# ON THE THEORY OF THE ELECTRONIC STRUCTURE OF CYCLIC MOLECULES

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**Abstract**

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# ON THE THEORY OF THE ELECTRONIC STRUCTURE OF CYCLIC MOLECULES

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Modern theory of cyclic molecules either does not take into account the Coulomb repulsion of $\pi$-electrons at all, or takes it into account as a perturbation. But even one-electron orbitals in the multicenter field of the molecular framework are not calculated exactly. The calculations contain parameters that are fitted to achieve agreement with experiment. A number of molecular properties cannot be explained, predictions are difficult to make, and therefore in the literature doubts are often expressed concerning the existing theory, or it is simply asserted that there is as yet no theory. It is therefore worthwhile to develop a theory based on alternative assumptions ([1]), and to compare its predictions with experiment. We consider that, in quasione-dimensional motion along the molecular framework, Coulomb repulsion makes the probability of tunneling passage of one $\pi$-electron "through" another very small, i.e. $T_r \ll 1$. This is reasonable, since for one-dimensional motion around a ring of radius $r > r_0 = 0.53$ Å, $T_r \ll 1$ so long as the relative energy of two electrons $E_\xi \ll 1\ Ry = 27.2$ eV. At $T_r \ll 1$ the electrons line up into a one-dimensional Wigner ([2]) chain, which performs hindered rotation relative to the molecular framework as a single quasiparticle of total mass. We shall not consider the excitation of Wigner phonons (electronic vibrations), since their energy is large, $\sim 10$ eV. It has proved possible to find the exact solution of the one-dimensional problem at $T_r = 0$. Let us write the Schrödinger equation for $n$ particles in a cyclic field $U(\varphi_i)$

$$-\frac{\hbar^2}{2mr^2}\sum_{i=1}^{n}\frac{\partial^2\psi}{\partial\varphi_i^2}+\sum_{i=1}^{n}U(\varphi_i)\psi+\frac{1}{2}\sum_{i\neq k=1}^{n}V(|\varphi_i-\varphi_k|)\psi=E\psi; \qquad (1)$$

the $\psi$-function and the repulsion potential $V$ have period $2\pi$ in each angular variable $\varphi_i$; $U$ has period $2\pi/\nu$, $\nu$ an integer. After the substitution

$$\varphi=\sum_{i=1}^{n}\varphi_i/n, \qquad \xi_j=\varphi_{j+1}-\varphi_1 \quad (j=1,2,\ldots,n-1)$$

we obtain

$$-\frac{\hbar^2}{2(nm)r^2}\frac{\partial^2\psi}{\partial\varphi^2}-\frac{\hbar^2}{2(m/2)r^2}\left[\sum_{j=1}^{n-1}\frac{\partial^2}{\partial\xi_j^2}+\frac{1}{2}\sum_{j\neq k=1}^{n-1}\frac{\partial^2}{\partial\xi_j\partial\xi_k}\right]\psi+$$

$$+\left\{U\left(\varphi-\sum_{j=1}^{n-1}\xi_j/n\right)+\sum_{k=1}^{n-1}U\left[\left(\varphi-\sum_{j=1}^{n-1}\xi_j/n\right)-\xi_k\right]\right\}\psi+$$

$$+\left[\sum_{j=1}^{n-1}V(|\xi_j|)+\frac{1}{2}\sum_{j\neq k=1}^{n-1}V(|\xi_j-\xi_k|)\right]\psi=E\psi. \qquad (2)$$

This Hill-type equation for $n=\nu$ has the solution

$$\psi=\exp(iM\varphi)\exp\left(i\frac{M}{n}\sum_{j=1}^{n-1}\xi_j\right)F_M(\varphi,\xi_1,\ldots,\xi_{n-1}),\qquad M=0,\pm1,\ldots, \quad (3)$$

where $F$ has period $2\pi$ in $\xi_j$ and $2\pi/\nu$ in $\varphi$.

For $T_r=0,\ U=0$ we have $E=(\hbar M)^2/2(nm)r^2+E_\xi$. For zero vibrational oscillations $E_\xi^0$, to each $M$ there correspond $(n-1)!$ orthogonal functions (3), according to the number of cells in the $(n-1)$-dimensional cube cut by diagonal planes passing through one vertex. They serve as a basis of the representation $\tau_\psi$ of the permutation group $G_n$ of $n$ elements. Let us write out all nonzero characters $\tau_\psi$ for $n\leq 10$.

$n=3$. Classes $1^3,3$. Their characters: $2,\ 2\cos(2\pi M/3)$.

$n=4$. Classes $1^4,2^2,4$. Their characters: $3!,\ 2(-1)^M,\ 2\cos(\pi M/2)$.

$n=5$. Classes $1^5,5$. Characters: $4!,\ 2[\cos(2\pi M/5)+\cos(4\pi M/5)]$.

$n=6$. Classes $1^6,2^3,3^2,6$. Characters: $5!,\ 8(-1)^M,\ 6(-1)^M\cos(\pi M/3),\ 2(-1)^M\cos(2\pi M/3)$.

$n=7$. Classes $1^7,7$. Characters: $6!,\ 2[\cos(2\pi M/7)+\cos(4\pi M/7)+\cos(6\pi M/7)]$.

$n=8$. Classes $1^8,2^4,4^2,8$. Characters: $7!,\ 2^3\cdot3!(-1)^M,\ 8\cos(\pi M/2),\ 2[\cos(\pi M/4)+\cos(3\pi M/4)]$.

$n=10$. Classes $1^{10},2^5,5^2,10$. Characters: $9!,\ 2^4\cdot4!(-1)^M,\ 10[\cos(2\pi M/5)+\cos(4\pi M/5)],\ 2[\cos(\pi M/5)+\cos(3\pi M/5)]$.

The spin functions transform according to the representation $\tau_s$ of the group $G_n$ corresponding to the two-row Young diagram ([3]); their characters are known ([4]). The complete coordinate-spin functions transform according to the representation $\tau_\psi\times\tau_s$. By virtue of the Pauli principle, the number of antisymmetric

representations contained in the complete one is the multiplicity of the term; it is given in Table 1.

**Table 1**

*Multiplicity of terms with given $n$, $s$, $M$ for $E_\xi = E_\xi^0$*

| $n =$ | 1, | 2, | 2, | 3, | 3, | 4, | 4, | 4, | 5, | 5, | 5, | 6, | 6, | 6, | 6, | 7, | 7, | 7, | 7, | 8, | 8, | 8, | 8, | 8, | 10, | 10, | 10, | 10, | 10, | 10, | $s =$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $M$ | $\frac{1}{2}$ | 0 | 1 | $\frac{1}{2}$ | $\frac{3}{2}$ | 0 | 1 | 2 | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | 0 | 1 | 2 | 3 | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | 0 | 1 | 2 | 3 | 4 | 0 | 1 | 2 | 3 | 4 | 5 | |
| 0 | 1 | 1 | 0 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 2 | 1 | 1 | 0 | 2 | 2 | 0 | 1 | 3 | 3 | 3 | 1 | 0 | 6 | 8 | 8 | 3 | 1 | 0 | |
| 1 | | 0 | 1 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 2 | 1 | 0 | 2 | 2 | 1 | 0 | 1 | 4 | 2 | 1 | 0 | 3 | 10 | 7 | 4 | 1 | 0 | |
| 2 | | | | | | 1 | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 0 | 2 | 2 | 1 | 0 | 2 | 3 | 3 | 1 | 0 | 5 | 8 | 8 | 3 | 1 | 0 | |
| 3 | | | | | | | | | | | | 1 | 2 | 0 | 1 | 2 | 2 | 1 | 0 | 1 | 4 | 2 | 1 | 0 | 3 | 10 | 7 | 4 | 1 | 0 | |
| 4 | | | | | | | | | | | | | | | | | | | | 3 | 3 | 3 | 0 | 1 | 5 | 8 | 8 | 3 | 1 | 0 | |
| 5 | | | | | | | | | | | | | | | | | | | | | | | | | 4 | 10 | 7 | 4 | 0 | 1 | |

For $0 < T_r \ll 1$, multiply degenerate terms split into multiplets similar to those observed in the Shpol' skii effect ([5]). For $T_r = 0$, $U \neq 0$, Table 1 remains valid, while the energy is $E = E_M + E_\xi$; the hindered-rotation levels of the Wigner chain $E_M$ are obtained from the equation

$$-\frac{\hbar^2}{2(nm)r^2}\frac{d^2\zeta}{d\varphi^2} + \overline{U}(\varphi)\zeta = E_M\zeta, \qquad \overline{U}(\varphi) \simeq nU(\varphi), \tag{4}$$

obtained by averaging (2), with the aid of (3), over the fast vibrations $\xi$.

In cyclic molecules $2\pi r = na_0$, $a_0 \simeq 1.4$ Å. Assuming that $U$ consists of narrow standard barriers of area $\delta = 0.5$ eV · Å, the whole set of levels for different $n$ and $M$ is obtained from the equation

$$P_n\frac{\sin \varkappa a_0}{\varkappa a_0} + \cos \varkappa a_0 = \cos\left(2\pi\frac{M}{n}\right),$$

$$P_n = n^2\frac{ma_0\delta}{\hbar^2}, \qquad \varkappa a_0 = \left[E_{nM}\Big/\frac{\hbar^2}{2nma_0^2}\right]^{1/2}. \tag{5}$$

The levels are collected in Table 2. They are grouped into zones: in the first, $|M| \leq n/2$; in the second, $n/2 \leq |M| \leq n$. We identify the observed optical singlet ($s = 0$) absorption levels of molecules with different $n$ with transitions to levels of the second zone. Let us consider the predicted singlet levels of benzene, $C_6H_6$, symmetry $D_{6h}$, $n = 6$. First zone: the doubly degenerate ground level $E_{M=0} = 0$ of symmetry $A_{1g}$, the level $E_{M=2} = 1.04$ eV of symmetry $E_{2g}$, and the level $E_{M=3} = 1.68$ eV of symmetry $B_{1u}$. Second zone: the level $E_{M=3} = 4.7$ eV of symmetry $B_{2u}$, the level $E_{M=4} = 6.1$ eV of symmetry $E_{2g}$, and the doubly

degenerate level $E_{M=6} \sim 10$ eV of symmetry $A_{1g}$. The levels 1.04 and 1.68 eV have not previously been observed; their discovery would serve as proof of the correctness of the initial assumptions (see (6)). These levels should give very weak absorption in the near infrared and red regions, since the probability of a dipole transition grows proportionally to $T_r$, i.e., exponentially with energy. Transitions with $\Delta M = \pm 1$ are allowed.

**Table 2**

**Lower levels of hindered rotation of the Wigner chain (in electron-volts)**

| 4 | 5 | 6 | 7 | 10 | $n/M$ |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 1.13.5 | 0.6 | 0.29 | 0.18 | 0.038 | 1 |
| 6.1 | 1.84 | 1.04 | 0.68 | 0.13 | 2 |
| | 6.3 | 1.684.7 | 1.2 | 0.27 | 3 |
| | | 6.1 | 5.0 | 0.40 | 4 |
| | | | 6.4 | 0.46 | 5 |
| | | | | 4.04.13 | 6 |
| | | | | 4.48 | 7 |
| | | | | 5.0 | 8 |
| | | | | 5.6 | 9 |
| | | | | 5.7 | 10 |

Naphthalene $C_{10}H_8$ has chain levels with $n = 10$ plus the benzene levels; its isomer azulene should have chain levels with $n = 10, 7$, and 5. The red absorption of azulene corresponds to the level 1.84 eV for $n = 5$. Good agreement between calculation and experiment is obtained for many molecules; however, the discovery in benzene of the two new predicted levels should be of key importance for the theory.

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*Note: Figure translations are in progress. See original paper for figures.*