PHYSICAL REVIEW B VOLUME 51, NUMBER 8 15 FEBRUARY 1995-II

Electromagnetic fields and dielectric response in empirical tight-binding theory

M. Graf and P. Vogl

Walter Schottky Institut and Physik Department, Technische Universität München, 85748 Garching, Germany

(Received 20 September 1994; revised manuscript received 16 November 1994)

Relativistic and nonrelativistic empirical tight-binding theory is generalized to incorporate time-dependent electromagnetic fields in a gauge-invariant manner that does not introduce any extra adjustable parameters. Based on this approach, it is shown that explicit expressions can be derived for the effective mass tensor, the effective Landé g factor, the current, the frequency-dependent transverse dielectric function, and the wave-vector-, and frequency-dependent longitudinal dielectric function. A finite basis analogue of the optical f-sum rule is derived and shown to impose a condition on tight-binding parameters.

I. INTRODUCTION

Since the pioneering work of Harrison,[1] it has become evident that empirical tight-binding theory is the tool of choice when one is looking for a physically transparent, qualitative picture of electronic or structural properties of solids. Tight-binding theory has even been useful as a semiquantitative tool in solid-state physics and chemistry, particularly when applied to very large quantum mechanical systems involving hundreds or thousands of atoms. The empirical tight-binding method has been applied to bulk band structures,[2–4] superlattices,[5] amorphous solids,[6] surfaces,[7] transition metals,[8] structural phase transformations,[9] lattice dynamics,[10] molecular dynamics,[11,12] and many other situations, to cite just a few applications.

The crucial results of tight-binding theory as developed by Harrison[1] may be summarized as follows. While it is difficult to characterize the crystal Hamiltonian H and a basis of orthogonalized atomiclike functions $|I\rangle$ separately in any simple way, the combination of the two elements, i.e., the *Hamiltonian matrix elements* $\langle I|H|I'\rangle$, follow very simple chemical trends indeed. The diagonal matrix elements are proportional to atomic ionization energies and the off-diagonal matrix elements are, to a good approximation, universal functions of the interatomic distance. While many more refined tight-binding parametrizations have been developed (e.g., in Refs. 2, 4, and 13), it is this approximate universality that determines the overall chemical trends and ensures consistency between different calculated properties, at least within one scheme of parameters.

As a consequence of these results, most applications of tight-binding theory rest entirely on a formulation in terms of Hamiltonian matrix elements. Unfortunately, this is insufficient to incorporate electromagnetic fields $\Phi(\mathbf{r},t),\mathbf{A}(\mathbf{r},t)$ into the theory or to calculate linear response functions, since they require the knowledge of additional matrix elements such as momentum or current matrix elements. Therefore one usually introduces a fair number of extra parameters to calculate, for example, optical properties of solids.[14,15]

The purpose of this paper is to show that time-dependent electromagnetic fields can be incorporated in empirical tight-binding theory in a way that is manifestly gauge invariant, guarantees charge conservation, and does not introduce any extra free parameters. Within this scheme, response functions can be calculated without additional approximations or assumptions.

In the framework of one-band models and envelope function approaches, magnetic fields have been incorporated into tight-binding theory before by invoking the so-called Peierls substitution.[16–18] Static electric fields and static screening have also been treated in tight-binding before.[19–21] In this paper, we generalize these models to arbitrary electromagnetic fields and general multiband tight-binding Hamiltonians and focus on the aspects of gauge invariance, charge conservation, and sum rules. In fact, the present work was stimulated by a recent paper of Lew Yan Voon and Ram-Mohan[22] who showed that the momentum matrix elements can be expressed entirely in terms of Hamiltonian matrix elements. However, as we will show in detail below, this relation must be generalized to correctly yield observables such as effective masses or optical dielectric functions.

In Sec. II, we briefly set up our notation. In Sec. III, we show that $\mathbf{k}\cdot\mathbf{p}$ theory can be quite generally recast into a form that solely refers to Hamiltonian matrix elements. An explicit expression for the effective mass tensor is derived. In Sec. IV, the main section of this paper, a gauge-invariant modification of the tight-binding Hamiltonian matrix elements is proposed that takes into account electromagnetic fields. In Secs. V and VI, these results are used to derive explicit expressions for the transverse and longitudinal dielectric function, respectively. In Sec. A, we also derive a finite-basis analogue of the f-sum rule that imposes constraints on tight-binding parameters. In Sec. VI, the longitudinal dielectric function is calculated, including charge self-consistency in the tight-binding Hamiltonian. Electromagnetic fields can also be incorporated by means of an envelope function approach, as shown in Sec. VII. This method is used to derive a tight-binding expression for the Landé factor. The proofs of gauge invariance and charge conservation are given in the Appendixes.

II. NOTATION

In the empirical tight-binding scheme,[1] the Hamiltonian is represented in terms of an orthogonal basis set of atomiclike orbitals $|\alpha, I\rangle$ that are characterized by a site index I and a symmetry-related index α that specifies the angular-momentum and spin quantum numbers of the atomic orbitals on that site. In the two-center approximation, the Hamiltonian matrix elements depend only on the difference vector between sites; additionally, they are usually restricted to first or second neighbors. Both approximations greatly reduce the number of free parameters. We invoke the two-center approximation throughout this paper, mainly to be able to use a simple notation.

The on-site and off-site Hamiltonian matrix elements are denoted by, respectively,

$$\begin{aligned} \epsilon_{\alpha I} &= \langle \alpha, I|H|\alpha, I\rangle \ , \\ t_{\alpha'\alpha}(\mathbf{R}_{I'} - \mathbf{R}_I) &= \langle \alpha', I'|H|\alpha, I\rangle \ . \end{aligned} \tag{1}$$

Following the work of Chadi,[23] we assume relativistic effects to affect only intra-atomic Hamiltonian matrix elements, $I' = I$. In particular, the spin-orbit interaction is assumed to couple only intra-atomic states with nonzero angular momentum.[23]

In this paper, we focus on periodic crystals and denote the lattice vectors by $\mathbf{R}_I = \mathbf{R}_L + \mathbf{R}_\tau$ where L labels the unit cells and τ the different atoms within the unit cell. In order to avoid too many indices in the matrix elements, it is convenient to lump together the orbital index α and the intracell site index τ into a single index that we also label α. Henceforth, a sum over α implies a sum over *all* orbital states in the unit cell. The lattice vectors are written as $\mathbf{R}_I = \mathbf{R}_{\alpha L}$.

We now form Bloch basis functions that are characterized by the crystal momentum $\mathbf{k}$,

$$|\alpha, \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_L e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha L}} \, |\alpha, L\rangle \ , \tag{2}$$

where N is the number of unit cells. In this basis, the Hamiltonian matrix reads

$$\begin{aligned} H_{\alpha',\alpha}(\mathbf{k}) &= \langle \alpha', \mathbf{k}|H|\alpha, \mathbf{k}\rangle \\ &= \sum_L e^{i\mathbf{k}\cdot(\mathbf{R}_{\alpha' L} - \mathbf{R}_\alpha)} \, t_{\alpha',\alpha}(\mathbf{R}_{\alpha' L} - \mathbf{R}_\alpha) \\ &\quad + \epsilon_\alpha \, \delta_{\alpha'\alpha} \ , \end{aligned} \tag{3}$$

where $\mathbf{R}_\alpha = \mathbf{R}_{\alpha 0}$. Its dimension equals the number of orbitals per atom times the number of atoms within the unit cell. The Bloch eigenfunctions of this Hamiltonian are denoted by $|n\mathbf{k}\rangle$, where n labels the energy bands and includes the Kramers index if spin is included. We expand these eigenfunctions in terms of the Bloch basis functions of Eq. (2), and define the coefficients $\mathbf{C}(n\mathbf{k})$ by the relation

$$|n\mathbf{k}\rangle = \sum_\alpha C_\alpha(n\mathbf{k})|\alpha, \mathbf{k}\rangle \ . \tag{4}$$

III. EFFECTIVE MASS TENSOR

The standard $\mathbf{k}\cdot\mathbf{p}$ theory is based on the expansion of $\mathbf{H}(\mathbf{k})$ in Eq. (3) around some wave vector $\mathbf{k}^*$ and utilizes the fact that the kinetic energy is quadratic in wave vector. In a tight-binding representation, however, the Hamiltonian matrix in Eq. (3) contains terms to all orders in $\mathbf{k}$. In order to derive an explicit expression for the effective mass in this situation, we therefore expand Eq. (3) in powers of $(\mathbf{k} - \mathbf{k}^*)$. This gives, in matrix notation,

$$\begin{aligned} \mathbf{H}(\mathbf{k}) &= \mathbf{H}(\mathbf{k}^*) + \nabla_{\mathbf{k}^*}\mathbf{H}(\mathbf{k}^*)\cdot(\mathbf{k} - \mathbf{k}^*) \\ &\quad + \frac{1}{2}(\mathbf{k} - \mathbf{k}^*)\cdot\nabla_{\mathbf{k}^*}\nabla_{\mathbf{k}^*}\mathbf{H}(\mathbf{k}^*)\cdot(\mathbf{k} - \mathbf{k}^*) \\ &\quad + O[(\mathbf{k} - \mathbf{k}^*)^3] \ . \end{aligned} \tag{5}$$

For the effective mass, we only need $\mathbf{H}(\mathbf{k})$ up to the second order in $(\mathbf{k} - \mathbf{k}^*)$. We now define an *effective* momentum operator $\mathbf{p}$ and a kinetic-energy-related operator $\mathbf{T}$,

$$\begin{aligned} \mathbf{p}_{nn'}(\mathbf{k}^*) &= \frac{m_0}{\hbar}\mathbf{C}^\dagger(n\mathbf{k}^*)\nabla_{\mathbf{k}^*}\mathbf{H}(\mathbf{k}^*)\mathbf{C}(n'\mathbf{k}^*) \\ &= \frac{m_0}{\hbar}\sum_{\alpha',\alpha} C^*_{\alpha'}(n\mathbf{k}^*)\sum_L i(\mathbf{R}_{\alpha' L} - \mathbf{R}_\alpha) \\ &\quad \times e^{i\mathbf{k}^*\cdot(\mathbf{R}_{\alpha' L} - \mathbf{R}_\alpha)} t_{\alpha',\alpha}(\mathbf{R}_{\alpha' L} - \mathbf{R}_\alpha) \\ &\quad \times C_\alpha(n'\mathbf{k}^*) \ , \\ \mathbf{T}_{nn'}(\mathbf{k}^*) &= \frac{m_0}{\hbar^2}\mathbf{C}^\dagger(n\mathbf{k}^*)\nabla_{\mathbf{k}^*}\nabla_{\mathbf{k}^*}\mathbf{H}(\mathbf{k}^*)\mathbf{C}(n'\mathbf{k}^*) \ , \end{aligned} \tag{6}$$

where m_0 is the free electron mass. With these definitions, the matrix elements of $\mathbf{H}(\mathbf{k})$ in the Bloch basis $|n\mathbf{k}^*\rangle$ can now be written as

$$\begin{aligned} H_{n,n'}(\mathbf{k}) &= E_n(\mathbf{k}^*)\delta_{n,n'} + \frac{\hbar}{m_0}\mathbf{p}_{nn'}(\mathbf{k}^*)\cdot(\mathbf{k} - \mathbf{k}^*) + \frac{\hbar^2}{2m_0}(\mathbf{k} - \mathbf{k}^*)\cdot\mathbf{T}_{nn'}(\mathbf{k}^*)\cdot(\mathbf{k} - \mathbf{k}^*) \\ &\quad + (\mathbf{k} - \mathbf{k}^*)\cdot\frac{\hbar^2}{m_0^2}\sum_{m\neq n,n'}\frac{\mathbf{p}_{nm}(\mathbf{k}^*)\mathbf{p}_{mn'}(\mathbf{k}^*)}{E_n(\mathbf{k}^*) - E_m(\mathbf{k}^*)}\cdot(\mathbf{k} - \mathbf{k}^*). \end{aligned} \tag{7}$$

For a nondegenerate band edge state, this expression yields the effective mass tensor in terms of the operators $\mathbf{p}$ and $\mathbf{T}$,

$$\left(\frac{1}{\mathbf{m}_n(\mathbf{k}^*)}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E_n(\mathbf{k}^*)}{\partial k_i^* \partial k_j^*}$$
$$= \frac{1}{m_0}[\mathbf{T}_{nn}(\mathbf{k}^*)]_{ij} + \frac{1}{m_0^2}\sum_{m\neq n}\frac{\mathbf{p}^i_{nm}(\mathbf{k}^*)\mathbf{p}^j_{mn}(\mathbf{k}^*) + \mathbf{p}^j_{nm}(\mathbf{k}^*)\mathbf{p}^i_{mn}(\mathbf{k}^*)}{E_n(\mathbf{k}^*) - E_m(\mathbf{k}^*)} . \tag{8}$$

This equation has a similar form as the standard expression in the Kohn-Luttinger basis but there are several significant differences. First, there is an intraband term $\mathbf{T}_{nn}$ which is unity in the Kohn-Luttinger basis. This additional term in the tight-binding basis is of the same order as or even larger than the interband term in Eq. (8) as will be seen later (Sec. V). This term was not taken into account in Ref. 22. Second, the operator $\mathbf{p}$ is related to but not equal to the momentum operator. One of the consequences is that the spin-orbit interaction enters Eq. (6) only via the eigenfunction coefficients; there is no separate additive term to the operator $\mathbf{p}$ in the tight-binding basis. Further properties of $\mathbf{p}$ and $\mathbf{T}$ will be discussed in Secs. V and VI.

IV. TIGHT-BINDING HAMILTONIAN WITH ELECTROMAGNETIC FIELDS

First, we discuss the incorporation of vector potentials into the tight-binding approach. Given a general Hamiltonian $H(\mathbf{r},\mathbf{p})$ that is a function of the position and momentum operators, minimal coupling to a vector potential $\mathbf{A}(\mathbf{r},t)$ can be achieved by the transformation[16]

$$\exp\left[-\frac{ie}{\hbar c}\int^{\mathbf{r}} \mathbf{A}(\mathbf{s},t)\cdot d\mathbf{s}\right] H(\mathbf{r},\mathbf{p}) \times \exp\left[\frac{ie}{\hbar c}\int^{\mathbf{r}} \mathbf{A}(\mathbf{s},t)\cdot d\mathbf{s}\right] = H\left(\mathbf{r},\mathbf{p}+\frac{e}{c}\mathbf{A}(\mathbf{r},t)\right) . \tag{9}$$

In the spirit of the two-center approximation, this becomes in a tight-binding representation

$$\langle\alpha',L'|H\left(\mathbf{r},\mathbf{p}+\frac{e}{c}\mathbf{A}(\mathbf{r},t)\right)|\alpha,L\rangle = \exp\left[-\frac{ie}{\hbar c}\int^{\mathbf{R}_{\alpha'L'}} \mathbf{A}(\mathbf{s},t)\cdot d\mathbf{s}\right]\langle\alpha',L'|H(\mathbf{r},\mathbf{p})|\alpha,L\rangle \exp\left[\frac{ie}{\hbar c}\int^{\mathbf{R}_{\alpha L}} \mathbf{A}(\mathbf{s},t)\cdot d\mathbf{s}\right]$$
$$= \exp\left[-\frac{ie}{\hbar c}\int_{\mathbf{R}_{\alpha L}}^{\mathbf{R}_{\alpha'L'}} \mathbf{A}(\mathbf{s},t)\cdot d\mathbf{s}\right]\langle\alpha',L'|H(\mathbf{r},\mathbf{p})|\alpha,L\rangle . \tag{10}$$

For nonzero magnetic fields, the contour integral in this equation is path dependent and we have to select a concrete path. For all field strengths of interest in a solid, we can safely assume the fields to excite only extended states. Consequently, we require this integral to vanish for $\mathbf{R}_I = \mathbf{R}_{I'}$. Obviously, the simplest path that obeys this condition is the line connecting the two lattice sites. Assuming $\mathbf{A}(\mathbf{r},t)$ does not vary strongly along this path, one is led to

$$\int_{\mathbf{R}}^{\mathbf{R}'} \mathbf{A}(\mathbf{s},t)\cdot d\mathbf{s} = (\mathbf{R}'-\mathbf{R})\cdot\frac{1}{2}[\mathbf{A}(\mathbf{R}',t)+\mathbf{A}(\mathbf{R},t)] , \tag{11}$$

where we have omitted the site indices in $\mathbf{R},\mathbf{R}'$ for brevity. Even though alternative paths could be chosen as well, Eq. (11) does have the advantage of avoiding extra adjustable parameters. In any case, Eq. (11) is the only essential assumption we make. From now on, gauge invariance dictates all further steps.

In particular, it is consistent with this treatment of the vector potential to assume that a scalar potential $\Phi(\mathbf{r},t)$ modifies only the diagonal matrix elements of the tight-binding Hamiltonian matrix, and adds a term $-e\Phi(\mathbf{R},t)$ to the on-site energies. In Appendix A we show that this addition, together with Eqs. (10) and (11), indeed satisfies gauge invariance. This treatment of a scalar potential implies the assumption that the potential is constant across an atom. Thus, local field effects on an intra-atomic scale are neglected.

To summarize, a gauge-invariant modification of the tight-binding Hamiltonian matrix elements by electromagnetic potentials is given by

$$\epsilon_{\alpha,\mathbf{R}} = \epsilon^0_{\alpha,\mathbf{R}} - e\,\Phi(\mathbf{R},t) ,$$
$$t_{\alpha',\alpha}(\mathbf{R}'-\mathbf{R}) = t^0_{\alpha',\alpha}(\mathbf{R}'-\mathbf{R}) \times \exp\left[-\frac{ie}{2\hbar c}(\mathbf{R}'-\mathbf{R})\cdot[\mathbf{A}(\mathbf{R}',t) + \mathbf{A}(\mathbf{R},t)]\right] , \tag{12}$$

where the field-free matrix elements are ϵ^0 and t^0. When spin is included, the intra-atomic diagonal matrix elements are to be augmented by the spin contribution to the magnetic moment, $\mu_B \boldsymbol{\sigma}\cdot\mathbf{B}$, where μ_B is the Bohr magneton.

Two limitations of this scheme should be pointed out. First, Eq. (12) is only valid up to field strengths that do not significantly affect intra-atomic states. This is because we use only a small number of (field-independent) basis states.[24] Fortunately, intra-atomic Stark shifts or intra-atomic diamagnetic shifts barely reach the meV scale even for the highest attainable electric or magnetic fields. Second, the present scheme also neglects intra-atomic excitations in the limit of isolated atoms. In fact, the valence states in a solid are extended and one cannot unambiguously discriminate between intra- and inter-atomic transitions. Moreover, the dominant peaks in the optical absorption spectra of nonmetallic systems can often be interpreted as bonding-antibonding or anion-to-cation transitions and these are adequately reproduced by the present model (see Sec. V).[1]

A. Example: magnetic band structure

As a first example, we consider GaAs in an extremely high magnetic field along the [001] direction in order to illustrate a situation where the periodic potential and the magnetic field are of comparable magnitude.[18] Realistically, such a situation can be reached in antidot lattices.[25] Since the present approach applies to any arrangement of atoms and we only wish to illustrate the method, we use the symmetry and tight-binding parameters of bulk GaAs. We have taken the latter parameters from Ref. 4. It is advantageous to choose the magnetic field B in such a way that the flux $\Phi = \mathbf{B} \cdot (\mathbf{a}_1 \times \mathbf{a}_2)/2$ is a rational multiple of the flux quantum $\Phi_0 = hc/e$. Here, $\mathbf{a}_i (i = 1, 2, 3)$ are the bulk primitive lattice vectors with $\mathbf{a}_3$ chosen along the field direction. In this way, the Hamiltonian remains periodic, albeit in a very large supercell.[26] We choose a magnetic flux ratio of

$$\frac{\Phi}{\Phi_0} = \frac{a^2 B}{8\Phi_0} = \frac{1}{160} , \tag{13}$$

where a is the bulk lattice constant. This gives a magnetic unit cell with primitive lattice vectors that are 160 times larger than those of bulk GaAs in the two directions perpendicular to the field. The resulting magnetic Brillouin zone reduces practically to a line when plotted on the same scale as the Brillouin zone of the bulk lattice (see Fig. 1) and leads to a highly degenerate folded band structure along the z direction. Figure 1 shows this energy band structure for the lowest conduction bands, the top of the valence band (at $B = 0$) representing the zero of energy.

The minimum of the conduction band at the Z point in the magnetic Brillouin zone originates in the L point of the underlying bulk zone. Since the effective mass at L is larger than at Γ, the magnetic-field-induced shift of the lowest band state pushes the conduction band minimum at the Γ point *above* the L minimum. In bulk GaAs, this transition to an indirect gap would require rather unrealistic magnetic fields (637 T) but analogous effects in antidot lattices may be observable.

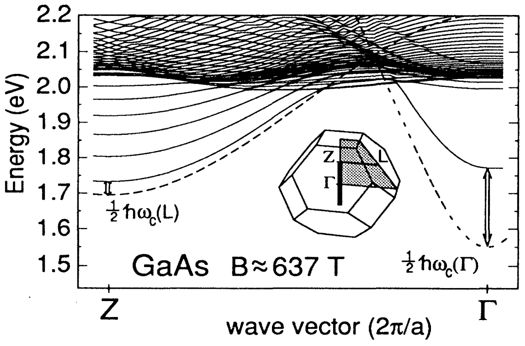

FIG. 1. Calculated magnetic conduction band structure of GaAs in a magnetic field parallel to the [001] direction that corresponds to 637 T (full lines). This magnetic field would be required to make GaAs an indirect gap material. For comparison, we also show the lowest conduction bands for zero magnetic field and for **k** vectors near Γ and L in the fcc Brillouin zone. The latter is depicted as inset. Also shown in the inset is the magnetic Brillouin zone that appears as a thick line along the [001] direction. The cyclotron frequency is denoted by ω_c.

B. Example: Landau states in quantum disk

As a second rather tutorial but elucidating example, we consider a finite nonperiodic structure, namely, a disk-shaped arrangement of atoms on a square lattice [see inset of Fig. 2(a)]. We take into account only a single s orbital per atom, a diagonal matrix element $\epsilon^0 = 4t^0$, and the nearest-neighbor hopping $-t^0$. We apply a magnetic field B perpendicular to the disk, using Eq. (12). For comparison, we additionally solve the two-dimensional effective mass Schrödinger equation

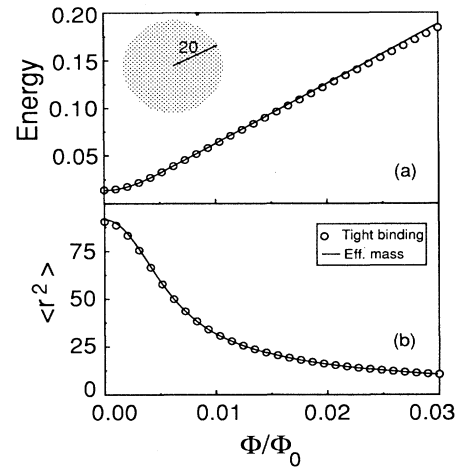

FIG. 2. Energy (in units of the nearest-neighbor matrix element t^0) and mean square radius (in units of the lattice constant a) of the lowest electronic state for atoms arranged in a two-dimensional disk of radius $20a$, as shown in the inset. The full lines have been calculated with the real space effective mass equation and the circles are obtained with the present tight-binding approach.

$$H = \frac{1}{2m^*}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + V(x,y) \qquad (14)$$

in real space, where the potential is taken as $V = 0$ inside the disk and $V = \infty$ at its rim. For low B, nonparabolicity effects are small and thus both approaches should give the same results provided we choose the same band edge effective mass. This amounts to taking $m^* = \hbar^2/(2a^2t^0)$ in Eq. (14). In Fig. 2(a), we depict the ground-state level energy as a function of the flux ratio Φ/Φ_0 ($\Phi = a^2B$), as calculated within the tight-binding approach and Eq. (14), respectively. Indeed, both methods agree excellently with one another. The energy is approximately $\hbar\omega_c/2 = 4\pi t^0\Phi/\Phi_0$ except for $\Phi \to 0$ due to the boundary condition at the rim of the disk. For higher Φ, the tight-binding calculation gives slightly lower energies due to nonparabolicity effects that are neglected in Eq. (14). In Fig. 2(b), we show the mean square radius of the electron density in the ground state, which illustrates the shrinkage of the wave function with increasing B and the diamagnetic susceptibility. Again, both methods yield the same results.

It has previously been pointed out that the total electronic energy in this model does not continuously increase with increasing flux and that this result is likely to be an artifact that stems from the severe truncation of the basis to a single s state with a field-independent coupling matrix element t^0.[24] This effect becomes appreciable only for extremely high fields of the order of 10^4 T (taking $t^0 = 1$ eV and $m^*/m = 0.1$).

V. TRANSVERSE DIELECTRIC FUNCTION

The general results of Sec. IV allow us to derive an explicit expression for the current-current response or, equivalently, the transverse dielectric function without any additional approximations or assumptions. In this section, we limit ourselves to the long-wavelength limit which is the most useful case.

First, we need to calculate the tight-binding matrix elements of the current $\mathbf{j}(\mathbf{r})$ that is induced by a small vector potential $\delta\mathbf{A}(\mathbf{r},t)$. The change in the Hamiltonian is

$$\delta H = -\frac{1}{c}\int \mathbf{j}(\mathbf{r}) \cdot \delta\mathbf{A}(\mathbf{r},t)\; d^3r \,. \qquad (15)$$

In the present context, this equation serves as a definition of the current operator since it provides a relation between the change δH of the Hamiltonian by a field $\delta\mathbf{A}(\mathbf{r},t)$, which can be calculated from Eq. (12), and the field itself. Using Eq. (12), one obtains to first order in $\delta\mathbf{A}(\mathbf{r},t)$

$$\begin{aligned}\langle\alpha', L'|\mathbf{j}(\mathbf{R}_{\alpha''L''},t)|\alpha, L\rangle = {}& \frac{ie}{2\hbar\Omega_{pa}} t^0_{\alpha',\alpha}(\mathbf{R}_{\alpha'L'} - \mathbf{R}_{\alpha L})(\mathbf{R}_{\alpha'L'} - \mathbf{R}_{\alpha L})\;(\delta_{\alpha L,\alpha''L''} + \delta_{\alpha'L',\alpha''L''}) \\ & \times \left\{1 + \frac{ie}{2\hbar c}(\mathbf{R}_{\alpha'L'} - \mathbf{R}_{\alpha L}) \cdot [\delta\mathbf{A}(\mathbf{R}_{\alpha'L'},t) + \delta\mathbf{A}(\mathbf{R}_{\alpha L},t)]\right\}. \qquad (16)\end{aligned}$$

Here, t^0 are the transfer matrix elements for $\delta\mathbf{A} = 0$ and $\Omega_{\rm pa}$ is the volume per atom. When the vector potential is spatially uniform, only the total current operator

$$\langle\alpha', L'|\mathbf{J}(t)|\alpha, L\rangle = \Omega_{\rm pa}\sum_{\alpha'',L''}\langle\alpha', L'|\mathbf{j}(\mathbf{R}_{\alpha''L''},t)|\alpha, L\rangle \qquad (17)$$

enters the correlation functions. Note that the total current averages over all atoms in the unit cell. In the Bloch basis, Eq. (2), this total current matrix can be converted into a more transparent expression. From Eq. (16), one easily obtains

$$\begin{aligned}\langle\alpha', \mathbf{k}|\mathbf{J}(t)|\alpha, \mathbf{k}\rangle &= \mathbf{J}_{\alpha',\alpha}(\mathbf{k},t) \\ &= \frac{e}{\hbar}\nabla_{\mathbf{k}}H_{\alpha',\alpha}(\mathbf{k}) \\ &\quad + \frac{e^2}{\hbar^2 c}\nabla_{\mathbf{k}}\;[\nabla_{\mathbf{k}}H_{\alpha',\alpha}(\mathbf{k}) \cdot \delta\mathbf{A}(t)]\;. \qquad (18)\end{aligned}$$

Therefore the current matrix element becomes in the basis of the Hamiltonian eigenfunctions, Eq. (4),

$$\mathbf{J}_{n',n}(\mathbf{k},t) = \frac{e}{m_0}\mathbf{p}_{n'n}(\mathbf{k}) + \frac{e^2}{m_0^2 c}\mathbf{T}_{n'n}(\mathbf{k}) \cdot \delta\mathbf{A}(t)\;, \qquad (19)$$

where the operators $\mathbf{p}$ and $\mathbf{T}$ have been defined in Eq. (6).

Standard linear response theory gives the thermodynamic average of the total current in terms of the current-current response function,

$$\langle\mathbf{J}(t)\rangle = \langle\mathbf{J}(t)\rangle_0 + \frac{i}{\hbar c}\int_{-\infty}^{t}\langle[\tilde{\mathbf{J}}(t), \tilde{\mathbf{J}}(t')]\rangle_0 \cdot \delta\mathbf{A}(t')\; dt'. \qquad (20)$$

Here, the tilde denotes the interaction picture and $\langle\,\rangle_0$ implies the average to be taken with the equilibrium density matrix. The frequency-dependent transverse conductivity tensor $\boldsymbol{\sigma}$ is defined by $\langle J_i\rangle = \Omega\sum\sigma_{ij}(\omega)\delta E_j(\omega)$, where Ω is the crystal volume, i, j are Cartesian components, and δE is the transverse electric field given by $\delta A_j = ic\delta E_j/\omega$ in the Coulomb gauge. Inserting the current from Eq. (19) into Eq. (20), one obtains the real and imaginary parts of the transverse dielectric susceptibility tensor $\boldsymbol{\chi}(\omega) = i\boldsymbol{\sigma}(\omega)/\omega$, respectively,

$$\begin{aligned}\mathrm{Re}\chi_{ij}(\omega) = {}& \frac{-e^2}{\omega^2 m_0\Omega}\sum_{n,\mathbf{k}} f_n(\mathbf{k})T^{ij}_{nn}(\mathbf{k}) + \frac{e^2}{\omega^2 m_0^2\Omega} \\ & \times\mathcal{P}\sum_{n,m,\mathbf{k}}\frac{[f_n(\mathbf{k}) - f_m(\mathbf{k})]\;p^i_{nm}(\mathbf{k})p^j_{mn}(\mathbf{k})}{\hbar[\omega_{mn}(\mathbf{k}) - \omega]}, \qquad (21)\end{aligned}$$

$$\mathrm{Im}\chi_{ij}(\omega) = \frac{e^2\pi}{\omega^2\hbar m_0^2\Omega}\sum_{n,m,\mathbf{k}}[f_n(\mathbf{k}) - f_m(\mathbf{k})] \times p^i_{nm}(\mathbf{k})\, p^j_{mn}(\mathbf{k})\, \delta(\omega - \omega_{mn}(\mathbf{k})). \tag{22}$$

In this equation, $\mathcal{P}$ denotes the principal value and $\hbar\omega_{mn}(\mathbf{k}) = E_m(\mathbf{k}) - E_n(\mathbf{k})$. The Fermi distribution function in the Bloch eigenstates $|n\mathbf{k}\rangle$ is denoted by $f_n(\mathbf{k})$. In deriving these equations, we have used $f_n(\mathbf{k}) = f_n(-\mathbf{k})$ and $\nabla_\mathbf{k}H(-\mathbf{k}) = -\nabla_\mathbf{k}H(\mathbf{k})$. These relations only hold if the unperturbed Hamiltonian does not contain a finite electromagnetic field.

The second term on the right hand side of Eq. (21) is actually regular for $\omega \to 0$, in spite of its singular appearance. This can be shown explicitly by an algebraic rearrangement of terms, as has been recently pointed out by Sipe and Ghahramani.[27] Following the same steps as in their paper,[27] one ends up with

$$\begin{aligned}\mathrm{Re}\chi_{ij}(\omega) &= \frac{e^2}{\omega^2\Omega}\sum_{n,\mathbf{k}} f_n(\mathbf{k})\left[\frac{-1}{m_0}T^{ij}_{nn}(\mathbf{k}) + \frac{1}{m_0^2}\sum_{m\neq n}\frac{p^i_{nm}(\mathbf{k})p^j_{mn}(\mathbf{k}) + p^j_{nm}(\mathbf{k})p^i_{mn}(\mathbf{k})}{\hbar\omega_{mn}(\mathbf{k})}\right] \\ &\quad + \frac{e^2}{m_0^2\Omega}\mathcal{P}\sum_{n,m,\mathbf{k}}\frac{[f_n(\mathbf{k}) - f_m(\mathbf{k})]\, p^i_{nm}(\mathbf{k})p^j_{mn}(\mathbf{k})}{\omega^2_{nm}(\mathbf{k})\hbar[\omega_{mn}(\mathbf{k}) - \omega]} \\ &= -\frac{e^2}{\omega^2\Omega}\sum_{n,\mathbf{k}} f_n(\mathbf{k})\left(\frac{1}{m_n(\mathbf{k})}\right)^{ij} + \frac{e^2}{m_0^2\Omega}\mathcal{P}\sum_{n,m,\mathbf{k}}\frac{[f_n(\mathbf{k}) - f_m(\mathbf{k})]\;p^i_{nm}(\mathbf{k})p^j_{mn}(\mathbf{k})}{\omega^2_{nm}(\mathbf{k})\hbar(\omega_{mn}(\mathbf{k}) - \omega)}.\end{aligned} \tag{23}$$

Here, Eq. (8) for the effective mass tensor has been used. This final expression for χ or, equivalently, for the transverse dielectric function $\epsilon(\omega) = 1 + 4\pi\chi(\omega)$, is identical to the standard random phase expression, except that the momentum operator is replaced by the operator $\mathbf{p}(\mathbf{k})$ from Eq. (6).

In the case of full bands (e.g., a semiconductor at zero temperature), the first term on the right hand side of the final expression in Eq. (23)—i.e., the $\mathbf{k}$ sum over the inverse effective mass—is zero, since the latter is proportional to the second derivative of a function that is periodic in $\mathbf{k}$.[27] Consequently, this term vanishes for an insulator and χ only contains interband contributions in this case.

In this section, we have focused on the frequency-dependent dielectric response in the long-wavelength limit. The procedure can staightforwardly be generalized to finite wave vectors. If we assume a perturbing vector potential of the form $\delta\mathbf{A}(\mathbf{r},t) = \exp(i\mathbf{q}\cdot\mathbf{r})\delta\mathbf{A}(\mathbf{q},t)$, the current operator follows from Eq. (15), leading to $\mathbf{j}(-\mathbf{q},t) = -c\delta H/\delta\mathbf{A}(\mathbf{q},t)$. In this way one obtains the orbital contributions to the current, in analogy to Eq. (18). In addition, the $\mu_B\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r},t)$ term in the diagonal part of the Hamiltonian leads to a spin contribution to the current that is relevant for the magnetic permeability and is given by

$$\langle\alpha',\mathbf{k}'|\mathbf{j}(\mathbf{q},t)|\alpha,\mathbf{k}\rangle = -\delta_{\mathbf{k}'+\mathbf{q},\mathbf{k}}c\mu_B\mathbf{q} \times\langle\alpha',\mathbf{R}_{\alpha'}|\boldsymbol{\sigma}|\alpha,\mathbf{R}_\alpha\rangle.$$

f-sum rule

The f-sum rule for the diagonal components of the transverse dielectric function $\epsilon(\omega)$ reads

$$\int_0^\infty d\omega\omega\;\mathrm{Im}\epsilon_{ii}(\omega) = \frac{2\pi^2e^2}{m_0\,\Omega_0}N_{\mathrm{val}}\,, \tag{24}$$

where Ω_0 and N_{val} are the volume and number of valence electrons per unit cell, respectively, and $\mathrm{Im}\epsilon$ is the imaginary part of the dielectric function. This equation is usually derived by forming matrix elements on the right and left hand sides of the commutator relation $[x_i,H] = i\hbar p_i/m_0$ and invoking the orthogonality and completeness of the Hamiltonian eigenfunctions. This relation cannot hold in a representation with only a finite number of basis states. First of all, x_i and p_i cannot obey the commutator relation $[\mathbf{x},\mathbf{p}] = i\hbar\mathbf{1}$ in any finite basis set. This can be seen by taking the trace of both sides and noting that $\mathrm{Tr}(AB) = \mathrm{Tr}(BA)$ holds for any finite matrices A, B. Second, assume that all energy bands are completely occupied. Then it follows that $\mathrm{Im}\epsilon = 0$, in contradiction to Eq. (24).

Nevertheless, an analog of Eq. (24) for the present finite tight-binding basis can be derived. Consider a semiconductor at zero temperature where the Fermi factors of the energy bands are either 1 or zero. With the help of Eqs. (8) and (22), one obtains the identity

$$\int_0^\infty d\omega\;\omega\;\mathrm{Im}\epsilon_{ii}(\omega) = \frac{2\pi^2e^2}{m_0\Omega_0}\frac{1}{N}\sum_{\mathbf{k},\,n\in\mathrm{VB}}T^{ii}_{nn}(\mathbf{k})\,, \tag{25}$$

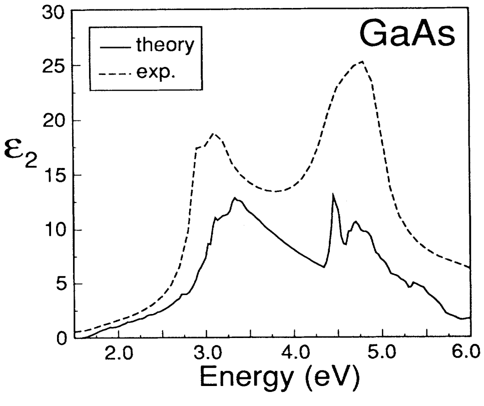

FIG. 3. Calculated imaginary part of the transverse dielectric function as function of energy in bulk GaAs. The experimental results (dashed line) are from Ref. 33.

where the summation on the right hand side extends over the valence bands (VB's) only. While this equation is automatically obeyed for any set of tight-binding parameters, it is clear from the analysis given above that in general

$$\frac{1}{N}\sum_{\mathbf{k},\, n\in \mathrm{VB}} T^{ii}_{nn}(\mathbf{k}) \neq N_{\mathrm{val}} \,. \tag{26}$$

However, if one requires this relation to become an equality, it provides an additional condition for good tight-binding parameters. This may be useful in the calculation of optical properties. Actually, most published sets of parameters do not do too well in this respect since $\mathrm{Im}\epsilon_{\perp}$ depends sensitively on the joint density of valence and conduction bands near the L point and the conduction bands are usually not very accurately modeled in tight binding. As an example, we show the dielectric function of GaAs in Fig. 3, as obtained with the parameters of Priester *et al.*[4] These authors employed a relativistic sp^3s^* nearest-neighbor tight-binding model. In this case, the left hand side of Eq. (26) gives 9.15 instead of 8. Still, the dielectric function is seen to be somewhat smaller than the experimental one for small frequencies (Fig. 3). Other tight-binding parametrizations, such as Ref. 2, give similar results.

VI. LONGITUDINAL DIELECTRIC FUNCTION

Simple tight-binding models for the static longitudinal dielectric function have already been developed in Refs. 19 and 20. In the framework of the bond-orbital approximation (which neglects the coupling between bonding and antibonding states), an illustrative analytic expression has been derived in Ref. 19.

In this section, we derive a general expression for the longitudinal susceptibility and dielectric function in a crystal. Linear response functions are, in a Wannier or tight-binding representation, matrices of the form $\chi_{\alpha\alpha'}(\mathbf{R}_{\alpha L}, \mathbf{R}_{\alpha' L'}, t)$ and give the density response at αL due to a perturbation at $\alpha' L'$. It is more convenient, however, to work in Fourier space and to calculate $\chi_{\alpha\alpha'}(\mathbf{q}, t)$. In contrast to the situation in a plane wave representation, however, these response functions are periodic functions of the wave vector in a complete Wannier basis and local field effects are reflected by the off-diagonal matrix elements $\alpha \neq \alpha'$.

We consider an infinitesimal external scalar potential of reduced wave vector $\mathbf{q}$ and frequency ω,

$$\delta\Phi^{\mathrm{ext}}(\mathbf{R}_{\alpha L}, t) = \delta\Phi^{\mathrm{ext}}_{\alpha}(\mathbf{q},\omega)\, \exp\left[-i(\mathbf{q}\cdot\mathbf{R}_{\alpha L} + \omega t)\right] \,. \tag{27}$$

This potential alters the electronic occupancies in the perfect crystal,

$$Q(\mathbf{R}_{\alpha L}) = \sum_{n\mathbf{k}\in \mathrm{VB}} f_{n\mathbf{k}} |\langle \alpha L | n\mathbf{k}\rangle|^2 \,, \tag{28}$$

by an amount $\delta Q(\mathbf{R}_{\alpha L}, t)$ and induces a total self-consistent potential $\delta\Phi = \delta\Phi^{\mathrm{ext}} + \delta\Phi^{\mathrm{ind}}$ that enters the perturbed Hamiltonian according to Eq. (12). This induced charge density can easily be determined invoking standard linear response theory for longitudinal perturbations (see, e.g., Ref. 28). Adapting this approach to the present tight-binding basis, one easily obtains the first order change of the statistical density operator $\delta\rho$ by the perturbed Hamiltonian,

$$\begin{aligned}\langle n'\mathbf{k}|\delta\rho(\omega)|n\mathbf{k}+\mathbf{q}\rangle &= \frac{f_{n'\mathbf{k}} - f_{n\mathbf{k}+\mathbf{q}}}{E_{n'\mathbf{k}} - E_{n\mathbf{k}+\mathbf{q}} - \hbar\omega - i\hbar\eta} \\ &\quad \times \sum_{\alpha} C^*_{\alpha}(n'\mathbf{k}) C_{\alpha}(n\mathbf{k}+\mathbf{q})\,\delta\Phi_{\alpha}(\mathbf{q},\omega) \,. \end{aligned}\tag{29}$$

In addition, one can write the induced charge density as

$$\begin{aligned}\delta Q(\mathbf{R}_{\alpha L}, t) &= \mathrm{Tr}\,(\delta\rho\, |\alpha L\rangle\langle \alpha L|\,) \\ &= \delta Q_{\alpha}(\mathbf{q},\omega)\, \exp\left[-i(\mathbf{q}\cdot\mathbf{R}_{\alpha L} + \omega t)\right] \,. \end{aligned}\tag{30}$$

Calculating the trace in this equation with the Bloch eigenstates and combining Eqs. (29) and (30), one obtains the longitudinal susceptibility matrix $\boldsymbol{\chi}$,

$$\begin{aligned}&\delta\mathbf{Q}(\mathbf{q},\omega) = \boldsymbol{\chi}(\mathbf{q},\omega)\,\delta\boldsymbol{\Phi}(\mathbf{q},\omega) \,, \\ &\chi_{\alpha,\alpha'}(\mathbf{q},\omega) \\ &\quad = \frac{1}{N}\sum_{n,n',\mathbf{k}} \frac{f_{n'\mathbf{k}} - f_{n\mathbf{k}+\mathbf{q}}}{E_{n'\mathbf{k}} - E_{n\mathbf{k}+\mathbf{q}} - \hbar\omega - i\hbar\eta} \\ &\qquad \times C_{\alpha}(n'\mathbf{k}) C^*_{\alpha}(n\mathbf{k}+\mathbf{q}) C^*_{\alpha'}(n'\mathbf{k}) C_{\alpha'}(n\mathbf{k}+\mathbf{q}) \,. \end{aligned}\tag{31}$$

The size of this susceptibility matrix equals the number of ions per unit cell times the number of orbitals per site. Actually, the matrix dimension can be reduced to the number of ions per unit cell since we assume that the perturbing potential is independent of the atomic orbital it acts on.

In order to calculate the longitudinal dielectric function, one needs to establish a relation between the induced charge density δQ and the induced potential $\delta\Phi^{\mathrm{ind}}$. In a continuous real space basis, this relation is simply provided by the Poisson equation. In a tight-binding framework, however, one needs to specify how the on-site Hamiltonian matrix elements depend on charge transfer.[9,19,29,30] A quite general ansatz is

$$\epsilon_{\alpha L} = w_{\alpha L} - \sum_{\alpha', L'} (Z_{\alpha' L'} - Q_{\alpha' L'}) U_{\alpha\alpha'}(\mathbf{R}_{\alpha L} - \mathbf{R}_{\alpha' L'}) \,, \tag{32}$$

where $Z_{\alpha L} e$ is the core charge of the ion at site $\mathbf{R}_{\alpha L}$ and $w_{\alpha L}$ are the orbital energies of the neutral atoms. The coefficients U reflect the on-site Coulomb repulsion for $\mathbf{R}_{\alpha L} = \mathbf{R}_{\alpha' L'}$ and must tend to a Coulomb potential for long distances in order to ensure charge conservation (see Appendix B). When the ion is neutral, $Q_{\alpha L} = Z_{\alpha L}$. Equations (31) and (32) imply the matrix relation

$$\delta\boldsymbol{\Phi}(\mathbf{q},\omega) = \delta\boldsymbol{\Phi}^{\mathrm{ext}}(\mathbf{q},\omega) + \mathbf{U}(\mathbf{q})\boldsymbol{\chi}(\mathbf{q},\omega)\delta\boldsymbol{\Phi}(\mathbf{q},\omega) \,, \tag{33}$$

where $\mathbf{U}(\mathbf{q})$ is the Fourier transform of $\mathbf{U}(\mathbf{R})$. The dielectric matrix is then given by

$$\boldsymbol{\epsilon}(\mathbf{q},\omega) = \mathbf{1} - \mathbf{U}(\mathbf{q})\boldsymbol{\chi}(\mathbf{q},\omega). \tag{34}$$

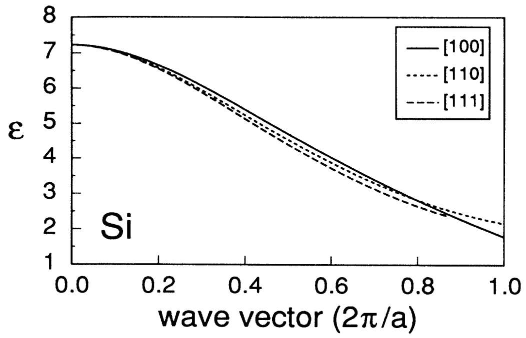

FIG. 4. Calculated longitudinal macroscopic dielectric function $\epsilon(\mathbf{q},0)$ of Si along different directions of the wave vector in the Brillouin zone.

Finally, we may define a scalar macroscopic dielectric function by averaging over all N_b orbital states in the unit cell,

$$\epsilon_{\mathrm{macro}}(\mathbf{q},0)=\frac{1}{N_b}\sum_{\alpha,\alpha'=1}^{N_b}\epsilon_{\alpha\alpha'}(\mathbf{q},0)\ . \tag{35}$$

We illustrate these results for bulk Si. We have used a strictly Coulombic interatomic potential U in Eq. (32),

$$U_{\alpha\alpha'}(\mathbf{q})=e^2\sum_L{}'\frac{\exp[i\mathbf{q}\cdot(\mathbf{R}_{\alpha L}-\mathbf{R}_{\alpha'})]}{|\mathbf{R}_{\alpha L}-\mathbf{R}_{\alpha'}|}\ , \tag{36}$$

where the prime indicates that the sum excludes the intra-atomic term. The intra-atomic Coulomb repulsion has been taken as $U_{\alpha\alpha}=7.64$ eV.[9] The resulting dielectric function is shown in Fig. 4 where the tight-binding parameters of Ref. 2 have been used. The long-wavelength limit of $\epsilon(\mathbf{q})$ gives $\epsilon_\infty=7.2$ which somewhat underestimates the experimental value of 12.0 but, since no parameters have been adjusted, the present results are in the expected range of accuracy.

Finally, we turn to the important question of consistency between the longitudinal and transverse dielectric function in the present tight-binding framework. As a consequence of charge conservation, these two functions should become equal in the limit of long wavelengths.[28] Indeed, we show in Appendix B that the present formalism obeys charge conservation.

VII. LUTTINGER-KOHN APPROXIMATION AND EFFECTIVE LANDÉ FACTOR

Within an envelope function approach,[17,32] there is an alternative way to introduce electromagnetic fields, namely, to replace the wave vector in the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian, Eq. (7), by an operator.[17] Let us consider a semiconductor in a magnetic field $\mathbf{B}=\mathrm{rot}\mathbf{A}$ and apply this substitution to Eq. (7),

$$\mathbf{k}\to\hat{\mathbf{k}}=-i\nabla+\frac{e}{\hbar c}\mathbf{A}(\mathbf{x},t)\ . \tag{37}$$

This substitution is sometimes also termed Peierls substitution[24] but is not equivalent to Eq. (12) since it relies on a one-band effective mass description that breaks down when the applied fields introduce significant mixing between different valleys or bands.

As an illustration, we calculate the effective Landé g factor for a band edge state.[31,32] To this end, we first add the Pauli term $\mu_B g_0\boldsymbol{\sigma}\cdot\mathbf{B}/2$ to the Hamiltonian Eq. (7), where $g_0=2$ is the gyromagnetic factor of electrons, and write the product of the wave vectors—which are now operators—in this equation as

$$\begin{aligned}\hat{k}_i\hat{k}_j&=\frac{1}{2}\left([\hat{k}_i,\hat{k}_j]_+ + [\hat{k}_i,\hat{k}_j]_-\right)\\&=\hat{k}_i\hat{k}_j+\hat{k}_j\hat{k}_i-\frac{ie}{\hbar c}\sum_m\epsilon_{ijm}B_m\ ,\end{aligned} \tag{38}$$

where ϵ_{ijm} is the Levi-Cività index or unit antisymmetric tensor. For simplicity, we consider only $\mathbf{k}^*=\mathbf{0}$ and insert the symmetric and antisymmetric combinations of $\hat{\mathbf{k}}$ into the Hamiltonian matrix,

$$\begin{aligned}H_{n,n'}(k)=E_n\delta_{n,n'}&+\sum_{i,j}\frac{\hbar^2}{2}(\hat{k}_i\hat{k}_j+\hat{k}_j\hat{k}_i)\\&\times\left(\frac{1}{2m_0}T^{ij}_{nn'}+\frac{1}{m_0^2}\sum_{m\neq n,n'}\frac{p^i_{nm}p^j_{mn'}}{E_n-E_m}\right)\\&+\frac{1}{2}\mu_B\sum_m\Bigg(g_0(\boldsymbol{\sigma}_m)_{n,n'}\\&-i\frac{2}{m_0}\sum_{\substack{m\neq n,n'\\ i\ j}}\frac{p^i_{nm}p^j_{mn'}}{E_n-E_m}\epsilon_{ijm}\Bigg)B_m\ .\end{aligned} \tag{39}$$

The last two terms on the right hand side of this equation are the spin and orbital contributions to the effective magnetic moment, respectively, and define the effective Landé factor. In the case of an sp^3s^* nearest-neighbor tight-binding model and a diamond structure, this expression can be evaluated analytically and gives

$$g=g_0+\frac{m_0}{12\hbar^2}a^2t^2_{sp\sigma}\left[\frac{1}{E_{\Gamma_{7c}}-E_{\Gamma_{7v}}}-\frac{1}{E_{\Gamma_{7c}}-E_{\Gamma_{8v}}}\right]\ . \tag{40}$$

Here a is the lattice constant and $t_{sp\sigma}$ is the transfer matrix element between neighboring s and p states. Note that the interband contribution in this equation is always negative, since the Γ_{8v} state forms the top of the valence band whereas Γ_{7v} is the split-off band.

Narrow-gap semiconductors are known to have very large and negative effective Landé factors associated with the lowest conduction band. We have numerically computed the effective g factor from Eq. (39) for InSb, again employing the tight-binding model of Ref. 4. We obtain $g=-26.6$, which is too small compared to the experimental value, $g=-50$, but does reflect the correct sign and order of magnitude.

In summary, we have extended the empirical tight-binding method to incorporate electromagnetic fields in a gauge-invariant manner. Based on this method, we have derived explicit expressions for the effective mass tensor, the effective Landé g factor, and linear response functions for transverse and longitudinal fields.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (SFB 348), Bayerische Forschungsverbund (FOROPTO), and Volkswagenstiftung is gratefully acknowledged.

APPENDIX A: GAUGE INVARIANCE

In a shorthand notation, the fields Φ and $\mathbf{A}$ modify the zero-field tight-binding parameters ϵ_I^0 and $t_{J,I}^0$ according to Eq. (12),

$$\begin{aligned} \epsilon_I &= \epsilon_I^0 - e\Phi_I \;, \\ t_{J,I} &= t_{J,I}^0 \exp\left[-\frac{ie}{\hbar c}\int_I^J \mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right] \;. \end{aligned} \qquad \text{(A1)}$$

Under the gauge transformation of the potentials and the wave function,

$$\begin{aligned} \mathbf{A} &\rightarrow \mathbf{A}' = \mathbf{A} + \nabla\Lambda \;, \\ \Phi &\rightarrow \Phi' = \Phi - \frac{1}{c}\delta_t\Lambda \;, \\ |\psi\rangle &= \sum_I C_I\, |I\rangle \\ &\rightarrow |\psi'\rangle = \sum_I C_I \,\exp\left[-\frac{ie}{\hbar c}\Lambda_I(t)\right] |I\rangle \;, \end{aligned} \qquad \text{(A2)}$$

the tight-binding matrix elements transform into

$$\begin{aligned} \epsilon_I' &= \epsilon_I^0 - e\Phi_I' = \epsilon_I^0 - e\Phi_I + \frac{e}{c}\delta_t\Lambda_I = \epsilon_I + \frac{e}{c}\delta_t\Lambda_I \;, \\ t_{J,I}' &= t_{J,I}^0 \exp\left[-\frac{ie}{\hbar c}\int_I^J \mathbf{A}'(\mathbf{s})\cdot d\mathbf{s}\right] \\ &= t_{J,I}^0 \exp\left[-\frac{ie}{\hbar c}\int_I^J \mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right] \exp\left[-\frac{ie}{\hbar c}(\Lambda_J - \Lambda_I)\right] \\ &= t_{J,I} \exp\left[-\frac{ie}{\hbar c}(\Lambda_J - \Lambda_I)\right] \;. \end{aligned} \qquad \text{(A3)}$$

Therefore, the Schrödinger equation in the gauge transformed system reads

$$\begin{aligned} \langle J|i\hbar\delta_t\, \psi'\rangle &= i\hbar \exp\left[-\frac{ie}{\hbar c}\Lambda_J\right]\left[\frac{-ie}{\hbar c}(\delta_t\Lambda_J) + \delta_t\right] C_J \\ &= \exp\left[-\frac{ie}{\hbar c}\Lambda_J\right]\left[\frac{e}{c}(\delta_t\Lambda_J)C_J + i\hbar\; \delta_t C_J\right] , \\ \langle J|H'\, \psi'\rangle &= \sum_{I\neq J} t_{J,I}' C_I' + \epsilon'_J C_J' \\ &= \exp\left[-\frac{ie}{\hbar c}\Lambda_J\right]\left[\sum_{I\neq J} t_{J,I}C_I + \epsilon_J C_J + \frac{e}{c}(\delta_t\Lambda_J)\; C_J\right] \;. \end{aligned} \qquad \text{(A4)}$$

This shows the gauge invariance of the field-dependent tight-binding Hamiltonian. We note that this invariance is independent of the approximation that is used to evaluate the contour integral, Eq. (11). For example, $(\mathbf{R}'-\mathbf{R})$ in Eq. (11) may be multiplied by a universal constant.

APPENDIX B: CHARGE CONSERVATION

We show that the longitudinal macroscopic dielectric function, as defined in Eq. (35), tends towards the transverse dielectric function as defined in Sec. V in the limit $\mathbf{q} \rightarrow \mathbf{0}$. More precisely, we show that

$$\epsilon_{ii}(\omega) = \lim_{\mathbf{q}\rightarrow 0} \epsilon_{\text{macro}}(\mathbf{q},\omega) \;, \qquad \text{(B1)}$$

where the limit is taken with $\mathbf{q}$ parallel to the direction i of a principal axis. For simplicity, we only consider the case of an insulator at zero temperature. The Fourier transform of the electron density operator is

$$\hat{n}(\mathbf{q}) = \sum_{\alpha L} e^{i\mathbf{q}\cdot\mathbf{R}_{\alpha L}} |\alpha, L\rangle\langle\alpha, L| \;. \qquad \text{(B2)}$$

We calculate the commutator of this operator with the Hamiltonian and obtain

$$\begin{aligned} [H,\hat{n}(\mathbf{q})] = \sum_{\alpha' L',\alpha L} & |\alpha', L'\rangle t_{\alpha'\alpha}(\mathbf{R}_{\alpha' L'} - \mathbf{R}_{\alpha L}) \\ & \times (e^{i\mathbf{q}\cdot\mathbf{R}_{\alpha L}} - e^{i\mathbf{q}\cdot\mathbf{R}_{\alpha' L'}})\langle\alpha, L| \;. \end{aligned} \qquad \text{(B3)}$$

The Bloch function matrix element of this commutator can be written as

$$\begin{aligned} &\langle n\mathbf{k}|[H,\hat{n}(\mathbf{q})]|n'\mathbf{k}+\mathbf{q}\rangle \\ &\quad = (E_{n\mathbf{k}} - E_{n'\mathbf{k}+\mathbf{q}}) \sum_\alpha C_\alpha^*(n\mathbf{k})C_\alpha(n'\mathbf{k}+\mathbf{q}) \;. \end{aligned} \qquad \text{(B4)}$$

Alternatively, by using directly Eq. (B3) in the matrix element, one finds

$$\begin{aligned} &\langle n\mathbf{k}|[H,\hat{n}(\mathbf{q})]|n'\mathbf{k}+\mathbf{q}\rangle \\ &\quad = \sum_{\alpha' L',\alpha L} C_{\alpha'}^*(n\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{R}_{\alpha L} - \mathbf{R}_{\alpha' L'})} t_{\alpha'\alpha}(\mathbf{R}_{\alpha' L'} - \mathbf{R}_{\alpha L}) \left[e^{2i\mathbf{q}\cdot\mathbf{R}_{\alpha L}} - e^{i\mathbf{q}\cdot(\mathbf{R}_{\alpha' L'} + \mathbf{R}_{\alpha L})}\right] C_\alpha(n'\mathbf{k}+\mathbf{q}) \;. \end{aligned} \qquad \text{(B5)}$$

We expand this expression in powers of $\mathbf{q}$ and obtain to first order

$$\langle n\mathbf{k}|[H,\hat{n}(\mathbf{q})]|n'\mathbf{k}+\mathbf{q}\rangle = \frac{\hbar}{m_0}\mathbf{q}\cdot\mathbf{p}_{nn'}(\mathbf{k}) + O(q^2) \ . \quad \text{(B6)}$$

Using the expression Eq. (19) for the current, one finally obtains in the Schrödinger picture

$$\lim_{\mathbf{q}\to 0}\left(i\hbar\partial_t\langle n\mathbf{k}|\hat{n}(\mathbf{q})|n'\mathbf{k}+\mathbf{q}\rangle - \frac{\hbar}{e}\mathbf{q}\cdot\mathbf{J}_{nn'}(\mathbf{k})\right) = 0 \ , \quad \text{(B7)}$$

which proves the charge conservation. Following Ref. 28, one can now easily establish Eq. (B1) by using this result and the long-wavelength limit of the intersite Coulomb interaction $\mathbf{U}(\mathbf{q})$ in Eq. (32),

$$U_{\alpha\alpha'}(\mathbf{q}) = \frac{4\pi e^2}{q^2\Omega_0} + O(q^0) \ . \quad \text{(B8)}$$

---

[1] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[2] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Chem. Solids **44**, 365 (1983).

[3] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[4] C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **37**, 8519 (1988).

[5] D. L. Smith and C. Mailhiot, Rev. Mod. Phys. **62**, 173 (1990), and references therein.

[6] S. K. Bose, K. Winer, and O. Andersen, Phys. Rev. B **37**, 6262 (1988).

[7] G. Lengel, R. Wilkins, G. Brown, M. Weimer, J. Gryko, and R. E. Allen, Phys. Rev. Lett. **72**, 836 (1994).

[8] W. A. Harrison and G. K. Straub, Phys. Rev. B **36**, 2695 (1987).

[9] J. A. Majewski and P. Vogl, Phys. Rev. B **35**, 9666 (1987).

[10] A. Mazur and J. Pollmann, Phys. Rev. B **39**, 5261 (1989).

[11] O. F. Sankey and R. E. Allen, Phys. Rev. B **33**, 7164 (1986); M. Menon and R. E. Allen, *ibid.* **33**, 7099 (1986); R. E. Allen and M. Menon, *ibid.* **33**, 5611 (1986).

[12] L. Goodwin, J. Phys. Condens. Matter **3**, 3869 (1991).

[13] J. N. Schulman and Y.-C. Chang, Phys. Rev. B **31**, 2056 (1985).

[14] G. D. Sanders and Y.-C. Chang, Phys. Rev. B **45**, 9202 (1992).

[15] H. M. Polatoglou, G. Theodorou, and C. Tserbak, Phys. Rev. B **49**, 8132 (1994).

[16] R. Peierls, Z. Phys. **80**, 763 (1933).

[17] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955); J. M. Luttinger, *ibid.* **84**, 814 (1951).

[18] D. R. Hofstadter, Phys. Rev. B **14**, 2239 (1976).

[19] W. A. Harrison and J. E. Klepeis, Phys. Rev. B **37**, 864 (1988).

[20] J. C. Durán, F. Flores, C. Tejedor, and A. Muñoz, Phys. Rev. B **36**, 5920 (1987).

[21] A. Di Carlo and P. Vogl, Phys. Rev. B **50**, 8358 (1994).

[22] L. C. Lew Yan Voon and L. R. Ram-Mohan, Phys. Rev. B **47**, 15 500 (1993).

[23] D. J. Chadi, Phys. Rev. B **16**, 790 (1977).

[24] A. S. Alexandrov and H. Capellmann, Phys. Rev. Lett. **66**, 365 (1991).

[25] G. Petschel and T. Geisel, Phys. Rev. Lett. **71**, 239 (1993).

[26] E. Brown, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 22, p. 313.

[27] J. E. Sipe and Ed Ghahramani, Phys. Rev. B **48**, 11 705 (1993).

[28] S. L. Adler, Phys. Rev. **126**, 413 (1962).

[29] C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **38**, 9870 (1988).

[30] G. K. Straub and W. A. Harrison, Phys. Rev. B **39**, 10 325 (1989).

[31] Y. Yafet, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 1.

[32] G. L. Bir and G. E. Pikus, *Symmetry and Strain-induced Effects in Semiconductors* (Keterpress, Jerusalem, 1974).

[33] D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).