

Calculations of the Optical Properties of Metals by LMTO Method

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Because of the variational character of the most of the modern band structure calculation methods, including LMTO, the calculated electron energies are much more accurate than the wave functions. This affects greatly the optical matrix elements calculations. We investigated the problem of the accurate calculation of the matrix elements in the frameworks of usual band structure methods, basing on the continuity equation for the charge density operator. We have derived an analytical expression for corrections to the common-used formulas for the optical matrix elements. These allow to compute the matrix elements with the same accuracy as the band structure so that the intraband matrix elements are exactly equal to the band electron velocities. A specific prescription is proposed for the optical matrix elements calculation in the frameworks of the LMTO method. The imaginary parts of the dielectric functions are calculated for Cu and Pd in the energy range 0.1–20 eV, which agree well with available experimental data.

I. Introduction

The *ab initio* calculation of the optical properties of metals is a complicated but interesting and important problem. In recent years some papers on this subject have been published, e.g. [1–5] where one has used the KKR, APW, LCAO and model Hamiltonian methods, respectively. There is also a good deal of papers in which the calculations of the optical properties of simple metals have been made by the pseudopotential method (see reviews [6, 7]). Sometimes the results obtained by various authors differ greatly though the energy structure is proved to be nearly independent on the band structure calculation method. So the accuracy of the band structure calculation cannot serve as a good criterion of the accuracy of the optical properties calculations. The usual way to judge of the correctness of the calculation is to compare them to experiment, but it is desirable to verify the accuracy of the optical properties calculation in a self-consistent way, e.g. by checking the fulfillment of some sum rules.

It is desirable also because of the following: First, all modern band structure calculations are based on the

density functional formalism. Strictly speaking, they refer to a system of some fictitious particles which are to be used only for the calculations of the equilibrium properties of the real metals and their static response functions. It is not yet clear if it is possible to describe in such a manner the dynamical response functions which define the optical properties.

Second, the electron gas in metals is not uniform so that screening is described by the dielectric matrix $\epsilon(\omega, \mathbf{G}, \mathbf{G}')$, where \mathbf{G} and \mathbf{G}' are the reciprocal lattice vectors. It is difficult to say how important is the difference between the inversed element of the dielectric matrix $1/\epsilon(\omega, 0, 0)$ which is usually calculated and the element of the inversed matrix $[\epsilon^{-1}(\omega, \mathbf{G}, \mathbf{G}')]_{\mathbf{G}=\mathbf{G}'=0}$, which is measured in experiments.

To find out how important these factors are, one could compare the calculated and experimental values. As we shall see, in some cases the error of approximations may be so large that such a comparison cannot be informative.

The goal of this article is the calculation of the optical properties of metals using LMTO – one of

the most effective methods of band structure calculations proposed by Andersen [8].

The weakest point of the one-particle calculations of the optical properties of metals is the matrix element computation. It will be shown below that they are extremely sensitive to the accuracy of the wave functions. The second section of our paper is concerned to the difficulties arising in optical matrix element computations and some ways are proposed to overcome them. In the third section we propose a prescription for the computation of the matrix element in the frameworks of the LMTO method. As an example the results of our LMTO calculations of the imaginary part of the dielectric function of Cu and Pd in the energy region 0.1–20 eV are presented in the fourth section.

II. Matrix Elements of Current Density Operator and the Accuracy of the Wave Functions

The optical properties of metals are defined by the dielectric function $\varepsilon(\omega, \mathbf{q}=0)$. In the frameworks of the random phase approximation it is given for cubic metals by

$$\begin{aligned} \varepsilon(\omega, \mathbf{q} \rightarrow 0) &= \varepsilon_{\text{intra}}(\omega, \mathbf{q} \rightarrow 0) + \frac{8\pi e^2}{3\omega^2} \\ &\cdot \sum_{\mathbf{k}, \lambda \neq \lambda'} \frac{|\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}|^2 (E_{\mathbf{k}\lambda'} - E_{\mathbf{k}\lambda}) f_{\mathbf{k}\lambda} (1 - f_{\mathbf{k}\lambda'})}{(E_{\mathbf{k}\lambda'} - E_{\mathbf{k}\lambda})^2 - \hbar^2 \omega^2 + i\delta} \end{aligned} \quad (1)$$

where $\varepsilon_{\text{intra}}$ is the dielectric function with only intraband transitions included, $f_{\mathbf{k}\lambda}$ is the Fermi distribution function, $E_{\mathbf{k}\lambda}$ is the energy of the electron in the band λ with the wave vector \mathbf{k} , $\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}$ is the matrix element of the current density operator (CDO). We shall deal in this paper only with cubic metals where there is no difference between the longitudinal and transverse dielectric functions, so we shall suppose that $\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}$ in (1) refers to the longitudinal current which is easier to deal with.

It is known that it is possible to write a number of equivalent expressions for the CDO matrix element [10], but this equivalence is just only for the exact wave functions, so it is an important question which expression to choose. We think that the most logical way is to start from the continuity equation relating the \mathbf{q} -component of CDO to the time derivative of the \mathbf{q} -component of the electron density operator:

$$-i\hbar\dot{\rho}_{\mathbf{q}} = \mathbf{q}\mathbf{j}_{\mathbf{q}} \quad (2)$$

The left side of (2) may be derived from the equation of motion

$$-i\hbar\dot{\rho}_{\mathbf{q}} = [H, \rho_{\mathbf{q}}] \quad (3)$$

where $H = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})$, is the one-particle Hamiltonian.

With regard to (2) and (3) we can define the CDO as

$$\lim_{\mathbf{q} \rightarrow 0} \mathbf{j}_{\mathbf{q}} = \lim_{\mathbf{q} \rightarrow 0} \frac{\mathbf{q}}{\hbar|\mathbf{q}|^2} [H, \rho_{\mathbf{q}}] = \frac{\hbar \nabla}{im}. \quad (4)$$

Therefore in many papers such an expression as

$$j_{\lambda\lambda'}^{\mathbf{k}} = \langle \mathbf{k}\lambda | \frac{\hbar \nabla}{im} | \mathbf{k}\lambda' \rangle \quad (5)$$

is used directly for the numerical computation of CDO matrix element.

How adequate is such an approach when $|\mathbf{k}\lambda\rangle$ are approximate wave functions computed within the frameworks of a band structure method?

Usually in band structure calculations the wave function is obtained as a linear combination of basis functions $|\mathbf{k}n\rangle$ which we shall suppose orthonormalized, for the sake of simplicity,

$$|\mathbf{k}\lambda\rangle = \sum_n a_n^{\mathbf{k}\lambda} |\mathbf{k}n\rangle, \quad (6)$$

Then the variational principle provides the matrix equation* for the eigenvectors $a_n^{\mathbf{k}\lambda}$ and eigenvalues $E_{\mathbf{k}\lambda}$

$$\sum_n \langle \mathbf{k}n | H | \mathbf{k}n' \rangle a_n^{\mathbf{k}\lambda} = E_{\mathbf{k}\lambda} a_n^{\mathbf{k}\lambda} \quad (7)$$

where the sum is cut off because of the finite number of the basis functions. It means that the solution of the Schrödinger equation is searched not in the whole Hilbert space but in the subspace spanned by the finite number of the basis functions $|\mathbf{k}n\rangle$. This subspace may be obtained by the action of the projection operator $P = \sum_{\mathbf{k}n} |\mathbf{k}n\rangle \langle \mathbf{k}n|$, which differs from

the unity operator because of the incompleteness of the basis $|\mathbf{k}n\rangle$. The functions $|\mathbf{k}\lambda\rangle$ are the exact eigenfunctions of the projected Hamiltonian $\tilde{H} = PHP$. The electron density operator in this subspace is given by $\tilde{\rho}_{\mathbf{q}} = P\rho_{\mathbf{q}}P$.

Defining now the CDO as in (4), we have

$$\tilde{\mathbf{j}}_{\mathbf{q}} = \lim_{\mathbf{q} \rightarrow 0} \frac{\mathbf{q}}{\hbar|\mathbf{q}|^2} [\tilde{H}, \tilde{\rho}_{\mathbf{q}}]. \quad (8)$$

* In the KKR method the equation for $E_{\mathbf{k}\lambda}$ and $a_n^{\mathbf{k}\lambda}$ is usually derived in terms of the multiply scattering theory, but it may be formulated also in the same manner [11]

Generally speaking the projection of the commutator of two operators is not equal to the commutator of their projections, so the operator defined by (8) is not equal to the Pj_qP , i.e.

$$\tilde{\mathbf{j}}_{\lambda\lambda'}^{\mathbf{k}} \neq \langle \mathbf{k} \lambda | \frac{\hbar \nabla}{im} | \mathbf{k} \lambda' \rangle.$$

Let us concentrate our attention on this question and compute the commutator

$$\begin{aligned} & \lim_{\mathbf{q} \rightarrow 0} \frac{\mathbf{q}}{\hbar |\mathbf{q}|^2} [\tilde{H}, \tilde{\rho}_{\mathbf{q}}] \\ &= \lim_{\mathbf{q} \rightarrow 0} \frac{\mathbf{q}}{\hbar |\mathbf{q}|^2} \sum_{\mathbf{k}_1 \mathbf{k}_2} [|k_1 n_1\rangle H_{n_1 n_2}^{\mathbf{k}_1} \langle \mathbf{k}_1 n_2 |, \\ & \quad | \mathbf{k}_2 + \mathbf{q}, n_3\rangle \rho_{\mathbf{q}, n_3 n_4}^{\mathbf{k}_2} \langle \mathbf{k}_2 n_4 |] \\ &= \sum_{\mathbf{k}, n, n'} \frac{1}{\hbar} | \mathbf{k} n \rangle \left\{ \frac{\partial H_{nn'}^{\mathbf{k}}}{\partial \mathbf{k}} + \lim_{\mathbf{q} \rightarrow 0} \sum_{n_1} \left[H_{nn_1}^{\mathbf{k}} \frac{\partial \rho_{\mathbf{q}, n_1 n'}^{\mathbf{k}}}{\partial \mathbf{q}} \right. \right. \\ & \quad \left. \left. - \frac{\partial \rho_{\mathbf{q}, nn_1}^{\mathbf{k}}}{\partial \mathbf{q}} H_{n_1 n'}^{\mathbf{k}} \right] \right\} \langle \mathbf{k} n' | \end{aligned} \quad (9)$$

where $H_{nn'}^{\mathbf{k}} = \langle \mathbf{k} n | H | \mathbf{k} n' \rangle$ and $\rho_{\mathbf{q}, nn'}^{\mathbf{k}} = \langle \mathbf{k} + \mathbf{q}, n | \rho_{\mathbf{q}} | \mathbf{k} n' \rangle$, where $\rho_{\mathbf{q}} = e^{i\mathbf{q}\mathbf{r}}$ and we have taken into account that

$$\rho_{\mathbf{q}=0, nn'}^{\mathbf{k}} = \langle \mathbf{k} n | \mathbf{k} n' \rangle = \delta_{nn'}.$$

Equation (9) may also be obtained if the current density is defined in the gradient-invariant way

$$\tilde{\mathbf{j}} = \lim_{|\mathbf{A}| \rightarrow 0} \frac{\delta \tilde{H}(\mathbf{A})}{\delta \mathbf{A}} \left(\frac{-c}{e} \right) \quad (10)$$

where \mathbf{A} is the vector potential. Derivation of the CDO elements gives

$$\begin{aligned} \tilde{\mathbf{j}}_{\lambda\lambda'}^{\mathbf{k}} &= \langle \mathbf{k} \lambda | \tilde{\mathbf{j}} | \mathbf{k} \lambda' \rangle \\ &= \frac{1}{\hbar} \sum_{\mathbf{k}, nn'} (a_n^{\mathbf{k}\lambda})^* a_n^{\mathbf{k}\lambda'} \left\{ \frac{\partial H_{nn'}^{\mathbf{k}}}{\partial \mathbf{k}} + (E_\lambda - E_{\lambda'}) \right. \\ & \quad \left. \cdot \lim_{\mathbf{q} \rightarrow 0} \frac{\partial \rho_{\mathbf{q}, nn'}^{\mathbf{k}}}{\partial \mathbf{q}} \right\}. \end{aligned} \quad (11)$$

It may be noted that Smith [5] has used the matrix elements without the second term in (11). This approach is not self-consistent and may give rise to considerable errors.

It is convenient to rewrite the wave function in Bloch form

$$| \mathbf{k} \lambda \rangle = e^{i\mathbf{k}\mathbf{r}} | u_{\mathbf{k}\lambda} \rangle,$$

$$| \mathbf{k} n \rangle = e^{i\mathbf{k}\mathbf{r}} | u_{\mathbf{k}n} \rangle.$$

Then

$$\begin{aligned} \frac{\partial H_{nn'}^{\mathbf{k}}}{\partial \mathbf{k}} &= \langle \mathbf{k} n | -\frac{i\hbar^2 \nabla}{m} | \mathbf{k} n' \rangle \\ &+ \left\langle \frac{\partial u_{\mathbf{k}n}}{\partial \mathbf{k}} \middle| e^{-i\mathbf{k}\mathbf{r}} H | \mathbf{k} n' \right\rangle + \langle \mathbf{k} n | H e^{i\mathbf{k}\mathbf{r}} \middle| \frac{\partial u_{\mathbf{k}n'}}{\partial \mathbf{k}} \right\rangle \end{aligned} \quad (12)$$

and

$$\begin{aligned} \lim_{\mathbf{q} \rightarrow 0} \frac{\partial \rho_{\mathbf{q}, nn'}^{\mathbf{k}}}{\partial \mathbf{q}} &= \left\langle \frac{\partial u_{\mathbf{k}n}}{\partial \mathbf{k}} \middle| u_{\mathbf{k}n'} \right\rangle \\ &= - \left\langle u_{\mathbf{k}n} \middle| \frac{\partial u_{\mathbf{k}n'}}{\partial \mathbf{k}} \right\rangle. \end{aligned} \quad (13)$$

From (12) and (13) it follows that

$$\begin{aligned} \tilde{\mathbf{j}}_{\lambda\lambda'}^{\mathbf{k}} &= \mathbf{j}_{\lambda\lambda'}^{\mathbf{k}} + \delta \mathbf{j}_{\lambda\lambda'}^{\mathbf{k}} \\ &= \langle \mathbf{k} \lambda | \frac{\hbar \nabla}{im} | \mathbf{k} \lambda' \rangle + \frac{1}{\hbar} \sum_n (a_n^{\mathbf{k}\lambda})^* a_n^{\mathbf{k}\lambda'} \\ & \quad \cdot \left\{ \left\langle \frac{\partial u_{\mathbf{k}n}}{\partial \mathbf{k}} \middle| e^{-i\mathbf{k}\mathbf{r}} (H - E_{\mathbf{k}\lambda}) | \mathbf{k} \lambda' \right\rangle \right. \\ & \quad \left. + \langle \mathbf{k} \lambda | (H - E_{\mathbf{k}\lambda}) e^{i\mathbf{k}\mathbf{r}} \middle| \frac{\partial u_{\mathbf{k}n}}{\partial \mathbf{k}} \right\rangle \right\}. \end{aligned} \quad (14)$$

The last two terms in (14) are the corrections to the commonly used expression (5) for the CDO matrix elements. These corrections may be written as

$$\begin{aligned} \delta \mathbf{j}_{\lambda\lambda'}^{\mathbf{k}} &= \frac{1}{\hbar} \sum_n (a_n^{\mathbf{k}\lambda})^* a_n^{\mathbf{k}\lambda'} \\ & \quad \cdot \left\{ \left\langle \frac{\partial u_{\mathbf{k}n}}{\partial \mathbf{k}} \middle| e^{-i\mathbf{k}\mathbf{r}} (I - P) (H - E_{\mathbf{k}\lambda}) | \mathbf{k} \lambda' \right\rangle \right. \\ & \quad \left. + \langle \mathbf{k} \lambda | (H - E_{\mathbf{k}\lambda}) (I - P) e^{i\mathbf{k}\mathbf{r}} \middle| \frac{\partial u_{\mathbf{k}n}}{\partial \mathbf{k}} \right\rangle \right\} \end{aligned} \quad (15)$$

where I is the unity operator and P is the projection operator.

Let us discuss these results. The corrections $\delta \mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}$ obviously vanish when the basis $| \mathbf{k} n \rangle$ is complete (operator P is then equal to I), i.e. when the functions $| \mathbf{k} \lambda \rangle$ are the exact eigenfunction of the Hamiltonian H . They vanish also when the function $| u_{\mathbf{k}n} \rangle$ does not depend on \mathbf{k} , as in the plane waves basis

$$| u_{\mathbf{k}n} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{G}_n \mathbf{r}}.$$

\mathbf{G}_n is a reciprocal lattice vector. Usually neither of these cases takes place. For example, the corrections do not vanish for many methods which use the basis function in form of the linear combination of localized orbitals:

$$| u_{\mathbf{k}n} \rangle = \sum_{\mathbf{R}} e^{-i\mathbf{k}(\mathbf{r}-\mathbf{R})} \phi_n(\mathbf{r}-\mathbf{R}).$$

The existence of the correction is not strange at all but probably it seems more unusual that the matrix elements calculated without this correction may be very inaccurate in spite of the accuracy of the eigen-energies. Often such a discrepancy is caused by the discontinuity of the wave functions. There are two interesting examples:

It is well known that the KKR method with $l_{\max}=2$ provides good accuracy of the band structure of simple and transition metals. Chen [2] have calculated matrix elements $\langle \mathbf{k}\lambda | \frac{\hbar \nabla}{im} | \mathbf{k}\lambda' \rangle$ for copper by

KKR method with $l_{\max}=2$ and $l_{\max}=4$. In the first case the matrix elements are 2-3 times less while the energies differ very little. The continuous wave function must have included all spherical harmonics, so if $l_{\max}=2$ the function is discontinuous, and the discontinuity is much more than if $l_{\max}=4$. Such a discontinuity leads to unexpectedly great error. Even more shocking is the example of the "canonical bands" method which is a variant of Andersen's LMTO method [8].

In this method the wave function of d -electron includes only the spherical harmonics with $l=2$. It is known that such a model provides a good qualitative description of the band structure in the d -band energy region. But the matrix elements of the gradient are exactly zero and without the corrections (15) any calculation of optical properties is impossible.

The role of the corrections $\delta \mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}$ may be demonstrated also by following reasoning:

From the equation of motion for $\tilde{\rho}$ and the continuity equation (2) it is easy to obtain the expression:

$$(E_{\mathbf{k}+\mathbf{q},\lambda} - E_{\mathbf{k},\lambda}) \langle \mathbf{k}+\mathbf{q},\lambda | e^{i\mathbf{q}\mathbf{r}} | \mathbf{k},\lambda \rangle = \hbar \mathbf{q} \langle \mathbf{k}+\mathbf{q},\lambda | \mathbf{j}_{\mathbf{q}} | \mathbf{k},\lambda \rangle.$$

In the limit of $q \rightarrow 0$ the usual expression for the electron velocity may be derived:

$$\tilde{\mathbf{j}}_{\lambda\lambda}^{\mathbf{k}} = \mathbf{j}_{\lambda\lambda}^{\mathbf{k}} + \delta \mathbf{j}_{\lambda\lambda}^{\mathbf{k}} = \frac{1}{\hbar} \frac{dE_{\mathbf{k},\lambda}}{d\mathbf{k}} = \mathbf{v}_{\mathbf{k},\lambda} \quad (16)$$

which is valid however only for the corrected CDO matrix elements. It means that the corrected CDO matrix elements are as accurate as the energy structure.

The equation (16) may be used as a good test of the accuracy of the diagonal matrix elements when they are calculated without the corrections. We have done this in our LMTO calculation as it is described below (in the optical properties calculations the non-diagonal matrix elements are used but it is natural

to suppose that their accuracy is of the same order as of the diagonal ones).

Some authors make use of other expressions for the matrix elements, which are equivalent to (4) when the wave functions are exact, namely

$$\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}} = \langle \mathbf{k}\lambda | \frac{i\mathbf{r}}{\hbar} | \mathbf{k}\lambda' \rangle \times (E_{\mathbf{k},\lambda} - E_{\mathbf{k},\lambda'}), \quad (17)$$

$$\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}} = \langle \mathbf{k}\lambda | \frac{i\hbar \nabla \nabla}{m} | \mathbf{k}\lambda' \rangle \frac{1}{E_{\mathbf{k},\lambda} - E_{\mathbf{k},\lambda'}}. \quad (18)$$

It is easy to show that the proper formulas of this kind must include the correction of the same type as (15) and also some other corrections, namely,

$$\frac{i}{\hbar} \{ \langle \mathbf{k}\lambda | (H - E_{\mathbf{k},\lambda})(I - P)\mathbf{r} | \mathbf{k}\lambda' \rangle - \langle \mathbf{k}\lambda | \mathbf{r}(I - P)(H - E_{\mathbf{k},\lambda'}) | \mathbf{k}\lambda' \rangle \}$$

for (16) and

$$\frac{i\hbar}{m} \{ \langle \mathbf{k}\lambda | (H - E_{\mathbf{k},\lambda})(I - P)\nabla \nabla | \mathbf{k}\lambda' \rangle - \langle \mathbf{k}\lambda | \nabla \nabla (I - P)(H - E_{\mathbf{k},\lambda'}) | \mathbf{k}\lambda' \rangle \}$$

for (17). So the formulas (17) and (18) are not more accurate than (5).

It must be noted that the problem of the self-consistent definition of the CDO and its matrix elements arises not only in the optical properties calculation, but in the calculations of the oscillator strengths in atoms [12], of the X-ray absorption and in some other problems. For example, Volkov et al. [14] have discussed the question of the self-consistent definition of the CDO in the Kohn-Luttinger representation for the finite number of energy bands in connection with the problem of excitonic insulator.

III. The LMTO Calculation of the Optical Matrix Element

Let us survey briefly the LMTO calculation of the matrix element $\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}} = \langle \mathbf{k}\lambda | \frac{\hbar \nabla}{im} | \mathbf{k}\lambda' \rangle$. The LMTO wave functions are given by [8]:

$$\psi_{\mathbf{k},\lambda}(\mathbf{r}) = \sum_L a_L^{\mathbf{k},\lambda} \chi_L^{\mathbf{k}}(\mathbf{r}) \quad (19)$$

where $\chi_L^{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \chi_L(\mathbf{r} - \mathbf{R})$ are the Bloch sums of the MT-orbitals. In the atomic sphere approximation (ASA) they may be written as

Table 1. Test of diagonal matrix elements in ASA

λ	1	2	3	4	5	6	7	8
$E_\lambda(l_{\max}=2)$	0.107	0.335	0.381	0.397	0.428	0.456	1.981	2.435
$\xi_\lambda(l_{\max}=2)$	0.987	-0.233	-0.524	0.439	0.863	0.486	0.644	0.580
$E_\lambda(l_{\max}=3)$	0.107	0.331	0.377	0.393	0.424	0.452	1.810	2.158
$\xi_\lambda(l_{\max}=3)$	1.011	0.984	0.776	1.101	1.040	1.010	0.659	0.499

λ	9	10	11	12	13	14	15	16
$E_\lambda(l_{\max}=2)$	2.826	-	-	-	-	-	-	-
$\xi_\lambda(l_{\max}=2)$	0.506	-	-	-	-	-	-	-
$E_\lambda(l_{\max}=3)$	2.679	2.780	3.253	3.737	4.083	4.241	4.785	5.480
$\xi_\lambda(l_{\max}=3)$	0.498	-0.277	-0.088	0.072	0.279	0.307	-1.575	0.079

$$\chi_L^{\mathbf{k}(\text{ASA})}(\mathbf{r}) = \sum_{L'}^{l' \leq l_{\max}} [\pi_{L'L}^{\mathbf{k}} \Phi_{L'}(\mathbf{r}, E_\nu) + \Omega_{L'L}^{\mathbf{k}} \dot{\Phi}_{L'}(\mathbf{r}, E_\nu)]. \quad (20)$$

The coefficients $\pi_{L'L}^{\mathbf{k}}$ and $\Omega_{L'L}^{\mathbf{k}}$ are given in the Andersen's paper ([8]; see formulas (4.21a) and (4.21b)). The function $\Phi_{L'}(\mathbf{r}, E_\nu)$ is the solution of the radial Schrödinger equation for the energy E_ν and $\dot{\Phi}_{L'}(\mathbf{r}, E_\nu)$ is its energy derivative. The matrix elements $\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}$ in the atomic sphere approximation are given by:

$$\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}(\text{ASA})} = \sum_{LL'} (a_L^{\mathbf{k}\lambda})^* a_{L'}^{\mathbf{k}\lambda'} \langle \chi_L^{\mathbf{k}(\text{ASA})} | \frac{\hbar \nabla}{im} | \chi_{L'}^{\mathbf{k}(\text{ASA})} \rangle \quad (21)$$

where the acute-angle brackets denote the integration over the atomic sphere. They may be easily derived by use of the well-known formula for the gradient of the spherical harmonics [15]. It should be noted that $\chi_L^{\mathbf{k}(\text{ASA})}$ is well-defined only inside atomic sphere of the radius S (Wigner-Seitz sphere). But being expanded over the whole space these functions are discontinuous due to the cut-off of the sum in (19) at l_{\max} .

For estimating the values of the corrections $\delta \mathbf{j}_{\lambda\lambda'}$ in (16) we shall compare the diagonal matrix element $\mathbf{j}_{\lambda\lambda}^{\mathbf{k}(\text{ASA})}$ and the electron velocity $\frac{1}{\hbar} \frac{dE_{\mathbf{k}\lambda}}{d\mathbf{k}}$. It follows from the previous consideration that such a comparison characterizes the consistency of the CDO matrix elements with the energy structure.

The results of the calculations of the ratio $\xi_\lambda^{\mathbf{k}} = \hbar (j_{\lambda\lambda}^{\mathbf{k}})_x \left/ \frac{dE_{\mathbf{k}\lambda}}{dk_x} \right.$ are shown in Table 1. The calculations were carried out at the \mathbf{k} -point (0.2, 0.1, 0.05) for the cases of $l_{\max}=2$ and $l_{\max}=3$ using the self-consistent potential from [16].

From this table it may be seen that the energies $E_{\mathbf{k}\lambda}$ in the lowest six bands are almost the same when $l_{\max}=2$ and $l_{\max}=3$ and hence the quantity $\frac{1}{\hbar} \frac{dE_{\mathbf{k}\lambda}}{d\mathbf{k}}$

does not change much neither. But the matrix elements $j_{\lambda\lambda}^{\mathbf{k}}$ differ greatly in these two cases. In higher bands the quantity $j_{\lambda\lambda}^{\mathbf{k}}$ differs from $\frac{1}{\hbar} \frac{dE_{\mathbf{k}\lambda}}{d\mathbf{k}}$ significantly even when $l_{\max}=3$.

Within the frameworks of the LMTO method the continuity of the wave function and its derivative may be achieved by using the LMTO wave functions $\chi_L^{\mathbf{k}(\text{LMTO})}$ instead of the ASA wave functions $\chi_L^{\mathbf{k}(\text{ASA})}$

$$\chi_L^{\mathbf{k}(\text{LMTO})}(\mathbf{r}) = [\chi_L^{\mathbf{k}(\text{ASA})}(\mathbf{r}) - \tilde{\chi}_L^{\mathbf{k}(\text{ASA})}(\mathbf{r})] \theta(S - |\mathbf{r}|) + \chi_L^{\mathbf{k}(\text{ASA})}(|\mathbf{r}|=S) \sum_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} F_L(\mathbf{k}+\mathbf{G}), \quad (22)$$

$$F_L(\mathbf{k}+\mathbf{G}) = 3(2l+1)(2l+3) \frac{j_{l+1}(|\mathbf{k}+\mathbf{G}|S)}{(|\mathbf{k}+\mathbf{G}|S)^3} Y_L(\widehat{\mathbf{k}+\mathbf{G}}) \quad (23)$$

where $\tilde{\chi}_L^{\mathbf{k}(\text{ASA})}$ is given by the expression (20) for the zero crystal potential. They are normalized by the condition $\tilde{\chi}_L^{\mathbf{k}(\text{ASA})}(|\mathbf{r}|=S) = \chi_L^{\mathbf{k}(\text{ASA})}(|\mathbf{r}|=S)$. Using (21) and (22) we get that

$$\begin{aligned} \mathbf{j}_{\lambda\lambda'}^{\mathbf{k}(\text{LMTO})} \approx \sum_{LL'} \left\{ \langle \chi_L^{\mathbf{k}(\text{ASA})} | \frac{\hbar \nabla}{im} | \chi_{L'}^{\mathbf{k}(\text{ASA})} \rangle \right. \\ \left. - \langle \tilde{\chi}_L^{\mathbf{k}(\text{ASA})} | \frac{\hbar \nabla}{im} | \tilde{\chi}_{L'}^{\mathbf{k}(\text{ASA})} \rangle \right. \\ \left. + \chi_L^{\mathbf{k}(\text{ASA})}(|\mathbf{r}|=S) \chi_{L'}^{\mathbf{k}(\text{ASA})}(|\mathbf{r}|=S) \Omega \right. \\ \left. \cdot \sum_{\mathbf{G}} F_L^*(\mathbf{k}+\mathbf{G}) F_{L'}(\mathbf{k}+\mathbf{G})(\mathbf{k}+\mathbf{G}) \right\} (a_L^{\mathbf{k}\lambda})^* a_{L'}^{\mathbf{k}\lambda'}. \quad (24) \end{aligned}$$

This formula turns out to be computable enough because the sum in (24) may be computed by the slightly modified LMTO subroutine for the calculation of the structure constants $F_{LL'}$ [8].

It should be noted that the (24) looks like the formula (4.13) of the Andersen paper [8] for the overlap matrix. As we now use the continuous wave

Table 2. Test of diagonal matrix elements in LMTO

λ	1	2	3	4	5	6	7	8
$E_{\lambda}(l_{\max}=2)$	0.107	0.336	0.379	0.396	0.426	0.454	1.880	2.240
$\xi_{\lambda}(l_{\max}=2)$	0.989	0.354	0.273	0.628	0.858	0.636	0.714	0.574
$E_{\lambda}(l_{\max}=3)$	0.107	0.335	0.378	0.395	0.425	0.453	1.800	2.150
$\xi_{\lambda}(l_{\max}=3)$	0.998	1.008	1.028	0.907	0.923	0.922	0.746	0.656

λ	9	10	11	12	13	14	15	16
$E_{\lambda}(l_{\max}=2)$	2.629	-	-	-	-	-	-	-
$\xi_{\lambda}(l_{\max}=2)$	0.645	-	-	-	-	-	-	-
$E_{\lambda}(l_{\max}=3)$	2.583	2.616	2.965	3.480	3.664	3.922	4.409	4.769
$\xi_{\lambda}(l_{\max}=3)$	0.708	0.565	0.188	0.404	0.443	0.876	0.891	0.462

Table 3. The comparison of the matrix elements calculated using LMTO method (24) and KKR [2] method (18)–(5)

transition	$L_1 \rightarrow L_2$	$L_3 \rightarrow L_2$	$L_3'' \rightarrow L_2$	$L_2 \rightarrow L_1'$	$X_1' \rightarrow X_4'$	$X_5 \rightarrow X_4'$	$X_4' \rightarrow X_1''$
$E_{\lambda} - E_{\lambda}'$	0.354	0.224	0.113	0.341	0.555	0.298	0.394
$P_{\lambda\lambda'}(\text{LMTO})$ $l_{\max}=3$	0.240	0.108	0.322	0.820	0.218	0.472	0.911
$P_{\lambda\lambda'}(\text{KKR})$ $l_{\max}=4$	0.214–0.220	0.081–0.104	0.302–0.384	0.857–0.843	0.201–0.203	0.350–0.350	0.977–0.963

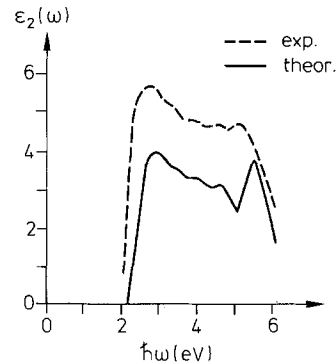
functions, the ratio $\hbar(j_{\lambda\lambda'}^k)_x / \frac{dE_{\mathbf{k}\lambda}}{dk_x}$ is much closer to unity in LMTO than in ASA (see Table 2). Above we supposed that the accuracy of the calculations of the nondiagonal matrix elements is of the same order than that of the diagonal ones. Now we can verify this supposition. The comparison between the calculated optical matrix elements for copper $\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}(\text{LMTO})(l_{\max}=3)$ (with the potential from the book [16]) and the matrix elements of [2], at the points of high symmetry confirms this estimation (see Table 3).

IV. Numerical Results

As an example of the application of the above-described technique we present the calculations of $\varepsilon_2(\omega)$ in comparison with the experimental measurements for FCC metals Cu and Pd. We have computed the interband part of $\varepsilon_2(\omega)$ for the energy range $\hbar\omega \lesssim 20$ eV using the formula

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{3\omega^2} \sum_{\mathbf{k}, \lambda \neq \lambda'} |\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}|^2 \delta(E_{\mathbf{k}\lambda'} - E_{\mathbf{k}\lambda} - \hbar\omega) f_{\mathbf{k}\lambda}(1 - f_{\mathbf{k}\lambda'}) \quad (25)$$

where the matrix elements $\mathbf{j}_{\lambda\lambda'}^{\mathbf{k}}$ are given by (24).

**Fig. 1.** Calculated and experimental [17] dielectric function of Cu

The reciprocal space integration was performed by the tetrahedron method using 215 points in the irreducible part of the Brillouin zone.

The optical properties of copper have been measured by many authors [17–19]. The experimental results for $\varepsilon_2(\omega)$ have been obtained by the Kramers-Kronig inversion of the reflectivity data. They are in good agreement with each other. The actual comparison between the calculated results for ε_2 and the curve of [17] is shown in Fig. 1 (in the energy range $\hbar\omega \lesssim 6$ eV). It may be seen that the positions of the main features of the theoretical curve almost coincides with the experimental ones.

The interband absorption edge lies about $\hbar\omega \sim 2.1$ eV. The first significant peak $\hbar\omega \sim 2.7$ eV on

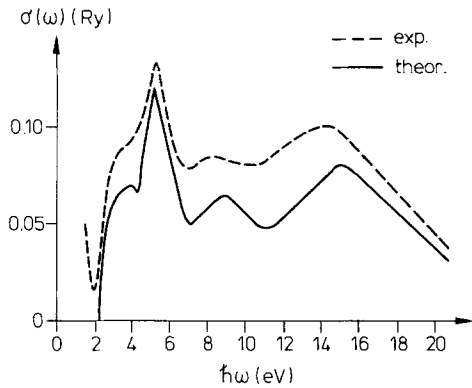


Fig. 2. Calculated and experimental [20] optical conductivity of Cu

the calculated curve corresponds to the experimental $\hbar\omega \sim 2.6$ eV. The positions of the features at 3.9 eV and 4.6 eV may be almost identified and the position ($\hbar\omega \sim 5.5$ eV) of the right theoretical peak corresponds to the value $\hbar\omega \sim 5.2$ eV of the experimental one.

There are the experimental data obtained by Beaglehole et al. [20] by the use of the multiangle reflectance technique from which $\varepsilon_2(\omega)$ could be extracted without the Kramers-Kronig integration. The comparison of the experimental measurements

of the optical conductivity $\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega)$ for Cu with the calculations in the energy region $\hbar\omega \lesssim 20$ eV is shown in Fig. 2.

The broad humps in the theoretical $\sigma(\omega)$ at about 9 eV and 15 eV correspond well to the similar broad features in the experimental curve at 8 eV and 14 eV.

Thus one can say that the theory allows us to establish the positions of the features observed in the experiment for the energy interval $\hbar\omega \lesssim 20$ eV. However, in general the theoretical magnitudes of $\varepsilon_2(\omega)$ and $\sigma(\omega)$ for Cu are lower than experimental ones.

The numerous measurements of the optical properties of Pd [21–23] give rather full picture of the positions of the main anomalies of $\varepsilon_2(\omega)$. The comparison between the theoretical $\varepsilon_2(\omega)$ for Pd and experiments [21] ($\hbar\omega = 1$ –13 eV) and [22] ($\hbar\omega = 2$ –30 eV) is shown in Fig. 3.

The theoretical curve displays a significant feature at $\hbar\omega \sim 1.5$ eV in accordance with [21]. At the points $\hbar\omega \sim 3.3$ eV and $\hbar\omega \sim 4.5$ eV both calculations and experiment [21] display two peaks, and the curve [22] has rather visible shoulders. At $\hbar\omega \sim 7.2$ eV there are peaks both in the theoretical and in the experimental [21] curves and at $\hbar\omega \sim 9.7$ eV our cal-

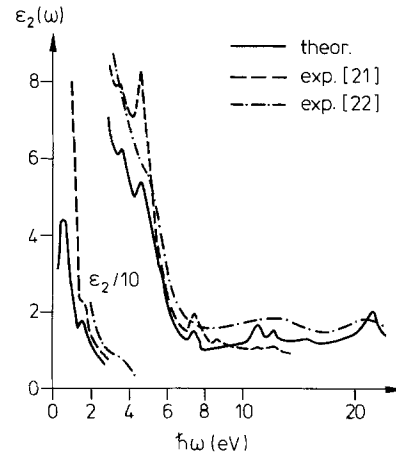


Fig. 3. Calculated and experimental [21, 22] imagine part of dielectric function of Pd

culations and [22] give plateau ([21] has a peak). At $\hbar\omega \sim 10.7$ eV the theoretical curve and [21] have peaks and at $\hbar\omega \sim 12.5$ eV all three curves have features. At $\hbar\omega \sim 17$ eV $\varepsilon_2(\omega)$ has a minimum and at 20.5 eV a maximum in accordance with [22]. It is also easily seen that the overall agreement of $\varepsilon_2(\omega)$ with the experiment, in the positions and the intensities of the features is rather good for Pd.

V. Conclusions

In this paper we show that some difficulties arise in the definition of the current density matrix elements because of the approximate nature of the wave functions obtained by the band structure calculations. Possible ways of solving these problems are either taking into account the corrections (15) directly or the further improvement of the wave functions, paying a special attention to the continuity. We think the second way is preferable, particularly because it does not require the revision of the existing theoretical equations. It will be important if one would like to take into account the many-particle effects and the matrix nature of the dielectric screening. Comparison of the calculated $\varepsilon_2(\omega)$ with the experimental values displays good qualitative and quantitative agreement. It is difficult to say now what is the origin of the existing discrepancy: the insufficient accuracy of the wave function or the many-particle effects. This question requires following investigations.

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