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Energy bands, optical conductivity, and Compton profile of sodium*

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A self-consistent calculation of energy bands in sodium has been performed using the linear-combination-of-atomic-orbitals method. The principal basis set contained eleven s-type, seven p-type, and five d-type Gaussian orbitals. Some calculations were also performed with smaller basis sets. Exchange was included according to the $X\alpha$ method with $\alpha = 2/3$. Results are presented for the band structure, Fermi-surface properties, and the Compton profile. No appreciable distortion of the Fermi surface was found. The optical- and thermal-effective-mass ratios are found to be (both) 1.03. The interband contribution to the optical conductivity was calculated including the $\vec{k}$ variation of the optical matrix elements, which is quite important. Direct interband transitions begin at 2.0 eV. A region of strong absorption is predicted to occur near 14 eV.

I. INTRODUCTION

The band structure of sodium has been the subject of calculations for more than 40 years.[1–21] Our interest centers on the Compton profile and the optical conductivity. Comparison of calculated values for these quantities with experiment tests the quality of computed wave functions as well as energies. It appears to be relatively easy to obtain reasonable agreement with experiment with respect to the Compton profile but quite difficult, because excited states are involved, to treat the conductivity adequately.

Our calculation employs a self-consistent form of the LCAO (linear-combination-of-atomic-orbitals) method in which the wave function is expanded in a set of independent Gaussian orbitals. Gaussian orbitals were introduced into energy-band calculations by Lin and co-workers.[22] It is possible to perform analytically all integrals required in a band calculation when these basis functions are used. In addition, explicit expressions are readily obtained for matrix elements of the momentum operator required in a calculation of the optical conductivity.[23] In fact, the major advantage of the LCAO method with Gaussian orbitals is the ease of computation with the wave functions. We have previously used a basis set of Gaussian orbitals in calculations of the band structure of lithium[24] and aluminum.[25]

The assumed crystal potential used to initiate the iterative procedure leading to self-consistency was formed by the superposition of atomic charge densities determined by Veillard.[26] Exchange was included according to the $X\alpha$ method with $\alpha = \frac{2}{3}$. Self-consistent band structures were found for three different sets of orbitals of increasing size. The principal results reported here were computed using a set of 11 s-type orbitals, seven p-type orbitals, and five d-type orbitals. The orbital exponents of this set are listed in Table I. At general points of the Brillouin zone, the Hamiltonian and overlap matrices are of dimension 57×57. These matrices are of somewhat larger dimensionality than we employed in our previous calculation of the band structure of lithium (42×42).[24] Some results from a smaller basis set will be presented for comparison.

II. BAND STRUCTURE AND FERMI SURFACE

The procedures of the self-consistent calculation are described in Refs. 27 and 28. Only the first 50 rotationally independent Fourier coefficients of the Coulomb and exchange potentials were allowed to change in the iterative procedure. The charge density was sampled at 90 points in $\frac{1}{48}$ of the Brillouin zone. The iterations were continued until the change in any $V(k)$ was not greater than 10^{-6} Ry. The lattice constant was taken to be $7.984a_0$. Energy bands are shown in several symmetry directions in Fig. 1. Energy levels, measured with respect to the lowest band state (Γ_1), are listed in Table II. For comparison, we give values of these quantities as computed (self-consistently) with a smaller basis set (nine s functions, six p functions, and three d functions) whose parameters are also listed in Table I. Results obtained by Dagens and Perrot[21] with the same exchange potential are also presented. Table III compares the present results for states in the lowest band with those of Dagens and Perrot.[21] In Table IV results of several calculations not necessarily using the same potential are presented for the band gap at N, the Fermi energy, and the width of the lowest band.

The degree of agreement between the present results and those obtained by Dagens and Perrot [self-consistent augmented plane wave (APW) with the Kohn-Sham exchange potential] is rather good in regard to states in the lowest band. The differences are of the order 0.001 Ry. However, we obtained better agreement with Ref. 21 in the case of lithium, in which the differences were of the

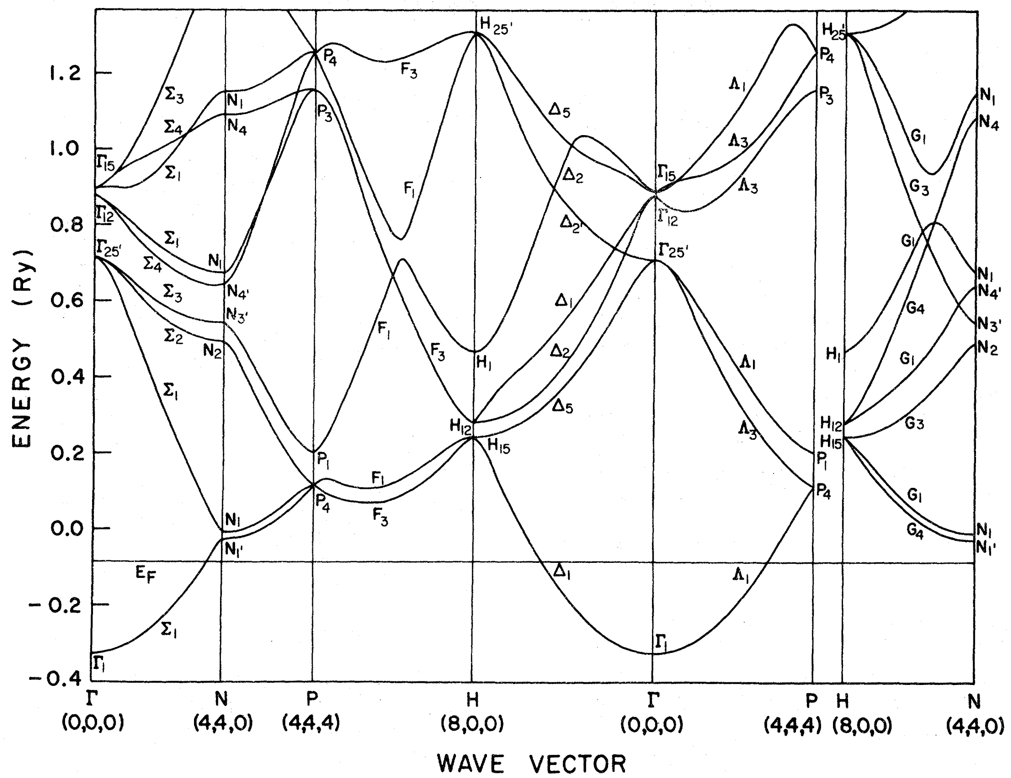

FIG. 1. Energy bands in sodium along symmetry directions.

order 10^{-4} Ry for states in the lowest band. The higher states present a more mixed pattern. Our values for energies of some p-like states (N_1', P_4, Γ_{15}) agree well with those of Ref. 21; however, there are more serious discrepancies in regard to other p states and the d-like states (Γ_{12}, Γ_{25}', H_{15}, N_2, H_{12}). We have no specific explanation for these discrepancies; but the use of a muffin-tin potential in Ref. 21 may be significant. We performed a plane-wave calculation of the energy of the d-like state H_{12} (which is orthogonal by reason of symmetry to all core states). The energy as calculated with 168 plane waves was larger by 4×10^{-4} Ry than that obtained with basis set 1. The difference between our results and those of Ref. 21 is much larger than this (4×10^{-2} Ry). Finally,

TABLE I. Orbital exponents for Gaussian orbitals. Set 1 is the principal basis set used in this calculation. Some results with the smaller set 2 are presented in order to indicate the degree to which some results depend on the basis.

s-type		p-type		d-type	
Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
36631	25000	145.0	120.0	10.0	2.8
5385	3000	34.0	25.0	2.5	0.3
1216	600	9.1	4.8	0.73	0.075
339.5	80	2.6	1.0	0.24	
109.6	15	0.78	0.18	0.084	
38.0	3.5	0.26	0.08		
13.0	0.7	0.088			
2.8	0.15				
0.7	0.07				
0.22					
0.07					

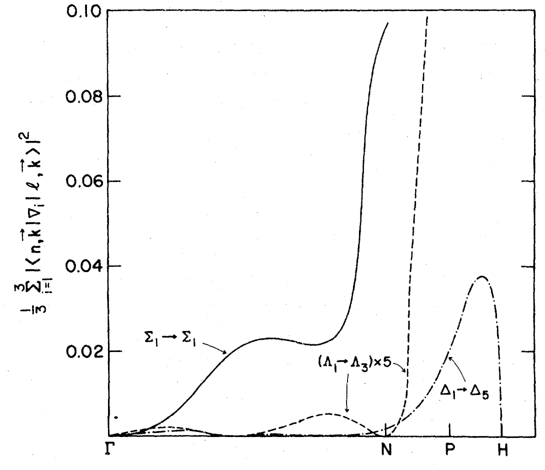

FIG. 2. Variation of the square of the momentum matrix element for transitions along the [110] direction ($\Sigma_1\rightarrow\Sigma_1$), [111] ($\Lambda_1\rightarrow\Lambda_3$), and [100] ($\Delta_1\rightarrow\Delta_5$).

TABLE II. Energies of selected states at symmetry points (relative to Γ_1) in Ry. Results obtained with two basis sets (see Table I) are compared with those of Dagens and Perrot (Ref. 21).

$a\vec{k}/2\pi$	State	Basis Set 1	Basis Set 2	Ref. # 21
(0, 0, 0)	Γ_{12}	1.2020	1.2078	1.1577
	Γ_{15}	1.2131	1.2260	1.2175
	Γ_{25}'	1.0334	1.0439	1.0922
$(\frac{1}{2}, \frac{1}{2}, 0)$	N_1'	0.2973	0.3034	0.2941
	N_1	0.3174	0.3178	0.3251
	N_1	0.9985	0.9995	0.9851
	N_2	0.8127	0.8214	0.8377
	N_3'	0.8655	0.8727	0.8988
	N_4'	0.9662	0.9588	0.9072
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	P_4	0.4376	0.4440	0.4361
	P_1	0.5263	0.5208	0.5491
(1, 0, 0)	H_{15}	0.5667	0.5738	0.5943
	H_{12}	0.6024	0.6075	0.5666

we see from Table IV that the agreement between the calculations of different authors in regard to properties relating to the lowest band is of the order of ± 0.01 Ry, even though the potentials used may be rather different.

The results reported here for basis sets 1 and 2 differ by the order of 0.01 Ry. These involve complete self-consistent calculations, hence different potentials, so that the variational theorem can not be intuitively applied to assert that energies for basis set 1 must be lower than for set 2. In fact, the larger basis does lead to a reduction of the energy differences with respect to Γ_1 in most cases. However, the effect on the wave functions is more significant, as determined in the calculation of the optical conductivity. This is apparently due to the better representation of the core part of the s-type wave functions produced by the improvement of the basis.

The density of states was computed by the Gilat-Raubenheimer[29] method. The density of states at the Fermi energy (− 0.09027 Ry) was found to be 6.50 electrons/atom Ry. The distortion of the Fermi surface from spherical symmetry is quite small (less than one part in 10^3); in fact, too small for us to calculate accurately. The Fermi surface as observed in the de Haas–van Alphen effect is close to spherical, with distortions of the order of 0.1% or less.[30]

TABLE III. Energies (Ry) of states in the lowest band (relative to Γ_1). Our present results are compared with those of Dagens and Perrot (Ref. 21).

$2a\vec{k}/\pi$	State	Present (basis set 1)	Ref. # 21
(1, 0, 0)	Δ_1	0.03965	0.03981
(2, 0, 0)	Δ_1	0.15607	0.15681
(1, 1, 0)	Σ_1	0.07892	0.07920
(1, 1, 1)	Λ_1	0.11777	0.11820
(2, 1, 0)		0.19420	0.19501
(2, 1, 1)		0.23198	0.23276

TABLE IV. Gap at N, Fermi energy, and width of the lowest band in Rydbergs. Present results are compared with those of Ham (Ref. 14), Lawrence (Ref. 18), Kenny (Ref. 17) and Dagens and Perrot (Ref. 21).

	Present	Ref. 14	Ref. 18	Ref. 17	Ref. 21
$E(N_1)-E(N_1')$	0.020	0.018	0.024	0.029	0.031
$E_F-E(\Gamma_1)$	0.238	0.233	0.228	0.239	
$E(N_1')-E(\Gamma_1)$	0.297	0.308	0.284	0.292	0.294

The optical and thermal effective masses were determined with the use of a Kubic harmonic expansion through sixth order:

$$E(k)=E_0+E_2k^2+k^4(E_4^{(1)}+E_4^{(2)}K_{4,1})+k^6(E_6^{(1)}+E_6^{(2)}K_{4,1}+E_6^{(3)}K_{6,1})\,, \tag{1}$$

in which $K_{4,1}$ and $K_{6,1}$ are normalized fourth- and sixth-order Kubic harmonics. The values of the coefficients are given in Table V. Only states with energies less than the Fermi energy were included in this fit. The optical and thermal effective masses are determined from the usual formulas

$$(m_{\text{op}}/m)=6(2\pi/a)^3\left[\int d^3k\, \nabla^2E(k)\right]^{-1} \tag{2}$$

and

$$\left(\frac{m_{\text{th}}}{m}\right)=\frac{1}{2\pi k_F}\int\frac{dS_F}{|\nabla_k E(k)|}\ . \tag{3}$$

We found $m_{\text{op}}/m = 1.031$, $m_{\text{th}}/m = 1.033$. Quoted experimental values of the optical-effective-mass ratios are (1.00,[31] 1.01,[32] 1.07,[33] 1.17[34]). Measurements of the low-temperature specific heat give $m_{\text{th}}/m = 1.27$,[35] while cyclotron resonance yields a mass ratio 1.24 ± 0.02.[36] Comparison of the calculated and measured thermal effective masses indicates a mass enhancement of 23%.

III. OPTICAL CONDUCTIVITY

The optical properties of sodium have been studied for many years. Early experimental observations were reported by Duncan and Duncan[37] and Ives and Briggs.[38] Measurements by Mayer and

TABLE V. Coefficients of the Kubic harmonic expansion of $E(k)$ for the lowest band [Eq. (1)].

E_0	−0.3279	$E_6^{(1)}$	0.0675
E_2	1.0303	$E_6^{(2)}$	0.0697
$E_4^{(1)}$	−0.1504	$E_6^{(3)}$	0.0115
$E_4^{(2)}$	−0.0299		

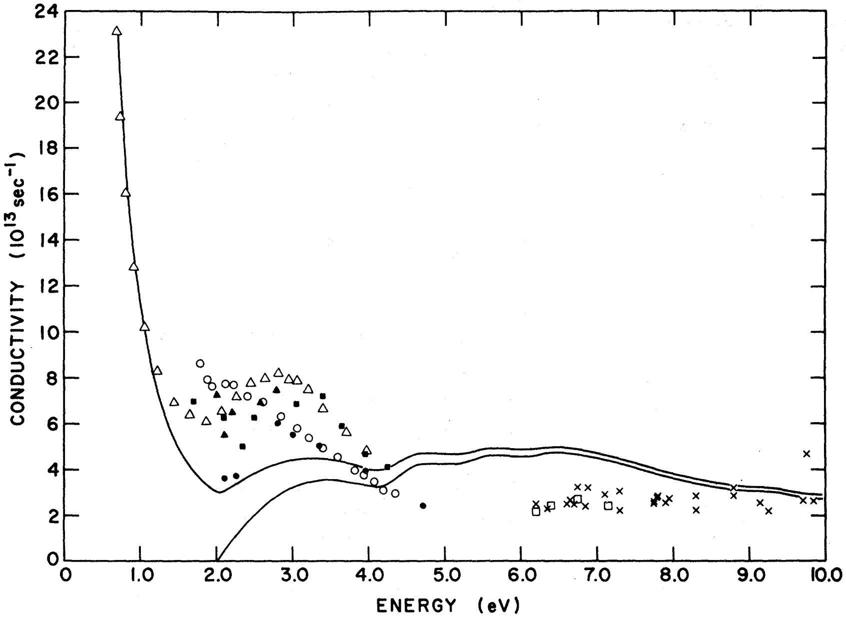

FIG. 3. Optical conductivity of sodium in the range 1–10 eV. The lower solid curve is the interband contribution; the upper curve contains a phenomenological Drude term. Experimental results are shown as follows: open triangles, Ref. 34; open circles, Ref. 31; open squares, Ref. 44; filled triangles, Ref. 37; filled circles, Ref. 38; filled squares, Ref. 39; crosses, Ref. 33.

co-workers[39,40] showed unexpectedly large optical absorption for photon energies below the interband threshold. Considerable theoretical interest was stimulated by these reports. More recent work[31,34] with improved experimental techniques has lead to more consistent results and showed that there was no anomalous absorption of the type reported by Mayer and co-workers. Most previous theoretical work has employed an OPW (orthogonalized-plane-wave) pseudopotential approach. Bennett and Vosko[41] have analyzed this procedure in detail and have shown that, if applied carefully, good agreement with experiment near the interband threshold is obtained. However, the pseudopotential method is limited to energies relatively close to threshold.

We have calculated the frequency-dependent interband optical conductivity according to

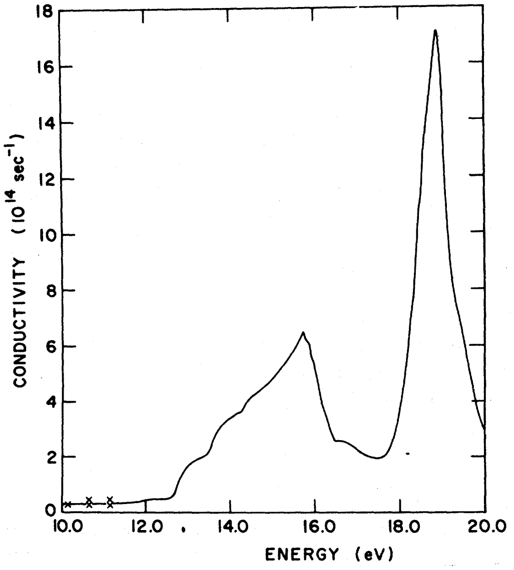

FIG. 4. Optical conductivity of sodium from 10 to 20 eV. Only the interband contribution is shown. Experimental points are the same as in Fig. 3.

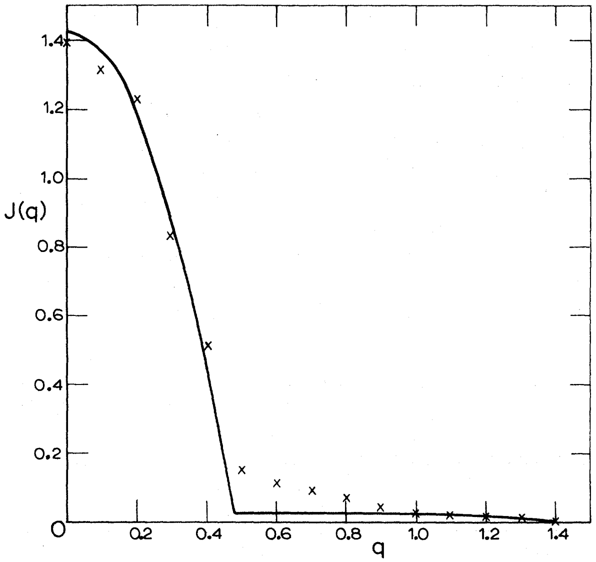

FIG. 5. Compton profile of Na. The calculated and directionally averaged Compton profile of the band electrons is shown (solid curve). The crosses are experimental results from Ref. 47. The anisotropy is too small to be shown on the scale of this graph.

$$\sigma_I(\omega)=\frac{2\pi e^2}{3m^2\omega}\sum_{ln}\int\frac{d^3k}{(2\pi)^3}\,|\langle l\vec{k}|\vec{p}|n\vec{k}\rangle|^2 f_l(\vec{k})$$

$$\times[1-f_n(\vec{k})]\,\delta(E_n(\vec{k})-E_l(\vec{k})-\hbar\omega)\quad ; \qquad (4)$$

in this equation ω is the frequency of the light and $f_l(\vec{k})$ is the Fermi distribution function for the state $|l\vec{k}\rangle$ (wave vector $\vec{k}$, band l). The energies and wave functions obtained previously were used to evaluate (4). It was found that the $\vec{k}$ dependence of the momentum matrix elements was quite important. Figure 2 shows the variation of the square of the momentum matrix element for transitions involving states in three different directions in the Brillouin zone. The strong $\vec{k}$ dependence of these matrix elements indicates that this quantity must not be treated as constant in the conductivity calculation.

The integration over the Brillouin zone was performed using the Gilat-Raubenheimer method based on energies and matrix elements obtained for 1785 points in $\frac{1}{48}$ of the Brillouin zone. The conductivity near threshold is dominated by transitions involving states near the [110] axis. In order to obtain a total conductivity, we added an approximate Drude term,

$$\sigma(\omega)=\sigma_I(\omega)+\sigma_D(\omega)\quad , \qquad (5)$$

where

$$\sigma_D(\omega)=\frac{Ne^2\tau}{m_{\text{op}}}\,\frac{1}{1+\omega^2\tau^2}\quad , \qquad (6)$$

in which N is the number of electrons per unit volume, m_{op} is the optical effective mass, and τ is a phenomenological relaxation time obtained by fitting the experimental results of Smith[34] in the infrared region. We found τ to be 2.53×10^{-14} sec. The calculated conductivity is shown in Figs. 3 and 4. Experimental results are included.

Our calculation predicts an interband threshold of 2.0 eV and a peak in the interband absorption near 3 eV. These are consistent with the results of Smith.[34] However, our absorption peak is too small compared to experiment. This may be due in part to our wave functions (basis set 2 yields a conductivity which is only about 15% of the experimental peak value). However, we have neglected a potentially significant contribution to the conductivity from indirect (phonon-assisted) interband transitions.[42] Stevenson has recently estimated that at 2.4 eV the contributions of Drude, direct, and indirect interband transitions to the optical absorption should be about equal.[43]

We are not aware of any experimental results for the conductivity from 4.5 to 6.0 eV. Sutherland and co-workers have reported some results in the range 6–11 eV.[33,34] Our results agree well in magnitude with their measurements. We predict that the optical absorption should increase rapidly beginning at about 13 eV. The peaks shown in Fig. 4 may be blended by large lifetime-broadening effects at these energies, as is apparently the case in potassium.[45] These transitions involve excitation to the group of bands emerging from the Γ'_{25}, Γ_{12}, and Γ_{15} levels. In potassium the d bands are much lower, and these transitions begin near 6 eV. In lithium such transitions would be expected near 20 eV.

IV. COMPTON PROFILE

The Compton-profile function

$$J_{\hat{k}}(q)=\frac{\Omega}{2\pi^3}\int d^3p\,\rho(\vec{p})\,\delta\,(q-\vec{p}\cdot\hat{k}) \qquad (7)$$

has been computed and is shown in Fig. 5. In this equation $\rho(\vec{p})$ is the momentum density, $\vec{k}$ is the change in momentum after a Compton scattering, $\hat{k}=\vec{k}/|\vec{k}|$, and

$$q=(m\,\omega/|\vec{k}|)-\tfrac{1}{2}|\vec{k}|\quad , \qquad (8)$$

where $\hbar\omega$ is the energy transferred to the electron. The evaluation of $J_{\hat{k}}(q)$ is straightforward with wave functions of the LCAO type. Details have been given elsewhere.[46] Experimental results of Eisenberger *et al.* are also shown.[47] There is a small amount of directional anisotropy in the calculated curves.

The agreement between theory and experiment is quite good, except that the experimental results show more high-momentum components in the tail than theory produces. This effect is expected, and is presumably a consequence of electron interactions. Finally, we note that our calculations seem to be in good agreement with the APW results of Wakoh and Yamashita.[48]

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[1] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).

[2] J. C. Slater, Phys. Rev. 45, 794 (1934).

[3] J. Bardeen, J. Chem. Phys. 6, 367 (1938).

[4] W. A. Bowers, Ph.D. thesis (Cornell University, 1943) (unpublished).

[5] F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

[6] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950).

[7] P. O. Lowdin, J. Chem. Phys. 19, 1579 (1951).

[8] D. J. Howarth and H. Jones, Proc. Phys. Soc. Lond. A 65, 355 (1952).

[9] H. Brooks, Phys. Rev. 91, 1027 (1953).

[10] S. Raimes, Proc. Phys. Soc. Lond. A 67, 52 (1954).

[11] J. Callaway, Phys. Rev. 112, 322 (1958); 123, 1255 (1961).

[12] F. Stern, Ph.D. thesis (Princeton University, 1955) (unpublished).

[13] M. M. Saffren, Ph.D. thesis (MIT, 1959) (unpublished).

[14] F. S. Ham, Phys. Rev. 128, 82, 2524 (1962).

[15] W. A. Harrison, Phys. Rev. 131, 2433 (1963).

[16] A. J. Hughes and J. Callaway, Phys. Rev. 136, A1390 (1964).

[17] J. Kenny, Quart. Progr. Rept. (Solid State and Molecular Theory Group, MIT 53, 38 (1964); 66, 3 (1967).

[18] M. J. Lawrence, J. Phys. F 1, 836 (1971).

[19] S. T. Inoue, S. Asano, and J. Yamashita, J. Phys. Soc. Jpn. 30, 1456 (1971).

[20] A. M. Boring, Intern. J. Quant. Chem. 2S, 265 (1968).

[21] L. Dagens and F. Perrot, Phys. Rev. B 8, 1281 (1973).

[22] R. C. Chaney, T. K. Tung, C. C. Lin, and E. Lafron, J. Chem. Phys. 52, 361 (1970).

[23] W. Y. Ching, Ph.D. thesis (Louisiana State University, 1974) (unpublished).

[24] W. Y. Ching and J. Callaway, Phys. Rev. B 9, 5115 (1974).

[25] R. A. Tawil and S. P. Singhal, Phys. Rev. B (to be published).

[26] A. Veillard, Theor. Chem. Acta 12, 405 (1968).

[27] J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).

[28] J. Callaway and J. L. Fry, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1972), p. 512.

[29] G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966).

[30] M. J. G. Lee, Phys. Rev. 128, 953 (1969); Proc. R. Soc. Lond. A 295, 440 (1966).

[31] R. E. Palmer and S. E. Schnatterly, Phys. Rev. B 4, 2329 (1971).

[32] M. H. Cohen, Phil. Mag. 3, 762 (1958).

[33] J. C. Sutherland, R. N. Hamm, and E. T. Arakawa, J. Opt. Soc. Am. 59, 1581 (1969).

[34] N. V. Smith, Phys. Rev. 183, 634 (1969); Phys. Rev. Lett. 21, 96 (1968); Phys. Rev. B 2, 2840 (1970).

[35] D. L. Martin, Phys. Rev. 124, 438 (1961).

[36] C. C. Grimes and A. F. Kip, Phys. Rev. 132, 1991 (1963).

[37] R. W. Duncan and R. C. Duncan, Phys. Rev. 1, 294 (1913).

[38] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. 27, 181 (1937).

[39] H. Mayer and M. H. J. Naby, Z. Phys. 174, 289 (1963).

[40] H. Mayer and B. Hietel, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland, Amsterdam, 1966), p. 47.

[41] B. I. Bennett and S. H. Vosko, Phys. Rev. B 6, 2119 (1972).

[42] S. Nettel, Phys. Rev. 150, 421 (1966).

[43] D. J. Stevenson, Phys. Rev. B 7, 2348 (1973).

[44] J. C. Sutherland, E. T. Arakawa, and R. N. Hamm, J. Opt. Soc. Am. 57, 645 (1967); 58, 1080 (1968).

[45] W. Y. Ching and J. Callaway, Phys. Rev. Lett. 30, 441 (1973).

[46] J. Rath, C. S. Wang, R. A. Tawil, and J. Callaway, Phys. Rev. B 8, 5139 (1973).

[47] P. Eisenberger, L. Lam, P. M. Platzman, and P. Schmidt, Phys. Rev. B 6, 3671 (1972).

[48] S. Wakoh and J. Yamashita, J. Phys. Soc. Jpn. 35, 1402 (1973).