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[13] Although the equations of motion obtained involve the full Riemann tensor, obviously the Riemann tensor $f_{\mu\nu}{}^{k}$ should then be taken according to Eq. (3) with $\varphi_{ij}=\Lambda=0$.

[14] The Riemann tensor $f_{\mu\nu}{}^{k}$ is taken now according to Eq. (3) with $\varphi_{ij}\simeq T_{ij}$ and $\Lambda=T/24$, where T_{ij} is the energy-momentum tensor. That does not mean that the Ricci tensor part of the Riemann tensor is taken fixed. It is still a dynamical variable. It should be noted that in this paper no attempt is made to obtain the full set of field equations of the gravitational theory from a variational principle, such as Eqs. (20) to (22) of Ref. 1, when considering gravitation as a gauge theory. No attempt is also made, in fact, to discuss Yang'g gravitational Lagrangian at all [see, for example, A. H. Thompson, Phys. Rev. Lett. 34, 507 (1975)]. For example, among the equations that are *not* obtained in our theory are $R_{\mu\nu}=0$ or $R_{\mu\nu}=T_{\mu\nu}-\frac{1}{2}g_{\mu\nu}T$ (formally the Einstein equations), although these equations are not as central in the Newman-Penrose scheme as they are in the usual presentation of general relativity theory. However, it is worthwhile emphasizing that the Newman-Penrose dynamical equations (Bianchi equations and the definition of the Riemann tensor in terms of the spin coefficients) *are* obtained from our variational principle.

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Long-Range Interactions in Semiconductors*

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We derive an exponentially decaying interaction between atoms in semiconductors. The decay length is $\hbar[2(m_1+m_2)E_g]^{-1/2}$, where m_1 and m_2 are the valence-band and conduction-band effective masses and E_g is the minimum energy gap. We show that Weber's bond-charge model of lattice vibrations leads to exponentially decaying interactions. Comparing the experimental vibration spectrum and the theoretical decay length suggests that the flattening of the TA mode is due to this long-range interaction.

Weber[1] has extended Phillips's[2] bond-charge (BC) model of lattice vibrations in semiconductors to explain the characteristic flattening of the transverse acoustic phonon mode away from the zone center and the unusually low frequency of this mode at the zone boundary. To illustrate the model Weber considers a monatomic linear chain with lattice constant d where each atom is coupled to its nearest-neighbor BC by a force constant f, and the nearest-neighbor BC's are coupled with a force constant f'. A simple calculation gives the dispersion relation

$$M\omega^2=2f\frac{(f+2f')\sin^2(\pi k/2k_0)}{f+2f'\sin^2(\pi k/2k_0)}, \qquad (1)$$

where M is the atomic mass; k is the wave number of the mode and k_0 its value π/d at the zone boundary. (The mass of the BC's is set equal to zero.)

This model can be described equally well in terms of a Born–von Kármán expansion in which only two-body interactions between atoms are considered. The BC in Weber's model produces long-range forces. This can be seen by displacing atom i while keeping the positions of the other atoms fixed; one can then calculate the force transmitted through the BC's to atom j by minimizing the total energy of the distorted lattice with respect to the BC positions. This calculation defines the force constant λ_{ij} between atom i and atom j which is found to be

$$\lambda_{ij} = f \sinh(\pi\mu/k_0) \exp(-\mu|x_i - x_j|), \tag{2}$$

where

$$\cosh(\pi\mu/k_0) = 1 + f/f' \tag{3}$$

and x_i is the equilibrium position of the ith atom. These force constants reproduce Eq. (1).

Weber notes that significant flattening of the TA mode arises when $f'/f \gg 1$. This corresponds to a very long-range interaction ($\mu \ll k_0$) and consequently we may conclude that the flattening of the TA mode in semiconductors occurs because of long-range, exponentially decaying forces. The bond-charge model of Weber provides a rationalization of that interaction. Note that no Coulomb charge was included in the model; the long-range forces are not Coulombic but arise through the electronic structure.

It is a familiar fact that such interactions must be exponentially decaying in insulators (or semiconductors) with a decay length depending upon the band gap. These are the counterpart of the Friedel oscillations in a metal but with an imaginary wave number. Bloembergen and Rowland[3] have in fact speculated on a relation between the decay and the band structure. Our intent here is to derive the form and compare it with their expression and with the observed vibrational spectra of semiconductors.

We represent the occupied electronic states (valence-band states) by Bloch functions $|\vec{k}_1\lambda_1\rangle$, where $\vec{k}_1$ is a wave number in the Brillouin zone and λ_1 denotes the band index and spin; similarly we represent the unoccupied electronic states (conduction-band states) by $|\vec{k}_2\lambda_2\rangle$. We introduce as a perturbation the infinitesimal displacements of two atoms, one at $\vec{R}_i$ and the other at $\vec{R}_j$. The perturbation is taken to be a sum of two terms, $V(\vec{R}_i)$ and $V(\vec{R}_j)$, localized at the two sites. Then the shift in energy of the system, to second order in the perturbation, contains two terms which involve both displacements; these represent the interaction energy between the two atoms:

$$E^{(2)} = \sum_{\vec{k}_1\lambda_1\vec{k}_2\lambda_2} \frac{\langle\vec{k}_1\lambda_1|V(\vec{R}_j)|\vec{k}_2\lambda_2\rangle\langle\vec{k}_2\lambda_2|V(\vec{R}_i)|\vec{k}_1\lambda_1\rangle}{E_1 - E_2} + \text{c.c.} \tag{4}$$

The Bloch functions may be written in the form $\Omega^{-1/2}u_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{r}}$ and the factors of the form $\exp[i(\vec{k}_1 - \vec{k}_2)\cdot\vec{R}_i]$ extracted from the matrix elements. The remaining integrals are over atomic cells and are rigorously independent of the relative positions $\vec{R}_i$ and $\vec{R}_j$. Thus Eq. (4) can be written in the form

$$E^{(2)} = \Omega^{-2}\sum_{12} \frac{I_{12}\exp[i(\vec{k}_1 - \vec{k}_2)\cdot(\vec{R}_i - \vec{R}_j)]}{E_1 - E_2} + \text{c.c.} \tag{5}$$

The integrals over wave number will be continued into the complex plane and the exponentially decaying interactions will arise from poles in the complex plane.

We seek the pole closest to the real axis since it will correspond to the longest-range interaction. Any poles from I_{12} will lie a distance of the order of a lattice wave number from the axis since the integrals involve functions with lattice periodicity. The nearest pole will arise from the band edges leading to the smallest $E_1 - E_2$ so that it may be estimated by expanding the corresponding bands around their extrema; that is, by using an effective-mass description. In addition I_{12} may be taken out of the integral for this estimate. Taking first the case of band extrema at $\vec{k} = 0$, we write Eq. (5) in the form

$$E^{(2)} = -\frac{2}{(2\pi)^6} I_{12} \int d^3k_1\, d^3k_2\, \frac{\exp[i(\vec{k}_1 - \vec{k}_2)\cdot(\vec{R}_i - \vec{R}_j)]}{E_g + \hbar^2k_1^{\,2}/2m_1 + \hbar^2k_2^{\,2}/2m_2} + \text{c.c.}, \tag{6}$$

where m_1 and m_2 are the valence-band and conduction-band effective masses, respectively, and E_g is the energy gap. We next make the change of variables

$$\vec{q} = \vec{k}_1 - \vec{k}_2, \quad \vec{K} = (m_2/m_1)^{1/2}\vec{k}_1 + (m_1/m_2)^{1/2}\vec{k}_2. \tag{7}$$

With these substitutions Eq. (6) becomes

$$E^{(2)} = -\frac{2}{(2\pi)^6} \frac{1}{[(m_1/m_2)^{1/2} + (m_2/m_1)^{1/2}]^3} \frac{2(m_1 + m_2)}{\hbar^2} 2\, \mathrm{Re} \int d^3K\, d^3q\, \frac{\exp[i\vec{q}\cdot(\vec{R}_i - \vec{R}_j)]}{K^2 + q^2 + k_g^{\,2}}, \tag{8}$$

where

$$k_g^2 = 2(m_1 + m_2)E_g/\hbar^2. \tag{9}$$

The angular integral over $\hat{q}$ may be performed explicitly and the integral over $|\vec{q}|$ continued into the complex plane. The pole at $|\vec{q}| = \pm i(K^2 + k_g^2)^{1/2}$ gives a term proportional to $\exp(-|\vec{q}||\vec{R}_i - \vec{R}_j|)$. A subsequent integration over $\vec{K}$ gives the leading term proportional to $\exp(-k_g|\vec{R}_i - \vec{R}_j|)$. If an indirect band gap had been taken, with minima separated by a wave vector $\vec{q}_0$, this would simply have introduced a constant factor $\exp[i\vec{q}_0 \cdot (\vec{R}_i - \vec{R}_j)]$ (summed over the minima) and an oscillatory interaction, again modulated by the exponential decay as above.

Note that if either mass becomes infinite the interaction is destroyed, contrary to the finding of Bloembergen and Rowland[3] who take the valence band flat but still expect an interaction. We can see schematically how this error arose by returning to our Eq. (5) which they also obtained. By taking a flat valence band they took E_1 to be independent of k_1. Then, ignoring the I_{12} term as both treatments have done, the integral is of the form $\exp[i\vec{k}_1 \cdot (\vec{R}_i - \vec{R}_j)]$ over a Brillouin zone. With $\vec{R}_i - \vec{R}_j$ a translation of the perfect lattice, this integral vanishes identically. Because they approximate the Brillouin zone by a sphere they obtained a net interaction with an oscillatory term depending on the cutoff chosen. We believe that this contribution is not present in a correct theory.

It is of interest to compare the form we deduce with that obtained from the observed vibration spectrum using the two-parameter model of Weber. We determine f and f' by fitting the [100] TA dispersion curve at two points: $\omega_{\text{TA}}(k = k_0)$ and ω/k as k tends to zero. In this way we obtain

$$f'/f = \tfrac{1}{2}(16C_{44}/\rho a^2 \omega_{\text{TA}}^2 - 1), \tag{10}$$

where ρ is the density, C_{44} is the elastic shear constant, and a is the lattice constant. Combining this with Eq. (3) gives an empirical value of μ which may be compared with our calculated k_g.

Note that for a realistic band structure there are three valence bands which contribute to the interaction, but we include only the light-hole band which, as seen from Eq. (9), gives the longest-range interaction. For the indirect-band-gap semiconductors the mass is anisotropic and it is not difficult to carry out the analysis for that case. However, for simplicity we use for our comparison an isotropic conduction-band mass determined by $m_{\text{iso}} = (m_l m_t^2)^{1/3}$.

TABLE I. The second column gives the ratio of the screening length to the zone-boundary wave length based upon the minimum energy gap and effective masses. The third column gives an experimental estimate of this ratio based upon Weber's model of the vibration spectrum.

Material	k_0/k_g	k_0/μ
C	1.7	0.9
ZnS	1.6	1.8
GaP	2.1	2.0
Si	3.1	2.0
GaAs	4.7	2.1
Ge	4.8	2.3
InSb	22.4	2.9

The results for those materials for which we could find masses are shown in Table I. The values obtained from the vibrational spectra (k_0/μ) are of similar magnitude to those predicted from our theoretical expression for the decay length. In addition, the trend from material to material is essentially the same.

We also calculated k_g using an average gap[4] obtained from optical absorption peaks ($E_g = E_2$) and unit masses. This leads to a universal value for k_0/k_g of 0.7 for homopolar materials. The reason for this is the experimental fact noted by Harrison and Ciraci[4] that

$$E_2 = 3.6\hbar^2/md^2,$$

where d is the bond length.

The contrast with the values shown in the right-hand column in Table I suggests that it is indeed the minimum gap, rather than an average gap, which dominates the observed flattening of the TA acoustic mode.

The remaining discrepancies apparent in Table I reflect the crudeness of the linear-chain model of the vibrational modes which can only be regarded as schematic. We believe that the limiting long-range form of the interaction is rigorously correct and the uncertainty lies in the role of interactions of shorter range and of long-range electric multipole interactions. In fact if interactions between nearest-neighbor atoms were taken into account in a three-parameter model the values of k_0/μ would be increased, improving the agreement. It is also interesting to note that the flattening of the modes, which Weber accounted for through the use of a bond charge, can be reinterpreted in terms of long-range interactions in which the valence and conduction bands enter symmetrically.

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Some Comments on the Plasmon Spectrum of Tetrathiafulvalene Tetracyano-*p*-quinodimethane (TTF-TCNQ)*

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Our random-phase-approximation model calculation of the high-frequency dielectric response of a quasi-one-dimensional metal is generalized to the case of *n* conducting strands per unit cell. For a model of the two-band system tetrathiafulvalene tetracyano-*p*-quinodimethane we obtain good agreement with recent experiments, and also predict an acoustic-plasmon branch. Some implications for the physics of the material are discussed.

The first experimental determination of the plasmon spectrum in a quasi-one-dimensional conductor has recently been reported by Ritsko *et al.*[1] They found that the organic metal tetrathiafulvalene tetracyano-*p*-quinodimethane (TTF-TCNQ)[2] displays an unusual plasmon response qualitatively consistent with the predictions of our model calculation[3] for a simple quasi-one-dimensional metal in the random-phase approximation (RPA). The predictions include negative dispersion, the absence of Landau damping, and a strongly angle-dependent long-wavelength plasma frequency. Our model, however, was not designed to represent a two-band system such as TTF-TCNQ,[4-6] and detailed agreement with experiment was lacking.

Here we extend our calculation to a two-band model more nearly representative of TTF-TCNQ. We find that much of the discrepancy between theory and experiment is removed, and that comparison of the two provides fresh insight into the electronic structure and optical properties of the material. Further, our analysis predicts a second, low-frequency plasmon branch, acoustic in the limit of zero interchain bandwidth and experimentally signficant at short wavelengths.

The model of Ref. 3 consisted of a periodic array of parallel, infinite, metallic strands, embedded in a uniform medium of dispersionless dielectric constant ϵ_∞, and coupled to one another only by their mutual Coulomb interaction. As we remarked in Ref. 3, the model in this simple form does not apply directly to a material such as TTF-TCNQ, whose crystal structure consists of four conducting chains (two each of stacked TTF and TCNQ molecular ions) per cross-sectional unit cell.[7] To treat such cases, we generalize the model to include n distinguishable strands per unit cell.

Our analysis proceeds in parallel with our original work,[3] and employs essentially the same notation. If $\chi_j(q,\Omega)$ [Ref. 3, Eq. (6)] is the complex density-density response function[8] and $\beta_j(\vec{Q})$ [Ref. 3, Eq. (3)] the molecular form factor for conduction electrons on the jth strand of the unit cell, the total potential due to an applied potential $V_{\text{ext}}(\vec{Q})$ is

$$V_{\text{tot}}(\vec{Q})=\frac{1}{\epsilon_\infty}\left[V_{\text{ext}}(\vec{Q})-\frac{4\pi e^2}{Q^2}\sum_{j=1}^{n}\chi_j(q,\Omega)\beta_j(\vec{Q})S_j(\vec{Q})\right]. \tag{1}$$

Equation (1) replaces Eq. (5) of Ref. 3, and we have defined

$$S_j(\vec{Q})\equiv\sum_{\vec{G}}\beta_j^*(\vec{Q}+\vec{G})V_{\text{tot}}(\vec{Q}+\vec{G}). \tag{2}$$