

Some Considerations on the Electronic Spectra of Cyclic Polyenes

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Synopsis. The theoretical prediction of a convergence limit in the electronic spectra of cyclic polyenes is nicely borne out by experimental findings.

In a recent communication hole particle formalism¹⁾ has been used to explain the convergence limit in the π -electronic spectra of linear polyenes. The hole-particle pair creation operator expressed in terms of particle creation and destruction operators was written as

$$b_i = u_i c_i + v_i c_i^\dagger \quad (1)$$

in order to diagonalize the Hamiltonian. For Boglyubov-Valentin^{2,3)} transformation this should be written as

$$b_i = u_i^* c_i + v_i^* c_i^\dagger \quad (2)$$

where $-i$ is the time reversed partner of the state i . Since n is the only good quantum number in the FE function of linear polyenes there is no genuine time reversed partner for the states described by n . The transformation (1) was therefore an *ad-hoc* assumption. The FE function for cyclic polyenes in cylindrical coordinate may be written as⁴⁾

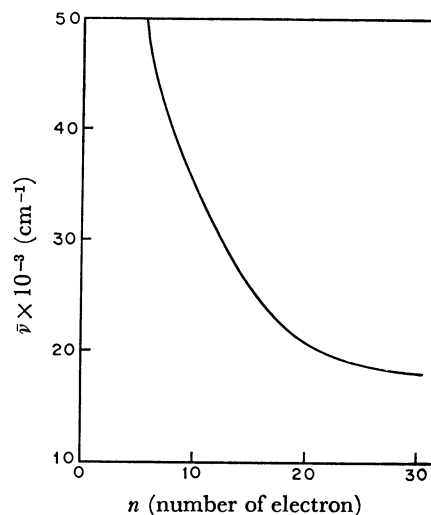
$$\Psi_{n_z n_r m}(Z, \rho, \Phi) = N e^{-Kz/2} H_{n_z}(\sqrt{K}Z) e^{-c\rho/2} F_{n_r}^m(\sqrt{C}\rho) e^{im\Phi}$$

where $C^2 = 1/R^{2\alpha}$ and $K^2 = 4\pi^2 mk/h^2$, where R is the radius of the ring and k and α are two parameters determined from experimental data. For these functions state m has a time reversed partner $-m$ and the transformation (2) may be written as

$$b_m = u_m^* C_m + v_m^* C_m^\dagger$$

which will be truly canonical. Rest of the deductions will be the same as given in a previous paper and we will get for hole-particle energy as

$$E = \sqrt{\epsilon_a - \epsilon_f + A^2}$$

Fig. 1. $\bar{\nu}$ vs. n .

This means that even for cyclic polyenes there should exist a convergence limit. In Fig. 1 is given the plot of longest wave length transition *versus* the ring size for a number of conjugated cyclic systems known as Sondheimer hydrocarbon.⁵⁾ It is evident that the convergence do exist.

References

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