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Collective Effects in Interband Optical Absorption

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Determination of the Fermi-surface anisotropy of alkali metals by the de Haas–van Alphen effect has provided reliable numerical values for electronic energy gaps at Brillouin-zone boundaries. These determinations allow a quantitative comparison of interband optical absorption power with theory. Serious discrepancies with standard theory are found. For Na, the theoretical absorption is too small by a factor of 4, whereas for Rb and Cs it is too large by a factor greater than 3. We observe that interband matrix elements must include not only the direct interaction with the photon field, but also the Hartree-Fock potential arising from collective motions of all electrons responding to that field. The interband matrix elements are calculated using time-dependent, self-consistent perturbation theory. If only the Hartree term arising from collective motion is added, matrix elements are reduced by a few percent. However, inclusion of the exchange potential profoundly alters the magnitude of the matrix element. For Na the theoretical absorption power is enhanced by a factor of 4, and for Rb and Cs it is suppressed by a factor of 6 or more. This apparent success of the time-dependent, Hartree-Fock method indicates that exchange interactions can contribute unexpectedly to electronic processes in solids.

I. INTRODUCTION AND DISCUSSION OF RESULTS

THE theory of interband optical absorption in simple metals has been given by Butcher.[1] Since the model employed was the nearly free-electron approximation, quantitative application of the theory is limited to the alkali metals. The vertical transitions in k space, corresponding to intrinsic absorption, are indicated in Fig. 1 for Na. The initial state of the transition must lie below the Fermi energy E_F, indicated by the dashed line. The object of the theory is to determine the energy dependence of the optical absorption power. This can be expressed in terms of an effective conductivity $\sigma_0(\hbar\omega)$. With the notation employed here, Butcher's theory is

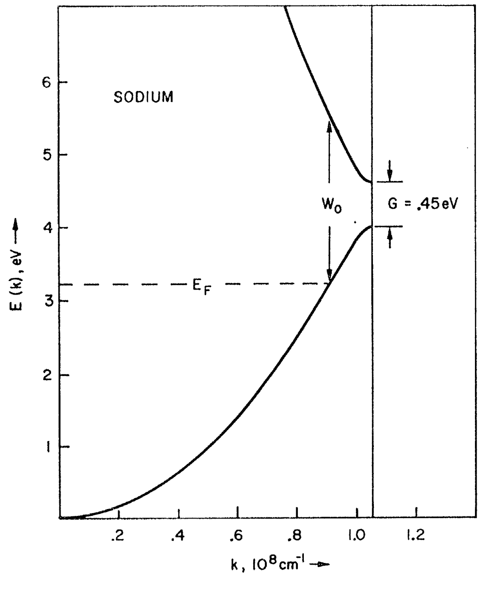

FIG. 1. Electronic energy spectrum of Na in the nearly-free-electron approximation. W_0 indicates the threshold energy of interband absorption.

$$\sigma_0(\hbar\omega)=\frac{me^2G^2(\hbar\omega-W_0)(W_1-\hbar\omega)}{4\pi\hbar^3Q(\hbar\omega)^3}. \tag{1}$$

Q is the wave vector of the (110) reciprocal lattice vector; $Q=2\sqrt{2}\pi/a$, where a is the lattice constant. G is the energy gap at the Brillouin-zone boundary.[2] W_0 and W_1 are the threshold and cutoff energies.

$$W_0=\hbar^2Q(Q-2k_F)/2m,$$
$$W_1=\hbar^2Q(Q+2k_F)/2m.$$

The expression for W_0 is valid for sufficiently small G/E_F; otherwise, the threshold energy is slightly larger.

The absorption power given by (1) cannot be compared with experiment quantitatively unless reliable values for the energy gap G are known. Such data have become available recently from precise determinations of the Fermi-surface anisotropy by the de Haas–van Alphen effect.[3–5] The analysis of Ashcroft[6] can then be used to deduce G. Table I summarizes the information relevant to a comparison between Eq. (1) and experiment.

TABLE I. Data pertinent to the interband absorption power of the alkali metals.

	$G=2V_{110}$ (eV)	Threshold (eV)	Max σ_0	Max σ, expt.
Li	1.0	3.0	0.6×10^{14}	$\sim1.2\times10^{14}$
Na	0.45	2.1	0.2	0.9
K	0.39	1.3	0.3	...
Rb	0.9	1.2	2.0	0.6
Cs	1.4	1.0	6.2	<2

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[1] P. N. Butcher, Proc. Phys. Soc. (London) **A64**, 765 (1951).

[2] The reader may elect to translate G, whenever it appears in this paper, into $G=2V_{110}$, where V_{110} is the pseudopotential coefficient for wave vector Q at the Fermi surface.

[3] D. Shoenberg and P. J. Stiles, Proc. Roy. Soc. (London) **A281**, 62 (1964).

[4] K. Okumura and I. M. Templeton, Proc. Roy. Soc. (London) **A287**, 89 (1965).

[5] M. J. G. Lee, Proc. Roy. Soc. (London) **A295**, 440 (1966).

[6] N. Ashcroft, Phys. Rev. **140**, A935 (1965).

The data for each alkali metal need individual discussion:

Lithium. The Fermi surface anisotropy of Li is not known, so the first row of Table I does not test the validity of Eq. (1). The value for G given here was deduced from the experimental value of σ, using the theory developed in this paper. Since this represents the only empirical determination of G in Li, it was included here to provide a complete summary. The experimental value for the interband contribution to σ was taken from the data of Hodgson,[7] and corresponds to the *increase* in $\sigma(\hbar\omega)$ between about 3 and 4 eV. Should optical data of greater resolution become available, the derived value of G should be altered by the square root of any correction factor to the quoted interband σ. It is noteworthy that $G\sim 1.0$ eV is about a factor 3 smaller than predictions of typical band calculations.[8]

Sodium. The Fermi surface anisotropy of Na has been determined recently by Lee.[5] $G=0.45$ eV is obtained from an Ashcroft analysis. The experimental σ is taken from Mayer and Hietel.[9] The significant discrepancy between σ_0 and σ, about a factor of 4, provides motivation for the present theoretical study. This disagreement was first pointed out by Appelbaum,[10] who investigated a modification of Butcher's theory based mainly on the use of orthogonalized plane wave (OPW) functions. He found that the discrepancy was not alleviated.[11]

Potassium. Shoenberg and Stiles[3] have measured the K Fermi-surface anisotropy by the de Haas–van Alphen effect. Their results indicate $G=0.39$ eV.[12] No value is given for the interband σ, although the optical absorption has been measured by Mayer and El Naby.[13] The reason is that the interband absorption is completely masked by the large optical absorption anomaly which occurs at $\hbar\omega=0.62$ eV. Such anomalies have been reported in all five alkali metals.[7,9] A quantitative theory of the anomaly in K has been published,[14] which attributes the absorption to magnetic interband transitions arising from a spin-density-wave ground state. Although this interpretation remains tentative, it accounts for the observed σ between 0.6 and 2.0 eV. This is surprising since the ordinary interband absorption σ_0 should be superposed additively between 1.3 and 2.0 eV. The standard theory, Eq. (1), cannot in any case account for the anomalous absorption.[15] Subtraction of a theoretical spin-density-wave contribution, normalized to the anomaly, leaves little if any remaining absorption attributable to interband processes.

Rubidium. The de Haas–van Alphen work of Shoenberg and Stiles[3] leads to an energy gap $G=0.9$ eV.[12] The experimental σ is taken from Mayer and Hietel,[9] and is about a factor of 3 smaller than that predicted by Eq. (1). This discrepancy is inverted relative to the one found above for Na.

Cesium. The Fermi-surface anisotropy, determined by Okumura and Templeton,[4] implies a value $G=1.4$ eV. Like K, the interband σ appears masked by an anomalous absorption of lower threshold. Here, however, the predicted σ_0, $\sim 6\times 10^{14}$, is about a factor of 3 larger than the *total* absorption observed[9] near $\hbar\omega=1.5$ eV. A discrepancy of at least a factor of 3 is indicated.

In summary, the standard theory of interband optical absorption fails to agree with observation where comparison is possible. Perhaps the nearly free-electron approximation is too crude for the heavier alkali metals, for which theoretical values are too large by at least a factor of 3. But such an excuse can hardly apply to Na, where theory underestimates the absorption by a factor of 4. The problem at hand is to discover a theoretical improvement that yields a correction factor, multiplying Eq. (1), with a range of variation (with electron density) of 12 or more.

It is not hard to find an omission in the standard theory which can be easily corrected. The interband matrix elements employed in the derivation of Eq. (1) are merely the matrix elements of the electronic interaction with the macroscopic photon field. However, the electric field of the photon causes all of the conduction electrons to oscillate adiabatically with the photon frequency. Since the conduction-electron density has a periodic spatial variation with wave vector Q, caused by the crystal potential, this collective motion will generate an oscillatory Hartree-Fock potential having spatial periodicity Q and temporal periodicity ω. The contribution of this potential must also be included in the transition matrix element. Since the collective motion depends on the total perturbation, the calculation

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[7] *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 60. (The data in Fig. 4 must be converted to esu by multiplying by c.)

[8] F. S. Ham, Phys. Rev. **128**, 82 (1962); V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[9] H. Mayer and B. Hietel, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 47, Fig. 6, $T=-183$°C.

[10] J. A. Appelbaum, Phys. Rev. **144**, 435 (1966).

[11] Appelbaum found a suppression of the interband matrix element by about 40%. We have repeated his work analytically and have found that his initial- and final-state wave functions were seriously nonorthogonal. We found that the suppression of the interband matrix element associated with core orthogonalization could be attributed almost entirely to those terms in the matrix element responsible for the above-mentioned nonorthogonality. Omission of such spurious terms leads to interband matrix elements essentially the same as those employed by Butcher. We have concluded that conduction-band wave functions based on the nearly-free-electron approximation are sufficiently accurate for the theoretical elaboration of the present paper.

[12] This value differs slightly from that quoted by Ashcroft, Ref. 6. The value given here is that which optimizes a fit to the Fermi surface in all three symmetry directions. Ashcroft's value was obtained by forcing an exact fit in the [110] and [100] directions, allowing an unnecessarily large deviation in the [111] direction.

[13] H. Mayer and M. H. El Naby, Z. Physik **174**, 269 (1963); **174**, 280 (1963); **174**, 289 (1963).

[14] A. W. Overhauser, Phys. Rev. Letters **13**, 190 (1964).

[15] M. H. Cohen and J. C. Phillips, Phys. Rev. Letters **12**, 662 (1964).

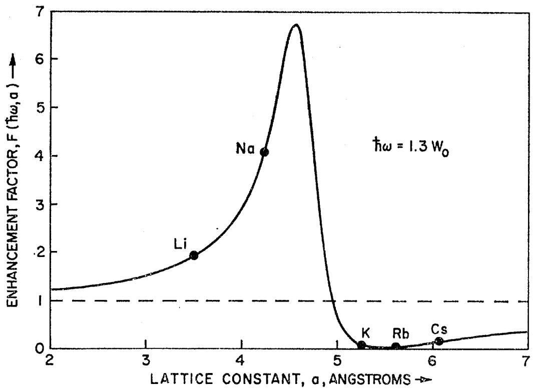

FIG. 2. Variation of the optical absorption enhancement factor F with lattice constant, for a monovalent bcc metal. Since F is also frequency-dependent, the value of F for $\hbar\omega$ 30% above threshold is shown. The points show the (theoretical) location of the alkali metals.

must be carried out by a self-consistent procedure. This is done in Sec. II. Collective effects in solid-state optical processes have been considered previously.[16] However, we are not aware of any prior calculation of interband matrix elements by the time-dependent, Hartree-Fock method.

Inclusion of the above-mentioned collective effects modifies the theoretical absorption power.

$$\sigma(\hbar\omega)=\sigma_0(\hbar\omega)F(\hbar\omega)\,. \tag{2}$$

The correction factor F depends only on frequency and electron density, and is independent of G. Figure 2 shows the density dependence of F for a photon energy 30% above threshold. This result predicts that the absorption power is enhanced by a factor of 4 in Na, and is significantly suppressed in K, Rb, and Cs. Since no adjustable parameter entered the derivation of F, this apparently successful explanation of the discrepancies cited above may have significance. The pronounced deviation of F from unity arises from exchange interactions. If only the Hartree term were included, F would have been a few percent less than unity throughout the density range. The apparently critical role of the time-dependent exchange potential warrants extensive discussion, given in Sec. III.

The theoretical $\sigma(\hbar\omega)$, Eq. (2), for an electron density appropriate to Na is shown in Fig. 3. The experimental data of Mayer and Hietel[7] and $\sigma_0(\hbar\omega)$, Eq. (1), are indicated. A more extensive analysis[17] of the Fermi-surface anisotropy of Na suggests that G may be as large as 0.50 eV. The corresponding $\sigma(\hbar\omega)$ is also shown. The somewhat larger maximum σ for this value of G agrees equally well with the data.

The rapid decrease of $\sigma(\hbar\omega)$ between 3 and 4 eV does not agree with experiment. This failure may possibly be caused by an oversimplification of the theory, which we now discuss. The Fermi surface and Brillouin zone in a $\{111\}$ plane are shown in Fig. 4. Consider a representation of interband optical processes in the extended zone scheme. Processes just above threshold correspond to transitions from A to B in Fig. 4. For $\hbar\omega$ 50% or more above threshold, transitions from C to D will participate. Note that energy states near D will be perturbed by the energy gap arising from the $(10\bar{1})$ crystal potential. The energy of states near D will be lowered. This will enhance the joint density-of-states factor that controls the transition rate. Such energy perturbations have been neglected in the elementary theory leading to Eqs. (1) and (2). Consequently, a much more elaborate calculation is required before discrepancies near $\hbar\omega = 2W_0$ can be held significant.

In Sec. II the only collective effects that are calculated are those arising from the conduction electrons. The ion-core electrons will also participate in collective motion. Their contribution will be proportional to the ionic polarizability. These effects are very small for Li and Na, but for Rb and Cs they are large enough to warrant inclusion. To do so would obscure the strategy of the calculation given below. We prefer to let this effect be the subject of a future study.

II. THEORY OF THE INTERBAND OPTICAL MATRIX ELEMENT

Consider conduction-electron states near one of the twelve equivalent faces of the Brillouin zone. A periodic potential

$$V(\mathbf{r})=G\cos\mathbf{Q}\cdot\mathbf{r}$$

generates an energy gap G at the zone face. The wave function $\varphi_{\mathbf{k}}$ of an electron near that face, below the

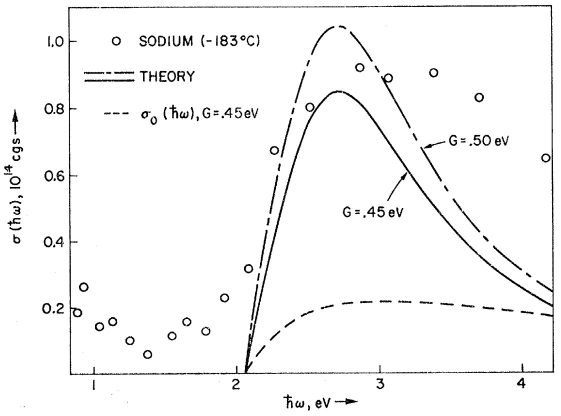

FIG. 3. Absorption power versus photon energy for Na. The data are taken from the work of Mayer and Hietel.

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[16] P. A. Wolff, Phys. Rev. **116**, 544 (1959); H. Ehrenreich, H. R. Philipp, and B. Segall, *ibid.* **132**, 1918 (1963); J. J. Hopfield, *ibid.* **139**, A419 (1965). The time-dependent, Hartree-Fock method has been applied to atomic polarizability problems by A. Dalgarno and G. A. Victor [Proc. Roy. Soc. (London) **A291**, 291 (1966)]. The reader is referred to this paper for earlier references to the time-dependent, Hartree-Fock equations.

[17] M. J. G. Lee, in Proceedings of the 10th International Conference on Low-Temperature Physics, Moscow, 1966 (to be published).

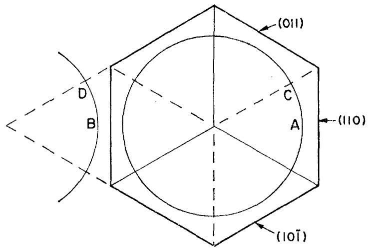

FIG. 4. Fermi surface and Brillouin zone of Na in a (111) plane. In the extended zone scheme, absorption processes near threshold correspond to transitions from A to B. For photon energies 50% or more above threshold, transitions from C to D contribute.

gap, can be adequately described by

$$\varphi_{\mathbf{k}}=\sin\theta \exp i\mathbf{k}\cdot\mathbf{r}-\cos\theta \exp i(\mathbf{k}-\mathbf{Q})\cdot\mathbf{r}. \tag{3}$$

The corresponding state above the gap, which is connected with (3) in an optical absorption event, is

$$\psi_{\mathbf{k}}=\cos\theta \exp i\mathbf{k}\cdot\mathbf{r}+\sin\theta \exp i(\mathbf{k}-\mathbf{Q})\cdot\mathbf{r}. \tag{4}$$

These are the wave functions associated with the nearly free-electron approximation. The coefficients obey the relation

$$\sin 2\theta=G/(E_+-E_-), \tag{5}$$

where

$$E_\pm=\tfrac{1}{2}[\epsilon(\mathbf{k})+\epsilon(\mathbf{k}-\mathbf{Q})]\pm\tfrac{1}{2}\{[\epsilon(\mathbf{k})-\epsilon(\mathbf{k}-\mathbf{Q})]^2+G^2\}^{1/2}$$

are the one-electron energies above and below the gap and $\epsilon(k)=\hbar^2k^2/2m$.

The macroscopic photon field in a metal can be described by a vector potential

$$\mathbf{A}(z)=A_0\mathbf{x}\exp(-k\omega z/c)\cos[(n\omega z/c)-\omega t],$$

where $\mathbf{x}$ is the unit polarization vector of the electric field, n and k are the optical constants, and A_0 is the amplitude of the vector potential at the surface $z=0$. Since the spatial variation of $\mathbf{A}$ is slow, it can be neglected. Accordingly, for a sufficiently small volume within the penetration depth of the light,

$$\mathbf{A}\approx A_0\mathbf{x}\cos\omega t.$$

The interaction Hamiltonian of an electron with this potential is

$$H'=(e/mc)\mathbf{A}\cdot\mathbf{p}. \tag{6}$$

This perturbation is employed to derive the interband conductivity, Eq. (1).

We observed previously that the correct perturbation must include, in addition to (6), the time-varying Hartree-Fock potential arising from conduction-electron collective motion. This must be found by a self-consistent procedure. The total self-consistent perturbation H_{sc} will have the form

$$H_{\mathrm{sc}}=(eA_0/mc)p_x\cos\omega t \\ +B[(1-u)\sin\omega t+v\cos\omega t]\sin Qx. \tag{7}$$

Without loss of generality we have chosen Q parallel to the polarization vector $\mathbf{x}$.

$$B\equiv eA_0GQ/mc\omega,$$

and u and v are dimensionless, real parameters (dependent on ω) to be determined by the requirement of self-consistency. The choice $1-u$ for the coefficient of $\sin\omega t$ is dictated by later convenience. Conceivably a term in $\cos Qx$, similar to the second term of (7), might also be required. We omit such a term from the outset only because, if included, its coefficient turns out to be zero.

The strategy of the calculation is to calculate the perturbed wave functions resulting from (7), compute from them the time-varying Hartree-Fock potential, and require that it equal the second term of (7).

The one-electron Hamiltonian, incorporating the self-consistent perturbation, is

$$H=(p^2/2m)+G\cos Qx+H_{\mathrm{sc}}.$$

We seek solutions, $\varphi'(t)\exp(-iEt/\hbar)$, of the time-dependent Schrödinger equation, correct to terms linear in H_{sc}. They are

$$\varphi'(t)=\varphi+\left[\frac{\langle\psi|H_{\mathrm{sc}}{}^+|\varphi\rangle}{E_--E_++\hbar\omega-i\eta}e^{-i\omega t}\right. \\ \left.+\frac{\langle\psi|H_{\mathrm{sc}}{}^-|\varphi\rangle}{E_--E_+-\hbar\omega}e^{i\omega t}\right]\psi, \tag{8}$$

where φ and ψ are the functions (3) and (4). The infinitesimal $i\eta$ defines the contour for future integrations. $H_{\mathrm{sc}}{}^+$ and $H_{\mathrm{sc}}{}^-$ are the positive and negative frequency parts of H_{sc}.

$$H_{\mathrm{sc}}\equiv H_{\mathrm{sc}}{}^+e^{-i\omega t}+H_{\mathrm{sc}}{}^-e^{i\omega t}.$$

The required elements are easily evaluated. (Wave functions are taken to be normalized in unit volume.)

$$\langle\psi|p_x|\varphi\rangle=\hbar Q\sin\theta\cos\theta=\hbar QG/2W.$$

The last equality follows from (5), where $W\equiv E_+-E_-$ is the transition energy. Also,

$$\langle\psi|\sin Qx|\varphi\rangle=i/2.$$

Accordingly, the matrix elements of H_{sc} are

$$\begin{aligned}\langle\psi|H_{\mathrm{sc}}{}^+|\varphi\rangle&=\tfrac{1}{4}B[(\hbar\omega/W)-1+u+iv],\\ \langle\psi|H_{\mathrm{sc}}{}^-|\varphi\rangle&=\tfrac{1}{4}B[(\hbar\omega/W)+1-u+iv].\end{aligned} \tag{9}$$

It is convenient to define real parameters $R(t)$, $S(t)$ by rewriting (8) as follows:

$$\varphi'(t)=\varphi+[R(t)+iS(t)]\psi.$$

The linear deviation in probability density of the state φ caused by the perturbation is

$$|\varphi'|^2-|\varphi|^2=2S\sin Qx+2R(\sin^2\theta-\cos^2\theta)\cos Qx. \tag{10}$$

The last term is disconcerting at first sight since it would give rise to a Hartree-Fock potential 90° out of phase (spatially) with the one assumed in (7). This new term is the one we have previously asserted would not arise. However, for every state φ near the gap where $\mathbf{k}-\frac{1}{2}\mathbf{Q}=0$, there is a corresponding state of equal energy near the gap where $\mathbf{k}+\frac{1}{2}\mathbf{Q}=0$. One can show that the coefficient of $\cos Qx$ for this corresponding state is the negative of that in (10). Consequently the $\cos Qx$ term drops out by pairwise cancellation when (10) is summed over all occupied states. From (8) and (9) the coefficient of $\sin Qx$ in (10) is evaluated.

$$2S=\left[\frac{\pi}{2}v\delta(W-\hbar\omega)+\frac{uW}{W^2-(\hbar\omega)^2}-\frac{1}{W}\right]B\sin\omega t$$
$$+\left[\frac{\pi}{2}u\delta(W-\hbar\omega)-\frac{vW}{W^2-(\hbar\omega)^2}\right]B\cos\omega t. \quad (11)$$

The Dirac delta functions arising from the infinitesimal $i\eta$ in the denominator of (8) have been exhibited explicitly. Integrals over the remaining singular terms of (11) are principal values.

The total change $\Delta N(\mathbf{r},t)$ in electron density caused by the collective motion is

$$\Delta N=4\sin Qx\int 2S(d^3k/8\pi^3). \quad (12)$$

The integration is over the occupied region of k space. The factor of 4 accounts for spin degeneracy and the contribution to the oscillatory electron density from excitations near the opposite Brillouin-zone face. The Hartree-Fock potential $U(\mathbf{r},t)$ associated with ΔN is

$$U=[(4\pi e^2/Q^2)-(9\pi e^2/2k_F^2)]\Delta N. \quad (13)$$

The first, or Hartree, term is derived from Poisson's equation. The second term is an approximate exchange potential, derived in Sec. III. In order that the time-dependent perturbation be self-consistent, U must equal the second term of (7).

$$U=B[(1-u)\sin\omega t+v\cos\omega t]\sin Qx. \quad (14)$$

Equation (14) generates a pair of linear equations for u and v, after substitutions from Eqs. (11), (12), and (13):

$$f_1u+f_2v=f_3,$$
$$f_2u-f_1v=0.$$

The functions appearing here are defined as follows:

$$f_1(\omega)=1+D\langle W/[W^2-(\hbar\omega)^2]\rangle_{\text{av}},$$
$$f_2(\omega)=\tfrac{1}{2}\pi D\langle\delta(W-\hbar\omega)\rangle_{\text{av}},$$
$$f_3=1+D\langle 1/W\rangle_{\text{av}}.$$

The indicated averages of the functions of $W(\mathbf{k})$ are over the $k_F^3/6\pi^2$ occupied states of k space. According to the definition given previously,

$$W(\mathbf{k})=\{[\epsilon(\mathbf{k})-\epsilon(\mathbf{k}-\mathbf{Q})]^2+G^2\}^{1/2}. \quad (15)$$

The coefficient D, which determines the feedback effect of the collective motion, is

$$D\equiv(8e^2k_F^2/3\pi Q^2)-(3e^2k_F/\pi).$$

The standard theory of interband absorption is recovered by setting $D=0$. The feedback effect of the Hartree term alone can be found by dropping the second term of D.

For the alkali metals, G can be neglected in (15) for states below the Fermi energy. This approximation, together with the almost spherical shape of the Fermi surface, allows analytic evaluation of the f's.

$$f_1(\omega)=1+\frac{3D}{8E_F}\left\{1+\frac{1-(p+w)^2}{4p}\ln\left|\frac{1+p+w}{1-p-w}\right|\right.$$
$$\left.+\frac{1-(p-w)^2}{4p}\ln\left|\frac{1+p-w}{1-p+w}\right|\right\},$$

$$f_2(\omega)=3\pi D(\hbar\omega-W_0)(W_1-\hbar\omega)/(8pE_F)^3,$$

$$f_3=1+\frac{3D}{8E_F}\left\{1+\frac{1-p^2}{2p}\ln\left|\frac{1+p}{1-p}\right|\right\},$$

where $p\equiv Q/2k_F=(2\pi^2/9)^{1/6}$ and $w\equiv m\omega/\hbar Qk_F$. The solution to the simultaneous equations for u and v is

$$\begin{aligned}u&=f_1f_3/(f_1^2+f_2^2),\\ v&=f_2f_3/(f_1^2+f_2^2).\end{aligned} \quad (16)$$

The interband matrix element with and without the Hartree-Fock terms can now be compared. The optical transition rate is of course proportional to the square magnitude of the positive-frequency matrix element. This is obtained for the bare interaction H', Eq. (6), by setting $u=1$ and $v=0$ in Eq. (9) and noting that $W=\hbar\omega$ for energy-conserving transitions.

$$|\langle\psi|H'^{+}|\varphi\rangle|^2=(\tfrac{1}{4}B)^2.$$

The square matrix element of the self-consistent perturbation is, from (9),

$$|\langle\psi|H_{\text{sc}}^{+}|\varphi\rangle|^2=(\tfrac{1}{4}B)^2(u^2+v^2).$$

The ratio, $F(\hbar\omega)=u^2+v^2$, of the latter to the former is the enhancement factor appearing in Eq. (2). Its final analytical form is obtained from (16).

$$F(\hbar\omega)=f_3^2/(f_1^2+f_2^2). \quad (17)$$

III. THE EXCHANGE POTENTIAL

Were it not for exchange interactions, the feedback parameter D would be positive and the enhancement factor (17) could never depart significantly from unity. The exchange potential employed in the foregoing derivation needs considerable discussion because it involves a crucial approximation. Furthermore there is wide variation of opinion on the proper way to treat exchange potentials and correlation potentials generally. A major difficulty in Hartree-Fock theory is that the exchange potential operator is a functional of the wave functions being sought. Consequently an exact formal treatment leads invariably to insolvable integral equations. Replacement of the exchange operator by a function of the local electron density—such as the Slater-Dirac approximation[18]—frequently allows one to carry on analytically. The appropriate manner of approximation depends, however, on the nature of the problem and on the particular one-electron wave function to be determined.

The exchange operator A that arises in the Hartree-Fock scheme is defined by the following operator equation for arbitrary ψ:

$$A\psi(\mathbf{r}_1)=-\sum_{\mathbf{k}}\left[\int(e^2/r_{12})\varphi_{\mathbf{k}}^*(\mathbf{r}_2)\psi(\mathbf{r}_2)d^3r_2\right]\varphi_{\mathbf{k}}(\mathbf{r}_1). \quad (18)$$

The sum is only over states $\mathbf{k}$ with the same spin direction as ψ. We are interested in the $\langle\mathbf{k}'-\mathbf{Q}|A|\mathbf{k}'\rangle$ matrix element of A when a set of wave functions having the form (8) is inserted in (18) for the φ's. It is sufficient, however, to consider a simpler set of wave functions having the form (3), which differ from (8) only in the spatial phase of the electron density modulation. The (off-diagonal) matrix element of A between the plane-wave states $\mathbf{k}'$ and $\mathbf{k}'-\mathbf{Q}$ is

$$\langle\mathbf{k}'-\mathbf{Q}|A|\mathbf{k}'\rangle =\sum_{\mathbf{k}}(4\pi e^2/|\mathbf{k}'-\mathbf{k}|^2)\sin\theta(\mathbf{k})\cos\theta(\mathbf{k}). \quad (19)$$

Now, the electron density associated with the set $\varphi_{\mathbf{k}}$ is

$$N(\mathbf{r})=N_0-2(e^{i\mathbf{Q}\cdot\mathbf{r}}+e^{-i\mathbf{Q}\cdot\mathbf{r}})\sum_{\mathbf{k}}\sin\theta(\mathbf{k})\cos\theta(\mathbf{k}),$$

where $N_0=k_F^3/3\pi^2$. The factor 2 is the spin degeneracy. Consequently, the Fourier coefficient ΔN_Q of the density deviation is

$$\Delta N_Q=-2\sum_{\mathbf{k}}\sin\theta(\mathbf{K})\cos\theta(\mathbf{K}).$$

Equation (19) can now be written symbolically:

$$\langle\mathbf{k}'-\mathbf{Q}|A|\mathbf{k}'\rangle\equiv-\tfrac{1}{2}\langle4\pi e^2/|\mathbf{k}'-\mathbf{k}|^2\rangle_{\mathrm{av}}\Delta N_Q. \quad (20)$$

This equation is really a definition of a *suitable* (weighted) average:

$$V_0\equiv\langle4\pi e^2/|\mathbf{k}'-\mathbf{k}|^2\rangle_{\mathrm{av}}.$$

The challenge of all problems, such as this, is to guess the numerical value of V_0. In principle V_0 will depend on Q,ω, and other characteristics of the deformation. For the problem at hand, Q is larger than the diameter $2k_F$ of the Fermi surface. Consequently, participation in the deformation is not restricted by the exclusion principle to a selected group of states in k space. With appropriate uncertainty, we take the unweighted average (over $\mathbf{k}$ and $\mathbf{k}'$) for V_0:

$$V_0\approx9\pi e^2/k_F^2.$$

Substitution of this value in Eq. (20) leads to the exchange potential term employed in Eq. (13).

It is well known that exchange interactions exaggerate magnetic instabilities of an electron gas. Many workers studying magnetic problems find it appropriate to use statically screened or dynamically screened interactions to avoid such exaggeration. The question of whether screened exchange should be used in the optical problem considered here arises naturally. We believe the answer is no. In Hartree-Fock theory the exchange potential is just the Coulomb interaction of, say, a spin-up electron with the surrounding correlation hole (of unit positive charge) in the spin-up electron gas. There is no corresponding correlation hole in the spin-down electron gas. The effect of dynamical corrections to the Hartree-Fock scheme is to ***redistribute*** this correlation hole, allowing some of the correlation potential to arise from the spin-down gas. Such dynamical effects could not occur if the total correlation potential were diminished in magnitude. This redistribution of the correlation potential between the up-spin and down-spin electrons, for an up-spin electron, can be represented heuristically by a parameter $\mu<1$, so that the total correlation potential $V_\uparrow$ is

$$V_\uparrow=-\mu V_0N_\uparrow-(1-\mu)V_0N_\downarrow, \quad (21)$$

where $N_\uparrow$ and $N_\downarrow$ are the spin-up and spin-down electron densities. A similar equation would apply to a spin-down electron. It is an instructive exercise to compute the spin susceptibility χ on the basis of this model. The result is

$$\chi=\chi_p\{1-[3(2\mu-1)N_0V_0/4E_F]\}^{-1},$$

where χ_p is the Pauli susceptibility. This indicates that χ is enhanced as long as $\mu>\frac{1}{2}$, an expected result. A phenomenological value for the redistribution parameter μ could be obtained by fitting χ either to a measured spin susceptibility or to values calculated[19] by employment of dynamically screened interactions.

We conclude from the foregoing discussion that screened exchange can be employed only if a correlation potential (with electrons of opposite spin) is added. For problems of the type we have considered in this paper, where variations in $N_\uparrow$ and $N_\downarrow$ are in phase and equal,

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the redistribution parameter in (21) cancels out. The distinction between a treatment using unscreened exchange, and one using screened exchange plus antiparallel correlation, is primarily semantic.

The apparently successful comparison of the theory developed in Sec. II with observed, interband optical absorption in the alkali metals can be interpreted in two ways. It is either an amusing coincidence, or it is a corroboration of the approximate treatment of exchange and correlation interactions given in Sec. III.[20]

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[20] The alert reader will surmise that the strength of exchange and correlation interactions employed in this paper leads to an adiabatic instability of the electron gas. This observation would be a serious objection were it taken for granted that such an instability does not occur experimentally. Many observed anomalies in alkali metal properties can be explained provided an exchange instability has in fact altered the electronic ground state.

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Excitons and the Absorption Edge in ZnSe

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The optical absorption threshold at about 2.7 eV, near the lowest-energy fundamental edge, was investigated for cubic ZnSe single crystals. Absorption spectra are reported for temperatures between 2 and 200°K, and absorption coefficients between 4 and 600 cm^{-1}. Although contributions associated with defects dominated the results in most crystals, intrinsic absorption could be observed for $T \gtrsim 60°\text{K}$ in the purest available crystals. This intrinsic absorption results from longitudinal-optical-phonon-assisted creation of excitons, as is shown by the good agreement between the observed magnitude, the temperature, and photon-energy dependence, and the absorption calculated for this mechanism. The relevant exciton states involve electrons and holes from band extrema near the center of the Brillouin zone; when created without phonon assistance, excitons from these same extrema also give the relatively very intense "direct transition" absorption lines. No evidence is found that any band gap is smaller than that at the zone center.

I. INTRODUCTION

OPTICAL absorption spectra at the low-energy threshold for intrinsic electronic excitation have been studied for several elemental and compound semiconductors. Analysis of the temperature and energy dependence of these spectra have shown that in some instances, e.g., Ge and Si,[1] the absolute extrema in the conduction and valence bands are at widely separated points in the Brillouin zone, while in others, e.g., CdS[2,3] and CdTe,[4–6] these extrema are at or very near the same point. In the former case (Ge and Si), the absorption processes and corresponding band gap are called "indirect" and absorption is forbidden unless assisted by the simultaneous emission or absorption of one or more phonons of wave vector comparable to the differences between the wave vectors at the two band extrema.[7] In the latter case (CdS and CdTe), the processes and corresponding band gap are called "direct" and absorption is allowed without phonon participation. Absorption processes assisted by phonons of small or zero wave vector are also allowed for a direct gap.[3,6] These are of central importance in the discussion of the absorption spectra of the cubic (zinc-blende) modification of ZnSe presented in this paper.

Low-temperature optical studies of ZnSe[8] have already shown the existence of a very intense, narrow absorption band at an energy a few millielectron volts below the absorption continuum due to interband electronic transitions. This band was interpreted[8] as resulting from the creation of excitons associated with a direct gap, without phonon participation. Some other electrical[9] and optical[10] studies also suggested that the absolute conduction-band minimum was at the center of the Brillouin zone, and since the fluorescence emission spectra[11] (presumably due to bound excitons) were not significantly broadened by auto-ionization to a lower-energy continuum state, it was suggested[9] that the direct band gap associated with the excitons was, in fact, the smallest so that the absolute valence-band maximum was also at the center of the zone. In contrast, optical transmission studies had been reported

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