begin{pmatrix}
\bar{4}^2 & b_1 & b_2 & b_3 \\
b_1 & \bar{1}^2 & b_1 & b_2 \\
b_2 & b_1 & 2^2 & b_1 \\
b_3 & b_2 & b_1 & 5^2
\end{pmatrix}. \quad (25)$$

The index l of $\mathbf{M}_l$ gives the quantum number l with the smallest absolute value among the quantum numbers of basis-functions of the submatrix. In this notation of $\mathbf{M}_l$ the dimension of the matrix $\mathbf{H}_{\tilde{2}}$ to which $\mathbf{M}_l$ belongs is not indicated explicitly. Inverting the sequence of the basis functions of one of the two submatrices it can be seen that $\mathbf{M}_{-1}$ and $\mathbf{M}_1$ have the same secular-equation. Thus the levels occurring in $\mathbf{M}_{-1}$ and $\mathbf{M}_1$ remain degenerate whatever the numerical values of the coefficients of $V'(\phi)$ (7) are. Increasing the dimension of $\mathbf{H}_{\tilde{n}}$ does not influence the scheme of the block-factorization. The new submatrices $\mathbf{M}_{-1}$ and $\mathbf{M}_1$ still have the same secular-equation. Therefore degeneracy can be removed only from pairs of levels which belong to $\mathbf{M}_0$, viz. with $k = \pm 3, \pm 6, \pm 9, \ldots, \pm(3m), \ldots, (m \in \mathbb{N})$.

Now the $(2\tilde{n}N+1) \times (2\tilde{n}N+1)$-dimensional matrix $\mathbf{H}_{\tilde{n}}^{(N)}$ of the $[N]$-annulene is considered. It can be seen from (10) that $\psi_k^{(0)}$ has non-zero matrix-elements with the functions $\psi^{(0)}_{k \pm mN}$ $(m \in \mathbb{N})$. Thus an arbitrary $\mathbf{H}_{\tilde{n}}^{(N)}$ can be block-factorized into N submatrices. The submatrix $\mathbf{M}_0$ in which the basis-function $\psi_0^{(0)}$ occurs, is $(2\tilde{n}+1)^2$-dimensional, the other submatrices are $(2\tilde{n})^2$-dimensional. In a similar way as in the example shown above the submatrices $\mathbf{M}_l$ are indicated by the quantum numbers l with the smallest absolute value among its basis functions. Contrary to the notation of the matrix $\mathbf{H}_{\tilde{n}}^{(N)}$, no superscript (N) is used to indicate the number N of C-atoms in the annulene to which the submatrix $\mathbf{M}_l$ belongs. The quantum numbers occurring in the various submatrices are

$$\begin{array}{llllllllll}
\mathbf{M}_0: & jN & (j-1)N & \ldots & N & 0 & -N & \ldots & -(j-1)N & -jN, \\
\mathbf{M}_1: & & (j-1)N+1 & \ldots & N+1 & 1 & -N+1 & \ldots & -(j-1)N+1 & -jN+1, \\
\mathbf{M}_{-1}: & jN-1 & (j-1)N-1 & \ldots & N-1 & -1 & -N-1 & \ldots & -(j-1)N-1\,, & \\
\mathbf{M}_2: & & (j-1)N+2 & \ldots & N+2 & 2 & -N+2 & \ldots & -(j-1)N+2 & -jN+2. \\
\vdots & & \vdots & & & & \vdots & & \vdots &
\end{array} \quad (26)$$

The matrix elements $M^{(l)}_{ij}$ of the submatrices $\mathbf{M}_l$ are

$$M^{(l)}_{ij} = a_{|i-j|} + k_j^2 \, \alpha \, \delta_{ij} \, , \quad a_0 = 0 \, , \tag{27}$$

where k_j is the quantum number of the j-th basis function of the submatrix. Here, the indices i and j of $M^{(l)}_{ij}$ must not be confused with the quantum numbers of the basis functions involved. Following the same arguments as above, it can be seen that pairs of matrices $\mathbf{M}_l$ and $\mathbf{M}_{-l}$ have the same secular equation. Thus the degeneracy of the basis functions of submatrices which occur as pairs $\mathbf{M}_{\pm l}$ cannot be removed.

The following values of l are possible:

$$l = 0, \pm 1, \pm 2, \ldots, \pm \left(\frac{N-1}{2} \right), \qquad N \text{ odd} \, , \tag{28}$$

$$l = 0, \pm 1, \pm 2, \ldots, \pm \left(\frac{N}{2} - 1 \right), + \frac{N}{2}, \qquad N \text{ even} \, . \tag{29}$$

Both $\psi^{(0)}_{+N/2}$ and $\psi^{(0)}_{-N/2}$, which exist only for even N, are basis-functions of the submatrix which is indicated as $\mathbf{M}_{N/2}$.

The functions $\psi^{(0)}_{\pm nN}$ ($n \in \mathbb{N}$) can be splitted for arbitrary N because they both occur in $\mathbf{M}_0$; $\psi^{(0)}_0$ has never been degenerate. For even N degeneracy can be removed from the $\psi^{(0)}_{\pm nN/2}$ which are basis functions of the submatrix $\mathbf{M}_{N/2}$. It has been shown in Sect. 5 that the levels $\psi^{(0)}_{\pm N}$ must be splitted for every N and that the $\psi^{(0)}_{\pm N/2}$ must be splitted for odd N.

It can be seen from (28) and (29) that in the MFE-model degeneracy cannot be removed from any pair levels which are degenerate in the HMO-model. For even N the level corresponding to the highest level in the HMO-model must be nondegenerate, as shown in Section 5.2. Thus for all levels relevant for the comparison between the HMO- and MFE-models, the sequence of degenerate and non-degenerate levels is identical.

It is worth noting that the numerical evaluation of the energies of the MFE-model is very effective, because the secular equation of $\mathbf{H}^{(N)}_{\tilde{n}}$ can be block-factorized. Instead of the large $(2\tilde{n}N+1)^2$-dimensional matrix $\mathbf{H}^{(N)}_{\tilde{n}}$ only about $N/2$ submatrices of dimension $(2\tilde{n})^2$ or $(2\tilde{n}+1)^2$ must be diagonalized.

7. Conclusion

In the approximation of the FE-model, the π-electrons of an annulene are described as particles in a ring. The lowest level ($k=0$) in this model is non-degenerate, whereas all other levels are twofold degenerate ($k = \pm l$). The FE-model can be improved by the introduction of a potential $V'(\phi)$ (7) with N-fold symmetry which takes into account the N C-atoms of an [N]-annulene. Lowering the C_∞-symmetry of the FE-model to the C_N-symmetry of the MFE-model removes degeneracy from some of the levels of the FE-model.

The effect of $V'(\phi)$ has been investigated using perturbation theory up to the second order. The only Fourier coefficient in $V'(\phi)$ which must not vanish is a_1. Thus the levels $\psi^{(0)}_{\pm N}$ are certainly splitted in second order PT for every annulene (22); the levels $\psi^{(0)}_{\pm N/2}$ must be splitted in first order PT only for annulenes with an even number N of C-atoms in the ring (11).

In a variational approach, the matrix $\mathbf{H}_{\tilde{n}}$ of the Hamiltonian of the MFE-model is set up using the complex basis functions $\psi^{(0)}_k$ of the particle in a ring up to a certain maximal quantum number $k = \pm \tilde{n} N$. The secular equation of $\mathbf{H}_{\tilde{n}}$ can be block-factorized yielding N sub-matrices. From the structure of the submatrices it follows that all levels except $\psi^{(0)}_{\pm nN/2}$ ($n \in \mathbb{N}_0$) for even N or $\psi^{(0)}_{\pm nN}$ ($n \in \mathbb{N}_0$) for odd N remain twofold degenerate if they are perturbed by a potential of N-fold symmetry.

The sequences of degenerate and non-degenerate levels of the HMO-model and of the N lowest levels of the MFE-model are identical. The qualitative chemical consequences, especially the prediction of aromaticity and anti-aromaticity, which follow from degeneracy are therefore the same for the MFE- and the HMO-model.

The qualitative sequence of levels known from the application of HMO-theory to N-annulenes is a consequence of the symmetry due to the N C-atoms in the ring. No further assumptions on the potential beyond symmetry are necessary.

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