f-Sum Rule and Effective Masses in Superlattices

N. F. Johnson, H. Ehrenreich, and K. C. Hass[a]
Division of Applied Sciences and Physics Department, Harvard University, Cambridge, Massachusetts 02138

and

T. C. McGill
T. J. Watson, Sr., Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125
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The f-sum rule, relating effective masses to oscillator strengths, is extended to semiconducting superlattices and applied to GaAs-(Ga,Al)As and HgTe-CdTe. This novel approach is implemented analytically by use of the envelope-function approximation to calculate both parallel and perpendicular masses and is used to account for their difference physically. Agreement with experiment is excellent, but in HgTe-CdTe only if the valence-band offset is small.

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The f-sum rule has been extremely useful for the extraction of a wide range of physical information pertaining to condensed matter. As shown here, this is equally true for superlattices, in particular, GaAs-(Ga,Al)As and HgTe-CdTe. Specifically, we (1) relate the parameters in the formal, exact expression for the f-sum rule to those of the bulk constituents using the envelope-function approximation[1]; (2) obtain oscillator strengths relevant to optical absorption and show that only a small number of superlattice (SL) bands contribute to the sum; (3) derive values of both $m_{\parallel}$ and $m_{\perp}$ (the effective masses in the plane of the SL and along the growth or z axis, respectively) simultaneously and show that they compare well with experimental information; (4) comment on band-offset values that yield effective masses consistent with cyclotron resonance experiments. It should be emphasized that these results can all be obtained from physically transparent, analytic expressions without extensive numerical computation.

For superlattices characterized by eigenstates $|L,\mathbf{K}\rangle$ and energies $E_L(\mathbf{K})$, where $\mathbf{K}$ and L are the SL wave vector and band index, respectively, the f-sum rule takes the form

$$(m/m_L)_\alpha = 1 + \sum_{L'}{}' f^{\alpha}_{L'L}, \tag{1}$$

where

$$f^{\alpha}_{L'L} = \frac{2}{m}\frac{|\langle L,0|p_\alpha|L',0\rangle|^2}{E_L(0)-E_{L'}(0)}$$

is the oscillator strength. The valence- and conduction-band extrema are assumed to be at $\mathbf{K}=0$. p_α is the momentum operator component along the principal axis α ($\alpha = z$ or $\perp$ for the growth axis and x, y, or $\parallel$ within the layers, respectively), and $(m_L/m)_\alpha$ is the corresponding effective mass in units of the electron mass m.

Equation (1) is exact as it stands. Here we evaluate the relevant SL quantities analytically in terms of bulk electronic structure parameters using the envelope-function approximation.[1] The envelope function $F_n(L,\mathbf{K};\mathbf{r})$ is defined by the coefficients of the expansion of $\langle \mathbf{r}|L,\mathbf{K}\rangle$ in terms of bulk Bloch functions $\langle \mathbf{r}|n\rangle$ for band n at $\mathbf{k}=0$. $F_n(L,\mathbf{K};\mathbf{r})$ varies slowly with $\mathbf{r}$ on the scale of the unit-cell size. For the well-lattice-matched SL's considered here, $\langle \mathbf{r}|n\rangle$ may be assumed the same in each constituent. This easily generalizable assumption is justified here by the similarity of the bulk pseudopotentials and momentum matrix elements.[2]

For the energy region of interest here, the envelope function may be calculated with the Kane model including finite spin-orbit coupling.[3] A finite heavy-hole mass is obtained by the inclusion of the next higher conduction band by perturbation theory. The function $\mathbf{F}(L,\mathbf{K};\mathbf{r})$ with components $F_n(L,\mathbf{K};\mathbf{r})$ in an A (B) layer is determined from

$$H_{A(B)}[k_x,k_y,k_z \rightarrow -i(\partial/\partial z)]\mathbf{F}(L,\mathbf{K};\mathbf{r}) = E_L(\mathbf{K})\mathbf{F}(L,\mathbf{K};\mathbf{r}),$$

where $H_{A(B)}$ is the 8×8 Hamiltonian matrix.[3] For $\mathbf{K}=(0,0,K_z)$ only bulk states with the same m_J mix, where J is the total angular momentum, and each F_n becomes independent of x and y. These simplifications[1] do not occur for $\mathbf{K}=(K_x,0,0)$ since the bulk states being mixed correspond to $\Delta m_J = \pm 1,0$. Both effective masses $m_\perp$ and $m_\parallel$ can be calculated from the f-sum rule if $\mathbf{F}(L,0;z)$ is known. The involvement of only $\mathbf{K}=0$ states reduces the number of coupled differential equations,[1] thereby permitting an analytical solution to the problem for arbitrary direction. The boundary conditions used are equivalent to those of Bastard and Mailhiot and coworkers.[3-5]

The relevant matrix elements are given by

$$\langle L,0|p_z|L',0\rangle = \sum_{nn'}[P^z_{nn'}\alpha_{nn'}(L,L') + \delta_{nn'}\pi_n(L,L')], \quad \langle L,0|p_x|L',0\rangle = \sum_{nn'}P^x_{nn'}\alpha_{nn'}(L,L'), \tag{2}$$

$E_{L'}(0)$ (eV)	L'	Envelope Functions	$f^{\perp}_{L',CI}$ ($\Sigma f^{\perp}$)	$f^{\parallel}_{L',CI}$ ($\Sigma f^{\parallel}$)
	Higher Bands		-0.17	~0
1.72	C2		-4.89	~0
1.56	C1		— (CB -5.06)	— (CB 0.00)
-0.006	HH1		0	6.85
-0.017	LH1		8.90	2.48
	LH2→LH15		0.60	0.43
	HH2→HH7		0	0.27
-0.36	LH16		3.36	3.35
	Lower Bands		~0 (VB 12.86)	~0 (VB 13.38)
			$m_{\perp}/m$ = 0.114	$m_{\parallel}/m$ = 0.070

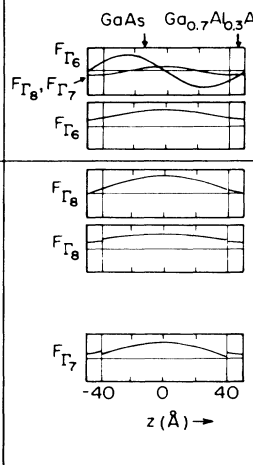

FIG. 1. Contributions to f-sum rule for 80-Å GaAs, 20-Å $Ga_{0.7}Al_{0.3}As$ superlattice. Envelope functions shown for important superlattice $\mathbf{K}=0$ states $|L',0\rangle$ at energies $E_{L'}(0)$. Partial sums of oscillator strengths over superlattice conduction and valence bands (CB and VB) in parentheses. Masses calculated from Eq. (1).

where $P^{\alpha}_{nn'}=\langle n|p_{\alpha}|n'\rangle$ is the bulk momentum matrix element, and

$$\alpha_{nn'}(L,L')=d^{-1}\left[\int_{-l_A/2}^{l_A/2}+\int_{l_A/2}^{l_A/2+l_B}\right]dz\,F_n^*(L,0;z)F_{n'}(L',0;z),$$
$$\pi_n(L,L')=(\hbar/i)d^{-1}\left[\int_{-l_A/2}^{l_A/2}+\int_{l_A/2}^{l_A/2+l_B}\right]dz\,F_n^*(L,0;z)(\partial/\partial z)F_n(L',0;z). \tag{3}$$

Here $l_{A(B)}$ is the A (B) layer width and $d=l_A+l_B$ is the superlattice period. The F_n's are trigonometric functions within each layer; the integrations are therefore straightforward.

Figure 1 shows the dominant F's for an 80-Å GaAs, 20-Å $Ga_{0.7}Al_{0.3}As$ SL over an energy range $-0.36 < E_{L'0} < 1.72$ eV. The condition-band–valence-band offset ratio is taken to be 70:30,[6] and standard bulk input parameters are employed.[2] The large number of SL valence bands are associated with the zone-folding due to the smaller SL Brillouin zone. The few $|L',0\rangle$'s of primary importance to the f-sum rule, whose F's are sketched in Fig. 1, have substantially the atomic symmetry of the bulk bands from which they originate, although small admixtures of other bands included in the Kane model are present. This behavior is associated with the small curvature of the F's (for a bulk crystal they would be constant). The closely spaced SL conduction-band states $|C1,0\rangle$ and $|C2,0\rangle$ have F's resembling the ground and first excited states of standing waves in a box. Even though they derive primarily from the same bulk symmetry Γ_6, they can have nonvanishing momentum or optical matrix elements coupling them because of the crystal momentum supplied by the barriers.

Values for the electron masses $m_{\parallel}$ and $m_{\perp}$ may be calculated with the oscillator strengths shown in Fig. 1. The results are shown in Fig. 2 as functions of Al concentration x for the layer widths used in Fig. 1 and compared to the $T=75$ K experimental cyclotron resonance values of Duffield *et al.*[7] As expected, the $m_{\perp}$ value increases with x, i.e., with the barrier height separating the GaAs layers, and agrees well with that obtained by differentiation of the dispersion relation derived in Ref. 3. By contrast, $m_{\parallel}$ is nearly proportional to the band gap, also shown in Fig. 2, much as in bulk GaAs. The agreement between theory and experiment, although excellent, could be improved by the addition of temperature corrections to the $T=0$ K theoretical results.[7]

It is clear that $m_{\perp}>m_{\parallel}$ because of the barriers. A more subtle explanation of this inequality is provided by consideration of the oscillator strengths $f_{L',C1}$ and their sums, as shown in Fig. 1. We note first that the principal contributions to the f-sum rule determining $m_{\perp}$ and $m_{\parallel}$ come from SL states near the GaAs bulk Γ_6, Γ_7, and Γ_8 levels. The total *valence*-band contributions to $m_{\perp}$ and $m_{\parallel}$ obtained by summation of $f^{\perp}_{L',C1}$ and $f^{\parallel}_{L',C1}$, respectively, are the same and are nearly to the bulk value. Individual f's differ, however, just as in the bulk Kane model where the z direction is given special significance.

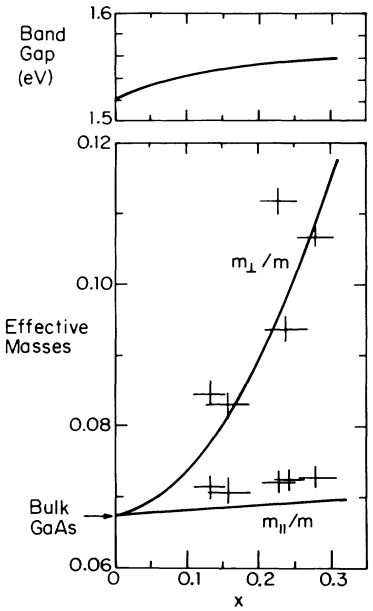

FIG. 2. Comparison of experimental (crosses, Ref. 7) and theoretical (solid lines) values of electron masses for 80-Å GaAs, 20-Å $Ga_{1-x}Al_xAs$ superlattice. Top: theoretical superlattice band gap.

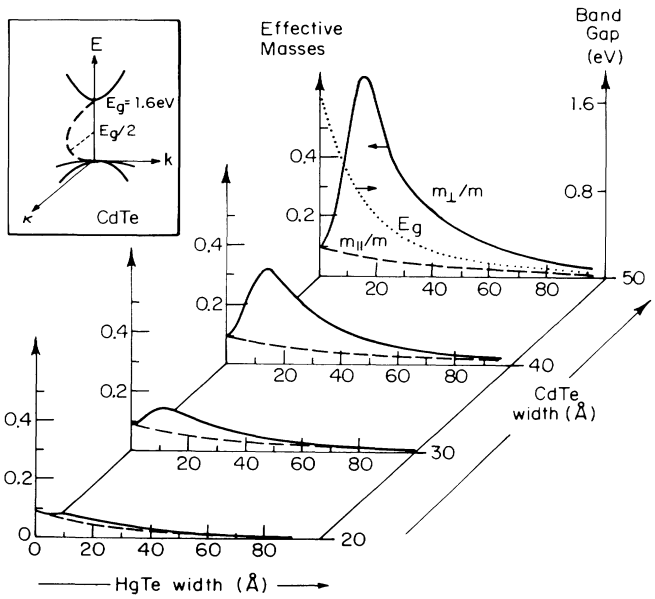

FIG. 3. Variation of effective masses as functions of layer widths in HgTe-CdTe superlattice. The superlattice band-gap behavior corresponds to 50-Å CdTe. Inset: Schematic complex band structure of bulk CdTe near $\mathbf{k}=0$.

The difference between $\sum f^\perp$ and $\sum f^\parallel$ is seen to arise from the negative contribution of $C2$ to $\sum f^\perp$, which has no analog in the bulk band structure. The $\langle C1,0 \mid p_z \mid C2,0\rangle$ matrix element, while smaller than typical bulk values, gives rise to an appreciable oscillator strength because of the energy proximity of $C1$ and $C2$.

Results for HgTe-CdTe are obtained with standard bulk parameters[2] and a variable valence-band offset Λ (defined to be positive if the Γ_8 level of HgTe lies above that of CdTe). Values of $m_\perp/m$ and $m_\parallel/m$ calculated for the controversial common-anion-rule value $\Lambda=0$ are plotted in Fig. 3 as functions of HgTe layer width (l_A) for a series of CdTe widths (l_B). The behavior of the SL band gap E_g is shown for a single representative CdTe width of 50 Å For thick CdTe widths, E_g corresponds physically to the kinetic energy of confinement in the HgTe quantum well. E_g increases with decreasing l_A as expected. For narrow CdTe widths (e.g., $l_B=20$ Å), for which the extent of the F's is greater than l_B, the SL case can be shown to be substantially equivalent to that of the alloy $Hg_{1-x}Cd_xTe$ ($x=l_B/d$) and $m_\parallel \approx m^*_{\text{alloy}}$ to better than 10%.

The remarkable peak in $m_\perp$ as a function of HgTe thickness for fixed CdTe width (e.g., $l_B=50$ Å) can be explained by reference to the inset in Fig. 3 showing the complex band structure of bulk CdTe near $\mathbf{k}=0$. Note that the SL gap E_g(SL) lies inside the CdTe gap E_g(CdTe). The imaginary wave vector κ, which characterizes the decay length of F in the CdTe barriers, increases as E_g(SL) becomes larger and causes F to decay more rapidly. This effect is most pronounced when the SL gap is $\frac{1}{2}E_g$(CdTe), i.e., at E_g(SL) = 0.8 eV. Figure 3 shows the peak in $m_\perp$ to occur at that energy. For l_A values smaller than that for which the peak occurs, $m_\perp$ decreases and approaches the CdTe value as l_A approaches zero. Values of $m_\perp$ are within 5% of those obtainable from the dispersion relation of Ref. 3.

Magnetoabsorption measurements of Berroir *et al.*[8] for a 100-Å HgTe, 36-Å CdTe SL have yielded $m_\parallel/m = 0.017 \pm 0.003$. The present theoretical results for a positive band offset Λ (in electronvolts) can be empirically represented by $m_\parallel/m = 0.014 - 0.046\Lambda$. Good agreement with experiment is thereby achieved for small Λ but not for the value $\Lambda \approx 0.36$ eV suggested by recent photoemission experiments.[9] We are not suggesting that any of these experiments is flawed; neither is it likely that the results of $\mathbf{k}\cdot\mathbf{p}$ calculations can be seriously in error. (Large band offsets, however, have been obtained from first-principles band calculations,[10] which do not address effective mass values.) These inconsistencies pose an interesting dilemma which remains unresolved.[11]

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[a]Present address: Research Staff, Ford Motor Co., Dear-

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[10]See, for example, S. H. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 (1987), and references therein.

[11]Note that while the recent empirical pseudopotential calculations of M. Jaros, A. Zoryk, and D. Ninno, Phys. Rev. B **35**, 8277 (1987), for $\Lambda=0.37$ eV claim consistency with experimental SL band gaps, we find that the present $\mathbf{k}\cdot\mathbf{p}$ model, in fact, yields much better agreement, particularly for *small* Λ.