PLASMA OSCILLATIONS OF π ELECTRONS IN MOLECULES

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The plasmon energy of the π-electron system is calculated for very long conjugated molecules with unequal CC-bond lengths.

IN the investigation of the spectra of electron absorption in organic molecules with conjugated bonds, it is usually assumed that three valence electrons of each carbon atom are described by hybrid wave functions and form σ-bonds; the wave function of the fourth valence electron is assumed not localized near a definite atom, but extending over the entire core of the molecule, i.e., it is assumed that this last π electron can move relatively easily from one carbon atom to the other.

The theory of collective effects in the π-electron system was considered by Araki and Murai[1] and by Mizuno and Izuyma[2]. It was found[2] that in long molecules, unlike in metals, the limiting frequency of the plasma oscillations vanishes. This circumstance should emphasize the importance of collective effects in the long-wave region of the electron-absorption spectra and by the same token the need for developing a more complicated theory of π-electron states. In this connection, a more accurate estimate of the plasma frequency is of interest.

We note first that in the usual analysis the molecule is likened to a one-dimensional metal, but such a state, as would follow from most general considerations, turns out to be unstable against deformations that lead to doubling of the period and consequently to the occurrence of a forbidden band, if we deal with long molecules. Numerical calculations[3] give for the resultant differences in the bond lengths a value of the order $0.04 \, \text{Å}$. The existence of a forbidden band explains also the singularities in the absorption spectrum in polyene chains[4].

We proceed to an examination of the collective effects. If we impose cyclic boundary conditions, then the π-electron wave function will have the property of one-dimensional Bloch functions

$$\chi_k(\mathbf{r}) = e^{ikx} L^{-1/2} u_k(\mathbf{r}), \qquad u_k(x + c, y, z) = u_k(x, y, z), \tag{1}$$

where x is the direction along which the potential of the core is periodic. The function $u_k(\mathbf{r})$ decreases relative to the coordinates y and z just as rapidly as the atomic wave functions.

The π-electron total energy operator can be written in the form

$$H = H_0 + H_c - \Gamma,$$

where H_0 is the operator of single-particle energy in the Hartree-Fock approximation and H_c the π-electron Coulomb interaction energy operator; the operator is due to the fact that H_0 already includes in part the interaction between electrons[5]. In the calculation of the Coulomb potential matrix elements it is convenient to go over to the well known Fourier representation

$$\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l, f} \Phi(l, f) \, e^{il(x - x') + if(\rho - \rho')},$$

$$\Phi(l, f) = 4\pi e^2 / (l^2 + f^2) L^3,$$

with $\mathbf{q} = (l, f)$ and $\mathbf{r} = (x, \rho)$.

We write, in analogy with the three-dimensional case[6], the wave function of the collective excited state of the system in the form

$$\Psi = A^* \Psi_0, \qquad [H, A^*] = \hbar \Omega A^*, \tag{2}$$

where A* is the operator

$$A^* = \sum_{p,l} \{\alpha_{p,l} \, a_p^* b_l^* + \beta_{p,l} \, b_p a_l\}, \tag{3}$$

$a_p (a_p^*)$ and $b_p (b_p^*)$ are the ordinary electron hole annihilation (creation) operators.

By substituting (3) in (2) we obtain for the coefficients $\alpha_{p,l}$ and $\beta_{p,l}$ in the approximation of the random-phase method, a closed system of equations from which we obtain, taking the periodicity properties of the Bloch functions into account, the following integral equation for the determination of the frequency $\hbar \Omega$

$$S_l(\mathbf{f}) = \sum_{\substack{p,\,\mathbf{f}' \\ |p+l|>p_F;\,|p|<p_F}} \Phi(l,\mathbf{f}')\,S_l(\mathbf{f}')\,Q_l(p,\mathbf{f}'), \qquad (4)$$

where the kernel $Q_l(p,\mathbf{f}')$ is of the form

$$Q_l(p,\mathbf{f}') = 2\frac{W_{p+l,\,p}(-\mathbf{f}')\,W_{p,\,p+l}(\mathbf{f})}{(\hbar\Omega)^2 - (\varepsilon_c(p+l) - \varepsilon_v(p))^2}\{\varepsilon_c(p+l) - \varepsilon_v(p)\},$$

ε_c and ε_v are single-particle energies which are larger or respectively smaller than the Fermi energy. The function $W_{k,\,l}(\mathbf{f})$ is of the form

$$W_{k,\,l} = \frac{N}{L}\int_{V_c} u_k^*(\mathbf{r})\,e^{i\mathbf{f}\rho}\,u_l(\mathbf{r})\,dv,$$

the integration extends over the volume of the unit cell V_c.

For small l we can represent the function $W_{k,\,l}$, using the Bloch equation, in the form

$$W_{\substack{p+l,\,p \\ l\to 0}} = \frac{q\Pi}{\varepsilon_c(p) - \varepsilon_v(p) + \hbar^2 f^2/2m},$$

$$\Pi = \frac{\hbar^2}{m}\frac{N}{L}\int_{V_c} e^{i\mathbf{f}\rho}\,u_k(i\nabla)u_k^*\,dv.$$

From this, in accordance with (4), we obtain as $l\to 0$

$$S_l(\mathbf{f}) \approx q\mathbf{c}/(1 + \hbar^2 f^2/2m\Delta), \qquad \Delta = \varepsilon_c(0) - \varepsilon_v(0),$$

where $\mathbf{c}$ is a constant vector.

Using the theorem on the sums of oscillator strengths, we can obtain from (4) the following estimate for $\hbar\Omega$:

$$\hbar\Omega < \{\tfrac{2}{3}e^2 N\Delta/L + \Delta^2\}^{1/2}, \qquad (5)$$

where Δ is the width of the forbidden band and N/L the linear density of the electrons. If we take Δ equal to 2.5 eV[7], we obtain in the case

of polyene chains $\hbar\Omega \approx 5$ eV. Thus, the spectrum of the collective excitations lies much higher than the single-particle levels.

The foregoing estimate for the plasmon energy $\hbar\Omega$ is obtained by substituting in (4) the approximate expressions for $S_l(\mathbf{f})$ and $W_{p+l,p}$ and replacing the upper limit of integration with respect to $|\mathbf{f}'|$ by infinity. On the other hand, for finite but sufficiently long molecules, the wavelengths along the molecule are limited by the dimensions of the molecule and by the same token the quasi-momentum l is bounded from below and has some minimum value. Since, furthermore, $d\Omega/dl > 0$, the plasma frequency for finite molecules will by the same token be larger than its limiting value for an infinitely long molecule. For $N \sim 15-20$ both corrections approximately cancel each other, and the plasma frequency will therefore have the order of magnitude indicated above.

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