Microscopic polarization and magnetization fields: Including spin effects

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We extend a microscopic theory of polarization and magnetization to include the spin degree of freedom of the electrons. We include a general spin orbit coupling and Zeeman interaction term to account for the modifications to the dynamics upon treating the electrons as spinful particles. The microscopic polarization and magnetization fields are introduced throughout an extended system using a set of orthogonal orbitals associated with each site. As well free charge and current density fields are introduced associated with charge movement from site to site. The sites act as natural expansion points for the microscopic fields, allowing for the evaluation of multipole moments associated with the polarization and magnetization fields. From the macroscopic polarization and magnetization fields we can extract various response tensors. We limit our study to insulators for which it is possible to construct exponentially localized Wannier functions, in the limit of uniform fields, to recover the magnetoelectric polarizability (MP) tensor, which contains the accepted expression for the orbital magnetoelectric polarizability (OMP) tensor as well as an added explicitly spin dependent contribution. This general framework can then be extended to finite frequency responses.

I. INTRODUCTION

Macroscopic polarization and magnetization are familiar quantities in the description of the physical properties of materials and the phenomena they exhibit. At an elementary level, the situation appears straightforward. In the case of a material consisting of neutral atoms, an applied electric field can induce dipole moments. Or, in the case of a material made up of polar molecules, each permanent dipole experiences a torque attempting to align it with the applied field. These effects lead to an overall polarization, \( \mathbf{P} \), defined as the dipole moment per unit volume \([1]\). In the case of magnetization, electrons are orbiting around nuclei, and possess an intrinsic spin, both of which can lead to magnetic dipole moments. As in the approach to polarization, one defines an overall magnetization, \( \mathbf{M} \), as the magnetic dipole moment per unit volume \([1]\).

When analysing systems composed of stable, separate units – the “molecular crystal” limit of a crystalline solid – one can introduce microscopic polarization and magnetization fields via the Power-Zienau-Wooley (PZW) gauge transformation \([2,3]\) to go beyond just the dipole moments. An expansion of the electromagnetic fields about the center of such a unit, the “special point” in the analysis, leads in a natural way to multipole moments coupling directly to the electromagnetic field and its derivatives at the special point, thus avoiding a description of the dynamics in terms of the electromagnetic potentials.

Such an approach cannot be immediately extended to crystalline solids, where electrons are free to move between sites. Indeed, in a bulk periodic solid there are fundamental difficulties even in introducing a dipole moment per unit volume. First, if the polarization is defined based on the charges in a unit cell, the result depends on the choice of unit cell. As well, even in an insulator, the electrons are usually associated with Bloch functions that extend throughout the crystal. If a field is applied, what sense does it make to talk about the displacement of the electron from a particular nucleus? Until the last decades of the last century the precise definition of even the macroscopic polarization was elusive \([1,5]\).

The “modern theory of polarization and magnetization” \([4,5]\) was developed to address these difficulties. It was argued that only a change in the macroscopic polarization is of physical significance, as this change can be associated with a current density induced by an adiabatic variation of the Hamiltonian; the change in polarization is then calculated via \( \mathbf{J} = \frac{\mathrm{d}\mathbf{P}}{\mathrm{d}t} \). The polarization in the ground state of an insulator could then be linked to dipole moments associated with the filled Wannier functions \([6,5]\), and there exists a “quantum of ambiguity” in the polarization since there is freedom in how the Wannier functions are associated with lattice sites \([6]\). The treatment for describing magnetization is more complicated; even in the ground state there can be both “atomic-like” and “itinerant” contributions due to movement between sites \([7]\), but much progress has been made in describing them \([8]\). Yet, since the “modern theory” relies upon adiabatic variations to the Hamiltonian, it generally does not treat applied fields that vary over the unit cell, or fields at arbitrary frequency.

A more recent treatment of polarization and magnetization in extended systems harks back to the work of Lorentz \([10]\). Microscopic polarization and magnetization fields are introduced, and the associated macroscopic fields are identified with their spatial averages \([11]\). “Free” charges and currents are also introduced, and the whole strategy can be understood as a generalization of a lattice gauge theory. Such an approach can describe the effects on the optical response of variations of the electromagnetic field over the unit cell, can be applied for arbitrary frequencies, and is sensitive to the topological properties of the band structure as well as its spectral properties \([12,13]\).

But to date, work along these lines has neglected the electron spin. Although suitable for exploring the response properties of interesting models, such as that of Haldane \([14]\), if this new approach is to serve as the basis
of a full response theory then electron spin must be included, since spin effects generally make a large contribution to the magnetic properties of materials. For example, in systems where magnetism arises on 3d transition metal ions the spin contribution due to unpaired electrons is usually assumed to dominate over orbital magnetic effects.

The inclusion of electron spin in the description of the electromagnetic response of materials, within an approach starting with microscopic polarization and magnetization fields, is the subject of this paper. The starting point is necessarily a Hamiltonian. There are a number of derivations of non-relativistic Pauli-Hamiltonians starting from the Dirac equation, with differences as to the preferred approach, and as to which terms are kept. We choose a Pauli-like Hamiltonian which, in the absence of applied electromagnetic fields, includes the standard spin-orbit coupling term due to the strong static field near the nuclei; in condensed matter systems this is often responsible for the largest consequences of electron spin. Applied electromagnetic fields, which we treat classically, are then included by the usual minimal coupling procedure, and as well we include a Zeeman-like term to account for the interaction of the electron’s intrinsic angular momentum with the magnetic field. The full electronic current density that results includes both the well-understood magnetization current as well as a contribution associated with the spin-orbit interaction.

In Section II we begin by introducing our choice of Hamiltonian and its associated charge and current density operators. We make the frozen ion approximation for the nuclei, and the independent particle approximation for the electrons. The second of these involves the neglect of interactions between the electrons, except as they can be included by employing an effective potential due to the nuclei, and by understanding the “applied” electromagnetic field we introduce to be the macroscopic Maxwell electromagnetic field. Then in calculating the dynamical response to such an electromagnetic field we can rely on the equal-time, single particle Green function.

In this paper we focus on zero temperature insulators for which exponentially localized Wannier functions can be constructed, and outline how the site quantities are constructed, highlighting the modifications that must be made from earlier work in which the spin-full nature of the particles was neglected.

In Section III we outline the form of the ground state site electric dipole moment and the magnetic dipole moments. We highlight two explicit changes to the ground state magnetization due to the presence of spin: The first is due to the intrinsic spin magnetic moment, and the second is due to a modification of the current density by the spin-orbit coupling.

In Section IV a perturbative expansion of the response of electric and magnetic dipole moments to applied uniform and constant fields is determined, again generalizing earlier work where spin was neglected. We obtain the response of the polarization to an applied uniform electric and magnetic field, and of the magnetization to an applied uniform electric field. The last two of these responses are both characterized by the magneto-polarizability tensor (MP) we introduce.

In Section V we discuss how the MP tensor consists of an orbital magneto-polarizability tensor (OMP), a generalization of the OMP tensor introduced earlier for spinless systems, and an explicitly spin dependent contribution that we identify. In the limit of uniform fields our result agrees with the spin magneto-electric response found via a semiclassical theory that treats various responses, including that of spin to weak electric fields, due to the adiabatic evolution of Bloch electronic states. Thus the MP tensor can be written as the sum of the usual Chern-Simons and cross gap contributions that, taken together, form the OMP response tensor, and the explicitly spin dependent contribution.

In Section VI we summarize the modifications to the earlier formalism to include the spin degree of freedom, and identify possibilities for future extensions to this work.

We relegate some technical details to Appendices A and B. In Appendix C we confirm that the MP tensor is non-vanishing only when both spatial-inversion and time-reversal symmetry are broken in the unperturbed system, with the caveat that the MP is only defined modulo a “quantum of ambiguity” that is sensitive to the choice of Wannier functions one uses as a basis for calculations. All the ambiguity is found only in the Chern-Simons contribution.

II. MICROSCOPIC FORMALISM

A. Hamiltonian

The electronic response of a crystalline insulator is a consequence of the evolution of the fermionic electron field operator, $\hat{\psi}(\mathbf{x},t)$. In the Heisenberg picture the dynamics are governed by...
\[ i\hbar \frac{\partial \psi(x,t)}{\partial t} = \mathcal{H}(x,t)\psi(x,t), \]  

(1)

where \( \psi(x,t) \) is a two-component Pauli spinor operator. We make the frozen ion and independent particle approximations, and begin by taking the electrons to be subject to a potential energy term \( V(x) \) that has the same periodicity as the crystal lattice. \( V(x) = V(x + \mathbf{R}) \) for all Bravais lattice vectors \( \mathbf{R} \). The potential \( V(x) \) can include electron-electron interactions in a mean field approximation. We can then include the first relativistic correction that involves the spin by taking the differential operator associated to a potential energy term due to the spin. Defining \( \mathcal{H}^0 \) to be

\[ \mathcal{H}^0_{\text{TR}}(x) = -\frac{\hbar^2}{2m} \nabla^2 + V(x) + \mathcal{H}^0_{\text{SOC}}(x). \]  

(2)

\( \mathcal{H}^0_{\text{SOC}} \) is the spin-orbit coupling term [15, 17], which we write in a general form as

\[ \mathcal{H}^0_{\text{SOC}}(x) = -\frac{i\hbar^2}{4mc^2} \sigma \cdot \nabla V(x) \times \nabla, \]  

(3)

where \( \sigma \) is the vector of Pauli matrices that act on spinor wavefunctions. Other relativistic corrections, such as the Darwin and mass-velocity terms [17], are neglected.

We use the subscript \( \text{TR} \) to indicate that \( \mathcal{H}^0_{\text{TR}}(x) \) satisfies time-reversal symmetry. Even before any electromagnetic fields are applied, we can allow for this symmetry to be broken by introducing a possible “internal”, static, cell-periodic magnetic field described by a vector potential \( \mathbf{A}_{\text{static}}(x) \), where \( \mathbf{A}_{\text{static}}(x) = \mathbf{A}_{\text{static}}(x + \mathbf{R}) \). While its presence breaks time-reversal symmetry, the inclusion of this static vector potential does not break the translational symmetry of the Hamiltonian, and thus Bloch’s theorem can still be applied.

We also consider the system to be perturbed by an applied electromagnetic field characterized by a scalar potential \( \phi(x,t) \) and a vector potential \( \mathbf{A}(x,t) \). We treat the applied electromagnetic field and the internal magnetic field classically, and adjust the Hamiltonian for their inclusion following the standard minimal coupling prescription, as well as adding in the magnetic dipole energy term due to the spin. Defining

\[ p(x) = -i\hbar \nabla - eA_{\text{static}}(x), \]  

(4)

where we take the charge of the electron to be \( e = -|e| \)

the full differential operator \( \mathcal{H}(x,t) \) is then given by

\[
\mathcal{H}(x,t) = \left( \frac{p(x) - \frac{e}{c} A_{\text{static}}(x)}{2m}\right)^2 + V(x) + e\phi(x,t) - \frac{e\hbar}{2mc} \sigma \cdot B(x,t) - \frac{e\hbar}{2mc} \sigma \cdot B_{\text{static}}(x) \\ + \frac{\hbar}{4mc^2} \sigma \cdot \nabla V(x) \times (p(x) - \frac{e}{c} A(x,t))
\]

(5)

where the applied magnetic field is \( \mathbf{B}(x,t) = \nabla \times \mathbf{A}(x,t) \), and the static magnetic field is \( \mathbf{B}_{\text{static}}(x) = \nabla \times \mathbf{A}_{\text{static}}(x) \). We assume the applied electric field is much smaller than the gradient of \( V(x) \), in regions of space where that term is important, and therefore the spin-orbit interaction is not modified by the applied electric field at our level of approximation. At times when the applied electromagnetic field vanishes, the expression for \( \mathcal{H}(x,t) \) reduces to \( \mathcal{H}^0(x) \), where the latter is obtained from the former by setting \( \phi(x,t) \) and \( \mathbf{A}(x,t) \) equal to zero.

The full Hamiltonian is then given by

\[
\mathcal{H}_{ji}(x,t) = \left( \frac{p(x) - \frac{e}{c} A_{\text{static}}(x)}{2m}\right) \delta_{ji} + V(x)\delta_{ji} + e\phi(x,t)\delta_{ji} - \frac{e\hbar}{2mc} \sigma_{ji} \cdot B(x,t) - \frac{e\hbar}{2mc} \sigma_{ji} \cdot B_{\text{static}}(x) \\ + \frac{\hbar}{4mc^2} \sigma_{ji} \cdot (\nabla V(x) \times (p(x) - \frac{e}{c} A(x,t))).
\]  

(6)

where \( \mathcal{H}(x,t) \) is a 2x2 matrix with in general four non-zero components. In the usual spin-z basis we denote the matrix elements by two spin-arrow labels; however, in general we introduce sans-serif subscripts to indicate spinor components. Hence the matrix components of the differential operator are identified as

\[
\mathcal{H}(x,t) = \begin{bmatrix} \mathcal{H}^{\uparrow\downarrow}(x,t) & \mathcal{H}^{\uparrow\downarrow}(x,t) \\ \mathcal{H}^{\downarrow\uparrow}(x,t) & \mathcal{H}^{\downarrow\downarrow}(x,t) \end{bmatrix},
\]  

(7)

where

\[
\hat{\mathcal{H}}(t) = \int \hat{\psi}^\dagger(x,t) \mathcal{H}(x,t) \hat{\psi}(x,t) d\mathbf{x},
\]  

(6)

\[
\mathcal{H}(x,t) = \begin{bmatrix} \mathcal{H}^{\uparrow\downarrow}(x,t) & \mathcal{H}^{\uparrow\downarrow}(x,t) \\ \mathcal{H}^{\downarrow\uparrow}(x,t) & \mathcal{H}^{\downarrow\downarrow}(x,t) \end{bmatrix},
\]  

(7)

where

\[
\hat{\mathcal{H}}(t) = \int \hat{\psi}^\dagger(x,t) \mathcal{H}(x,t) \hat{\psi}(x,t) d\mathbf{x},
\]  

(6)
B. Charge and Current Densities

In the quantum field theoretic approach we adopt for the electrons \[20\], the equations for the charge and current densities are obtained via

\[
\dot{\rho}(x,t) = \frac{\delta H(t)}{\delta \phi(x,t)} + \rho^{\text{ion}}(x),
\]

and

\[
\dot{j}(x,t) = -c \frac{\delta H(t)}{\delta A(x,t)},
\]

where to the electronic charge density in (9) we have added a charge density for the (assumed fixed) ions so that \(\dot{\rho}(x,t)\) is the full charge density. Here the ion charge density \(\rho^{\text{ion}}(x)\) can be written as

\[
\rho^{\text{ion}}(x) = \sum_{\text{R}} \rho^{\text{ion}}_{\text{R}}(x),
\]

where \(\rho^{\text{ion}}_{\text{R}}(x)\) is the ion density associated with lattice site \(\text{R}\). If the ions are approximated as point charges, we have

\[
\rho^{\text{ion}}_{\text{R}}(x) = \sum_{N} q_{N} \delta(x - \text{R} - \text{d}_{N}),
\]

where we assume that in each unit cell there are \(N\) ions with charges \(q_{N}\) located at \(\text{R} + \text{d}_{N}\).

The charge and current densities \([9,10]\) satisfy the continuity equation, and are given by

\[
\dot{\rho}(x,t) = e \hat{\psi}^\dagger(x,t) \hat{\psi}(x,t) + \rho^{\text{ion}}(x),
\]

and

\[
\dot{j}(x,t) = \frac{e}{2m} (\hat{\psi}^\dagger(x,t)(p(x) - \frac{e}{c} A(x,t)) \hat{\psi}(x,t) + ((p(x) - \frac{e}{c} A(x,t)) \hat{\psi}(x,t))^\dagger \hat{\psi}(x,t))
\]

\[
+ \frac{e\hbar}{4m^2c^2} \hat{\psi}^\dagger(x,t)(\sigma \times \nabla V(x)) \hat{\psi}(x,t) + \hat{j}_m(x,t).
\]

The first line on the right-hand-side of (13) is the standard current density that one would expect from a minimal coupling Hamiltonian. The second line has two additional contributions that are associated with spin: The second, \(\hat{j}_m(x,t)\), is the magnetization current that would be present even for a free electron gas; it is given by

\[
\hat{j}_m(x,t) = e \hat{\psi}^\dagger(x,t) \sigma \hat{\psi}(x,t),
\]

where

\[
\hat{m}_\sigma(x,t) = \frac{e\hbar}{2mc} \hat{\psi}^\dagger(x,t) \sigma \hat{\psi}(x,t).
\]

The remaining contribution to the charge current density in (14) is transverse to the spin magnetization of the system and to the electric field \(E_{\text{lattice}} = -e^{-1}\nabla V\) created by the crystal environment. It arises because the spin-orbit coupling introduces a correction to the relation between the velocity and momentum of an electron. Physically, this can be understood as a consequence of the effective electric dipole moment \(\mu = c^{-1} \nu \times \nu\) in the laboratory frame of a magnetic dipole moment \(\nu\) moving with velocity \(\nu\) \([31]\). The full Lagrangian of a single electron interacting with the electromagnetic field, which is specified in the laboratory frame, is then

\[
L = \frac{1}{2} m \nu \cdot \nu + \frac{e}{c} \nu \cdot (A + A_{\text{static}}) + \mu \cdot E_{\text{lattice}},
\]

together with contributions from the scalar potential and from the interaction of the magnetic dipole moment with the magnetic field. Since the last two terms on the right-hand-side of (17) both involve the velocity \(\nu\), they will both lead to a difference between the canonical momentum and the product of the mass and the velocity. Putting the spin magnetic moment \(\nu = eS/(mc)\), where \(S\) is the spin angular momentum, and including in this term the Thomas factor \(\frac{1}{2}\) to account for Thomas precession \([32]\), we find

\[
p = m \nu + \frac{e}{c} (A + A_{\text{static}}) - \frac{1}{2mc}(S \times \nabla V),
\]

(18)
Taking $S \to \hbar \sigma/2$, we can write this equation as

$$eV = \frac{e}{m} (p - \frac{e}{c} \mathbf{A} + \mathbf{A}_{\text{static}}) + \frac{e\hbar}{4mc^2} (\mathbf{\sigma} \times \nabla \mathbf{V}).$$  \hfill (19)

The first term in the second line of the expression (14) for the current density is the field theory analogue of the last term on the right-hand-side of (19).

C. Wannier functions

Our approach employs a Wannier function basis for calculations [3, 32]. To construct these we begin with the two component spinor wave functions

$$\psi_{nk}(x) \equiv \langle x | \psi_{nk} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i \mathbf{k} \cdot \mathbf{x}} \left[ \frac{u_{nk,\uparrow}(x)}{u_{nk,\downarrow}(x)} \right],$$  \hfill (20)

which are the Bloch eigenfunctions of the unperturbed Hamiltonian $\mathcal{H}^0(x)$ introduced after (15). The Bloch eigenfunctions are normalized over the infinite crystal such that $\langle \psi_{nk'} | \psi_{nk} \rangle = \delta_{nk} \delta(k - k')$; when sans-serif spinor component indices are omitted the object is understood to be the full two-component spinor. Associated with each Bloch eigenvector is an energy $E_{nk}$ and a cell-periodic spinor function $u_{nk}(x)$. The $n$ are band indices and $\mathbf{k}$ the crystal momentum. The cell-periodic functions $u_{nk}(x) = \langle x | n \mathbf{k} \rangle$ satisfy the orthogonality condition $(mk|nk) = \delta_{nn'}$, where we adopt the notation that

$$(g|h) \equiv \frac{1}{\Omega_{uc}} \int_{\Omega_{uc}} g^*_x(x) h_x(x) dx,$$  \hfill (21)

where $\Omega_{uc}$ is the unit cell volume. Repeated spinor indices are implicitly summed over.

It is useful to introduce sets of Wannier functions, where the Wannier functions in a particular set are associated with a particular set of “isolated bands” that may intersect amongst themselves, but where no band from the set intersects with bands from different sets. For the Wannier functions associated with a particular set of isolated bands, the prescription for doing that is

$$|\alpha\mathbf{R}\rangle = \sqrt{\frac{\Omega_{uc}}{(2\pi)^3}} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{R}} \sum_n U_{n\alpha}(\mathbf{k}) |\psi_{nk}\rangle,$$  \hfill (22)

where the unitary matrix $U(\mathbf{k})$ and the Bloch eigenvectors $|\psi_{nk}\rangle$ are chosen to be periodic over the first Brillouin zone. The sum over band indices in (22) is only over the relevant set of isolated bands, and each Wannier function $|\alpha\mathbf{R}\rangle$ is labeled by a type index $\alpha$ and a lattice site $\mathbf{R}$ with which it is identified.

As a first example, in this paper we consider an insulator, and so we can introduce two sets of isolated bands: One consists of the valence bands, and the other of the conduction bands. In studies of insulators involving scalar wave functions, if the band structure is “topologically trivial” then one can construct one set of exponentially localized Wannier functions (ELWF) \cite{34,38} from the valence bands, and another set from the conduction bands. For the scalar case the restriction is to insulators where the set of bands chosen has net zero Chern invariant; and work has been done to develop a procedure for constructing Wannier functions for Z2 insulators \cite{36,39}. In the generalization to spinor wave functions developed here we consider the analogous scenario, assuming that we can associate a set of spinor ELWF with the valence bands and another set with the conduction bands.

Even with the restriction to ELWFs, the Wannier functions are not uniquely defined, due to the freedom in choosing the unitary transformations $U(\mathbf{k})$. Thus there is an unavoidable “gauge freedom” – to be distinguished from the gauge freedom in choosing the scalar and vector potentials that identify the electromagnetic field – when identifying the Wannier functions. In this paper we refer to quantities as being gauge-dependent, in this sense, if they depend on the matrices $U(\mathbf{k})$ or their derivatives. This gauge freedom does not extend to physical quantities such as the charge and current densities.

The expression (22) for the Wannier functions provides a mapping from the set of filled energy eigenstates to the set of filled ELWFs; likewise, we can map the unoccupied states to unoccupied ELWFs. The ground state filling factors $f_n$ for the bands are either 0 or 1. Likewise the orbital filling factors $f_\alpha$ are either 0 or 1, and if $U_{n\alpha} \neq f_n$ then $f_n = f_\alpha$.

The Wannier functions $W_{\alpha\mathbf{R}}(x) \equiv \langle x | \alpha\mathbf{R}\rangle$ form an orthogonal set,

$$\int W_{\alpha\mathbf{R}}^{\ast}(x) W_{\beta\mathbf{R}}(x) dx = \delta_{\beta\alpha} \delta\mathbf{R} \cdot \mathbf{R}.$$  \hfill (23)

If a vector potential is applied it is useful to work with Wannier functions multiplied by a generalized Peierl phase factor. Moreover, if the vector potential is nonuniform, such as what we want to consider in general, those modified Wannier functions are neither orthonormal nor gauge-invariant in the electromagnetic sense. Thus, we use Lowdin’s method of symmetric orthogonalization \cite{40} to construct an orthonormal set of functions \{\bar{W}_{\alpha\mathbf{R}}(\mathbf{x},t)\}. We call these the set of “adjusted Wannier functions”. In the limit of a weak applied magnetic field we can construct a perturbative expansion for a set of functions \{\chi_{\alpha\mathbf{R}}\}, which are gauge-invariant in the electromagnetic sense and are related to the “adjusted Wannier functions” by

$$\bar{W}_{\alpha\mathbf{R}}(\mathbf{x},t) = e^{i\Phi(\mathbf{x},\mathbf{R};t)} \chi_{\alpha\mathbf{R}}(\mathbf{x},t).$$  \hfill (24)

The phase factor is a generalized Peierl phase, with the function $\Phi(\mathbf{x},\mathbf{R};t)$ a line integral of the vector potential over an arbitrary path from $\mathbf{R}$ to $\mathbf{x}$,
where the function $s(w; x, R)$ is a so-called “relator” \(^1\), and is defined as

$$s^i(w; x, R) = \int_{C(x, R)} dz^i \delta(w - z),$$

where $C(x, R)$ specifies a path from $R$ to $x$. The first two terms of the perturbative expansion of the set $\{\chi_{\alpha R}\}$ in powers of the magnetic field are given by

$$\chi_{\alpha R,i}(x) = W_{\alpha R,i}(x) - \frac{i}{2} \sum_{\beta R'} \int W_{\beta R',i} \Delta(x', z, R, t; x) W_{\alpha R',i}(z) + \ldots$$

Here the function $\Delta(x, y, z; t) = \Phi(z; x, t) + \Phi(x, y; t) + \Phi(y, z; t)$, which is simply a closed line integral of the vector potential. By Stokes’ theorem this is an integral of the magnetic flux passing through the surface identified by the paths connecting $x$, $y$, and $z$. Both $\Phi(x, R; t)$ and $\Delta(x, y, z)$ have been discussed earlier \(^1\).

We introduce a new set of cell-periodic functions $\{|\alpha k\rangle\}$ that are associated with Wannier functions of type $\alpha$,

$$|\alpha k\rangle = U_{\alpha n}(k)|n k\rangle. \tag{28}$$

In the case of a multi-band unitary transformation relating the original set of Bloch functions $\{|n k\rangle\}$ to the new set $\{|\alpha k\rangle\}$, the set $\{|\alpha k\rangle\}$ are not identified with eigenstates of the Hamiltonian. Matrix elements of the position operator between Wannier functions can be related to the non-Abelian Berry connection \(^1\) associated with this new set of cell-periodic functions

$$\int W^*_{\beta R,i}(x) x^a W_{\alpha 0,i}(x) dx = \frac{\Omega_{ac}}{(2\pi)^3} \int_{BZ} dke^{ikR} \tilde{S}_{\alpha a\beta}(k), \tag{29}$$

where $\tilde{S}_{\alpha a\beta}(k) \equiv i(\beta k) \partial_a \alpha k)$. \(^a\)

and $\partial_a$ indicates a partial derivative with respect to the Cartesian component $a$ of $k$. One could instead view the components of the non-Abelian Berry connection as a 2x2 matrix, with rows and columns indicating the spinor component of the bra or the ket state respectively. Then equation (30) is the trace over this matrix, since we implicitly sum over spinor components. The non-Abelian Berry connection associated with the set $\{|\alpha k\rangle\}$ is related to the non-Abelian Berry connection associated with the set $\{|n k\rangle\}$ via

$$\sum_{\alpha \beta} U_{\alpha \beta} \tilde{S}_{\alpha a\beta} U^\dagger_{\alpha n} = \xi_{mn} + W_{mn}, \tag{31}$$

where

$$W_{mn} = i \sum_{\alpha} (\partial_n U_{\alpha m}) U^\dagger_{\alpha n}. \tag{32}$$

Just as there is a relation (29) between the position matrix elements of the Wannier functions and the non-Abelian Berry connection, there is a relation between the spin matrix elements in the Wannier function basis and the $k$ dependent spin matrix elements in the Bloch cell-periodic basis. This relationship follows from equations (28) \(^1\), (29), and dividing the integral over all space into a sum of integrals over unit cells,

$$\frac{\hbar}{2} \int dx W^*_{\alpha 0,i}(x) \sigma^a W_{\beta 0,j}(x) = \frac{\Omega_{ac}}{(2\pi)^3} \int_{BZ} dke^{ikR} \tilde{S}_{\alpha a\beta}(k), \tag{33}$$

where

$$\tilde{S}_{\alpha a\beta}(k) \equiv \frac{\hbar}{2}(\alpha k | \sigma^a \beta k). \tag{34}$$

The spin matrix elements in the basis of the cell-periodic Bloch functions and the new Wannier cell-periodic functions are related by the unitary transformation

$$S_{mn}^a = \sum_{\alpha \beta} U_{\alpha m} \tilde{S}_{\alpha a\beta} U^\dagger_{\beta n}. \tag{35}$$

These quantities \(^1\), \(^1\) are new to the formalism and are required due to the addition of the spin degree of freedom.

Another useful identify involves the velocity operator,

$$\int \psi^\dagger_{n'k'}(x) \left( p^a(x) + e \sigma^b \frac{\hbar}{4\Omega_{ac}} \partial_b V(x) \right) \psi_{nk}(x) dx = mv_{n' \alpha}(k) \delta(k - k'), \tag{36}$$

where the velocity matrix elements are

$$v_{n' \alpha}(k) = \frac{\hbar}{\delta_{n'n} \partial_{\alpha n} E_{nk} + i \hbar} (E_{n'k} - E_{nk}) \xi_{n'n}(k). \tag{37}$$

While the expression (37) for the velocity matrix element is identical to what is found in previous work \(^1\), when spin was not included, the velocity operator now appearing in equation (36) is modified by spin-orbit coupling. A derivation of the expression for the velocity matrix elements as a function of the crystal momentum can be found in Appendix A.\(^a\)
D. Global Green function

We now turn to establishing Green function expressions in a form that will allow us to focus on individual lattice site quantities. We begin by expanding our field operators in the Heisenberg picture in a basis formed by the “adjusted Wannier functions” \(^{(21)}\).

\[
\hat{\psi}(\mathbf{x}, t) = \sum_{\alpha, \mathbf{R}} \hat{a}_{\alpha \mathbf{R}}(t) \left[ \hat{W}_{\alpha \mathbf{R}} \right]_{\uparrow}(\mathbf{x}, t) \] \(=\left[ \hat{\psi}_\uparrow(\mathbf{x}, t) \right], \quad (38)
\]

where from the anticommutation relations that the field operators satisfy it follows that

\[
\{ \hat{a}_{\alpha \mathbf{R}}(t), \hat{a}_{\beta \mathbf{R}}^\dagger(\mathbf{r}) \} = 0, \quad \{ \hat{a}_{\alpha \mathbf{R}}(t), \hat{a}_{\beta \mathbf{R}}^\dagger(\mathbf{r}) \} = \delta_{\alpha \beta} \delta_{\mathbf{R R}'}. \quad (39)
\]

The lesser, equal time single-particle Green function matrix then has the spin-components

\[
G_{\mathbf{ij}}^{mc}(\mathbf{x}, \mathbf{y}; t) = i\langle \hat{\psi}_\downarrow(\mathbf{y}, t) \hat{\psi}_\uparrow(\mathbf{x}, t) \rangle. \quad (40)
\]

Following manipulations used in the spinless problem \(^{(11)}\), the dynamics of \(G^{pl}\) are found to be governed by

\[
i\hbar \frac{\partial G_{\mathbf{ij}}^{pl}(\mathbf{x}, \mathbf{y}; t)}{\partial t} = K_{\mathbf{ij}}(\mathbf{x}, \mathbf{y}; t) G_{\mathbf{kl}}^{pl}(\mathbf{x}, \mathbf{y}; t) - G_{\mathbf{ij}}^{pl}(\mathbf{x}, \mathbf{y}; t) \bar{\mathcal{K}}_{\mathbf{kl}}(\mathbf{y}, \mathbf{x}; t) - e\Omega_{\mathbf{ij}}^{pl}(\mathbf{x}, t) G_{\mathbf{kl}}^{pl}(\mathbf{x}, \mathbf{y}; t), \quad (43)
\]

where the modified Hamiltonian differential operator matrix elements are

\[
K_{\mathbf{ij}}(\mathbf{x}, \mathbf{y}, t) = \frac{(\mathbf{p}(\mathbf{x}) - e\mathbf{\Omega}(\mathbf{x}, t))^2}{2m} \delta_{\mathbf{ij}} + V(\mathbf{x}) \delta_{\mathbf{ij}} - \frac{e\hbar}{2mc} \mathbf{\sigma}_{\mathbf{ij}} \cdot \mathbf{B}(\mathbf{x}, t) - \frac{e\hbar}{2mc} \mathbf{\sigma}_{\mathbf{ij}} \cdot \mathbf{B}_{\text{static}}(\mathbf{x}) \quad \!
\]

where once there was the applied vector potential accompanying the momentum, there is now the new quantity \(\mathbf{\Omega}_y(\mathbf{x}, t)\), and the applied scalar potential term has been replaced by one involving \(\mathbf{\Omega}_x(\mathbf{x}, t)\). These quantities depend only on the electromagnetic fields and not the potentials, and are given by

\[
\Omega_{\mathbf{ij}}^{pl}(\mathbf{x}, t) = \int s^l(\mathbf{w}; \mathbf{x}, \mathbf{y}) E^i(\mathbf{w}, t) d\mathbf{w}, \quad (45)
\]

\[
\Omega_{\mathbf{ij}}^{k}(\mathbf{x}, t) = \int \alpha^{k}(\mathbf{w}; \mathbf{x}, \mathbf{y}) B^l(\mathbf{w}, t) d\mathbf{w}, \quad (46)
\]

where we have employed another “relator” \(\alpha^{jk}(\mathbf{w}; \mathbf{x}, \mathbf{y})\) \(^{(42)}\), defined as

\[
\alpha^{jk}(\mathbf{w}; \mathbf{x}, \mathbf{y}) = \epsilon^{jmn} \int_{C(\mathbf{x}, \mathbf{y})} dz^m \frac{\partial z^n}{\partial x^k} \delta(\mathbf{w} - \mathbf{z}). \quad (47)
\]

When spin-orbit coupling is included, the Hamiltonian differential operator in general contains off-diagonal elements that couple spinor components. Thus the off diagonal elements of the Green function matrix are non-zero. The dynamics of \(G_{\mathbf{ij}}^{mc}(\mathbf{x}, \mathbf{y}; t)\) are governed by the equation

\[
i\hbar \frac{\partial G_{\mathbf{ij}}^{mc}(\mathbf{x}, \mathbf{y}; t)}{\partial t} = \mathcal{H}_{\mathbf{ik}}(\mathbf{x}, t) G_{\mathbf{kl}}^{mc}(\mathbf{x}, \mathbf{y}; t) - G_{\mathbf{ij}}^{mc}(\mathbf{x}, \mathbf{y}; t) \bar{\mathcal{H}}_{\mathbf{kl}}(\mathbf{y}, \mathbf{x}), \quad (41)
\]

where the matrix \(\bar{\mathcal{H}}(\mathbf{x}, t)\) is identical to \(\mathcal{H}(\mathbf{x}, t)\), except that in the matrix elements of \(\bar{\mathcal{H}}(\mathbf{x}, t)\) the differential operators are taken as acting to the left.

To move from the minimal-coupling form \(G_{\mathbf{ij}}^{mc}(\mathbf{x}, \mathbf{y}; t)\) of the Green function matrix to one that is gauge-invariant with respect to the electromagnetic potentials, we introduce a global Green function according to

\[
G^{pl}(\mathbf{x}, \mathbf{y}; t) = e^{-i\mathbf{p}(\mathbf{x}, \mathbf{y}; t)} G^{mc}(\mathbf{x}, \mathbf{y}; t). \quad (42)
\]

The quantities \(\mathbf{\Omega}_y(\mathbf{x}, t)\), which are dependent on the magnetic field, and \(\mathbf{\Omega}_x^{pl}(\mathbf{x}, t)\), which are dependent on the electric field, have been discussed earlier \(^{(11)}\). In moving from \(G_{\mathbf{ij}}^{mc}(\mathbf{x}, \mathbf{y}; t)\) to \(G_{\mathbf{ij}}^{pl}(\mathbf{x}, \mathbf{y}; t)\), the gauge freedom of the electromagnetic potentials has been replaced by a freedom in choosing the path \(C(\mathbf{x}, \mathbf{y})\) involved in the definitions of the relators.

E. Site quantities

We now wish to decompose quantities like the charge and current densities into parts we can associate with each lattice site \(\mathbf{R}\). This allows us to identify motion within and between sites, and provides natural expansion points for quantities when we consider the optical response. To do this we begin by writing the expectation values of the charge and current density operators in terms of differential operators acting on the global Green
function,

\[ \langle \dot{\rho}(x, t) \rangle = -ie [G^{gl}_{\alpha}(x, y, t)]_{y \to x} + \rho^{\text{ion}}(x), \] (48)

and

\[ \langle \dot{j}(x, t) \rangle = -ie \left[ J^{gl}_{ij}(x, y, t)G^{gl}_{ij}(x, y, t) \right]_{y \to x}. \] (49)

Here we have introduced a differential operator for the global charge current,

\[ J^{gl}_{ij}(x, y, t) = J^{gl}_{ij}(x, p(x, y, t)) + J^{gl}_{ij}(y, p^*(y, x, t)), \] (50)

with

\[ J^{gl}_{ij}(x, p(x, y, t)) = \frac{e}{2m} p(x, y, t) \delta_{ij} + \hat{e} \epsilon_{abc} \frac{e\hbar}{2m} \partial_{x^a} \delta_{ij} + \hat{e} \epsilon_{abc} e\hbar \frac{\hbar}{8m^2 c^2} \sigma^{gl}_{ij} \nabla V(x))^b. \] (51)

and where we have defined a modified momentum operator by

\[ \hbar \frac{\partial}{\partial t} = \sum_{\lambda \lambda'_{\rho \rho'}} e^{i\Delta(R, R', t)} (\hat{H}_{\alpha R;\lambda \lambda'; R'} t) \eta_{\lambda \lambda'; R'} t (t) - \eta_{\lambda \lambda'; R'} t (t) \hat{H}_{\lambda \lambda'; R'} t (t) - e^{i\Delta(R, R', t)} \Omega^{\lambda_{\rho \rho'}}_{R}(t) \eta_{\lambda \lambda'; R'} t (t). \] (55)

The matrix \( \hat{H} \) is Hermitian, and its matrix elements are

\[ \hat{H}_{\alpha R;\lambda \lambda'; R'} t (t) = \frac{1}{2} \int d\chi_{\lambda \lambda'; R'} t (x, t) e^{i\Delta(R, R', t)} (K_{\alpha R; R'} t (x, t)) \chi_{\lambda \lambda'; R'} t (x, t). \] (56)

Since all the terms appearing in the dynamics of \( \eta_{\lambda \lambda'; R'} t \) are gauge-invariant in the electromagnetic sense, if its initial conditions are set before any fields are applied then it will remain so at all later times. The matrix elements \( \hat{H}_{\alpha R;\lambda \lambda'; R'} t \) are effectively hopping matrix elements and on-site energies. While the matrix elements between different sites \( (R \neq R') \) are in general non-zero, for \( R \) far from \( R' \) they can be reasonably expected to be zero. Additionally, on the same site there are hopping matrix elements between different orbital types \( \alpha \).

We are now ready to decompose the global Green function into site specific Green functions labelled by a lattice site \( R \),

\[ G^{gl}_{ij}(x, y, t) = \sum_{R} e^{-i\Delta(x, y, R, t)} G_{ij}^{R}(x, y, t), \] (57)

where

\[ p(x, y, t) = p(x) - \frac{e}{c} \Omega_{y}(x, t). \] (52)

The global Green function can then be expanded in the adjusted Wannier function basis as

\[ G^{gl}_{ij}(x, y, t) = i e^{-i\Phi(x, y, t)} \sum_{\alpha, \beta, R, R'} \langle \hat{a}^\dagger_{\beta R'} t (t) \hat{a}_{\alpha R} t (t) \rangle \times W_{\beta R'} t (y, t) W_{\alpha R} t (x, t), \] (53)

where we define the single particle density matrix as

\[ \eta_{\alpha R;\beta R'} t (t) = \langle \hat{a}^\dagger_{\beta R'} t (t) \hat{a}_{\alpha R} t (t) \rangle e^{i\Phi(R', R, t)}, \] (54)

The phase factor is chosen to ensure the dynamics of the single particle density matrix are gauge-invariant in the electromagnetic sense, as was done with the global Green function. The dynamics are governed by
\[ G_R^\mathbf{R}(\mathbf{x}, \mathbf{y}; t) = \frac{i}{2} \sum_{\alpha, \beta, \mathbf{R}'} \eta_{\alpha \mathbf{R}, \beta \mathbf{R}'}(t) e^{i\Delta(R', \mathbf{R}, \mathbf{x}, \mathbf{y}, t)} \chi^{*}_{\beta \mathbf{R}, j}(\mathbf{y}, t) \chi_{\alpha \mathbf{R}, i}(\mathbf{x}, t) \]

With the identification of \( G^\mathbf{R} \) we can proceed to write the microscopic charge and current densities as the sum of individual site contributions,

\[ \langle \dot{\rho}(\mathbf{x}, t) \rangle = \sum_{\mathbf{R}} \rho_R(\mathbf{x}, t), \]
\[ \langle \dot{j}(\mathbf{x}, t) \rangle = \sum_{\mathbf{R}} j_R(\mathbf{x}, t). \]

Site quantities such as \( j_R(\mathbf{x}, t) \) in general involve differential operators acting on the site Green functions \( G^\mathbf{R}(\mathbf{x}, \mathbf{y}; t) \). Expressions for the site charge and current density are found in Appendix B.

As was outlined earlier [11], we must also identify a free charge density \( p_F(\mathbf{x}, t) \) and a free charge current density \( j_F(\mathbf{x}, t) \). “Free” charges at each site are constructed by placing all the charge associated with a site \( \mathbf{R} \) at that site. Since the total charge associated with each site is not necessarily constant in time, link currents are identified, and from these we identify the free current density. The expressions for these quantities can be found in Appendix B.

The charge density \( \rho_R(\mathbf{x}, t) \) associated with each site can be considered as the sum of the total charge associated with site \( \mathbf{R} \) localized at that lattice site [14], and contributions from a microscopic polarization field associated with the site that captures the multipole moments of the charge distribution,

\[ p_R(\mathbf{x}, t) \equiv \int s(\mathbf{x}; \mathbf{y}, \mathbf{R}) \rho_R(\mathbf{y}, t) d\mathbf{y}. \]

We also introduce magnetization fields associated with each site, which are further split into three contributions,

\[ m_R(\mathbf{x}, t) \equiv \tilde{m}_R(\mathbf{x}, t) + m_R(\mathbf{x}, t) + \tilde{m}_R(\mathbf{x}, t). \]

These are the “atomic,” “itinerant,” and “spin” contributions respectively. The atomic magnetization is related to the site current density \( j_R(\mathbf{x}, t) \) in the way that the magnetization in an isolated atom would be related to its current density. The itinerant magnetization arises because there are corrections to this in a solid, since the sites are not isolated; this is discussed in Appendix B.

For brevity we omit these expressions in the main body of the text, since their derivation follows exactly what was done earlier [11], with the understanding that operators such as the charge current and the Hamiltonian matrix elements are different, and the Wannier functions are now spinors. The spin contribution to the magnetization, however, is a new term here and arises due to including the spin degree of freedom. It is given by

\[ \mathbf{m}_R(\mathbf{x}, t) = \frac{e\hbar}{4mc} \sum_{\alpha, \beta, \mathbf{R}', \mathbf{R}''} (\delta_{\mathbf{RR}'} + \delta_{\mathbf{RR}''}) e^{i\Delta(R', \mathbf{x}, \mathbf{R}'')} \chi^{*}_{\beta \mathbf{R}' \mathbf{j}}(\mathbf{x}, t) \sigma_i \chi_{\alpha \mathbf{R}' \mathbf{j}}(\mathbf{x}, t) \eta_{\alpha \mathbf{R}' \beta}(t). \]

The total microscopic polarization and magnetization fields are simply the sum over their respective site quantities,

\[ p(\mathbf{x}, t) = \sum_{\mathbf{R}} p_R(\mathbf{x}, t), \]
\[ m(\mathbf{x}, t) = \sum_{\mathbf{R}} m_R(\mathbf{x}, t). \]

We can write the expectation value of the total charge density and current density in terms of the polarization, magnetization, and free charge and current:

\[ \langle \dot{\rho}(\mathbf{x}, t) \rangle = -\nabla \cdot p(\mathbf{x}, t) + \rho_F(\mathbf{x}, t), \]
\[ \langle \dot{j}(\mathbf{x}, t) \rangle = \frac{\partial p(\mathbf{x}, t)}{\partial t} + e\nabla \times m(\mathbf{x}, t) + j_F(\mathbf{x}, t). \]

The expressions for all the aforementioned site quantities, and for the free charge and current densities, can be found in Appendix B.

At this point, spatial averaging can be employed to construct the macroscopic analogues of the microscopic quantities defined above, and the macroscopic version of (65) follows immediately; the treatment of light propagating through the crystal, taking into account its variation over a unit cell if necessary, can then be addressed [12]. However, for the rest of this paper we focus on ground state quantities and the linear response to constant and uniform applied fields. Then the macroscopic polarization and magnetization are uniform throughout the crystal, and given by

\[ P = \frac{\mu_R}{\Omega_{uc}}, \quad M = \frac{\nu_R}{\Omega_{uc}}, \]

where

\[ \mu_R = \int d\mathbf{x} p_R(\mathbf{x}), \]
\[ \nu_R = \int d\mathbf{x} (\mathbf{x} - \mathbf{R}) \rho_R(\mathbf{x}). \]
is the electric dipole moment of site \( \mathbf{R} \), and

\[
\nu_{\mathbf{R}} = \int dx \, m_{\mathbf{R}}(x) \tag{67}
\]

is the magnetic dipole moment of site \( \mathbf{R} \); in our cases of interest these will be the same for all \( \mathbf{R} \). In [65] and below we employ the usual straight-line paths in the integrals used to construct the relators [66-67] [11].

### III. GROUND STATE POLARIZATION AND MAGNETIZATION

We first consider the ground state polarization and magnetization. The expressions for these generally follow those found earlier [13], with the understanding that the Wannier functions are now spinors, but will be quoted for completeness and continuity; more serious changes to those found earlier [13], with the understanding that the magnetization. The expressions for these generally follow those found earlier [11].

#### A. Polarization

In the ground state we have \( \mu_{\mathbf{R}} = \mu_{\mathbf{R}}^{(0)} \), where

\[
\mu_{\mathbf{R}}^{(0)} = \int d\mathbf{x} (\mathbf{x} - \mathbf{R}) \rho_{\mathbf{R}}^{(0)}(\mathbf{x})
= e \sum_\alpha f_\alpha \int d\mathbf{x} W_{\alpha 0}^*(\mathbf{x}) \mathbf{x} W_{\alpha 0}(\mathbf{x}) + \sum_N q_N d_N,
\tag{68}
\]

and where in the second line we have used the point-charge approximation [12] for the ions. Using the relationship between the matrix elements of the position operator and the non-Abelian Berry connection, we can write the electronic contribution to the dipole moment as a k-space integral, and then from the first of (65) we find

\[
P^{(0)} = e \sum_n f_n \int \frac{dk}{(2\pi)^3} (\xi_n^a + \mathcal{W}_{nn}^a) + \sum_N \frac{q_N}{\Omega_{uc}} d_N^a \tag{69}
\]

for the ground state polarization. This expression illustrates the useful correspondence between the non-Abelian Berry connection and the position matrix elements in the Wannier function basis. Additionally, it depends on the diagonal elements of the matrix \( \mathcal{W} \), and hence is gauge dependent. The macroscopic polarization is only unique modulo a “quantum of ambiguity” that originates from this gauge dependence [3]. When using the Wannier functions as a basis for calculations, the ambiguity arises because one can change which “home cell” to associate to each orbital type via a unitary transformation.

#### B. Magnetization

The magnetic dipole moment (67) of a site is the sum of the atomic, itinerant, and spin contributions [31]. From each one can find the respective macroscopic magnetization fields

\[
\tilde{\mathbf{M}} = \frac{1}{\Omega_{uc}} \int d\mathbf{x} \, \tilde{m}_{\mathbf{R}}(\mathbf{x}), \tag{70}
\]

A detailed discussion of the ground state atomic and itinerant magnetic dipole moments was presented earlier [11]. The real space integral expression for the first can be simplified to

\[
\tilde{\mathbf{M}}^{(0)} = \frac{e \epsilon_{\alpha\beta}}{2\hbar c} \sum_{\alpha} f_\alpha \int d\mathbf{x} (\mathbf{x}^a - R^a) W_{\alpha R}(\mathbf{x}) \times \left( e^{ibm} \frac{\hbar}{8m^2c^2} \gamma_l \nabla_m \mathbf{V}(\mathbf{x}) \right) W_{\alpha R}(\mathbf{x}), \tag{71}
\]

where compared to earlier work [11] we note the new velocity operator in the brackets; it has been altered by the spin-orbit coupling in the Hamiltonian, which results in a contribution that is transverse to the gradient of the crystal potential and the spin of the electron. The corresponding expression for the itinerant contribution to the magnetic dipole moment is

\[
\tilde{\mathbf{M}}^{(0)} = \frac{e \epsilon_{\alpha\beta}}{2\hbar c \Omega_{uc}} \sum_{\alpha\beta R} f_\alpha \text{Im} \left\{ \int d\mathbf{x} \mathbf{R}^{a,b} \times W_{\mu R}(\mathbf{x}) W_{\alpha 0}(\mathbf{x}) H^{(0)}_{\alpha 0,\beta R} \right\}, \tag{72}
\]

where the zero-order Hamiltonian matrix elements are

\[
H^{(0)}_{\alpha R;\beta R'} = \int W_{\alpha R}^*(\mathbf{x}) \mathcal{H}^{(0)}(\mathbf{x}) W_{\beta R'}(\mathbf{x}) d\mathbf{x}. \tag{73}
\]

As done earlier [11], these can be converted to k-space integrals and, using [65], expressions for \( \tilde{\mathbf{M}}^{(0)} \) and \( \tilde{\mathbf{M}}^{(0)} \) can be constructed. Despite the appearance of the spin-orbit contribution in (71), the k-space expression for \( \tilde{\mathbf{M}}^{(0)} \) is formally the same as if there were no spin, because the velocity matrix element takes the same form in both cases (see Appendix A); the expression for \( \tilde{\mathbf{M}}^{(0)} \) is the same as well.

However, we have a new contribution to the total magnetization due the spin degree of freedom. The spin magnetic dipole moment is just as one would expect, and is given by
\[ \tilde{\eta}_{\mathbf{R}}^{(0)} = \frac{e\hbar}{2mc} \sum \int dx W_{\alpha\mathbf{R}}^*(x) \sigma W_{\alpha\mathbf{R}}(x). \] (74)

Using equations (33), (35) and (65) we find

\[ \tilde{\mathbf{M}}^{(0)} = \frac{e}{mc} \sum \frac{d\mathbf{k}}{(2\pi)^3} S_{\mathbf{m}\mathbf{n}}(\mathbf{k}), \] (75)

which is gauge-invariant in the sense of how one constructs the Wannier functions.

### IV. LINEAR RESPONSE TO UNIFORM FIELDS

We now turn to the first order perturbative modifications to the polarization and magnetization (65), due to static and uniform applied electric and magnetic fields. The expressions for the electric and magnetic dipole moments, \(\mu_{\mathbf{R}}\) and \(\nu_{\mathbf{R}}\), which must be evaluated, take the form

\[ \Lambda_{\mathbf{R}} \equiv \sum_{\alpha\beta_{\mathbf{R}'\mathbf{R}}} \Lambda_{\beta\mathbf{R}'\alpha\mathbf{R}}(\mathbf{R}) \eta_{\alpha\mathbf{R}'\beta\mathbf{R}} + \Lambda_{\mathbf{R}m}^{nm}, \] (76)

where \(\eta_{\alpha\mathbf{R}'\beta\mathbf{R}}\) is the single particle density matrix, \(\Lambda_{\beta\mathbf{R}'\alpha\mathbf{R}}(\mathbf{R})\) is the “site quantity matrix element,” and \(\Lambda_{\mathbf{R}m}^{nm}\) is a contribution from the ions that arises only for \(\mu_{\mathbf{R}}\). For example, the contribution to \(\nu_{\mathbf{R}}\) due to \(\nu_{\mathbf{R}}\) arises from the integral of \(\tilde{\mathbf{m}}_{\mathbf{R}}(x)\) (see (62)) over all space, which indeed takes the form (70), with no ion contribution since the ions are assumed fixed. A perturbative modification to a site quantity, such as \(\mu_{\mathbf{R}}\) or \(\nu_{\mathbf{R}}\), will then depend on how both the site quantity matrix element and the single particle density matrix are perturbed. If we take \(\Lambda_{\alpha\mathbf{R}'\beta\mathbf{R}}\) to zeroth order in the applied field and the single particle density matrix to first order, we obtain what we call the “dynamical modification,” with the phrase chosen because the single particle density matrix characterizes the electron hopping amplitude between various lattice sites and orbital types in response to applied fields. The other first order contribution to a site quantity is obtained by taking the single particle density matrix to zeroth order, \(\eta_{\alpha\mathbf{R}'\beta\mathbf{R}}^{(0)} = \delta_{\alpha\beta} \delta_{\mathbf{R}'\mathbf{R}}\), and the modification of the site quantities \(\Lambda_{\alpha\mathbf{R}'\beta\mathbf{R}}\) to first order in the applied fields. We call this the “composition” modification. In a compositional modification the populations have not changed, but the site quantity itself is altered by the applied fields.

We annotate first order perturbative modifications by a superscript \(I\) if the response is dynamical in nature, and by a superscript \(II\) if the response is compositional in nature. And we use \((E)\) or \((B)\) to indicate a response to the electric field or magnetic field, respectively.

#### A. First order response

The dynamical modifications are determined by the response of the single particle density matrix to an external electromagnetic field. A detailed treatment of this has been presented earlier (11), so here we quote the results where they are the same – but with the understanding that quantities now involve spinor functions – and note changes where necessary. While we present the result for the response of the polarization to an applied electric field, our main focus is on the response of the polarization to the magnetic field, and on the response of the magnetization to the electric field.

The first order response of the single particle density matrix to an applied DC electric field is given by \(\eta_{\alpha\mathbf{R}'\beta\mathbf{R}}^{(E)}\):

\[ \eta_{\alpha\mathbf{R}'\beta\mathbf{R}}^{(E)} = e E_{\mathbf{F}} \sum \frac{f_{nm}}{BZ} \int \frac{d\mathbf{k}}{(2\pi)^3} \left( \frac{\epsilon_{\mathbf{k}}^i \mathbf{R} - \mathbf{R}' \cdot \mathbf{k}^j}{E_{\mathbf{m}k} - E_{\mathbf{n}k}} \right) \xi_{\mathbf{m}\mathbf{n}}(\mathbf{k}), \] (77)

where \(f_{nm} = f_n - f_m\), while the first order response of the single particle density matrix to an applied DC magnetic field is given by:

\[ \eta_{\alpha\mathbf{R}'\beta\mathbf{R}}^{(B)} = \frac{e}{4\hbar c} \sum \int d\mathbf{k} e^{ik\cdot(\mathbf{R} - \mathbf{R}')^j} \left( \frac{U_{\mathbf{m}\mathbf{n}}^i(\mathbf{k}) \xi_{\mathbf{m}\mathbf{n}}^b(\mathbf{k})}{E_{\mathbf{m}k} - E_{\mathbf{n}k}} \right) \]

\[ + \frac{e}{4\hbar c} \sum \int d\mathbf{k} e^{ik\cdot(\mathbf{R} - \mathbf{R}')^j} \left( \frac{U_{\mathbf{m}\mathbf{n}}^i(\mathbf{k}) \xi_{\mathbf{m}\mathbf{n}}^b(\mathbf{k})}{E_{\mathbf{m}k} - E_{\mathbf{n}k}} \right), \] (78)

where

\[ \xi_{\mathbf{m}\mathbf{n}}^b(\mathbf{k}) = i \sum_s \left( \frac{E_{skk} - E_{sk}}{E_{skk} - E_{sk}} + \frac{E_{sk} - E_{skk}}{E_{skk} - E_{sk}} \right) \xi_{s\mathbf{m}}^a(\mathbf{k}) \xi_{s\mathbf{n}}^b(\mathbf{k}) - 2 \frac{\partial_{\mathbf{k}} E_{skk} + \partial_{\mathbf{k}} E_{sk}}{E_{skk} - E_{sk}} \xi_{s\mathbf{m}}^a(\mathbf{k}) \xi_{s\mathbf{n}}^b(\mathbf{k}). \] (79)

The last line of the response of the single-particle density matrix to an applied magnetic field (78) is a new contribution,
above and beyond what was shown in previous work \cite{13}. It arises due to the magnetic dipole energy term in the Hamiltonian.

1. Polarization response to $E$

There is only a dynamical modification of the electric dipole moment due to a constant and uniform electric field, and thus only a dynamical modification of the polarization due to that field, $P^{(E)} = P^{(E;I)}$; using \cite{65} we find

$$P^{(E;I)} = e^2 E^l \sum_{nm} f_{nm} \int_{BZ} \frac{dk}{(2\pi)^3} \frac{\epsilon_{i}^{nm} \xi_{nm}}{E_{mk} - E_{nk}}. \tag{80}$$

The expression has not qualitatively changed upon incorporating spin effects to the dynamics, and is a standard result. As was highlighted previously \cite{13}, this response is gauge-invariant.

2. Polarization response to $B$

There is both a dynamical and a compositional modification of the polarization due to an applied constant and uniform magnetic field, $P^{(B)} = P^{(B;I)} + P^{(B;II)}$. The dynamical modification is

$$P^{(B;I)} = \frac{e^2}{4\hbar c} \epsilon^{lab} B^l \sum_{mn} f_{nm} \int \frac{dk}{(2\pi)^3} \xi_{nm}(\epsilon)^{ab} + \frac{e^2}{\hbar c} \epsilon^{lab} B^l \sum_{mns} f_{nm} \int \frac{dk}{(2\pi)^3} \Re \left[ i \xi_{ns}(\epsilon)^{ab} \right]$$

$$+ \frac{e^2}{mc} B^a \sum_{mn} f_{nm} \int \frac{dk}{(2\pi)^3} \xi_{nm}(\epsilon)^{ab} \right]. \tag{81}$$

The first two terms of the right hand side of equation (81) follow what was previously found \cite{13}, with the understanding that the periodic part of the Bloch function is now a two-component spinor. The last term is new, and due to the added contribution to the first order linear response of the single particle density matrix to a constant and uniform magnetic field, the last line of (78).

The compositional modification to the polarization due to an applied constant and uniform magnetic field is

$$P^{(B;II)} = \frac{e^2}{2\hbar c} \epsilon^{lab} B^l \sum_{\alpha \beta} \Re \left[ \int \frac{dk}{(2\pi)^3} \xi_{\beta \alpha} \partial_{\alpha \beta} \right]. \tag{82}$$

This expression is identical to what is found earlier \cite{13}. Combining (81) and (82) we get the total response of the polarization to a constant and uniform magnetic field, which is characterized by the magneto-polarizability (MP) tensor, discussed in Section V. Previously \cite{13, 26, 27, 29} only the contribution to the MP tensor due to translational motion of the electrons was identified, the orbital magneto-polarizability (OMP) tensor; here we have a spin contribution to the full MP tensor as well.

3. Magnetization response to $E$

Using the contributions to the magnetic dipole moment (70) in \cite{65} we see that in general we can expect atomic, itinerant, and spin contributions to the response of the magnetization to a constant and uniform electric field, $M^{(E)} = M^{(E;I)} + M^{(E;II)}$. All three involve dynamical modifications, and the itinerant contribution also has a compositional modification. The atomic contribution, $M = M^{(E;I)}$, is given by

$$M^{(E;I)} = \frac{e^2}{4\hbar c} \epsilon^{lab} E^l \sum_{mn} f_{nm} \int \frac{dk}{(2\pi)^3} \frac{\partial E_{mk}}{E_{mk} - E_{nk}} \xi_{nm}(\epsilon)^{ab}$$

$$+ \frac{e^2}{2\hbar c} \epsilon^{lab} E^l \sum_{mns} f_{nm} \int \frac{dk}{(2\pi)^3} \Re \left[ i \xi_{ns}(\epsilon)^{ab} \right]$$

$$+ \frac{e^2}{2\hbar c} \epsilon^{lab} E^l \sum_{mns} f_{nm} \int \frac{dk}{(2\pi)^3} \Re \left[ i \xi_{ns}(\epsilon)^{ab} \right]. \tag{83}$$

while the itinerant contribution, $M = M^{(E;I)} + M^{(E;II)}$, is the sum of a dynamical modification,
\[
\tilde{M}^{(E,l)} = -\frac{e^2}{4\hbar c} E^i \epsilon^{iab} \sum_{mn} f_{nm} \int \frac{dk}{(2\pi)^3} \epsilon^{b}_{snm} \epsilon^{a}_{smn} \\
\times \int \frac{dk}{(2\pi)^3} \epsilon^{b}_{snm} \epsilon^{a}_{smn} \\
\times \partial_{\alpha} E_{mk} + \partial_{\alpha} E_{nk} \\
\times \Re \left[ i \epsilon^{b}_{snm} \mathcal{W}^{a}_{mn} \epsilon^{b}_{smn} \right] ,
\]
and a compositional modification,
\[
\tilde{M}^{(E,l)} = \frac{e^2}{2\hbar c} E^i \epsilon^{iab} \sum_{\alpha \beta} f_{\alpha} \Re \left[ \int \frac{dk}{(2\pi)^3} \epsilon^{b}_{snm} \epsilon^{a}_{smn} \right] .
\]
The spin contribution, \(\tilde{M} = \tilde{M}^{(E,l)}\) is
\[
\tilde{M}^{(E,l)} = \frac{e^2}{mc} E^i \sum_{mn} f_{nm} \int \frac{dk}{(2\pi)^3} \epsilon^{b}_{snm} \epsilon^{a}_{smn} \\
\times \partial_{\alpha} E_{mk} + \partial_{\alpha} E_{nk} \\
\times \Re \left[ i \epsilon^{b}_{snm} \mathcal{W}^{a}_{mn} \epsilon^{b}_{smn} \right] .
\]
Only the spin contribution is new. Combining all these modifications we find the total response of the magnetization to a constant and uniform electric field. This response is also characterized by the MP tensor.

The Chern-Simons contribution can be written as \[13\]
\[
\alpha_{CS}^{il} = \frac{e^2}{2\hbar c} \epsilon^{iab} \int_{BZ} \frac{dk}{(2\pi)^3} \left[ 2 \sum_{cv'} \Re \left( \partial_{\alpha} v(c) | c \partial_{\alpha} v' \right) \partial_{\beta} \mathcal{S}^{a}_{cv} \right] + \sum_{cv} \Re \left( \partial_{\alpha} v(c) | \partial_{\beta} v \right) \right] \\
+ \frac{e^2}{2\hbar c} \epsilon^{iab} \sum_{mn} f_{nm} \int \frac{dk}{(2\pi)^3} \epsilon^{b}_{snm} \epsilon^{a}_{smn} \\
+ \frac{e^2}{2\hbar c} \epsilon^{iab} \sum_{\alpha \beta} f_{\alpha} \int \frac{dk}{(2\pi)^3} \epsilon^{b}_{snm} \epsilon^{a}_{smn} \\
- \delta^{i}_{il} \frac{e^2}{2\hbar c} \epsilon^{abc} \int_{BZ} \frac{dk}{(2\pi)^3} \sum_{cv'} \left( \mathcal{S}^{a}_{cv} \partial_{\beta} \mathcal{S}^{b}_{cv} - \frac{2i}{3} \sum_{v} \epsilon^{a}_{cv} \epsilon^{b}_{cv} \mathcal{S}^{c}_{cv} \right) + \left( \partial_{\alpha} \mathcal{W}^{a}_{cv} \right) \partial_{\alpha} \mathcal{W}^{b}_{cv} - \frac{2i}{3} \sum_{v} \mathcal{W}^{a}_{cv} \mathcal{W}^{b}_{cv} \mathcal{W}^{c}_{cv} .
\]
This is the usual Chern-Simons contribution to the MP tensor \[24, 27, 29, 43\]. The “cross gap” contribution can be written as \[13\]
\[
\alpha_{C}^{il} = \frac{e^2}{h c} \epsilon^{iab} \int_{BZ} \frac{dk}{(2\pi)^3} \left\{ - \sum_{cv} \partial_{\beta} (E_{cv} - E_{cv}) \Re \left( \partial_{\alpha} v(c) | c \partial_{\beta} v \right) - \sum_{uv'} \frac{E_{uv} - E_{uv'}}{E_{uv} - E_{uv'}} \Re \left( \partial_{\alpha} v(c) | \partial_{\beta} v(c) \right) \\
+ \sum_{v'v \neq v' \neq v} \frac{E_{uv} - E_{uv'}}{E_{uv} - E_{uv'}} \Re \left( \partial_{\alpha} v(c) | \partial_{\beta} v(c) \right) \right\} .
\]

where \(v\) labels an occupied state and \(c\) labels an unoccupied state; when \(n, m, s\) are used the index runs over both occupied and unoccupied states. The Chern-Simons and cross gap contributions have not changed their form by adding the spin degree of freedom, the Zeeman term, and spin-orbit coupling. We do, however, now have a spin

V. MAGNETO-POLARIZABILITY

The magneto-polarizability tensor is defined as
\[
\alpha^{il} = \frac{\partial P^{l}}{\partial B^{i}} \bigg|_{B=0} = \frac{\partial M^{l}}{\partial E^{i}} \bigg|_{E=0} .
\]
If the response of the polarization to the magnetic field is calculated, the new spin contribution to the MP tensor identified here appears as a dynamical modification of the polarization due to the Zeeman term in the Hamiltonian. Alternately, if the response of the magnetization to the electric field is calculated, it appears as a dynamical modification to the magnetization due to the presence of \(\Omega_{R}^{il}\) in the Hamiltonian matrix elements \[16\].

The orbital contributions to the MP tensor are usually written as the sum of “cross gap contributions”, \(\alpha^{il}_{C}\), and the isotropic Chern-Simons contribution \(\alpha^{il}_{CS}\). In section IV of Mahon et al. \[11\] the splitting of the orbital contributions to the MP tensor derived there into \(\alpha^{il}_{C}\) and \(\alpha^{il}_{CS}\) is performed. That strategy is valid here as well, and so we can split the full MP tensor into the familiar Chern-Simons contribution, the cross gap contribution, and the new explicitly spin dependent contribution,
\[
\alpha^{il} = \alpha^{il}_{CS} + \alpha^{il}_{G} + \alpha^{il}_{S} .
\]
contribution to the MP tensor, which can be written as

$$\alpha_{il}^d = \frac{2e^2}{mc} \sum_{\nu c} \int \frac{dk}{(2\pi)^3} \text{Re} \left[ \frac{\xi_{\nu c}S_{\nu c}^l}{E_{\nu c} - E_{c k}} \right].$$

It is often stated that the OMP is non-zero only if the system breaks both time-reversal and inversion symmetry \([29]\). This statement is subject to the fact that the OMP tensor has a “quantum of ambiguity” through the gauge-dependent Chern-Simons contribution, somewhat analogous to the “quantum of ambiguity” of the polarization \([29]\). However, like the cross-gap contribution the spin contribution to the MP tensor vanishes unambiguously if either time-reversal or inversion is a symmetry. In Appendix \(C\) we confirm that when there is either inversion or time-reversal symmetry all the gauge-dependent part of the Chern-Simons contribution necessarily vanishes.

The molecular crystal limit is one that can be easily explored within the framework we have introduced here. In that limit the energy bands are now flat, and we choose the unitary matrix to be \(U_{\alpha\alpha} = \delta_{\alpha\alpha}\). The Wannier functions are now eigenstates of the molecular Hamiltonian, and have no compact support with Wannier functions at different lattice sites. These simplifications lead to very succinct expressions for the different contributions to the MP tensor, which we denote with a circle accent to distinguish quantities in the molecular crystal limit:

$$\hat{\alpha}_{CS}^d = \frac{e^2}{\Omega_{uc} \hbar c} \epsilon^{lab} \text{Re} \left[ i \sum_{\nu c'} \bar{x}_{\nu c}^a x_{\nu c'}^b \right],$$

and

$$\hat{\alpha}_{O}^d = \frac{e^2}{\Omega_{uc} \hbar c} \epsilon^{lab} \sum_{\nu c} \frac{E_{\nu c} - E_c}{E_c - E_{\nu c}} \text{Re} \left[ i x_{\nu c}^a x_{\nu c'}^b \right],$$

and

$$\hat{\alpha}_{S}^d = \frac{2e^2}{\Omega_{uc} mc} \sum_{\nu c} \text{Re} \left[ \frac{x_{\nu c}^i S_{\nu c}^l}{E_{\nu c} - E_{c k}} \right],$$

where

$$x_{\nu c}^i = \int dx W_{\nu \alpha i}(x) x^i W_{\nu \alpha i}(x).$$

Except for the expression for \(\hat{\alpha}_{S}^d\), the results are straightforward generalizations of what was found earlier for spinless systems \([11]\). In Appendix \(C\) we confirm that in the molecular crystal limit the full MP tensor vanishes (modulo a “quantum of ambiguity” contained in the Chern-Simons contribution) if either inversion or time-reversal symmetry is present, as it does in the general case.

VI. CONCLUSION

In this paper we have shown how to modify the formalism developed earlier \([11]\) to include electron spin. The Hamiltonian had to be modified to include an interaction term between the spin and an external magnetic field, and spin-orbit coupling. These changes had consequences for the electron probability current. The Zeeman term is linked to the magnetization current that must now be added. Additionally the spin-orbit coupling modifies the velocity operator, leading to an added contribution to the current that is transverse to the electron spin and transverse to the crystal electric field. We have neglected some of the effects of external fields on the spin-orbit coupling term. The dynamics and site quantities are now described in terms of a Green function matrix where the indices are the spinor components of the field operators. The site quantities are defined in the same manner as was previously discussed \([11]\) with the addition of a site spin magnetization. Some of the real space expressions for quantities, like the ground state atomic and itinerant spin magnetization, are different from what was found previously \([13]\). This is because they involve the modified velocity operator and a different unperturbed Hamiltonian. Interestingly, when converted to an integral over the Brillouin zone, they are identical to the previous work \([13]\). We find an expected addition to the MP tensor due to the spin-magnetization, and it is gauge-invariant. This new part of the MP vanishes if there is either inversion or time-reversal symmetry, as does the rest of the MP modulo the “quantum of ambiguity” that resides in the Chern-Simons contribution. Additionally, the formalism can be extended to treat finite frequency response calculations, as well as to treat fields that vary over the unit cell. Another natural extension of the formalism upon adding spin is to incorporate how spin-currents can be treated.

VII. ACKNOWLEDGEMENTS

We thank Jason Kattan and Perry Mahon for helpful comments and discussions. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).
Appendix A: VELOCITY MATRIX ELEMENTS

To determine the form of the velocity matrix elements as functions of \( \mathbf{k} \) we begin by manipulating the left side of equation (36),

\[
\begin{aligned}
&= \int \psi_{n'k'}^\dagger(x) \left[ \frac{\hbar}{im} \frac{\partial}{\partial x^a} - \frac{e}{mc} A_{stat}^a(x) + \frac{\hbar}{4im^2c^2} \epsilon^{abc} \sigma_b \frac{\partial V(x)}{\partial x^c} \right] \psi_{nk}(x) dx \\
&= \frac{1}{(2\pi)^3} \int u_{n'k'}^\dagger(x) e^{i(k - k') \cdot x} \left[ \frac{\hbar}{im} \frac{\partial}{\partial x^a} + \frac{\hbar}{m} k^a - \frac{e}{mc} A_{stat}^a(x) + \frac{\hbar}{4m^2c^2} \epsilon^{abc} \sigma_b \frac{\partial V(x)}{\partial x^c} \right] u_{nk}(x) dx \\
&= \frac{1}{(2\pi)^3} \int e^{i(k - k') \cdot x} K_{n'k';nk}^a(x) dx,
\end{aligned}
\]  

where

\[
K_{n'k';nk}^a(x) = u_{n'k'}^\dagger(x) \left[ \frac{\hbar}{im} \frac{\partial}{\partial x^a} + \frac{\hbar}{m} k^a - \frac{e}{mc} A_{stat}^a(x) + \frac{\hbar}{4m^2c^2} \epsilon^{abc} \sigma_b \frac{\partial V(x)}{\partial x^c} \right] u_{nk}(x).
\]

Then converting the integral over all space in equation (A1) to a sum of integrals over unit cells leads to

\[
\begin{aligned}
&= \sum_{\mathbf{R}} \frac{1}{(2\pi)^3} \int \Omega_{uc} e^{i(k - k') \cdot x} \left[ \frac{\hbar}{im} \frac{\partial}{\partial x^a} + \frac{\hbar}{m} k^a - \frac{e}{mc} A_{stat}^a(x) + \frac{\hbar}{4m^2c^2} \epsilon^{abc} \sigma_b \frac{\partial V(x)}{\partial x^c} \right] u_{nk}(x) dx \\
&= \delta(k - k') \frac{1}{\Omega_{uc}} \int_{\Omega_{uc}} K_{n'k';nk}^a(x) dx \\
&= \delta(k - k') v_{n'n}^a(k),
\end{aligned}
\]

where

\[
v_{n'n}^a(k) = \frac{1}{\Omega_{uc}} \frac{1}{m} \int_{\Omega_{uc}} u_{n'k'}^\dagger(x) \left[ \frac{\hbar}{im} \frac{\partial}{\partial x^a} + \frac{\hbar}{m} k^a - \frac{e}{mc} A_{stat}^a(x) + \frac{\hbar}{4m^2c^2} \epsilon^{abc} \sigma_b \frac{\partial V(x)}{\partial x^c} \right] u_{nk}(x) dx.
\]

To simplify the above integral we look at the effective Hamiltonian operator that acts on the cell-periodic part of the Bloch function

\[
\begin{aligned}
\hat{H}_k^0(x) &= \frac{1}{2m} \left( \frac{\hbar}{i} \frac{\partial}{\partial x^b} - \frac{e}{c} A_{stat}^b(x) + \hbar k^b \right)^2 + V(x) + \frac{\hbar}{4m^2c^2} \epsilon^{abc} \sigma_b \nabla_c V(x) \left( \frac{\hbar}{i} \frac{\partial}{\partial x^a} - \frac{e}{c} A_{stat}^a(x) + \hbar k^a \right) \\
&\quad - \frac{e\hbar}{2mc} \sigma^a \eta^0_{static}(x,t),
\end{aligned}
\]

and we take the derivative of the effective Hamiltonian with respect to \( \mathbf{k} \),

\[
\frac{\partial}{\partial k^a} \hat{H}_k^0(x) = \frac{\hbar}{m} \left( \frac{\hbar}{i} \frac{\partial}{\partial x^b} - \frac{e}{c} A_{stat}^b(x) + \hbar k^b + \frac{\hbar}{4m^2c^2} \epsilon^{abc} \sigma_b \nabla_c V(x) \right),
\]

which allows us to identify the velocity matrix element as

\[
v_{n'n}^a(k) = \frac{1}{\Omega_{uc}} \frac{1}{\hbar} \int_{\Omega_{uc}} u_{n'k'}^\dagger(x) \left[ \frac{\partial}{\partial k^a} \hat{H}_k^0(x) \right] u_{nk}(x) dx.
\]

The integral over the unit cell can be simplified

\[
\begin{aligned}
&= \frac{\partial}{\partial k^a} \int_{\Omega_{uc}} u_{n'k'}^\dagger(x) \hat{H}_k^0(x) u_{nk}(x) dx - \int_{\Omega_{uc}} u_{n'k'}^\dagger(x) \hat{H}_k^0(x) \frac{\partial u_{nk}(x)}{\partial k^a} dx \\
&\quad - \int_{\Omega_{uc}} \frac{\partial u_{n'k'}^\dagger(x)}{\partial k^a} \hat{H}_k^0(x) u_{nk}(x) dx.
\end{aligned}
\]
we get:

\[
\delta_{\alpha\beta} \Omega_{uc} \frac{\partial}{\partial k_\alpha} E_{n_k} - E_{n'_k} \int_{uc} \frac{\partial u_{nk}(x)}{\partial k_\alpha} dx - E_{n_k} \int_{uc} \frac{\partial u_{nk}(x)}{\partial k_\alpha} u_{nk}(x) dx = \Omega_{uc}\delta_{nn} \frac{\partial E_{n_k}}{\partial k_\alpha} + \frac{1}{i}(E_{n_k} - E_{n'_k}) \Omega_{uc} c_{\alpha\beta}'(k).
\]

Putting this all together we find equation (37). Thus we see that the expression for the \( k \) dependent velocity matrix elements hold when using spinors and including spin orbit coupling.

**Appendix B: Expressions for site quantities**

We begin by isolating the contribution to the total charge density due only to the electrons

\[
\rho^e(x, t) = \rho(x, t) - \rho^{\text{ion}}(x).
\]  

The electronic charge density \( \rho^e(x, t) \) can then be partitioned into contributions associated with the lattice sites \( R \),

\[
\rho^e(x, t) = \sum_R \rho^e_R(x, t).
\]  

The site electronic charge density and current densities are written in terms of the site Green function

\[
\rho^e_R(x, t) = -ie \text{Tr}([G^R(x, y; t)]_{y \rightarrow x}),
\]

\[
J^e_R(x, t) = \text{Tr}([J^R(x, y; t)G^R(x, y; t)]_{y \rightarrow x}).
\]

We can re-express the microscopic charge density in terms of the single particle density matrix and a site quantity matrix

\[
\rho^e_R(x, t) = \sum_{\alpha, \beta, R', R''} \rho^{\alpha R'_{\alpha R''}}(x, R; t) \eta_{\alpha R'' \beta R'},
\]  

where

\[
\rho^{\alpha R'_{\alpha R''}}(x, R; t) = \frac{e}{2} \sum_{\alpha, \beta, R', R''} (\delta_{RR'} + \delta_{RR''}) x e^{iE_{R''}(x, R; t)} \chi^\ast_{\beta R'' \beta R'}(x, t) \chi_{\alpha R'' \beta R'}(x, t).
\]

The total charge density associated with a site \( R \) is the sum of the electronic and nuclei contributions associated with said site (\( \text{(B4)} \) and \( \text{(12)} \))

\[
\rho_R(x, t) = \rho^e_R(x, t) + \rho^{\text{ion}}_R(x).
\]  

The charge current density is composed of two separate parts, one we wish to separately identify with the “magnetization current” that arises from the electron spin, as well as the more standard velocity charge current.

\[
J^e_R(x, p(x, y; t)) = \frac{e}{2m} \left( \frac{e}{c} \Omega_y(x, t) \right) \delta_{ij} + \epsilon_{abc} \delta_{ij} \frac{e\hbar}{8m^2c^2} \sigma_b \frac{\partial V(x)}{\partial x_b},
\]

and

\[
J^M_R(x, p(x, y; t)) = \epsilon_{abc} \frac{e\hbar}{2m} \sigma_b \frac{\partial J(x)}{\partial x_a},
\]

and their sum

\[
J^R_R(x, p(x, y; t)) = J^e_R(x, p(x, y; t)) + J^M_R(x, p(x, y; t)).
\]  

Using \( \text{(B7)} \), \( \text{(B8)} \), and \( \text{(B9)} \) we can identify the microscopic charge current operator \( J^R \) as

\[
J^R_R(x, y; t) = -ie [J^R_R(x, p(x, R; t)) + J^R_R(y, p^\ast(y, R; t))].
\]

This natural splitting of the current density allows one to identify two contributions to the expectation value of the site current

\[
J_R(x, t) = J^e_R(x, t) + J^M_R(x, t),
\]

where the microscopic velocity charge current is defined as

\[
J^e_R(x, t) = \sum_{\alpha, \beta, R', R''} J^{\alpha R'_{\alpha R''}}(x, R; t) \eta_{\alpha R'' \beta R'}(t),
\]  

with

\[
J^m_R(x, t) = \sum_{\alpha, \beta, R', R''} J^{\alpha R'_{\alpha R''}}(x, R; t) \eta_{\alpha R'' \beta R'}(t),
\]
As well the magnetization current is given by
\[ J^M_{\beta\gamma}(x, R; t) = \sum_{\alpha, \lambda, \lambda'} \langle [\hat{H}_{\alpha R} - \hat{H}_{\lambda' R'}, t] \rangle_{\alpha R} \eta_{\lambda', \lambda} R_{\alpha R'}(x, t); \lambda' R'; t \rangle_{\lambda' R'} \phi_{\lambda R}(x, t) \]
\[ + \langle \delta_{\alpha R} \phi_{\lambda R}(x, t) \rangle_{\alpha R} \eta_{\lambda', \lambda} R_{\alpha R'}(x, t); \lambda' R'; t \rangle_{\lambda' R'} \phi_{\lambda R}(x, t) \]  
(B13)

As well the magnetization current is given by
\[ J^M_{\beta R}(x, t) = \sum_{\alpha, \beta' R'} \langle J^M_{\beta' R'}(x, R; t) \eta_{\alpha R'}; \beta' R'(t), \rangle \]  
(B14)

The expressions for the site specific current and charge density do not in general satisfy continuity,
\[ K_R(x, t) = \nabla \cdot J_R(x, t) + \frac{\partial \rho_R(x, t)}{\partial t} \neq 0. \]  
(B16)

This is because charges are free to travel from a region associated with site R to other regions. The total charge associated with a region R is in general a time-dependent quantity. However, since total charge is conserved the sum over all \( K_R \) is zero. Note that the divergence of the magnetization current is always zero since the magnetization current is the curl of a vector.

The total site charges are
\[ Q_R(t) = \int \rho_R(x, t) dx = e \sum_\alpha \eta_{\alpha R}; R(t) + \sum_N q_N, \]  
(B17)

which follows from how we defined \( \rho_R(x, t) \) and our ortho-normality condition for the Wannier functions. Link currents are introduced since the total charge associated with site R is not necessarily constant in time
\[ \frac{dQ_R(t)}{dt} = \int \int_{R'} I(R, R'; t), \]  
(B18)

with
\[ I(R, R'; t) = \frac{e}{i \hbar} \sum_{\alpha, \lambda} \left( \hat{H}_{\alpha R} - \hat{H}_{\lambda R'}(t) \right) \eta_{\lambda'; \lambda} R_{\alpha R'}(t) \]
\[ - \eta_{\alpha R; \lambda R'}(t) \hat{H}_{\lambda' R; \lambda R}(t) \]  
(B19)

With the total site charges and links currents identified in (B17) and (B18), we can now define the microscopic “free” charge and current densities
\[ \rho_F(x, t) = \sum_R \delta(x - R) Q_R(t), \]  
(B20)

and
\[ J_F(x, t) = \int \frac{1}{2} \sum_{R, R'} s(x; R, R') I(R, R'; t). \]  
(B21)

The free charge density is simply the sum of the charges associated with each lattice site placed at that lattice site. The second introduces a microscopic current density by distributing the net link current along a path from site R to R'. The factor of 1/2 is so one can sum over all R and R', compensating for double counting. These expressions satisfy continuity
\[ \nabla \cdot J_F(x, t) + \frac{\partial \rho_F(x, t)}{\partial t} = 0. \]  
(B22)

As can be seen in equation (B11), the magnetization has been split into three contributions. These contributions are termed the “atomic”, “itinerant”, and “spin” contribution. The atomic magnetization is defined as
\[ \tilde{m}_R^i(x, t) = \int \frac{1}{c} \alpha^i(k y, R) j^i_R(k y, t) dy. \]  
(B23)

The itinerant magnetization is included due to the possibility of charges being allowed to move between sites. The derivation is fairly involved, and we refer the reader to earlier work [11]. The relevant equations are
\[ m_i^k_R(x, t) = \int \frac{1}{c} \alpha^i(k y, R) j^k_R(y, t) dy, \]  
(B24)
where
\[ \tilde{j}_R(x, t) = \sum_{\alpha, \beta, R', R''} \tilde{j}_{\beta R', \alpha R''}(x, R; t) \eta_\alpha \eta_{R''} \beta R'(t). \] (B25)

With
\[ \tilde{j}_{\beta R', \alpha R''}(x, R; t) = \frac{1}{2} (\delta_{RR'} + \delta_{RR''}) \tilde{j}_{\beta R', \alpha R''}(x, t), \] (B26)

and
\[ \tilde{j}_{\beta R', \alpha R''}(x, t) = -\sum_R \int s(x; y, R) \Gamma_{\beta R'; \alpha R''}(y, t) dy - \frac{1}{2} \sum_{R, R'} s(x; R, R') \zeta_{\alpha R''} \beta R''(t), \] (B27)

where
\[ \zeta_{\alpha R''} \beta R''(t) = \frac{e}{i \hbar} \left( \delta_{RR'} \delta_{\beta R''} \tilde{H}_\beta R_{\alpha R'}(t) - \delta_{RR'} \delta_{\beta R''} \tilde{H}_\beta R_{\alpha R'}(t) \right), \] (B28)

and
\[ \Gamma_{\beta R'; \alpha R''}(x, t) = \nabla \cdot \tilde{j}_{\beta R', \alpha R''}(x, R; t) + \frac{\partial \tilde{j}_{\beta R', \alpha R''}(x, R; t)}{\partial t} + \frac{1}{i \hbar} \sum_{\mu, x, R_1, R_2} \rho_{\mu R_1, R_2} \nu R_1; \alpha R_1 \beta R_2(t), \] (B29)

with
\[ \delta_{\mu R_1, R_2}(t) = \delta_{\beta \rho} \delta_{R_1, R_2} \delta_{R_2} e^{i \Delta(R_2, R_1, R_2; t) \tilde{H}_{\rho R_1, \alpha R'; R''}(t)} - \delta_{\beta \rho} \delta_{R_2} e^{i \Delta(R_2, R_1, R_2; t) \tilde{H}_{\rho R_1, \alpha R'; R''}(t)} + e \delta_{\beta \rho} \delta_{R_1, R_2} \delta_{R_2} \Omega_{R_2}(t). \] (C1)

The spin contribution to the magnetization is given by
\[ \tilde{m}(x, t) = \frac{e \hbar}{2mc} (\psi^\dagger(x, t) \sigma \psi(x, t)) \]
\[ = \frac{e \hbar}{4mc} \sum_{\alpha, \beta, R, R', R''} (\delta_{RR'} + \delta_{RR''}) \eta_\alpha \eta_{R''} \beta R'(t) \chi_{\beta R''}(x, t) \sigma_{\beta R''}(x, t), \] (B31)

which can be broken up into site magnetizations in an obvious way,
\[ \tilde{m}(x, t) = \sum_R \tilde{m}_R(x, t). \] (B32)

The expression for \( \tilde{m}_R(x, t) \) has already been given in Section 11 equation 62.

The total microscopic polarization field is just the sum of all the site polarizations, and likewise the total microscopic magnetization field is just the sum of all the site magnetizations. This follows what was done earlier [11] when the formalism was outlined excluding electron spin. The key differences are that now the Wannier functions are spinors and there is an extra contribution to the magnetization explicitly due to the spin.

**Appendix C: MP Tensor with inversion or time reversal symmetry**

In this appendix we confirm that the MP tensor vanishes unless both time reversal and inversion symmetry are broken, with the caveat that the gauge-dependent part of the MP tensor, entirely contained in the Chern-Simons contribution, does not necessarily vanish. We consider both the full crystal expressions and the molecular crystal limit, where the Wannier functions can be taken to be the energy eigenstates of the isolated molecules constituting the crystal.

1. **Inversion symmetry - Bloch functions**

In the case of inversion symmetry one requires that the Hamiltonian satisfies \( H^0(x) = -H^0(-x) \). This implies that the eigenstate \( \psi_{\nu \nu}(x) \) has the same energy as the state \( \psi_{\nu \nu}(-x) \). Furthermore, the new state \( \psi_{\nu \nu}(-x) \) can in fact be identified with a Bloch state with wavevector \(-k\) [44]. Thus, we may choose the cell-periodic Bloch spinors at opposite momenta to be identical,

\[ u_n(k) = u_n(-k). \] (C1)

The relationship in equation (C1) could be altered by a \( k \) dependent phase factor. This represents an alternative gauge choice, only affecting the diagonal elements of \( U(k) \), seen in equation (22).

Choosing Bloch functions that satisfy (C1) the non-Abelian Berry connection at opposite momenta is related by

\[ \xi_{nm}^a(-k) = -\xi_{nm}^a(k). \] (C2)

As well the spin matrix elements at opposite momenta are the same

\[ S_{nm}^a(-k) = S_{nm}^a(k). \] (C3)

Now the question becomes what consequences these constraints have on the MP tensor. We can only make a definitive statement on the gauge-independent part of the MP. Split the integrals in half and perform a change of variables of \( k \to -k \). The result is as one would expect
zero, bar the gauge-dependent terms. Had we chosen the Bloch functions to be related by some $k$-dependent phase with a non-zero derivative the relationships (C2) and (C3) would be more complicated but the result for the MP tensor would be the same. This is because the MP tensor is insensitive to purely diagonal gauge transformations.

2. Inversion symmetry - Molecular Crystal Limit

If the Hamiltonian has inversion symmetry then we can choose the Wannier functions, which are eigenstates of the Hamiltonian in the molecular crystal limit, to have a definite parity, either even or odd under inversion. If we look at the position matrix elements (95) we see that if $W_{\alpha 0}(x)$ has the same parity as $W_{\beta 0}(x)$ the integral is over an odd function, and is thus zero. The spin matrix element behaves in the opposite manner. If the Wannier functions have opposite parity the integral is over an odd function, and is thus zero. In the MP tensor we see the functions have opposite parity the integral is over an odd function, and is thus zero. The spin expectation value of $\psi_{\alpha k}$ is the negative of $\psi_{\alpha' -k}$.

We also have the relationship between the energy of the time reversed states [46],

$$E_n(k) = E_{n'}(-k). \quad (C7)$$

When we sum over all states we will have time reversed partners appearing. We assume the ground state is time-reversal symmetric, so if a state is filled in the ground state its time-reversed partner is also filled. If one takes the integrals in the MP and splits them in half, performs a change of variables from $k \to -k$ in one of them, one will find that all that remains are the gauge-dependent terms. As before these terms only appear in the Chern-Simons contribution.

4. Time reversal - Molecular Crystal Limit

According to Kramer’s theorem, when time reversal is a symmetry each state is now at least doubly degenerate, and these degenerate pairs are time-reversed partners. An example state would be

$$|\psi\rangle \rightarrow \begin{bmatrix} a \\ b \end{bmatrix}. \quad (C8)$$

Its time reversed partner $|\phi\rangle$, which would be orthogonal, would be

$$|\phi\rangle = T|\psi\rangle \rightarrow \begin{bmatrix} b^* \\ -a^* \end{bmatrix}, \quad (C9)$$

with

$$T^2|\psi\rangle = -|\psi\rangle. \quad (C10)$$

It is important to note that every time we sum over all orbital types we are implicitly summing over all the time reversed partners. I will denote one state the ‘$+$’ state, and the other as the ‘$-$’ state. Due to the anti-unitarity of the time-reversal operator we find a simple relationship between position matrix elements between two arbitrary states

$$\langle \alpha + |x|\beta+ \rangle = ((\alpha - |x|\beta-))^*, \quad (C11)$$

$$\langle \alpha + |x|\beta- \rangle = -((\alpha - |x|\beta+))^*. \quad (C11)$$
One can see that the position matrix elements $x_{\alpha \beta}$ could have been describing any of the four above inner products, so an additional label is necessary due to the two fold degeneracy of states. Likewise, the spin matrix elements between arbitrary states have the property:

$$\langle \alpha + | \sigma | \beta + \rangle = -(\langle \alpha - | \sigma | \beta - \rangle)^*,$$

$$\langle \alpha + | \sigma | \beta - \rangle = (\langle \alpha - | \sigma | \beta + \rangle)^*.$$  \hspace{1cm} (C12)

With time reversal symmetry the position matrix elements have the properties

$$x_{\alpha+\beta+} = x^*_{\alpha-\beta-},$$

$$x_{\alpha+\beta-} = -x^*_{\alpha-\beta+}. \hspace{1cm} (C13)$$

Looking at the Chern-Simons and cross gap contributions to the MP tensor we see a product of three position matrix elements; this can be expanded out by summing over time reversed partners, labelled with a $\pm$.

$$x_{\alpha\beta}x_{\gamma\delta}x_{\epsilon\alpha} \rightarrow$$

$$x_{\alpha+\beta+}x_{\gamma+\delta+} + x_{\alpha-\beta-}x_{\gamma-\delta-} + x_{\alpha+\beta-}x_{\gamma+\delta+} + x_{\alpha-\beta+}x_{\gamma-\delta-}$$

$$+ x_{\alpha+\beta-}x_{\gamma+\delta-} + x_{\alpha-\beta+}x_{\gamma-\delta+} + x_{\alpha-\beta-}x_{\gamma+\delta+} + x_{\alpha+\beta+}x_{\gamma-\delta-}$$

$$+ x_{\alpha+\beta+}x_{\gamma-\delta-} + x_{\alpha-\beta-}x_{\gamma+\delta+} + x_{\alpha-\beta+}x_{\gamma-\delta+} + x_{\alpha+\beta-}x_{\gamma+\delta-}$$

$$+ x_{\alpha+\beta-}x_{\gamma-\delta+} + x_{\alpha-\beta+}x_{\gamma+\delta-} + x_{\alpha-\beta-}x_{\gamma+\delta-} + x_{\alpha+\beta+}x_{\gamma-\delta+}. \hspace{1cm} (C14)$$

Using the relationship between the matrix elements of plus/minus states we see that the product of the three position matrix elements is a real quantity when we sum over time-reversed partners. A very important caveat is that in the MP tensor we have filling factors multiplying each of these products. For the eight terms in equation (C14) to actually appear in the sum over orbital types one requires that $f_{\alpha+} = f_{\alpha-} = f_{\alpha}$. This is true if the ground state has time-reversal symmetry. The fact that the product is real means that any expression involving $\Re[ix^i_j x^a_n x^b_m]$ is zero in the MP tensor.

The spin matrix elements obey a slightly different property to the position matrix elements

$$S_{\alpha+, \beta+} = -S^*_{\alpha-, \beta-},$$

$$S_{\alpha+, \beta-} = S^*_{\alpha-, \beta+}. \hspace{1cm} (C15)$$

Looking at the last line of the spin contribution to the MP we find that there are four terms to consider for each pair of orbital labels,

$$x^i_{\alpha+, \beta+} S^l_{\beta+, \alpha+} + x^i_{\alpha-, \beta-} S^l_{\beta-, \alpha-} + x^i_{\alpha+, \beta-} S^l_{\beta-, \alpha+} + x^i_{\alpha-, \beta+} S^l_{\beta+, \alpha-}. \hspace{1cm} (C16)$$

Using our relationships between matrix elements of plus and minus states the above expression is an entirely imaginary quantity. Since the MP tensor is real this term vanishes.

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