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# Electron Pairing Interaction and Electronic Spectra of Linear Polyene

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**Synopsis.** Assuming the pairing interaction which arises in Hartree-Fock-Bogolyubov formulation in many-electron system, to be due to attraction between two electrons of opposite spin it has been shown that the longest wavelength singlet transition in linear polyenes will show convergence limit while the corresponding triplet transition will not.

In a previous communication[1] it has been shown that the convergence limit in the electronic spectra of linear polyene may be understood in terms of $\Delta_{i-i}$ (the pairing interaction) value in the Hartree-Fock-Bogolyubov (HFB) equation for many electron system. Since the $\Delta_{i-i}$ term is positive, it was assumed that it may be looked upon as attraction between a particle and a hole. If we are prepared to accept a non-classical conclusion, that is, there is residual attraction between electrons in a many electron system, then we may consider $\Delta_{i-i}$ to arise from attraction between electrons in states i and $-$i. The states i and $-$i have the same principal quantum number but one has the projection quantum number reversed in sign from the other. In spherical systems which are characterised by quantum numbers $n$, $l$, and $m$, the states i and $-$i differ from each other in the sign of $m$ values. In linear polyene the good quantum number is $n$ only (which appears in the electron-in-a-box calculation). Only way the states i and $-$i can differ from each other in these systems is by having spin $+1/2$ and $-1/2$. It is to be remembered, however, that HFB calculation do not take spin into account at any stage. We can only say that there is electron pairing in the same level of polyene, but to satisfy some basic requirements of the HFB theory, the two electrons must have opposite projection quantum number, which we consider to be spin. But this term does not arise from spin-spin interaction in any way. With this basic prescription we may analyse the electronic properties of linear polyenes in greater detail.

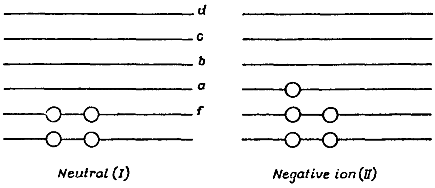

Fig. 1. Level scheme for neutral and mono-negative polyene.

Let us consider the level schemes for a neutral and a negatively charged polyene.

In the case (I) of Fig. 1 an electron from f (Fermi level) can go to a level c, such that $\varepsilon_c - \varepsilon_f \geq \Delta_{i-i}$ *i.e.* the low-lying excited levels cannot be populated as they are unable to break the pairing interaction. Therefore the minimum amount of energy which the system can take up is $\Delta_{i-i}$, *i.e.* the spectrum should show convergence limit. In the case II on the other hand, the unpaired electron in level a, may be excited to any of the vacant levels as there is no pairing interaction to break. So these systems will not show any convergence limit. The same argument should hold for positive ions. We reached the same conclusion considering $\Delta_{i-i}$ as hole-particle interaction energy in the previous paper.

Let us consider the neutral molecule again. The two electrons in the level f have the spin $+1/2$ and $-1/2$. When one is excited to a level c, without changing the spin, we get a singlet state. For a triplet state excitation we have the electrons in f and c having the same spin, say $+1/2$. We may suppose that we have arrived at this state by electron transition from a virtual Fermi level having both the spins $+1/2$. In the HFB formulation there cannot be any pairing interaction between two electrons of the same spin in the virtual orbital. So the triplet transitions in linear polyenes will show no convergence limit. We may go over from the ground state to the virtual orbital by some type of spin-orbital interaction. Further when the energy difference $\varepsilon_f - \varepsilon_a$ becomes small, $\varepsilon_a$ may be thermally populated by a triplet mechanism. So very large linear molecule may become paramagnetic and the magnetic moment increases with increasing temperature.[2]

This pairing interaction, however, fails to explain the convergence behaviour of cyanines for which hole-particle attraction model appears to be a better one.

## References

1) S. Basu, This Bulletin, **47**, 735 (1974).
2) A. A. Berlin, G. A. Vinogradov, A. A. Ovchinnikov, *Int. J. Quantum Chem.*, **6**, 263 (1972).