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# Optical properties studied using linear muffin-tin orbital theory

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**Abstract.** A new method is presented for calculating optical properties within the framework of the self-consistent linear muffin-tin orbital (LMTO) band-structure theory. We show how Green's second identity along with the commutation relation between the position and Hamiltonian operators may be used to calculate, independently of the gauge, the velocity matrix elements required for optical properties. The method has been applied to calculate the imaginary part of the dielectric function  $\epsilon_2(E)$  for FeSi and Si. Notably, the new expressions for matrix elements are also valid for Hamiltonians in which non-local potentials are included.

## 1. Introduction

In recent years a number of methods have been proposed for calculating optical properties within the framework of LMTO theory [1–3]. It has been shown that the optical properties of both metals [1, 2] and semiconducting materials [4, 5] may be calculated. Uspenski *et al* [1] proposed a method for the accurate calculation of the optical matrix elements based on the continuity equation for the charge-density operator. They were able to show that the same accuracy as in band-structure calculations could be achieved for the optical matrix elements. This was done by including the combined correction term to compensate for inaccuracies in the wavefunction due to the basis set in LMTO theory being finite. Their method was applied to calculate the optical spectra of the metals Cu and Pb showing good agreement with experimental values. These corrections were incorporated by Alouani *et al* [2, 4] and they have shown how satisfactory optical spectra can be obtained for Al and Fe in the low-energy range, i.e. less than 5 eV. Subsequently they have applied their method to calculate the optical properties of various semiconducting materials [4], namely Ge, GaAs, InSb and CdTe. They have also used their method to investigate the hydrostatic pressure dependence of the dielectric functions of Ge and GaAs. Another similar approach to determining the optical properties within the LMTO formalism has been given by Zemach *et al* [3]. They showed that the matrix elements may be evaluated using a spherical wave expansion and Racah algebra [6]. Subsequently they have applied their method to calculate the optical properties of *trans*-polyacetylene [5].

In all of the above calculations however, the gradient operator has been employed for the determination of the momentum matrix. In this paper we shall show how the momentum matrix may be constructed using a gauge-independent formalism which avoids the determination of the gradient operator and allows for the inclusion of non-local potentials

in the Hamiltonian. In our method we have employed Green's second identity and the commutation relation between the position and Hamiltonian operators. We then show how the momentum matrices may be written in terms of a sum over Gaunt coefficients [6] and potential parameters which are defined within the LMTO method [7, 8]. The optical spectrum is then evaluated by linear extrapolation [9] on a mesh of  $k$ -points in the irreducible wedge of the Brillouin zone using the tetrahedron method [10, 11]. We have linearly interpolated both the eigenvalues and the momentum matrix elements between mesh points on a given tetrahedra [11]. In order to demonstrate the validity of our method we have applied it to calculate the imaginary part of the dielectric function for FeSi and Si. The results obtained show good agreement with other calculations [4, 12] and experiment [13].

## 2. Optically induced transitions

In order to study the effect of a radiation field on the electronic states of a solid, one must determine the total energy involved which is described mathematically by the Hamiltonian of the system. The Hamiltonian is given as the sum of the kinetic,  $H_{KE}$ , and potential,  $H_{PE}$ , energies of a system of  $N$  electrons and the energy of interaction,  $H_{int}$ , of the system with the perturbing electromagnetic field, i.e.

$$H = H_{KE} + H_{int} + H_{PE} = \frac{1}{2m_e} \sum_{i=1}^N \left( P_i + \frac{eA(\mathbf{r}_i, t)}{c} \right)^2 + H_{PE} \quad (1)$$

where  $e$  is the absolute value of the electron charge and  $A$  is the vector potential of the electromagnetic field. Using the normal Coulomb gauge  $\nabla \cdot A(\mathbf{r}_i, t) = 0$  it may be shown [15] that the interaction Hamiltonian, neglecting squared terms in the vector potential, is given by [14]

$$H_{int} = \frac{e}{c} \sum_{i=1}^N \mathbf{A} \cdot \mathbf{v}_i. \quad (2)$$

Within the standard quantum mechanical treatment, the effects of an electromagnetic field on the electronic states are studied using  $H_{int}$  as a time-dependent perturbation which causes electrons to make transitions between the energy bands. By using time-dependent perturbation theory one obtains the rate at which these transitions occur which may then be related to the standard optical response functions in crystals [15]. The absorption of radiation in solids is described by the absorption coefficient for cubic systems

$$\alpha(E) = \frac{\hbar e^2}{3nc\pi m^2 E} \sum_v \sum_c \int_{BZ} \left| \langle \Psi^{ck} | \mathbf{P} | \Psi^{vk} \rangle \right|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - E) d\mathbf{k}. \quad (3)$$

The imaginary part of the dielectric function may be related to this using the simple formula

$$\alpha(E) = \frac{E}{\hbar nc} \epsilon_2(E) \quad (4)$$

and hence

$$\epsilon_2(E) = \frac{\hbar^2 e^2}{3\pi m^2 E^2} \sum_v \sum_c \int_{BZ} \left| \langle \Psi^{ck} | \mathbf{P} | \Psi^{vk} \rangle \right|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - E) d\mathbf{k}. \quad (5)$$

One can see from this formula that at high-symmetry points and for allowed transitions, the optical properties can be described in terms of a contribution from the strength of the

matrix elements calculated at the high-symmetry points and a contribution from pairs of bands  $(1/E^2)J_{cv}(E)$ , where  $J_{cv}(E)$  is the joint density of states defined as

$$J(E) = \sum_v \sum_c J_{cv}(E) = \sum_v \sum_c \frac{1}{4\pi^3} \int_{\text{BZ}} \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - E) d\mathbf{k} \quad (6)$$

and is the density of pairs of states, one in the valence band, labelled  $v$ , and the other in the conduction band, labelled  $c$ . All over the energy range one has to calculate directly expression (5) and take into account the  $k$ -dependence of the matrix elements.

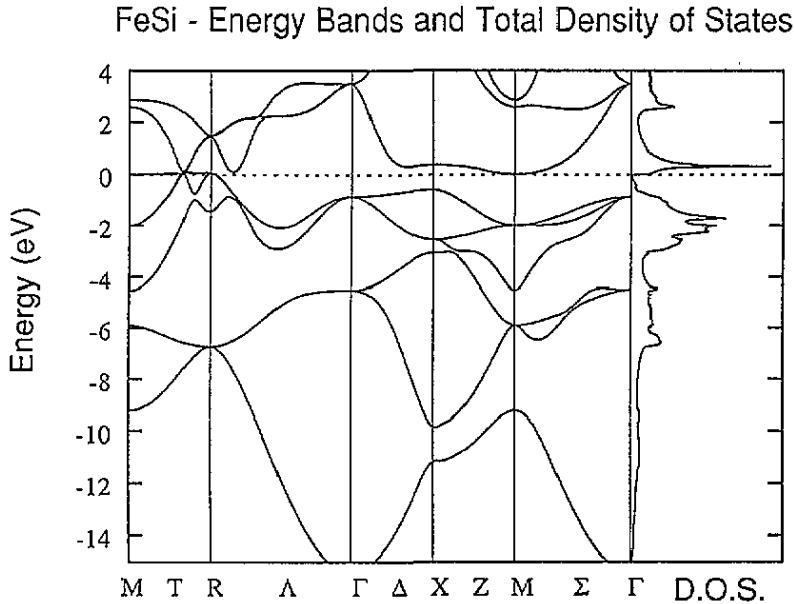


Figure 1. Electronic band structure of FeSi shown with the corresponding density of states.

### 3. The momentum matrix

In this section we will show how the optical matrix elements, and therefore the optical properties of solids, may be calculated within the framework of the self-consistent linear muffin-tin orbital band-structure method. As a starting point the momentum operator may be defined within the gauge-independent formalism by the commutation relation

$$\mathbf{P} = m_e \mathbf{v} \quad \text{where } \mathbf{v} = \frac{1}{i\hbar} [\mathbf{r}, H]. \quad (7)$$

Next we need to determine the one-electron wavefunction which has been defined within LMTO theory [7, 8]. This is achieved by using the variational principle for Schrödinger's equation with energy-independent basis functions which reduces the secular equations to those of a linear eigenvalue problem. The LMTO eigenvalue equation

$$\sum_L (H_{LL}^k - E^{jk} O_{LL}^k) \alpha_L^{jk} = 0 \quad (8)$$

is then solved numerically to obtain the eigenvalues  $E^{jk}$  at all required  $k$ -points and the corresponding eigenvectors  $\alpha_L^{jk}$ . The index  $L$  refers to the quantum numbers  $l$  and  $m$  and

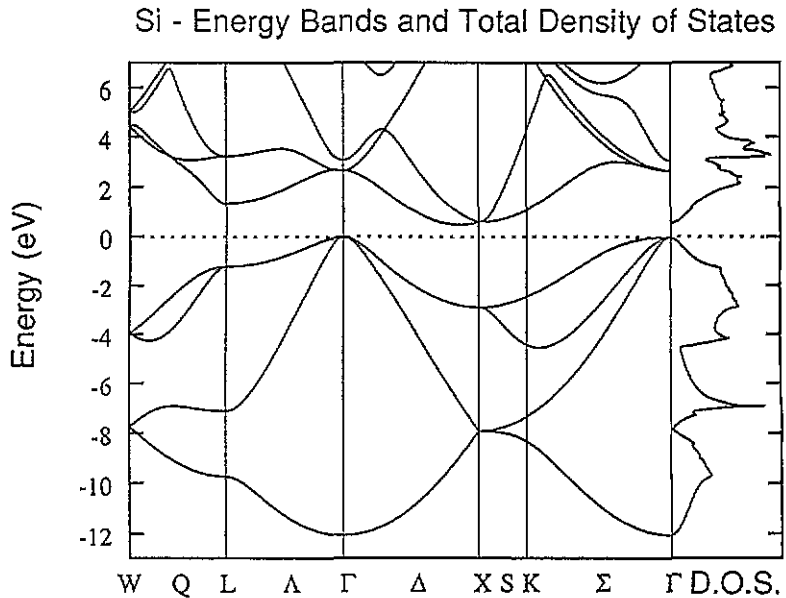


Figure 2. Electronic band structure of Si shown with the corresponding density of states.

also to each sphere  $q$  in the unit cell, i.e.  $L \Rightarrow qlm$ . The type of sphere  $t$  is then defined as a function of  $q$ . Using this we can construct the wavefunction corresponding to the  $j$ th eigenvalue at  $\mathbf{k}$  as a linear combination of the muffin-tin orbitals

$$\Psi^{jk}(\mathbf{r}) = \sum_L \Psi_L^{jk}(\mathbf{r}) \quad \Psi_L^{jk}(\mathbf{r}) = \alpha_L^{jk} \chi_L^k(\mathbf{r}) \quad (9)$$

where  $\Psi_L^{jk}(\mathbf{r})$  is the  $L$ -decomposed wavefunction and  $\chi_L^k(\mathbf{r})$  are the muffin-tin orbitals, defined in terms of potential parameters and canonical structure constants. By choosing some energy  $\varepsilon_{vlt}$  and assuming an energy-independent basis set, in the energy range surrounding  $\varepsilon_{vlt}$ , we can write

$$\phi_{vlt}(r) \equiv \phi_{lt}(\varepsilon_{vlt}, r). \quad (10)$$

This is the normalized solution of the radial Schrödinger equation for the potential  $v(r)$  and its energy derivative is defined by

$$\dot{\phi}_{vlt}(r) \equiv \left. \frac{\partial \phi_{lt}(E, r)}{\partial E} \right|_{\varepsilon_{vlt}}. \quad (11)$$

The radial derivatives of these functions are defined in terms of the corresponding radial logarithmic derivatives at the sphere boundaries:

$$\phi'_{vlt}(S_t) = \frac{1}{S_t} \phi_{vlt}(S_t) D_{vlt} \quad \dot{\phi}'_{vlt}(S_t) = \frac{1}{S_t} \dot{\phi}_{vlt}(S_t) D_{vlt}. \quad (12)$$

By using a linear combination of the energy-independent basis functions the  $L$ -decomposed wavefunction can be written as

$$\Psi_L^{jk}(\mathbf{r}) = A_L^{jk} \phi_{vL}(\mathbf{r}) + B_L^{jk} \dot{\phi}_{vL}(\mathbf{r}). \quad (13)$$

The coefficients  $A$  and  $B$  are also defined in terms of the potential parameters and the canonical structure constants [8]. The partial wave and its energy derivative are defined in terms of the energy-independent basis set

$$\phi_{vL}(\mathbf{r}) = i^l Y_l^m(\mathbf{r}) \phi_{vlt}(r) \quad (14)$$

$$\dot{\phi}_{\nu L}(\mathbf{r}) = i^l Y_l^m(\mathbf{r}) \dot{\phi}_{\nu l}(r). \tag{15}$$

The optical matrix elements are then given by

$$\langle \Psi^{j'k} | \mathbf{P} | \Psi^{jk} \rangle = m_e \sum_{L'L} \langle \Psi_{L'}^{j'k} | \mathbf{v} | \Psi_L^{jk} \rangle. \tag{16}$$

Let us now expand the optical matrix elements in terms of the  $L$ -decomposed wave function

$$\langle \Psi^{j'k} | \mathbf{P} | \Psi^{jk} \rangle = m_e \sum_{L'L} \langle A_{L'}^{j'k} \phi_{\nu L'}(\mathbf{r}) + B_{L'}^{j'k} \dot{\phi}_{\nu L'}(\mathbf{r}) | \mathbf{v} | A_L^{jk} \phi_{\nu L}(\mathbf{r}) + B_L^{jk} \dot{\phi}_{\nu L}(\mathbf{r}) \rangle. \tag{17}$$

After multiplication one obtains four separate terms which can be computed individually:

$$\begin{aligned} &\langle \Psi^{j'k} | \mathbf{P} | \Psi^{jk} \rangle \\ &= m_e \sum_{L'L} A_{L'}^{j'k*} A_L^{jk} \langle \phi_{\nu L'}(\mathbf{r}) | \mathbf{v} | \phi_{\nu L}(\mathbf{r}) \rangle \\ &\quad + m_e \sum_{L'L} A_{L'}^{j'k*} B_L^{jk} \langle \phi_{\nu L'}(\mathbf{r}) | \mathbf{v} | \dot{\phi}_{\nu L}(\mathbf{r}) \rangle \\ &\quad + m_e \sum_{L'L} B_{L'}^{j'k*} A_L^{jk} \langle \dot{\phi}_{\nu L'}(\mathbf{r}) | \mathbf{v} | \phi_{\nu L}(\mathbf{r}) \rangle \\ &\quad + m_e \sum_{L'L} B_{L'}^{j'k*} B_L^{jk} \langle \dot{\phi}_{\nu L'}(\mathbf{r}) | \mathbf{v} | \dot{\phi}_{\nu L}(\mathbf{r}) \rangle. \end{aligned} \tag{18}$$

We shall now consider the velocity matrix elements in this expression in detail.

By using the definitions of the partial wave and its energy derivative along with Green's second identity and the commutation relation between the position and Hamiltonian operators we shall show that the above relation may be solved in terms of potential parameters and Gaunt coefficients. So taking the first velocity matrix term

$$\begin{aligned} \langle \phi_{\nu L'}(\mathbf{r}) | \mathbf{v} | \phi_{\nu L}(\mathbf{r}) \rangle &= \frac{1}{i\hbar} \langle \phi_{\nu L'}(\mathbf{r}) | [\mathbf{r}, H] | \phi_{\nu L}(\mathbf{r}) \rangle \\ &= \frac{1}{i\hbar} \int \phi_{\nu L'}^*(\mathbf{r}) \mathbf{r} H \phi_{\nu L}(\mathbf{r}) d^3r - \frac{1}{i\hbar} \int \phi_{\nu L}^*(\mathbf{r}) H \mathbf{r} \phi_{\nu L'}(\mathbf{r}) d^3r. \end{aligned} \tag{19}$$

Now using

$$H \phi_{\nu L}(\mathbf{r}) = \epsilon_{\nu l} \phi_{\nu L}(\mathbf{r}) \tag{20}$$

and

$$H \dot{\phi}_{\nu L}(\mathbf{r}) = \dot{\phi}_{\nu L}(\mathbf{r}) + \epsilon_{\nu l} \dot{\phi}_{\nu L}(\mathbf{r}) \tag{21}$$

the first integral term in (19) may be expanded using the definition of the partial wave and its energy derivative, equations (14) and (15), giving

$$\frac{1}{i\hbar} \int \phi_{\nu L'}^*(\mathbf{r}) \mathbf{r} H \phi_{\nu L}(\mathbf{r}) d^3r = \frac{1}{i\hbar} \epsilon_{\nu l} i^{-l'} i^l \sqrt{\frac{4\pi}{3}} G \int_0^{s_l} \phi_{\nu l'}^*(x) x \phi_{\nu l}(x) x^2 dx \tag{22}$$

where  $G$  is defined in terms of the product of three spherical harmonics, (see appendix 1):

$$\begin{aligned} G &= \left[ \left[ \sqrt{\frac{1}{2}} \int Y_l^{m'*} Y_1^{-1} Y_l^m d\omega - \sqrt{\frac{1}{2}} \int Y_l^{m'*} Y_1^1 Y_l^m d\omega \right] \mathbf{x} \right. \\ &\quad + \left[ i\sqrt{\frac{1}{2}} \int Y_l^{m'*} Y_1^1 Y_l^m d\omega + i\sqrt{\frac{1}{2}} \int Y_l^{m'*} Y_1^{-1} Y_l^m d\omega \right] \mathbf{y} \\ &\quad \left. + \left[ \int Y_l^{m'*} Y_1^0 Y_l^m d\omega \right] \mathbf{z} \right] \end{aligned} \tag{23}$$

and the position vectors  $x$ ,  $y$ ,  $z$  are the unit vectors of the cartesian coordinate system, defined such that

$$\mathbf{r} = \sqrt{\frac{4\pi}{3}} \left[ \sqrt{\frac{1}{2}}(-Y_1^1 + Y_1^{-1})\mathbf{x} + \sqrt{\frac{1}{2}}i(Y_1^1 + Y_1^{-1})\mathbf{y} + Y_1^0\mathbf{z} \right] r. \quad (24)$$

The second integral term of expression (19) can be evaluated by using Green's second identity [16]:

$$\begin{aligned} & \int_{\text{volume}} [F_\alpha(\mathbf{r}) \nabla^2 \phi_{\nu L'}^*(\mathbf{r}) - \phi_{\nu L'}^*(\mathbf{r}) \nabla^2 F_\alpha(\mathbf{r})] d^3r \\ &= \int \int_{\text{surface}} [F_\alpha(\mathbf{r}) \mathbf{r} \cdot \nabla \phi_{\nu L'}^*(\mathbf{r}) - \phi_{\nu L'}^*(\mathbf{r}) \mathbf{r} \cdot \nabla F_\alpha(\mathbf{r})] S_r^2 d\omega \end{aligned} \quad (25)$$

We have taken  $F_\alpha(\mathbf{r})$  equal to the alpha component of  $\mathbf{r}\phi_{\nu L}(\mathbf{r})$ . By rearranging Green's second identity and again expanding in terms of the partial wave and its energy derivative we can see that the second term reduces to a contribution from the integration over the spheres and a surface integral contribution:

$$\begin{aligned} & \frac{1}{i\hbar} \int \phi_{\nu L'}^*(\mathbf{r}) H \mathbf{r} \phi_{\nu L}(\mathbf{r}) d^3r \\ &= \frac{1}{i\hbar} \left[ -\frac{\hbar^2}{2m_e} \int \phi_{\nu L'}^*(\mathbf{r}) \nabla^2 F(\mathbf{r}) d^3r + \int \phi_{\nu L'}^*(\mathbf{r}) v(r) F(\mathbf{r}) d^3r \right]. \end{aligned} \quad (26)$$

Then substituting in Green's second identity gives us

$$\begin{aligned} & \frac{1}{i\hbar} \int \phi_{\nu L'}^*(\mathbf{r}) H \mathbf{r} \phi_{\nu L}(\mathbf{r}) d^3r \\ &= \frac{1}{i\hbar} \left[ -\frac{\hbar^2}{2m_e} \int F(\mathbf{r}) \nabla^2 \phi_{\nu L'}^*(\mathbf{r}) d^3r + \int \phi_{\nu L'}^*(\mathbf{r}) v(r) F(\mathbf{r}) d^3r \right] \\ &+ \frac{i^{-1}\hbar}{2m_e} \int \int_{\text{surface}} [F(\mathbf{r}) \mathbf{r} \cdot \nabla \phi_{\nu L'}^*(\mathbf{r}) - \phi_{\nu L'}^*(\mathbf{r}) \mathbf{r} \cdot \nabla F(\mathbf{r})] S_r^2 d\omega. \end{aligned} \quad (27)$$

Finally by expanding in terms of the partial wave and its energy derivative, equations (14) and (15), and by using the fact that  $\phi$  and  $\dot{\phi}$  are real we obtain the result expressed in terms of an integral over the sphere and the potential parameters:

$$\begin{aligned} & \frac{1}{i\hbar} \int \phi_{\nu L'}^*(\mathbf{r}) H \mathbf{r} \phi_{\nu L}(\mathbf{r}) d^3r \\ &= \frac{i^{l'-l-1}}{\hbar} \epsilon_{\nu l l'} \sqrt{\frac{4\pi}{3}} \mathbf{G} \int_0^\infty \phi_{\nu l l'}(x) x \phi_{\nu l l'}(x) x^2 dx + \frac{\hbar i^{l'-l-1}}{2m_e} \sqrt{\frac{4\pi}{3}} \\ &\quad \times S_r^2 [S_r \phi_{\nu l l'}(S_r) \phi'_{\nu l l'}(S_r) - S_r \phi_{\nu l l'}(S_r) \phi'_{\nu l l'}(S_r) - \phi_{\nu l l'}(S_r) \phi_{\nu l l'}(S_r)] \mathbf{G}. \end{aligned} \quad (28)$$

The derivation of the other three terms in expression (18) is similar—one must simply incorporate the energy derivative of the partial wave. The results for all four terms are listed in the following section and may be used in conjunction with expression (18) to compute the optical matrix elements. The matrix elements of the velocity operator are as follows:

$$\begin{aligned} \langle \phi_{\nu L'}(\mathbf{r}) | \mathbf{v} | \phi_{\nu L}(\mathbf{r}) \rangle &= \frac{i^{l'-l-1}}{\hbar} \sqrt{\frac{4\pi}{3}} \\ &\quad \times \left[ (\epsilon_{\nu l l} - \epsilon_{\nu l l'}) \int_0^{S_r} \phi_{\nu l l'}(x) x \phi_{\nu l l}(x) x^2 dx \right. \end{aligned}$$

$$\begin{aligned}
& -\frac{\hbar^2}{2m_e} S_i^2 [S_i \phi_{vll'}(S_i) \phi'_{vll'}(S_i) - S_i \phi_{vll'}(S_i) \phi'_{vll}(S_i) - \phi_{vll'}(S_i) \phi_{vll}(S_i)] \Big] G \\
\langle \phi_{vL'}(\mathbf{r}) | v | \phi_{vL}(\mathbf{r}) \rangle &= \frac{i^{l'-l-1}}{\hbar} \sqrt{\frac{4\pi}{3}} \\
& \times \left[ \int_0^{S_i} \phi_{vll'}(x) x \phi_{vll}(x) x^2 dx + (\epsilon_{vll} - \epsilon_{vll'}) \int_0^{S_i} \phi_{vll'}(x) x \dot{\phi}_{vll}(x) x^2 dx \right. \\
& \left. - \frac{\hbar^2}{2m_e} S_i^2 [S_i \dot{\phi}_{vll}(S_i) \phi'_{vll'}(S_i) - S_i \dot{\phi}_{vll'}(S_i) \phi'_{vll}(S_i) - \dot{\phi}_{vll'}(S_i) \dot{\phi}_{vll}(S_i)] \right] G \\
\langle \dot{\phi}_{vL'}(\mathbf{r}) | v | \phi_{vL}(\mathbf{r}) \rangle &= \frac{i^{l'-l-1}}{\hbar} \sqrt{\frac{4\pi}{3}} \\
& \times \left[ (\epsilon_{vll} - \epsilon_{vll'}) \int_0^{S_i} \dot{\phi}_{vll'}(x) x \phi_{vll}(x) x^2 dx - \int_0^{S_i} \phi_{vll'}(x) x \phi_{vll}(x) x^2 dx \right. \\
& \left. - \frac{\hbar^2}{2m_e} S_i^2 [S_i \dot{\phi}_{vll}(S_i) \dot{\phi}'_{vll'}(S_i) - S_i \dot{\phi}_{vll'}(S_i) \dot{\phi}'_{vll}(S_i) - \dot{\phi}_{vll'}(S_i) \dot{\phi}_{vll}(S_i)] \right] G \\
\langle \dot{\phi}_{vL'}(\mathbf{r}) | v | \dot{\phi}_{vL}(\mathbf{r}) \rangle &= \frac{i^{l'-l-1}}{\hbar} \sqrt{\frac{4\pi}{3}} \\
& \times \left[ \int_0^{S_i} \dot{\phi}_{vll'}(x) x \phi_{vll}(x) x^2 dx - \int_0^{S_i} \phi_{vll'}(x) x \dot{\phi}_{vll}(x) x^2 dx \right. \\
& \left. + (\epsilon_{vll} - \epsilon_{vll'}) \int_0^{S_i} \dot{\phi}_{vll'}(x) x \dot{\phi}_{vll}(x) x^2 dx \right. \\
& \left. - \frac{\hbar^2}{2m_e} S_i^2 [S_i \dot{\phi}_{vll}(S_i) \dot{\phi}'_{vll'}(S_i) - S_i \dot{\phi}_{vll'}(S_i) \dot{\phi}'_{vll}(S_i) - \dot{\phi}_{vll'}(S_i) \dot{\phi}_{vll}(S_i)] \right] G.
\end{aligned}$$

Equation (2) remains valid in the presence of non-local potentials. If these potentials are expressed as  $tl$ -dependent functions of  $r$ , the above velocity matrix elements continue to be valid.

#### 4. Band-structure calculation

In our calculations we have used LMTO theory in the atomic-sphere approximation (ASA) [7, 8]. In this framework the matrix elements have been calculated using a fully self-consistent procedure. The self-consistency was imposed on total charge densities, the energies  $E_{vll}$  and the potential parameters. Included in the calculation are the combined corrections terms and relativistic corrections with the exception of spin-orbit coupling. For FeSi we have used the CsCl structure with a diatomic basis of Fe at (0, 0, 0) and Si at ( $a/2$ ,  $a/2$ ,  $a/2$ ). The lattice constant is  $a = 2.717 \text{ \AA}$  and the muffin-tin radius is  $0.4330a$ . In the atomic-sphere approximation for Si empty spheres have been introduced in order to obtain a satisfactory packing ratio for the crystal lattice. The cell of Si has the FCC structure with a basis composed of two silicon atoms respectively at (0, 0, 0) and ( $a/4$ ,  $a/4$ ,  $a/4$ ) and two empty spheres at ( $a/2$ ,  $a/2$ ,  $a/2$ ) and ( $-a/4$ ,  $-a/4$ ,  $-a/4$ ). The lattice constant,  $a$ , is  $5.429 \text{ \AA}$  and the muffin-tin radius is  $0.2165a$ . In order to perform the calculation we have used a uniform mesh of 220 and 240 points, for FeSi and Si respectively in the irreducible wedge of the Brillouin zone. Figures 1 and 2 show the band structures and densities of states corresponding to FeSi and Si respectively.



## The Imaginary Part of the Dielectric Function

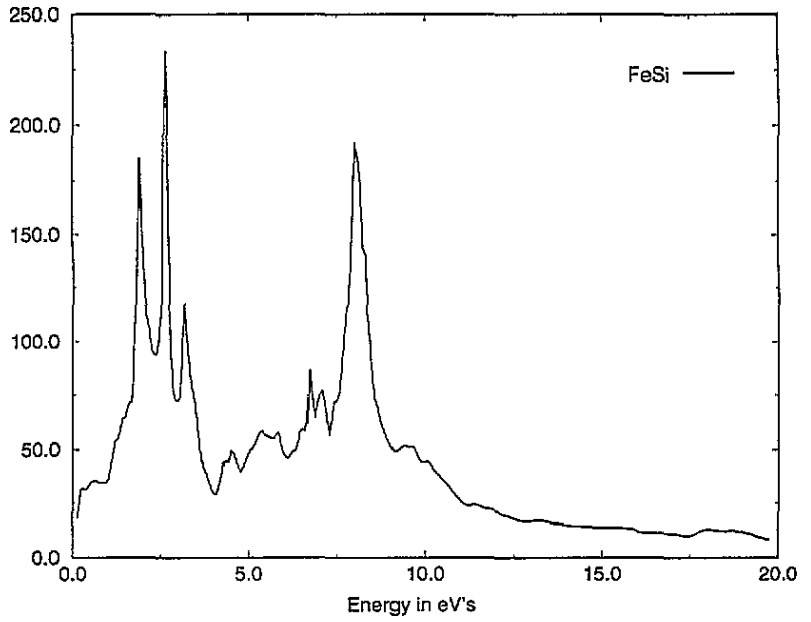


Figure 3. The imaginary part of the dielectric function calculated for FeSi.

## The Joint Density-of-States

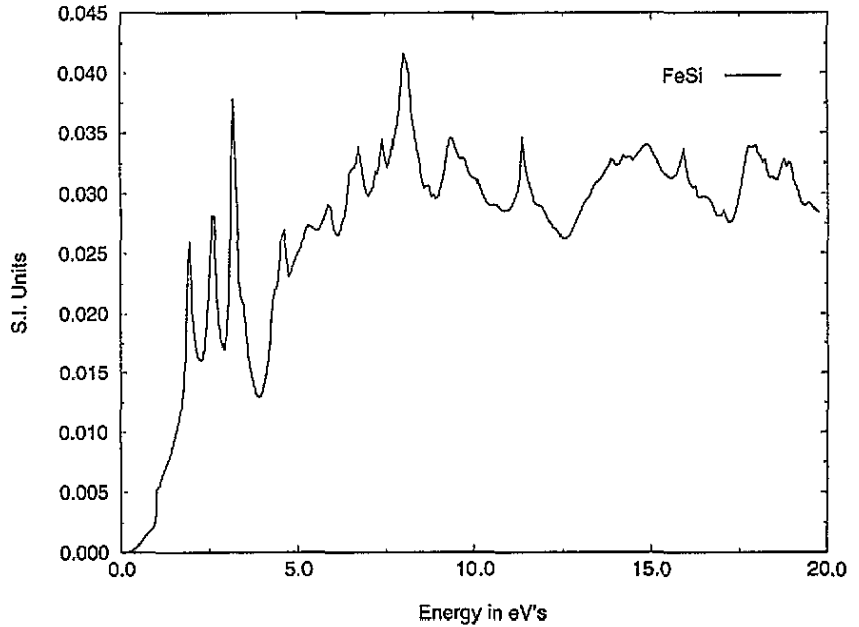


Figure 4. The joint density of states calculated for FeSi.

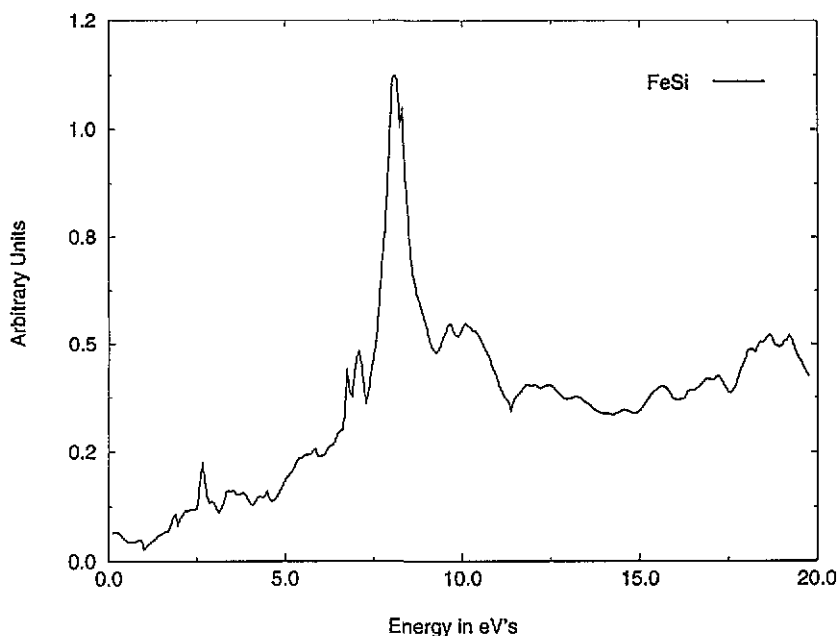
Contribution of Matrix Elements,  $M(E)$ 

Figure 5. An estimate of the energy dependence of the contribution of the matrix elements,  $M(E)$ , to the optical properties of FeSi.

### 5. Integration in $k$ -space

In order to compute the imaginary part of the dielectric function (5) and the joint density of states (6) one must perform an integration over the Brillouin zone. Within the formalism of LMTO theory the tetrahedron method [10, 11] is generally used. In this method the dielectric function is expressed as an integral over the constant-energy surface  $E_c(k) - E_v(k) = E$ :

$$\epsilon_2(E) = \frac{\hbar^2 e^2}{3\pi m^2 E^2} \sum_v \sum_c \int \frac{dS_E}{|\nabla_k(E_c(k) - E_v(k))|_{E_c(k) - E_v(k) = E}} \left| \langle \Psi^{ck} | \mathbf{P} | \Psi^{vk} \rangle \right|^2 \quad (29)$$

and the joint density of states is similarly defined by

$$J(E) = \sum_v \sum_c J_{cv}(E) = \frac{1}{4\pi^3} \sum_v \sum_c \int \frac{dS_E}{|\nabla_k(E_c(k) - E_v(k))|_{E_c(k) - E_v(k) = E}}. \quad (30)$$

The eigenvalues and eigenvectors are then calculated on a mesh in the irreducible Brillouin zone. This zone is divided into tetrahedra of equal volume (although this is not a necessary condition), the mesh of  $k$ -points defining the corners of each tetrahedron. The interpolated function is continuous at the boundaries of the tetrahedra and the irreducible Brillouin zone is completely divided into tetrahedra. The result of the interpolation is that the integrand depends only on the corner energies for a given energy band and the volume of the tetrahedra but not on their shape.

Lehmann and Taut [11] have shown how a function of  $k$  such as the  $tl$ -character (see, for example, Skriver [8]), used to calculate density of states, or the matrix elements squared  $|\langle \Psi^{ck} | \mathbf{P} | \Psi^{vk} \rangle|^2$ , used to calculate optical properties, may also be linearly interpolated within each tetrahedron. We have found that interpolating the  $tl$ -character produces no

### The Imaginary Part of the Dielectric Function

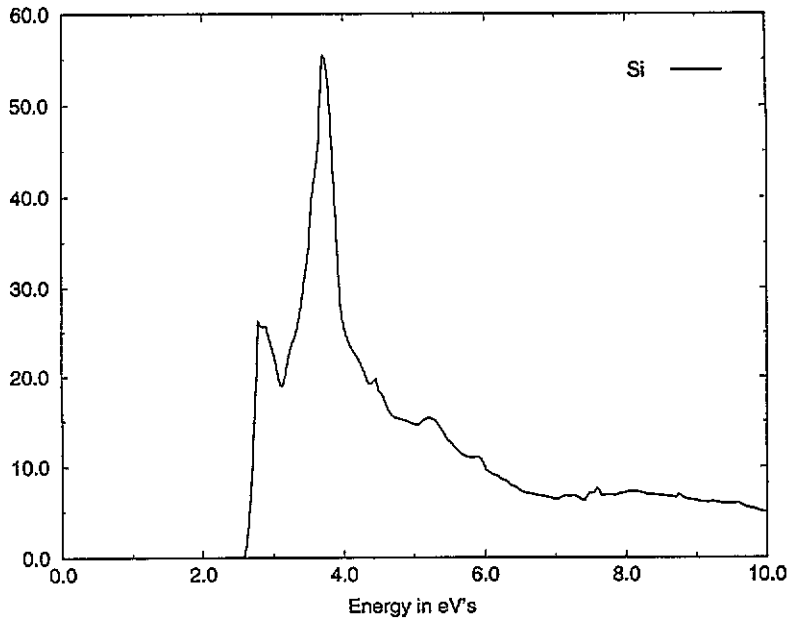


Figure 6. The imaginary part of the dielectric function calculated for Si.

visible difference in the density of states compared to using an average value for the  $tl$ -character. However, for optical properties a small but visible improvement in the spectra is obtained by linearly interpolating the matrix elements squared as opposed to using their average value.

### 6. Numerical results

To demonstrate the validity of our method we have applied it for calculating the imaginary part of the dielectric function for FeSi and Si. Figures 3 and 4 show  $\epsilon_2(E)$  and the corresponding joint density of states respectively for FeSi. The large resonance located at around 8 eV in the optical spectrum (figure 3) cannot be totally accounted for by the corresponding peak in the joint density of states (figure 4). In order to investigate this resonance further, we have crudely obtained the energy dependence of the contribution from the matrix elements,  $M(E)$ , by dividing the  $\epsilon_2(E)$  spectrum by that of the joint density of states, i.e.

$$M(E) \sim \epsilon_2(E) / \sum_v \sum_c J_{cv}(E). \quad (31)$$

This rough approximation can, however, yield useful information and it may be seen from figure 5 that the matrix elements have a strong contribution in the region from 7 to 11 eV for FeSi. This contribution encourages transitions over this energy range and hence the resonance at 8 eV in the optical spectrum. Nevertheless it is not possible to make any more definite conclusions as to which interband transitions contribute significantly.

The results for Si are shown in figure 6 the optical spectrum  $\epsilon_2(\omega)$  and in figure 7 the joint density of states. We are satisfied that our optical spectrum for Si shows reasonable

## The Joint Density-of-States

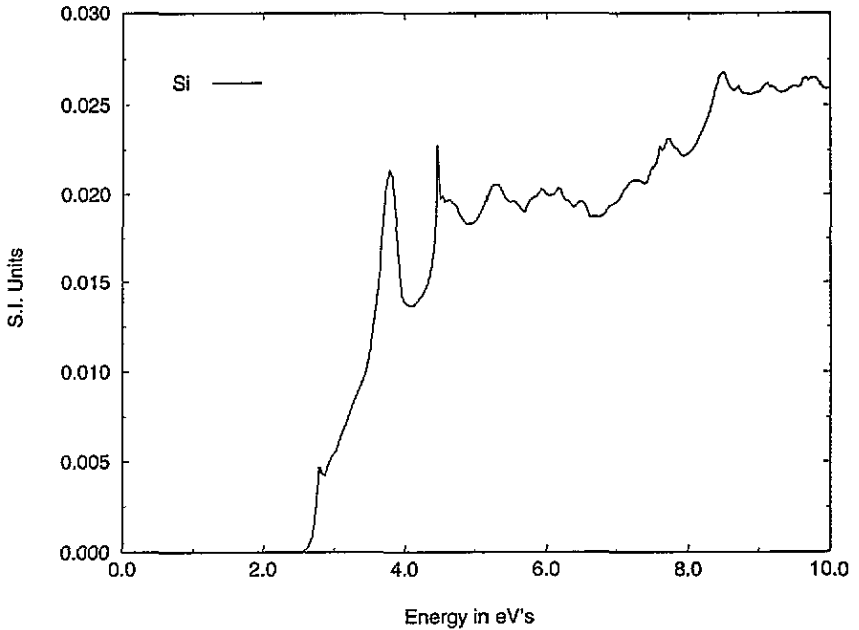


Figure 7. The joint density of states calculated for Si.

agreement with other theoretical calculations [12] and experimental results [13]. At energies above 4.5 eV for Si the contribution from the matrix elements and the  $1/E^2$ -term combine in principle to reduce the optical spectrum to zero at high energies. However, we can see from the optical spectrum of Si that this process does not work adequately and we are left with an unphysical 'high-energy tail'. At this point it is useful to consider what effect this high-energy tail will have on the normal sum rules [15]. Indeed if we use the Thomas-Reiche-Kuhn sum rule to calculate the effective number of valence electrons, termed  $n_{\text{eff}}(\infty)$  where  $N$  is the atomic density:

$$n_{\text{eff}}(E) = \frac{m_e}{2\pi^2 e^2 \hbar N} \int_0^E E \epsilon_2(E) dE \quad (32)$$

we find that the sum rule is violated at energies above  $\sim 8.44$  eV for FeSi and  $\sim 9.3$  eV for Si. The existence of these high-energy tails is not, however, unique to our calculations (see, for example, Del Sole and Girlanda [12]). Scissors operators may be used to adjust the spectra artificially for better agreement with experimental values; however, more rigorous theories must be developed in order to calculate the observed optical spectra.

## 7. Concluding remarks

We have shown in this paper how a new method may be used to calculate the optical properties of solids using a gauge-independent formalism for LMTO theory. The above theoretical expressions may be computed using output data from the LMTO band-structure package. The  $k$ -space integration is carried out using the tetrahedron method. This method is also suitable for Hamiltonians in which non-local potentials are included. The results

given here have been calculated for FeSi and for crystalline Si, in which empty spheres were employed.

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### Appendix 1

The product of three spherical harmonics may be calculated from the Gaunt formula

$$\int Y_{l_3}^{m_3} Y_{l_2}^{m_2} Y_{l_1}^{m_1} d\omega = \left[ \frac{(2l_1 + 1)(2l_2 + 2)}{4\pi(2l_3 + 1)} \right]^{1/2} C(l_1 l_2 l_3; m_1 m_2 m_3) C(l_1 l_2 l_3; 000) \quad (\text{A1})$$

where the Clebsch–Gordan coefficients for the coupling of two angular momenta may be calculated using

$$\begin{aligned} C(l_1 l_2 l_3; m_1 m_2 m_3) = & \delta_{m_1, m_1 + m_2} \left[ (2l_3 + 1) \frac{(l_1 + l_2 - l_3)! (l_3 + l_1 - l_2)! (l_3 + l_2 - l_1)!}{(l_1 + l_2 + l_3 + 1)!} \right. \\ & \left. \times (l_1 + m_1)! (l_1 - m_1)! (l_2 + m_2)! (l_2 - m_2)! (l_3 + m_3)! (l_3 - m_3)! \right]^{1/2} \\ & \times \sum_v \frac{(-1)^v}{v!} [(l_1 + l_2 - l_3 - v)! (l_1 - m_1 - v)! (l_2 + m_2 - v)! \\ & \times (l_3 - l_2 + m_1 + v)! (l_3 - l_1 - m_2 + v)!]^{-1} \end{aligned} \quad (\text{A2})$$

and the summation over  $v$  assumes all non-negative factorial arguments.

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