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Note

Plasma Oscillations in Large Ring Polyenes

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The possibility of collective motion of the π-electron system has been examined by many authors[1-3]. In this context it is interesting to note that much more attention has been devoted to the linear conjugated systems than to the ring ones. Recently Yomosa and Segawa studied collective oscillations (charge density or plasma waves) in ring polyenes using Tomonaga's[4] method. They concluded that the plasma wave exists and that the method satisfactorily predicts its wavelength and intensity. It is our intention to use a different model[5] and to show the limitation inherent in the above mentioned approach. The geometry of the ring polyene is determined by the cylindrical coordinates r, φ, z; the ring lies in a plane perpendicular to the z axis. The charge density can be written as:

$$\varrho (\varphi, t) = \sum_{i}^{N} e\, \delta [\varphi_i (t) - \varphi] = \sum_{i}^{N} \frac{e}{2\pi} \sum_{m} e^{-im(\varphi_i - \varphi)} = \sum_{m} \varrho_m e^{im\varphi} \tag{1}$$

The electron-electron repulsion potential is expanded as Fourier series:

$$V_{ij} = \frac{e^2}{(r_i - r_j)} = \sum_{m} f_m (r_{ij} r_j)\, e^{im(\varphi_i - \varphi_j)} \tag{2}$$

where

$$f_m (r_i ; r_j) = \frac{1}{2\pi} \int_{0}^{2\pi} \frac{e^2}{(r_i - r_j)} \cos m\varphi \, d\varphi$$

The first and the second time derivatives of ϱ_m are ($\omega_i = \dot{\varphi}_i$)

$$\dot{\varrho}_m = \frac{e}{2\pi} \sum_{i}^{N} (- im\, \omega_i)\, e^{-im\varphi_i} \tag{3}$$

$$\ddot{\varrho}_m = \frac{e}{2\pi} \sum_{i}^{N} [(-im\, \omega_i)^2 - im\, \dot{\omega}_i]\, e^{-im\varphi_i} \tag{4}$$

The force on the charge *i* due to the charges *j* is:

$$F_i = - \sum_{j} \frac{\partial V_{ij}}{\partial l_i} = - \frac{1}{R} \sum_{j} \frac{\partial V_{ij}}{\partial \varphi_i} = M \dot{\omega}_i R \tag{5}$$

Eq (5) and (2) give for $\dot{\omega}_i$

$$\dot{\omega}_i = -\frac{1}{M R^2} \sum_{j} \sum_{m'} f_{m'} (r_i ; r_j) (im') e^{im' (\varphi_i - \varphi_j)} \tag{6}$$

and eq (4) takes the form:

$$\ddot{\varrho}_m = -\frac{e}{2\pi} \sum_i (m \, \omega_i)^2 e^{-im \varphi_i} -$$

$$-\frac{e}{2\pi} \sum_i \sum_j \sum_{m'} \frac{1}{M R^2} m m' f_{m'} (r_i ; r_j) e^{im' (\varphi_i - \varphi_j)} e^{-im \varphi_i} \tag{7}$$

The random phase approximation (RPA) is introduced and the second sum in eq (7) averages to zero for $m \neq m'$. With this approximation the equation of motion for charge density is

$$\ddot{\varrho}_m + \frac{N m^2 f_m}{M R^2} \varrho_m = -\frac{e}{2\pi} \sum_i^N (m \, \omega_i)^2 \tag{8}$$

By using similar arguments as were introduced by Bohm and Pines[5] one can deduce that the right side factor is small for collective oscillations.
The plasma frequency is then

$$\omega_p^2 = \frac{N m^2 f_m}{M R^2} \tag{9}$$

The same result has been previously found by Yomosa and Segawa[3]. The consequence of this agreement is that the previous calculations[1,3] with Tomonaga's method are equivalent to the Bohm-Pines RPA approximation. This means that Tomonaga's method has the same type of the limitation as the usual RPA method.

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IZVLEČEK

Frekvenca plazma oscilacije v cikličnih polienih

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Z RPA[5] metodo je izračunana frekvenca plazma oscilacije v cikličnih polienih. Dobljeni rezultat se ujema z rezultatom izračunanim[3] po metodi Tomonaga. Rezultati za linearne in ciklične sisteme[1,3] izračunani po tej metodi vsebujejo vse predpostavke in omejitve običajne RPA metode.

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