Orbital magnetism and chemical shielding in the projector augmented-wave formalism

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We show how to compute the orbital magnetization, as the first-order change of the energy due to an homogeneous magnetic field, within the projector augmented-wave (PAW) formalism of density functional theory, for systems with periodic boundary conditions. To accomplish this, magnetic translation symmetry is invoked together with a perturbative treatment of the density operator, yielding well-posed expressions that account fully for all PAW terms. The terms may be computed in a standard PAW implementation using density functional perturbation theory to compute the necessary wavefunction derivatives, rather than the finite difference approach that has been used previously. In order to obtain nontrivial magnetization, we also impose nuclear magnetic dipole moments on atomic sites of interest, which gives direct access to the chemical shielding, as measured in nuclear magnetic resonance spectroscopy. The resulting expressions have been implemented and tested, and results are shown both for atoms and solids.

I. INTRODUCTION

The effect of an homogeneous magnetic field on a solid is manifested in several different observables. Probably the simplest is the magnetic susceptibility, which is an effect second order in the applied field strength and is, in insulators, typically a small negative value (the negative sign indicates that the field in the insulator is reduced from the applied value). Somewhat more complex, but much more important experimentally, is the chemical shielding, which is the mixed second-order interaction between the external field and a nuclear magnetic dipole as mediated by the electronic environment around the nucleus. The shielding, together with the direct Zeeman interaction of the field and dipole, are routinely measured by nuclear magnetic resonance spectroscopy.

Calculating the shielding from first principles is complicated both by the problem of insuring that all derived expressions are gauge invariant, and by the fact that the field is not periodic and hence not obviously compatible with Bloch wavefunctions and hence the planewave basis and periodic boundary conditions frequently employed in first-principles calculations.

One approach to calculating the shielding is to focus on the current density generated by a magnetic field. Then, using the Biot-Savart Law, the induced magnetic field at a point of interest (typically an atomic nucleus) may be obtained and thus the magnetic shielding. This approach has been developed by Pickard and Mauri [1, 2] and by Sebastiani and Parinello [3], using different approaches to the gauge invariance problem. The approach of Pickard and Mauri in particular is now in wide-spread use [4].

An alternative approach is the direct expansion of the total energy in terms of both the magnetic field and the nuclear magnetic dipole. Conceptual difficulties with the direct calculation of the first derivative of the energy with respect to the magnetic field (the magnetization) in a periodic system were resolved by Ceresoli, Vanderbilt, Resta and colleagues by using Wannier functions [5, 6], see as well ref. [7] where the orbital response in the presence of a finite magnetic field is treated. The resulting expression for the orbital magnetism could then be used to develop an approach to computing magnetic shielding, by comparing the magnetism with and without the presence of a nuclear magnetic dipole [8, 9].

In the present contribution we also focus on the energy to first order in an external homogeneous magnetic field, but our treatment is based on the density operator perturbation theory we developed previously [10]. We develop this approach in the PAW framework [11–13], developing expressions that allow for non-norm-conserving PAW (in contrast to earlier work [9]), and additionally take advantage of the gauge freedom [14] of the expressions to use density functional perturbation theory to avoid finite difference computation of the required wavefunction derivatives, thus greatly speeding convergence. We show how the theory is implemented in a DFT code, ABINIT [15], and provide examples on a variety of atomic and solid-state systems.

II. THEORY

A. Overview of theoretical approach

We obtain expressions for the energy in a magnetic field broadly as follows. In Section II B, the energy is developed, up to the first power in the magnetic field, based

on a variational treatment using the density operator, in presence of an overlap operator, as needed for PAW. Magnetic translation invariance is used to express the result in a form suitable for periodic solids. In Section II C, the translational invariance is completely restored with the gauge-including projector augmented-wave transform. In Section II D, the vector potential for a nuclear magnetic dipole is defined, in order to be able to compute the NMR shielding thanks to the converse NMR method.

In the last part of the theory description, Section II E, the explicit magnetic field-dependent terms of the Hamiltonian and energy within PAW are identified and described. The final result, Eq. 36, gives explicitly the first-order energy of a periodic solid due to an external homogeneous magnetic field, with the projector augmented-wave framework.

B. Energy derivative from a variational approach, including overlap

Quite generally the energy of a non-interacting electronic system (the Density-Functional Theory generalization will be presented later in the PAW section) is found from the usual trace formula, $\text{Tr}[\rho H]$, where H is the Hamiltonian and ρ is the density operator. For eigenstates $|\psi_n\rangle$, the density operator is

$$\rho = \sum_n f_n |\psi_n\rangle\langle\psi_n|, \tag{1}$$

where f_n is the occupancy of state n. Aiming towards a general PAW treatment, the normalization condition incorporates an overlap operator S and hence the idempotency condition on ρ becomes $\rho = \rho S \rho$, where $\langle\psi_m|S|\psi_n\rangle = \delta_{mn}$. Furthermore, $\text{Tr}[\rho S] = N$, where N is the number of electrons. Thus a constrained minimization problem emerges,

$$E[H,S] = \min_\rho \{\text{Tr}[\rho H - \Lambda(\rho - \rho S \rho)] - \\ \mu\left(\text{Tr}[\rho S] - N\right)\}, \tag{2}$$

with Lagrange multipliers Λ (an operator) and μ (a scalar).

As detailed in Appendix A, the Lagrange multiplier μ distinguishes between occupied and unoccupied states, and is linked to Λ through

$$\Lambda = -P_v^\dagger(H - \mu S)P_v + P_c^\dagger(H - \mu S)P_c, \tag{3}$$

where $P_v = \rho S$ projects onto occupied states and $P_c = 1 - P_v$ onto unoccupied ones.

In the presence of an homogeneous magnetic field B, all terms in Eq. 2 become B dependent, and moreover, B will be included in H through a vector potential. Indeed, the all-electron form of the Hamiltonian is

$$H = \frac{1}{2}\left(\mathbf{p} + \mathbf{A_0}\right)^2 + V(\mathbf{r}) \tag{4}$$

in atomic units. The resulting form is not compatible with periodic boundary conditions. Translation invariance can be recovered through application of magnetic translation symmetry, which can be achieved by working in the symmetric gauge [16]

$$\mathbf{A_0} = \frac{1}{2}\mathbf{B} \times \mathbf{r}. \tag{5}$$

In this case, as detailed in Appendix B, an operator O with spatial dependence can be formulated in terms of a periodic kernel $\bar{O}$ and a magnetic phase factor [16, 17]:

$$O_{\mathbf{r_1},\mathbf{r_2}} = \bar{O}_{\mathbf{r_1},\mathbf{r_2}} e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}\times\mathbf{r_2})}. \tag{6}$$

This procedure is detailed for the operators arising in the Hamiltonian in Appendix B. More complex are the operator products ρS and $\rho S \rho$, for which the application of Eq. 6 is considerably more involved. The procedure is detailed in reference [10] and Appendix C. The ultimate result will be gauge-invariant expressions for the energy per unit volume based on the density operator kernel and Hamiltonian kernel, as (schematically) $E = \text{Tr}[\bar{H}\bar{\rho}]$.

With translation invariance restored, the first-order derivative of the variational energy per unit cell with respect to the magnetic field B in direction α is given by (Appendix A):

$$E^{(1)} = \int \frac{d\mathbf{k}}{(2\pi)^3}\text{Tr}\left[\bar{\rho}_\mathbf{k}^{(0)}\left(\bar{H}_\mathbf{k}^{(1)} - \mu^{(0)}\bar{S}_\mathbf{k}^{(1)}\right)\right. \\ \left. + \bar{\Lambda}_\mathbf{k}^{(0)}\left(\bar{\rho}_\mathbf{k}^{(0)}\bar{S}_\mathbf{k}^{(1)}\bar{\rho}_\mathbf{k}^{(0)} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}\partial_{\beta\gamma}(\bar{\rho}_\mathbf{k}^{(0)}\bar{S}_\mathbf{k}^{(0)}\bar{\rho}_\mathbf{k}^{(0)})\right)\right], \tag{7}$$

where

$$\bar{\Lambda}_\mathbf{k}^{(0)} = -\bar{P}_{v\mathbf{k}}^{(0)\dagger}(\bar{H}_\mathbf{k}^{(0)} - \mu^{(0)}\bar{S}_\mathbf{k}^{(0)})\bar{P}_{v\mathbf{k}}^{(0)} \\ + \bar{P}_{c\mathbf{k}}^{(0)\dagger}(\bar{H}_\mathbf{k}^{(0)} - \mu^{(0)}\bar{S}_\mathbf{k}^{(0)})\bar{P}_{c\mathbf{k}}^{(0)}, \tag{8}$$

and $\partial_{\beta\gamma}()$ is short-hand for

$$\partial_{\beta\gamma}(\bar{U}\bar{V}\bar{W}) = \\ (\partial_\beta\bar{U})(\partial_\gamma\bar{V})\bar{W} + (\partial_\beta\bar{U})\bar{V}(\partial_\gamma\bar{W}) + \bar{U}(\partial_\beta\bar{V})(\partial_\gamma\bar{W}). \tag{9}$$

This first-order derivative of the energy per unit volume with respect to the magnetic field B in direction α is also the negative of the magnetization along direction α,

$$E^{(1)} = \frac{\partial E}{\partial B_\alpha} = -M_\alpha. \tag{10}$$

Integration over k-space is included in Eq. 7, because with translation invariance restored one can use Bloch theorem, and the different operators can be decomposed according to their wavevector content.

One must now carefully detail the zeroth and first-order Hamiltonian and overlap operators. We turn to that problem next.

C. Translation invariance

In addition to the magnetic translation invariance discussed above and in Appendix B, the PAW transform T itself includes projectors and orbitals centered on the atomic sites. In the vector potential of the homogeneous magnetic field, these terms must also be properly gauged, and this is accomplished with the so-called gauge-including projector augmented-wave transform [1]:

$$T_{\text{PAW}} = 1 + \sum_{Ri} \mathcal{G} \left(|\phi_{Ri}\rangle - |\tilde{\phi}_{Ri}\rangle \right) \langle \tilde{p}_{Ri}| \mathcal{G}^\dagger, \quad (11)$$

where

$$\mathcal{G} = \exp\left(i\mathbf{R} \cdot \mathbf{A_0}\right) = e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r}\times\mathbf{R})}, \quad (12)$$

for electrons in atomic units. We follow the notation for PAW objects of ref. [13], such that in the PAW transform operator T, R labels the ion locations, i the atomic basis states ϕ and $\tilde{\phi}$, and $\tilde{p}$ are the atomic projectors. Thus the on-site density contributions are modified by the presence of the field-dependent phase factors through

$$\rho_{Rij} = \sum_n \langle \tilde{\psi}_n | \mathcal{G} | \tilde{p}_{Ri}\rangle \langle \tilde{p}_{Rj} | \mathcal{G}^\dagger | \tilde{\psi}_n\rangle, \quad (13)$$

and the PAW overlap operator becomes

$$S = \mathbf{1} + \sum_{Rij} \mathcal{G}|\tilde{p}_{Ri}\rangle s_{ij} \langle \tilde{p}_{Rj}|\mathcal{G}^\dagger, \quad (14)$$

where

$$s_{ij} = \langle \phi_{Ri}|\phi_{Rj}\rangle - \langle \tilde{\phi}_{Ri}|\tilde{\phi}_{Rj}\rangle. \quad (15)$$

Expectation values in this picture become

$$\text{Tr}\left[\rho A\right] = \text{Tr}\left[\tilde{\rho}A\right] + \sum_{Rij} \rho_{Rij} \times$$
$$\left(\langle \phi_{Ri}|\mathcal{G}A\mathcal{G}^\dagger|\phi_{Rj}\rangle - \langle \tilde{\phi}_{Ri}|\mathcal{G}A\mathcal{G}^\dagger|\tilde{\phi}_{Rj}\rangle \right), \quad (16)$$

assuming the usual caveats of PAW, that the PAW spheres on neighboring atoms do not overlap, and that the set of projectors is complete [11–13].

Because of the dependence on $\mathbf{r}$ and not $\mathbf{r} - \mathbf{R}$ in both $\mathbf{A_0}(\mathbf{r})$ and ρ_{Rij}, applying these objects to periodic systems is not well-posed. This situation may be addressed by using the magnetic translation symmetry, as outlined in Appendix B. The PAW terms affected are the kinetic energy, due to the derivative operators, and those involving the projector functions. The kinetic energy operator becomes

$$\bar{T}_{\text{KE}} = \frac{1}{2} \left(-i\nabla\right)^2. \quad (17)$$

The on-site densities involve contraction with the translationally invariant projector kernel

$$\bar{p}_{ij,\bar{\mathbf{r}}_1,\bar{\mathbf{r}}_2} = e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2\times\bar{\mathbf{r}}_1} \tilde{p}_{Ri}(\bar{\mathbf{r}}_2)\tilde{p}_{Rj}^*(\bar{\mathbf{r}}_1), \quad (18)$$

and the overlap operator becomes

$$\bar{S} = \delta(\mathbf{r_2} - \mathbf{r_1}) + \sum_{Rij} e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2\times\bar{\mathbf{r}}_1} \tilde{p}_i(\bar{\mathbf{r}}_2)\tilde{p}_j^*(\bar{\mathbf{r}}_1)s_{ij}. \quad (19)$$

In the above the short-hand notation $\bar{\mathbf{r}} = \mathbf{r} - \mathbf{R}$ has been used. Thus by working with the density operator and exploiting magnetic translation symmetry, the PAW energy terms can be rendered explicitly lattice periodic.

D. Nuclear Magnetic Dipoles

In order to study diamagnetic insulators, which normally have no orbital magnetism, we add a nuclear magnetic dipole to sites of interest in the unit cell, as in the "converse NMR method" of Thonhauser and colleagues. [8, 9] In this approach, nuclear magnetic dipole moments $\mathbf{m_R}$ are associated with the ion positions $\mathbf{R}$, and described in the Hamiltonian by a vector potential

$$\mathbf{A_N}(\mathbf{r}) = \alpha^2 \sum_{\mathbf{R}} \frac{\mathbf{m_R} \times (\mathbf{r} - \mathbf{R})}{|\mathbf{r} - \mathbf{R}|^3}, \quad (20)$$

where the sum is over ion positions and α is the fine structure constant. Being ion-centered, this term is already translation-invariant.

E. PAW total energy, Hamiltonian and derivative

The total energy may now be assembled. In standard PAW notation [12, 13]:

$$\tilde{E} + (E^1 - \tilde{E}^1). \quad (21)$$

The first term is

$$\tilde{E} = \text{Tr}[\bar{\rho}\bar{T}_{\text{KE}}] +$$
$$\int v_H[\tilde{n}_{Zc}](\tilde{n} + \hat{n})d\mathbf{r} + E_{xc}[\tilde{n} + \tilde{n}_c] + E_H[\tilde{n} + \hat{n}], \quad (22)$$

where $\bar{T}_{\text{KE}} = \frac{1}{2}\left(\mathbf{p} + \mathbf{A_N}\right)^2$, the kinetic energy with periodicity restored. Note that the compensation charge density $\hat{n}$ is not considered to be part of the exchange and correlation energy [18].

The second, on-site term is given by

$$E^1 = \sum_{Rij} \rho_{Rij} \langle \phi_i | \frac{1}{2} \left[\mathbf{p} + \mathbf{A_0}(\mathbf{r} - \mathbf{R}) + \mathbf{A_N}\right]^2 |\phi_j\rangle$$
$$+ \int v_H[n_{Zc}]n^1 + E_H[n^1] + E_{XC}[n^1 + n_c], \quad (23)$$

where the on-site kinetic energy has been transformed by the GIPAW $\mathcal{G}$ operator (see Eq. 16). As the $\mathcal{G}$ operator commutes with position, it has no effect on the on-site density contributions.

The third, on-site term is

$$\tilde{E}^1 = \sum_{Rij} \rho_{Rij} \langle \tilde{\phi}_i | \frac{1}{2} \left[\mathbf{p} + \mathbf{A_0}(\mathbf{r} - \mathbf{R}) + \mathbf{A_N} \right]^2 | \tilde{\phi}_j \rangle$$
$$+ E_H[\tilde{n}^1 + \hat{n}] + E_{XC}[\tilde{n}^1 + \tilde{n}_c]$$
$$+ \int_{\Omega_R} v_H[\tilde{n}_{Zc}](\tilde{n}^1 + \hat{n})d\mathbf{r}. \quad (24)$$

In these equations, ρ_{Rij} is to be understood as expressed in periodic kernel form as found in Eq. B9. Note that ρ_{Rij} appears in the above expressions both explicitly, and implicitly in n^1 and $\tilde{n}^1$. As the compensation charge is used only to cancel the electrostatic moments of the PAW spheres in the zero field calculation of the wavefunctions and derivatives, we include it here only in its zeroth order form, that is, defined in terms of the zero field values of n^1 and $\tilde{n}^1$.

As the above energy contributions were determined from $\text{Tr}[\bar{\rho}\bar{H}]$, the Hamiltonian operator is found formally as $dE/d\bar{\rho}$ (reference [12]). The term $\tilde{E}$ yields, with a slight abuse of notation,

$$\bar{T} + v_H[\tilde{n} + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n} + \tilde{n}_c] +$$
$$\sum_{Rij} e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2 \times \bar{\mathbf{r}}_1} |\tilde{p}_{Ri}\rangle \hat{D}_{ij} \langle \tilde{p}_{Rj}|, \quad (25)$$

where v_H and v_{xc} are the Hartree and exchange and correlation potentials, and $\hat{D}_{ij}$ arises as usual from the $\hat{n}$ charge distribution, added to cancel sphere-sphere interactions [13]:

$$\hat{D}_{ij} = \sum_{LM} \int d\mathbf{r} v_H[\tilde{n} + \hat{n} + \tilde{n}_{Zc}] Q_{ij}^{LM}, \quad (26)$$

with Q_{ij}^{LM} the residual sphere multipole moments.

The term E^1 yields

$$\sum_{Rij} e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2 \times \bar{\mathbf{r}}_1} |\tilde{p}_{Ri}\rangle D_{ij}^1 \langle \tilde{p}_{Rj}|, \quad (27)$$

with

$$D_{ij}^1 = \langle \phi_{Ri} | \frac{1}{2} \left[\mathbf{p} + \mathbf{A_0}(\mathbf{r} - \mathbf{R}) + \mathbf{A_N} \right]^2 | \phi_{Rj} \rangle +$$
$$\langle \phi_{Ri} | v_H[n^1 + n_{Zc}] + v_{xc}[n^1 + n_c] | \phi_{Rj} \rangle. \quad (28)$$

Similarly, $\tilde{E}^1$ yields

$$\sum_{Rij} e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2 \times \bar{\mathbf{r}}_1} |\tilde{p}_{Ri}\rangle \tilde{D}_{ij}^1 \langle \tilde{p}_{Rj}|, \quad (29)$$

with

$$\tilde{D}_{ij}^1 = \langle \tilde{\phi}_{Ri} | \frac{1}{2} \left[\mathbf{p} + \mathbf{A_0}(\mathbf{r} - \mathbf{R}) + \mathbf{A_N} \right]^2 | \tilde{\phi}_{Rj} \rangle +$$
$$\langle \tilde{\phi}_{Ri} | v_H[\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n}^1 + \tilde{n}_c] | \tilde{\phi}_{Rj} \rangle$$
$$+ \sum_{LM} \int_{\Omega_R} v_H[\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc}] Q_{ij}^{LM}. \quad (30)$$

We now consider the above Hamiltonian terms perturbatively in the external magnetic field. From the above, the zeroth order Hamiltonian is

$$\bar{H}^{(0)} = \bar{T} + v_H[\tilde{n} + \hat{n} + \tilde{n}_{Zc}] + v_{xc}[\tilde{n} + \tilde{n}_c] +$$
$$\sum_{Rij} |\tilde{p}_{Ri}\rangle (\hat{D}_{ij}^{(0)} + D_{ij}^{1,(0)} - \tilde{D}_{ij}^{1,(0)}) \langle \tilde{p}_{Rj}|, \quad (31)$$

where the $D^{(0)}$ terms are just the D quantities given above, Eqs. 26, 28, and 30, evaluated at $\mathbf{A_0} = 0$. In other words, $\bar{H}^{(0)}$ is the standard PAW ground state Hamiltonian, including the magnetic dipole vector potential $\mathbf{A_N}$.

The first-order Hamiltonian is given, with the same abuse in notation as above, by

$$\bar{H}^{(1)} =$$
$$- \sum_{Rij} \frac{i}{2} \mathbf{e}_\alpha \cdot \bar{\mathbf{r}}_2 \times \bar{\mathbf{r}}_1 |\tilde{p}_{Ri}\rangle (\hat{D}_{ij}^{(0)} + D_{ij}^{1,(0)} - \tilde{D}_{ij}^{1,(0)}) \langle \tilde{p}_{Rj}|$$
$$+ \sum_{Rij} |\tilde{p}_{Ri}\rangle (D_{ij}^{1,(1)} - \tilde{D}_{ij}^{1,(1)}) \langle \tilde{p}_{Rj}|, \quad (32)$$

where

$$D_{ij}^{1,(1)} - \tilde{D}_{ij}^{1,(1)} =$$
$$\langle \phi_{Ri} | \mathbf{A_0}^{(1)}(\mathbf{r} - \mathbf{R}) \cdot \mathbf{p} + \mathbf{A_0}^{(1)}(\mathbf{r} - \mathbf{R}) \cdot \mathbf{A_N} | \phi_{Rj} \rangle -$$
$$\langle \tilde{\phi}_{Ri} | \mathbf{A_0}^{(1)}(\mathbf{r} - \mathbf{R}) \cdot \mathbf{p} + \mathbf{A_0}^{(1)}(\mathbf{r} - \mathbf{R}) \cdot \mathbf{A_N} | \tilde{\phi}_{Rj} \rangle, \quad (33)$$

with

$$\mathbf{A_0}^{(1)} = \frac{1}{2} \mathbf{e}_\alpha \times \mathbf{r}. \quad (34)$$

Note that only terms with explicit B dependence appear in Eq. 33: the exchange and correlation energies arising from the perturbed densities are fully accounted for in the first term of Eq. 32. This is because the first-order energy change due to a density perturbation can be expressed as the functional derivative of the energy with respect to the density evaluated at the zeroth-order density, multiplied by the first-order density [19]. The derivatives are just the zeroth-order potentials, and these are all included in the various contributions to $D^{1,(0)}$ and $\tilde{D}^{1,(0)}$. Finally, as noted previously, we use the compensation charge $\hat{n}$ only in its zeroth order form.

When the Hamiltonian terms above are applied in reciprocal space, we note [20] that $|\tilde{p}_{iRk}\rangle = e^{-i\mathbf{k}\cdot\mathbf{r}}|\tilde{p}_{iR}\rangle$, so that the bilinear term $\mathbf{e}_\alpha \cdot \bar{\mathbf{r}}_2 \times \bar{\mathbf{r}}_1$ in Eq. 32 can be written in terms of derivatives with respect to $\mathbf{k}$, yielding:

$$\bar{H}_\mathbf{k}^{(1)} =$$
$$- \frac{i}{2} \epsilon_{\alpha\beta\gamma} \sum_{Rij} |\partial_\beta \tilde{p}_{Rik}\rangle (\hat{D}_{ij}^{(0)} + D_{ij}^{1,(0)} - \tilde{D}_{ij}^{1,(0)}) \langle \partial_\gamma \tilde{p}_{Rjk}|$$
$$+ \sum_{Rij} |\tilde{p}_{Rik}\rangle (D_{ij}^{1,(1)} - \tilde{D}_{ij}^{1,(1)}) \langle \tilde{p}_{Rjk}|. \quad (35)$$

Finally, with $\bar{H}_\mathbf{k}^{(0)}$ and $\bar{H}_\mathbf{k}^{(1)}$ fully specified as in Eqs. 31 and 35, the expression for $E^{(1)}$, Eq. 7, can be completed as (App. A)

$$E^{(1)} = -M_\alpha = \int \frac{d^3k}{(2\pi)^3} \left[\sum_n^{\text{occ}} \langle \bar{u}_{n,\mathbf{k}}^{(0)} | \bar{H}_{\mathbf{k}}^{(1)} - \epsilon_{n\mathbf{k}} \bar{S}_{\mathbf{k}}^{(1)} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle \right.$$

$$+ \frac{i}{2} \epsilon_{\alpha\beta\gamma} \sum_n^{\text{occ}} \langle P_c \partial_\beta \bar{u}_{n,\mathbf{k}}^{(0)} | \bar{H}_{\mathbf{k}}^{(0)} + \epsilon_{n\mathbf{k}} \bar{S}_{\mathbf{k}}^{(0)} - 2\mu^{(0)} \bar{S}_{\mathbf{k}}^{(0)} | P_c \partial_\gamma \bar{u}_{n,\mathbf{k}}^{(0)} \rangle$$

$$+ \frac{i}{2} \epsilon_{\alpha\beta\gamma} \sum_n^{\text{occ}} (\epsilon_{n\mathbf{k}} - \mu^{(0)}) \left(\langle \bar{u}_{n,\mathbf{k}}^{(0)} | \partial_\beta \bar{S}_{\mathbf{k}}^{(0)} | P_c \partial_\gamma \bar{u}_{n,\mathbf{k}}^{(0)} \rangle + \langle P_c \partial_\beta \bar{u}_{n,\mathbf{k}}^{(0)} | \partial_\gamma \bar{S}_{\mathbf{k}}^{(0)} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle \right)$$

$$\left. - \frac{i}{2} \epsilon_{\alpha\beta\gamma} \sum_{n,n'}^{\text{occ}} (\epsilon_{n\mathbf{k}} - \mu^{(0)}) \langle \bar{u}_{n,\mathbf{k}}^{(0)} | \partial_\beta \bar{S}_{\mathbf{k}}^{(0)} | \bar{u}_{n',\mathbf{k}}^{(0)} \rangle \langle \bar{u}_{n',\mathbf{k}}^{(0)} | \partial_\gamma \bar{S}_{\mathbf{k}}^{(0)} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle \right]. \quad (36)$$

Eq. 36 is the primary theoretical result of this paper, and represents a complete PAW treatment of the first-order energy of a periodic system in the presence of an homogeneous magnetic field.

III. IMPLEMENTATION

The energy to first order in the magnetic field arises from the considerations outlined above, and is fully expressed by Eq. 36. Still, some issues, related to wavefunction gauge freedom, and the valence and core electron contributions are worth additional comments.

A. Energy arising from $\bar{H}_{\mathbf{k}}^{(0)}$ and $\bar{S}_{\mathbf{k}}^{(0)}$

The second term in Eq. 36 arises from both $\bar{H}_{\mathbf{k}}^{(0)}$ and $\bar{S}_{\mathbf{k}}^{(0)}$. As detailed above (Eq. 31), $\bar{H}_{\mathbf{k}}^{(0)}$ is the standard ground state Hamiltonian at $\mathbf{B} = 0$. Its eigenstates and eigenenergies are the $|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle$ and $\epsilon_{n\mathbf{k}}$ appearing in Eq. 36, that is,

$$\bar{H}_{\mathbf{k}}^{(0)} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle = \epsilon_{n\mathbf{k}} \bar{S}_{\mathbf{k}}^{(0)} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle. \quad (37)$$

These states are found from a standard ground-state computation in DFT using $\bar{H}_{\mathbf{k}}^{(0)}$. In standard perturbation theory, the eigenenergies will change at first order. However, this is not the case with the present approach to the magnetic field. In order to simplify the notation, the (0) superscript usually present for the eigenvalues of the non-perturbed Hamiltonian is omitted. From the states the projection operators onto the occupied and unoccupied subspaces may be constructed as

$$\bar{P}_{v\mathbf{k}}^{(0)} = \sum_n^{\text{occ}} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle \langle \bar{u}_{n,\mathbf{k}}^{(0)} | \bar{S}_{\mathbf{k}}^{(0)}, \quad (38)$$

$$\bar{P}_{c\mathbf{k}}^{(0)} = \mathbf{1} - \bar{P}_{v\mathbf{k}}^{(0)}. \quad (39)$$

Furthermore, the wavefunction derivatives with respect to components of $\mathbf{k}$, given by

$$| \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)} \rangle = \left| \frac{\partial \bar{u}_{n,\mathbf{k}}^{(0)}}{\partial k_\alpha} \right\rangle, \quad (40)$$

may be obtained through a standard density functional perturbation theory (DFPT) calculation. Then, the projectors $\bar{P}_{c\mathbf{k}}^{(0)}$ may be applied, and the Hamiltonian $\bar{H}_{\mathbf{k}}^{(0)}$ and overlap $\bar{S}_{\mathbf{k}}^{(0)}$ used to obtain the second line of Eq. 36.

We remark here that the derivative of the wavefunction with respect to the wavevector, Eq. 40, has an intrinsic arbitrariness, due to the freedom in the choice of phase for eigenfunctions of Eq. 37 at different wavevectors. However, this arbitrariness is strictly limited to the projection of $| \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)} \rangle$ on the subspace spanned by $| u_{n,\mathbf{k}}^{(0)} \rangle$, and possibly eigenfunctions degenerate with it, all other components of $| \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)} \rangle$ being fixed. This component has no influence on the final result in Eq. 36, due to the projection of such derivatives on conduction states. Because of the projection, the choice of how to fix the phase freedom can be made based on convenience. For example, one choice involves setting the projection of $| \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)} \rangle$ on $| u_{n,\mathbf{k}}^{(0)} \rangle$ to zero, which defines the so-called "diagonal gauge" for $| \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)} \rangle$ [14]. This "gauge choice" has nothing to do with the well-known vector potential "gauge choice", as made for example in Eq. 5. In addition to the intrinsic phase arbitrariness of the eigenfunctions, the energy is determined within a unitary transform among occupied wavefunctions. The derivative functions $| \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)} \rangle$ are routinely computed in density functional theory for convenience in the "parallel transport gauge" [14, 19], where mixing with the occupied states is minimized. This is an alternative choice to the diagonal gauge, and the one we make in the present work. Again, in the present application, given that the derivative functions are only used in Eq. 36 projected on the unoccupied space, the result is invariant to the phase choice made in computing the derivative functions. This observation also means that Eq. 36 need not be evaluated using a finite-difference ap-

proach to the derivatives, and so can also be used without modification with only a single **k** point, say for isolated atoms or molecules, or solids with very large periodic cells.

The third and fourth terms in Eq. 36 require also the ground state and derivative wavefunctions as described above, and application of the derivative of the overlap operator. This derivative operator is standard in DFPT.

B. Energy arising from $\bar{H}_{\mathbf{k}}^{(1)}$ and $\bar{S}_{\mathbf{k}}^{(1)}$

1. Valence electron contributions

The first term in Eq. 36 involves application of $\bar{H}_{\mathbf{k}}^{(1)}$ and $\bar{S}_{\mathbf{k}}^{(1)}$ to the ground state wavefunctions. $\bar{H}_{\mathbf{k}}^{(1)}$ is given by Eq. 35, while $\bar{S}_{\mathbf{k}}^{(1)}$ has a similar form and derived from Eq. 14 as

$$\bar{S}_{\mathbf{k}}^{(1)} = \frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{Rij}|\partial_\beta \tilde{p}_{Rik}\rangle s_{ij}\langle\partial_\gamma \tilde{p}_{Rjk}|. \quad (41)$$

Combining these terms give the contribution

$$-\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{nRij}\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\beta\tilde{p}_{Rik}\rangle\langle\partial_\gamma\tilde{p}_{Rjk}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle$$
$$\times\left(\hat{D}_{ij}^{(0)} + D_{ij}^{1,(0)} - \tilde{D}_{ij}^{1,(0)} - \epsilon_{n\mathbf{k}}s_{ij}\right). \quad (42)$$

The remaining parts of Hamiltonian $\bar{H}_{\mathbf{k}}^{(1)}$ are applied to the ground state wavefunctions. One part arises from $\mathbf{A_0}^{(1)}(\mathbf{r}-\mathbf{R})\cdot\mathbf{p}$. The corresponding linearized change of energy per cell for an imposed magnetic field **B** gives in atomic units the contribution $\frac{1}{2}\mathbf{L_R}\cdot\mathbf{B}$, where $\mathbf{L_R} = (\mathbf{r}-\mathbf{R})\times\mathbf{p}$ is the on-site orbital angular momentum. The term $\mathbf{A_0}(\mathbf{r}-\mathbf{R})\cdot\mathbf{A_N}(\mathbf{r}-\mathbf{R})$ results in the following contribution:

$$\frac{1}{2}\alpha^2\frac{[\mathbf{B}\times(\mathbf{r}-\mathbf{R})]\cdot[\mathbf{m_R}\times(\mathbf{r}-\mathbf{R})]}{|\mathbf{r}-\mathbf{R}|^3}. \quad (43)$$

Terms in $\mathbf{A_0^2}$ and $\mathbf{A_1^2}$ have been dropped.

2. Core electron contribution

Although as noted above we take the core electron densities n_c as magnetic field independent, there is neverthe-

less a significant core electron contribution to the orbital magnetic moment. The core electron densities are found during the PAW data set construction by solving for the atomic wavefunctions ψ_{Ri}^c using an all-electron atomic potential, which presumably in the core region, is very strong relative to the potential in the valence space. We can thus treat the effect of the magnetic field and the nuclear magnetic dipole through first order perturbation theory, using the core wavefunctions as the unperturbed set. The primary complication is that in the crystal, the core orbitals are referenced to the atomic locations R, and thus the orbitals must be gauged using the same $\mathcal{G}$ as used for the GIPAW transform above. The energy contributed by the core orbitals is thus determined by the Hamiltonian

$$H_{\text{cores}} = \left[\frac{1}{2}(\mathbf{p}+\mathbf{A_0}(\mathbf{r}-\mathbf{R})+\mathbf{A_N})^2 + V\right] \quad (44)$$

with V the atomic potential used in construction of the PAW dataset. Treating $\mathbf{A_0}$ as a perturbation, the only first order term that survives spherical averaging over the core orbitals is the scalar part of $\mathbf{A_0}\cdot\mathbf{A_N}$, which is just the Lamb shielding [21] σ_L,

$$\sigma_L = \frac{1}{3}\alpha^2\langle|\mathbf{r}-\mathbf{R}|^{-1}\rangle_{\text{cores}}. \quad (45)$$

The induced dipole moment is thus reduced by $-\sigma_L\mathbf{m_R}$.

C. Energy shifts and the Berry curvature

The Lagrange multiplier μ in our formulation is effectively an energy shift, and the magnetization should be invariant to this. This invariance has been noted elsewhere in the modern theory of orbital magnetization [6], where it is also noted that the derivative of the magnetization (or $E^{(1)}$) with respect to μ should be proportional to the Chern vector invariant. The Chern vector is zero in typical insulators. Differentiating Eq. 36 and simplifying (see App. A) yields

$$C_\alpha = -(2\pi)^2 \frac{dE^{(1)}}{d\mu^{(0)}} = i \int \frac{d^3k}{2\pi} \left[\epsilon_{\alpha\beta\gamma} \sum_n^{\text{occ}} \langle P_c \partial_\beta \bar{u}_{n,\mathbf{k}}^{(0)} | \bar{S}_{\mathbf{k}}^{(0)} | P_c \partial_\gamma \bar{u}_{n,\mathbf{k}}^{(0)} \rangle \right.$$

$$\left. + \frac{1}{2} \epsilon_{\alpha\beta\gamma} \sum_n^{\text{occ}} \left(\langle \bar{u}_{n,\mathbf{k}}^{(0)} | \partial_\beta \bar{S}_{\mathbf{k}}^{(0)} | P_c \partial_\gamma \bar{u}_{n,\mathbf{k}}^{(0)} \rangle + \langle P_c \partial_\beta \bar{u}_{n,\mathbf{k}}^{(0)} | \partial_\gamma \bar{S}_{\mathbf{k}}^{(0)} | \bar{u}_{n,\mathbf{k}}^{(0)} \rangle \right) \right]. \quad (46)$$

We compute this term at the same time as $E_\alpha^{(1)}$, as it provides a very useful convergence check on the overall calculation.

IV. RESULTS AND DISCUSSION

The theory and expressions outlined above give the first-order derivative of the energy in the applied magnetic field, $E^{(1)}$, with a finite nuclear magnetic dipole $\mathbf{m}$. We have implemented them in ABINIT [15], an open-source DFT code using a planewave basis, with a full PAW implementation [13]. The result is the negative of the magnetization induced by the nuclear dipole moment in the primitive cell. To make contact with the experimental NMR literature, we report below

$$\sigma_{ij} = \frac{\Omega}{\mathbf{m}_i} \frac{\partial E}{\partial B_j} = -\frac{\Omega}{\mathbf{m}_i} \mathbf{M}_j, \quad (47)$$

for dipole component $\mathbf{m}_i$ and field component B_j. Multiplication by the unit cell volume Ω yields the induced magnetic dipole moment, and division by $|\mathbf{m}|$ scales for the applied moment size.

A. Convergence

An example of the convergence with respect to k-point mesh is shown in Table I. The example presented is of the shielding around aluminum in solid AlP. The extremely fast convergence with k-point mesh is a feature of using DFPT to compute the wavefunction derivatives, rather than finite-difference methods. The final column shows the Chern vector convergence towards its theoretical value of zero. This value provides a useful subsidiary check on the convergence of the shielding, as it provides in a sense an upper bound on the precision that can be expected from the shielding.

The shieldings scale with both added magnetic moment strength and system size as expected [9], see Table II. Table II has two parts; the upper part shows the scaling with nuclear dipole size. In this case, the shielding around silicon in crystalline Si was computed, with various sizes of nuclear dipole moment added. As energy should be linear in the dipole size (at least for small dipoles), the shielding should be independent of dipole size (see Eq. 47), and it largely is. If the dipole is very

TABLE I. Convergence of the chemical shielding at aluminum in AlP, as a function of the k-point mesh density. The first column shows the minimum k-point grid spacing in Å^{-1}; the second column shows the chemical shielding in ppm at aluminum (the aluminum is on a site of tetrahedral point symmetry in AlP so the shieldings in all directions are equivalent); the third column shows the component of the Chern vector in the applied dipole direction, also in ppm.

mesh, Å^{-1}	σ, ppm	C_α, ppm
0.0649	412.944	0.182
0.0432	415.261	7.601×10^{-3}
0.0324	415.328	2.043×10^{-4}
0.0259	415.330	-7.563×10^{-5}
0.0216	415.329	-8.551×10^{-5}
0.0185	415.329	-8.7156×10^{-5}
0.0162	415.329	-8.706×10^{-5}

TABLE II. Scaling of the shielding with dipole strength (top part of table) and dipole separation (bottom part). The computation is for crystalline silicon.

$|\mathbf{m}|$, atomic units	σ, ppm
10^{-3}	414.321
10^{-2}	414.449
10^{-1}	414.439
1.0	414.436
10.0	414.442
100.0	415.022
Dipole-dipole distance, Å	
2.35	414.437
3.84	414.436
7.68	414.435
11.52	414.438

small, the energy effect is too small to compute accurately, while if it is large, the linearity approximation breaks down. We find good results at $|\mathbf{m}| = 1$ in atomic units, which is also the most convenient value to use.

Table II also shows the effect of dipole-dipole distance. In general one would like to compute the effect around an isolated dipole, as that most closely approximates experiment (due to the thermal averaging to which all nuclear dipoles in a realistic solid are subject to). Four cases are shown in Table II, all for $|\mathbf{m}| = 1$: the first, if both silicon atoms in the primitive unit cell carry the same dipole, so the interdipole separation is 2.35 Å; next is if a single

TABLE III. Chemical shieldings of noble gas atoms computed with ABINIT, CASTEP, CCSD(T) wavefunctions [22], and Dirac-Fock wavefunctions [22]. Values given in ppm.

Atom	ABINIT	CASTEP	CCSD(T)	DIRAC-FOCK
He	58.9	59.7	59.9	59.9
Ne	552.9	553.0	551.9	561.3
Ar	1242.2	1245.4	1237.7	1274.3
Kr	3321.0	3318.4	3245.4	3577.3
Xe	5941.9	5925.2	5642.2	6938

TABLE IV. Components of the shielding tensor in two systems: an isolated Ne atom, and aluminum in solid AlP.

Shielding term	Ne	Al*P
Core, Eq. 45	341.8	764.2
On-site, Eq. 35 $D^{1,(1)}$	-522.4	8.4
On-site, Eq. 35 $D^{1,(0)}$	-894.1	-181.0
Planewave, Eqs. A24 and A29	1627.5	-176.2
Total	552.8	415.4

silicon in the primitive cell carries a dipole, so the separation is 3.84 Å; and finally, $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells, with separation of 7.68 Å and 11.52 Å respectively. As the table shows, there is basically no dependence on separation, meaning that the shielding is a short-range effect and that large supercells are not needed. There is one caveat: as the computation is for the perturbed energy per cell, if multiple equivalent sites within a cell carry a dipole, as in the first case studied here, the results must be divided by the number of dipoles to obtain the shielding on individual sites. This also means that if several different site in a cell are of interest, the calculation should be carried out for each one independently of the others.

B. Shieldings

Table III shows shieldings for noble gas atoms, obtained with ABINIT, as well as a code that uses the GIPAW method (CASTEP) and wavefunction-based methods [22]. The wavefunction-based methods are post-Hartree-Fock coupled cluster with single and double excitations, and perturbative triple excitations, and a complete relativistic treatment based on the Dirac equation [22]. The CASTEP results were obtained using the real-space representation of the GIPAW theory, suitable for isolated systems such as here. In the ABINIT case, the reciprocal-space expressions as outlined above were used, but note that as the wavefunction derivatives are determined from a Sternheimer equation and not by finite differences, working with a single **k** point only (the Γ point in this case) causes no complications. The CASTEP calculations were performed with CASTEP's internal pseudopotential set, which includes scalar relativistic corrections, while the ABINIT calculations were done using the PAW datasets [23] obtainable from the pseudo-dojo.org web site (also including scalar relativistic corrections). Agreement between the methods is excellent for lighter atoms, while for heavier atoms (Kr and Xe), relativistic corrections are clearly important.

The various components that make up the total shielding in the current formalism are shown in Table IV for two systems, an isolated neon atom and the aluminum site in solid AlP. We have decomposed the total into four contributions. The first is due to the filled core or-

bitals, Eq. 45; here these are $1s^2$ for neon, and $1s^2 2s^2 2p^6$ for aluminum. The second and third arise from the ground state wavefunctions acting on the on-site PAW projectors, Eq. 35, first with the first-order on-site energies due to $\mathbf{A_0}$, and then with the perturbed projectors and the unperturbed on-site energies. The final term arises from the planewave contributions, summarized in Eqs A24 and A29. We show this breakdown into components for several reasons. The first is to emphasize that all the terms contribute significantly to the total shielding, so none could be easily ignored. Of course, the time-consuming part of the calculation is in computing the wavefunctions and their derivatives, assembling the terms in Eq. 36 takes just a few seconds.

The second aspect of Table IV to note is that the contributions do not align with "diamagnetic" and "paramagnetic" shielding terminology usually employed in simple treatments of shielding [24]. In this simplified picture, the diamagnetic shielding arises from the ground state wavefunctions and is expected to be positive, while the paramagnetic shielding arises from mixing in the excited state wavefunctions and is expected to be negative. In the present formalism, the planewave contribution (Eqs. A24 and A29) arise from the perturbed wavefunctions, in this case $\bar{P}^{(0)}_{c\mathbf{k}}|\partial_\alpha \bar{u}^{(0)}_{n,\mathbf{k}}\rangle$, but we can see that in neon, this term is positive, while it is negative in AlP. Likewise, the on-site terms arising from the ground state wavefunctions $|\bar{u}^{(0)}_{n,\mathbf{k}}\rangle$ sum to negative values in both cases. Only the filled-state Lamb term has the simple interpretation of a "diamagnetic" shielding. To be sure, the "simplified" treatment is clearly recognized in ref. [24] as, indeed, simplified, where it is noted in particular that the separation into diamagnetic and paramagnetic components is not gauge invariant, so these terms have no intrinsic meaning in the context of shielding. In our formalism, it is clear that interpreting the shielding through the different total contributions appears very challenging; we believe that a band-by-band decomposition will prove more fruitful but that will be the subject of a later publication.

Turning to the comparison of our calculations with experimental results, we show in Table V comparison between calculated and measured shifts for ^{29}Si in a variety of compounds, and in Table VI, a similar comparison for ^{17}O. We note that the ABINIT values do not include a shift contribution due to susceptibility and sample shape. However, such contributions vanish under magic angle

TABLE V. Isotropic chemical shifts obtained from ABINIT, compared with experiment, for ^{29}Si in several compounds. Experimental data obtained from refs. [25–28]. Referencing done by a linear fit between the calculated data and experiment, which yielded a slope of -1.066.

Formula	Compound	ABINIT	Experiment
Si	Silicon	-82.0	-81
SiO_2	α-Quartz	-105.7	-106.2
	Cristobalite	-114.5	-108.5
	Stishovite	-188.5	-191.4
$Li_2Si_2O_5$	Lithium disilicate	-95.0	-93
Mg_2SiO_4	Forsterite	-58.2	-62
Al_2SiO_5	Andalusite	-78.6	-80
	Sillimanite	-88.6	-87
	Kyanite	-81.1	-83

TABLE VI. Isotropic chemical shifts obtained from ABINIT, compared to experiment, for ^{17}O in several compounds. Experimental data from refs. [27, 29]. Referencing done by a linear fit between the calculated data and experiment, which yielded a slope of -0.866.

Compound	ABINIT	Experiment
BeO	27.0	26
MgO	55.5	47
SrO	405.7	390
BaO	619.9	629
SiO_2 (α-Quartz)	35.7	41
SiO_2 (Stishovite)	98.2	109

spinning conditions (MAS) [30], the experimental conditions used in Tables V and VI, and so are unnecessary for the comparison. For static samples with large magnetic anisotropies they would be important to include [31].

Agreement with experiment in both cases is quite good, and consistently as good or better than what is obtained using the GIPAW method with planewaves (CASTEP, ref. [25]) or with LAPW (WIEN2K, ref. [29]). It is important to note that the referencing done here, in order to compare with experiment, was carried out by a linear fit of the calculations to the experimental shift, as done in ref. [29]). Experimentally of course the referencing would be done against an experimental spectrum of tetramethyl silane, in the case of ^{29}Si, and water, in the case of ^{17}O. For the calculations, the linear fit reference would ideally have a slope of -1.0, while we find -1.066 for ^{29}Si and -0.866 for ^{17}O. These deviations from -1 indicate a systematic error, which very likely arises from the modest ability of the PBE exchange and correlation functional used here and in the cited studies [25, 29] to compute the band gap accurately. This has been shown in ref. [29], where even better agreement with experiment was obtained using the modified Becke-Johnson potential [32], which is known to give a better band-gap estimate. We will pursue this issue, also for the shielding tensor elements, in future work.

V. CONCLUSIONS

In this contribution we detailed the treatment of the energy to first order in a crystalline system, due to an homogeneous magnetic field. We developed the theory in the projector augmented-wave framework, using three major steps: the development of the energy using a constrained minimization based on the density operator, followed by application of magnetic translation symmetry to obtain expressions compatible with Bloch functions, and finally the development of expressions for how products of operators transform under magnetic translation symmetry. The resulting expressions were implemented in ABINIT, a DFT code based on on planewaves that includes a full implementation of PAW. Our approach takes advantage of the gauge invariance of the expressions to compute the necessary wavefunction derivatives in a DFPT computation, greatly accelerating convergence over finite-difference methods. Furthermore, because our treatment of PAW is complete, our implementation can be used directly with standard libraries of PAW atomic datasets. We also implemented on-site nuclear dipoles, so that the resulting first-order energies could be used to compute chemical shieldings as measured by NMR. We found that the computed shieldings compare very favorably both with other first-principles methods, and with experiment.

Future work will focus on developing the decomposition of the chemical shieldings in ways amenable to chemical interpretation; the inclusion of explicitly spin-dependent terms in the Hamiltonian; application to metals; and exploration of systematic errors due to the particular choice of exchange and correlation functionals.

Appendix A: Energy from a variational approach

Treating density functional theory problems through variational methods is standard, and has been discussed in a number publications, see for example [12, 14, 19, 33]. In the non-interacting electron case (fixed Hamiltonian), the total energy may be found by varying $\text{Tr}[\rho H]$ over all density operators ρ, subject to the constraints of idempotency,

$$\rho = \rho S \rho, \tag{A1}$$

and total number of electrons N,

$$\mathrm{Tr}[\rho S] = N, \tag{A2}$$

where S is the overlap operator. These constraints lead to the following minimization problem:

$$E[H, S] = \min_\rho \mathrm{Tr}[\rho H - \Lambda(\rho - \rho S \rho)] - \mu \left(\frac{1}{2} \mathrm{Tr}[\rho S + S \rho] - N \right), \tag{A3}$$

with Lagrange multipliers Λ and μ. Minimization with respect to ρ leads to

$$0 = H - \mu S - \Lambda + \Lambda(\rho S + S \rho). \tag{A4}$$

The generalization of this minimization problem to include the effect of a self-consistent Hamiltonian is trivial, and anyhow does not have any bearing on the forthcoming determination of the first-order energy, due to Hellmann-Feynman theorem [34, 35]. This is similar to the determination of forces in the PAW framework.

We now express the operators in the basis of states $|\psi_n\rangle$ that solve the generalized eigenvalue problem:

$$H|\psi_n\rangle = \epsilon_n S|\psi_n\rangle; \tag{A5}$$

$$\langle \psi_m | S | \psi_n \rangle = \delta_{mn}; \tag{A6}$$

$$\langle \psi_m | H | \psi_n \rangle = \delta_{mn} \epsilon_n. \tag{A7}$$

We thus use

$$H = \sum_n S|\psi_n\rangle \epsilon_n \langle \psi_n | S; \tag{A8}$$

$$\Lambda = \sum_n S|\psi_n\rangle \lambda_n \langle \psi_n | S; \tag{A9}$$

$$\rho = \sum_n |\psi_n\rangle \theta(\epsilon_F - \epsilon_n) \langle \psi_n |, \tag{A10}$$

where $\theta(\epsilon_F - \epsilon_n)$ is the Heaviside step function. Here ϵ_F is the Fermi energy differentiating between occupied and unoccupied states. Using these expressions in Eq. A4 leads to

$$0 = \epsilon_n - \mu - \lambda_n + 2\lambda_n \theta(\epsilon_F - \epsilon_n), \tag{A11}$$

or

$$\lambda_n = \begin{cases} \epsilon_n - \mu, & \epsilon_F < \epsilon_n \ \text{(unoccupied states)} \\ -(\epsilon_n - \mu), & \epsilon_F > \epsilon_n \ \text{(occupied states)}. \end{cases} \tag{A12}$$

Using this link between λ_n, ϵ_n and μ, we can write the operator Λ as

$$\Lambda = -P_v^\dagger (H - \mu S) P_v + P_c^\dagger (H - \mu S) P_c, \tag{A13}$$

where P_v projects onto occupied states and P_c onto unoccupied states.

When a magnetic field is present, Eq. A3 is modified in several ways. First, magnetic translation symmetry should be used, to render the various operators periodic (see Appendix B). We indicate the resulting operators with an overbar. Secondly, the various objects are (explicitly or implicitly) field dependent. The minimization problem becomes

$$E[H, S, B] = \min_{\bar\rho} \Big\{ \mathrm{Tr} \left[\bar\rho(B) \bar H(B) - \bar\Lambda(B)[\bar\rho(B) - \overline{\rho S \rho}(B)] \right] - \mu(B) \left(\frac{1}{2} \mathrm{Tr}[\overline{\rho S}(B) + \overline{S\rho}(B)] - N \right). \Big\} \tag{A14}$$

We seek to obtain the energy to first order in B from Eq. A14, so to that end we enumerate the explicit field dependence of the various terms. First, $\bar H$ and $\bar S$ might have explicit B field dependence, which is indeed present for PAW. In the former case, it comes through both the vector potential $\mathbf{A_0}$ and the onsite density ρ_{Rij}, and the latter also through ρ_{Rij}. The explicit B-field dependence of ρ_{Rij} is shown in Eq. B9. Next, operator products $\overline{\rho S \rho}$, $\overline{\rho S}$, and $\overline{S\rho}$ have first-order B dependence as detailed in Appendix C. In particular, we have

$$\overline{\rho S \rho} = \bar\rho \bar S \bar\rho - \frac{i}{2} \epsilon_{\alpha\beta\gamma} B_\alpha \partial_{\beta\gamma} (\bar\rho \bar S \bar\rho) + \dots, \tag{A15}$$

where we have used the abbreviated notation

$$\partial_{\beta\gamma} (\bar\rho \bar S \bar\rho) = (\partial_\beta \bar\rho)(\partial_\gamma \bar S) \bar\rho + (\partial_\beta \bar\rho) \bar S (\partial_\gamma \bar\rho) + \bar\rho (\partial_\beta \bar S)(\partial_\gamma \bar\rho). \tag{A16}$$

The products $\overline{\rho S}$ and $\overline{S\rho}$ have a similar first order dependence (Eq. C1), but because they appear symmetrically and the dependence is contracted with the antisymmetric $\epsilon_{\alpha\beta\gamma}$, the first-order term involving these product operators vanishes.

Both $\bar\Lambda$ and μ depend on B, but because in a perturbative treatment their first order terms multiply exactly the idempotency and electron count constraints, they do not contribute.

Finally, note that $\bar\rho$ does not have explicit B dependence, as it is transferred to the magnetic phase factor, see Eq. B4.

The first-order energy per unit volume is thus found by differentiating the energy per unit volume to first order in B, taking into account only the explicit B dependence. The following expression is obtained, where because we have applied magnetic translation symmetry we can also use Bloch states:

$$E^{(1)} = \int \frac{d^3 k}{(2\pi)^3} \mathrm{Tr} \left[\bar\rho_{\mathbf{k}}^{(0)} \left(\bar H_{\mathbf{k}}^{(1)} - \mu^{(0)} \bar S_{\mathbf{k}}^{(1)} \right) + \bar\Lambda_{\mathbf{k}}^{(0)} \left(\bar\rho_{\mathbf{k}}^{(0)} \bar S_{\mathbf{k}}^{(1)} \bar\rho_{\mathbf{k}}^{(0)} - \frac{i}{2} \epsilon_{\alpha\beta\gamma} \partial_{\beta\gamma} (\bar\rho_{\mathbf{k}}^{(0)} \bar S_{\mathbf{k}}^{(0)} \bar\rho_{\mathbf{k}}^{(0)}) \right) \right], \tag{A17}$$

where

$$\bar\Lambda_{\mathbf{k}}^{(0)} = -\bar P_{v\mathbf{k}}^{(0)\dagger} (\bar H_{\mathbf{k}}^{(0)} - \mu^{(0)} \bar S_{\mathbf{k}}^{(0)}) \bar P_{v\mathbf{k}}^{(0)} + \bar P_{c\mathbf{k}}^{(0)\dagger} (\bar H_{\mathbf{k}}^{(0)} - \mu^{(0)} \bar S_{\mathbf{k}}^{(0)}) \bar P_{c\mathbf{k}}^{(0)} \tag{A18}$$

and the B field is understood to be in direction α.

In order to evaluate the terms in Eq. A17, we first note that, using Bloch states, the density operator and its k-space derivative are written as

$$\bar{\rho}_{\mathbf{k}}^{(0)} = \sum_n^{\text{occ}} |\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\langle \bar{u}_{n,\mathbf{k}}^{(0)}|, \tag{A19}$$

$$\partial_\alpha \bar{\rho}_{\mathbf{k}}^{(0)} = \sum_n^{\text{occ}} |\partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)}\rangle\langle \bar{u}_{n,\mathbf{k}}^{(0)}| + |\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\langle \partial_\alpha \bar{u}_{n,\mathbf{k}}^{(0)}|. \tag{A20}$$

In contrast to the all-electron and norm-conserving cases, in PAW the derivative wavefunctions have both occupied space and unoccupied space components.

To evaluate the first two terms of Eq. A17, one notes that as $\bar{P}_{c\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)} = 0$, only the occupied space part of $\bar{\Lambda}_{\mathbf{k}}^{(0)}$ needs to be considered. This restriction leads to

$$\bar{\Lambda}_{\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)} \bar{S}_{\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)} =$$
$$- \bar{P}_{v\mathbf{k}}^{(0)\dagger}(\bar{H}_{\mathbf{k}}^{(0)} - \mu^{(0)} \bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)} \bar{S}_{\mathbf{k}}^{(1)} \bar{\rho}_{\mathbf{k}}^{(0)}. \tag{A21}$$

Upon taking the trace this term yields

$$- \sum_n^{\text{occ}} \langle \bar{u}_{n,\mathbf{k}}^{(0)}|\epsilon_{n\mathbf{k}} \bar{S}_{\mathbf{k}}^{(1)} - \mu^{(0)} \bar{S}_{\mathbf{k}}^{(1)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle, \tag{A22}$$

which, when combined with the first term of Eq. A17, leads to

$$\text{Tr}\left[\bar{\rho}_{\mathbf{k}}^{(0)} \left(\bar{H}_{\mathbf{k}}^{(1)} - \mu^{(0)} \bar{S}_{\mathbf{k}}^{(1)}\right) + \bar{\Lambda}_{\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)} \bar{S}_{\mathbf{k}}^{(1)} \bar{\rho}_{\mathbf{k}}^{(0)}\right] =$$
$$\sum_n^{\text{occ}} \langle \bar{u}_{n,\mathbf{k}}^{(0)}|\bar{H}_{\mathbf{k}}^{(1)} - \epsilon_{n\mathbf{k}} \bar{S}_{\mathbf{k}}^{(1)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle. \tag{A23}$$

For the terms arising from $\partial_{\beta\gamma}(\bar{\rho}_{\mathbf{k}}^{(0)} \bar{S}_{\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)})$, it is easiest to consider the occupied and unoccupied space parts of $\bar{\Lambda}_{\mathbf{k}}^{(0)}$ separately. For the unoccupied subspace, two of the three terms in $\partial_{\beta\gamma}(\bar{\rho}_{\mathbf{k}}^{(0)} \bar{S}_{\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)})$ are annihilated and

what remains is

$$-\frac{i}{2}\epsilon_{\alpha\beta\gamma}\text{Tr}\left[(\bar{H}_{\mathbf{k}}^{(0)} - \mu^{(0)} \bar{S}_{\mathbf{k}}^{(0)})\right.$$
$$\left.\bar{P}_{c\mathbf{k}}^{(0)}(\partial_\beta\bar{\rho}_{\mathbf{k}}^{(0)})\bar{S}_{\mathbf{k}}^{(0)}(\partial_\gamma\bar{\rho}_{\mathbf{k}}^{(0)})\bar{P}_{c\mathbf{k}}^{(0)\dagger}\right] =$$
$$+\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_n^{\text{occ}} \langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\bar{H}_{\mathbf{k}}^{(0)} - \mu^{(0)} \bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle. \tag{A24}$$

Here $|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle$ is an abbreviation for $\bar{P}_{c\mathbf{k}}^{(0)}|\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle$. The overall sign-change occurs because the original trace is cyclically reordered to a term of the form $(\partial_\gamma)H(\partial_\beta)$, followed by use of antisymmetry to relabel as $(\partial_\beta)H(\partial_\gamma)$.

When acting with the occupied space part of $\bar{\Lambda}_{\mathbf{k}}^{(0)}$, it is easiest to insert $1 = \bar{P}_{c\mathbf{k}}^{(0)} + \bar{P}_{v\mathbf{k}}^{(0)}$ between the derivatives of each of the three terms of $\partial_{\beta\gamma}(\bar{\rho}_{\mathbf{k}}^{(0)} \bar{S}_{\mathbf{k}}^{(0)} \bar{\rho}_{\mathbf{k}}^{(0)})$, and to simplify where possible through use of

$$\bar{P}_{v\mathbf{k}}^{(0)\dagger}\partial\rho\bar{P}_{v\mathbf{k}}^{(0)} = -\rho\partial S\rho, \tag{A25}$$

which is derived by differentiating the idempotency condition $\rho = \rho S \rho$ and projecting. With this approach we obtain for the three terms,

$$-\bar{P}_{v\mathbf{k}}^{(0)}\left[(\partial_\beta\bar{\rho}_{\mathbf{k}}^{(0)})(\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}\right]\bar{P}_{v\mathbf{k}}^{(0)\dagger} =$$
$$\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\beta\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}$$
$$-\bar{P}_{v\mathbf{k}}^{(0)}\left[(\partial_\beta\bar{\rho}_{\mathbf{k}}^{(0)})\bar{P}_{c\mathbf{k}}^{(0)\dagger}(\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}\right]\bar{P}_{v\mathbf{k}}^{(0)\dagger}; \tag{A26}$$

$$-\bar{P}_{v\mathbf{k}}^{(0)}\left[(\partial_\beta\bar{\rho}_{\mathbf{k}}^{(0)})\bar{S}_{\mathbf{k}}^{(0)}(\partial_\gamma\bar{\rho}_{\mathbf{k}}^{(0)})\right]\bar{P}_{v\mathbf{k}}^{(0)\dagger} =$$
$$-\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\beta\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}$$
$$-\bar{P}_{v\mathbf{k}}^{(0)}\left[(\partial_\beta\bar{\rho}_{\mathbf{k}}^{(0)})\bar{P}_{c\mathbf{k}}^{(0)\dagger}\bar{S}_{\mathbf{k}}^{(0)}(\partial_\gamma\bar{\rho}_{\mathbf{k}}^{(0)})\right]\bar{P}_{v\mathbf{k}}^{(0)\dagger}; \tag{A27}$$

and

$$-\bar{P}_{v\mathbf{k}}^{(0)}\left[\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\beta\bar{S}_{\mathbf{k}}^{(0)})(\partial_\gamma\bar{\rho}_{\mathbf{k}}^{(0)})\right]\bar{P}_{v\mathbf{k}}^{(0)\dagger} =$$
$$\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\beta\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)})\bar{\rho}_{\mathbf{k}}^{(0)}$$
$$-\bar{P}_{v\mathbf{k}}^{(0)}\left[\bar{\rho}_{\mathbf{k}}^{(0)}(\partial_\beta\bar{S}_{\mathbf{k}}^{(0)})\bar{P}_{c\mathbf{k}}^{(0)}(\partial_\gamma\bar{\rho}_{\mathbf{k}}^{(0)})\right]\bar{P}_{v\mathbf{k}}^{(0)\dagger}. \tag{A28}$$

Summing the three we obtain the following:

$$-\frac{i}{2}\epsilon_{\alpha\beta\gamma}\mathrm{Tr}\left[(\bar{H}_{\mathbf{k}}^{(0)}-\mu^{(0)}\bar{S}_{\mathbf{k}}^{(0)})\left(-\bar{P}_{v\mathbf{k}}^{(0)}\partial_{\beta\gamma}(\bar{\rho}_{\mathbf{k}}^{(0)}\bar{S}_{\mathbf{k}}^{(0)}\bar{\rho}_{\mathbf{k}}^{(0)})\bar{P}_{v\mathbf{k}}^{(0)\dagger}\right)\right]=$$

$$+\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}(\epsilon_{n\mathbf{k}}-\mu^{(0)})\langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle$$

$$+\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}(\epsilon_{n\mathbf{k}}-\mu^{(0)})\left(\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\beta\bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle+\langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\right)$$

$$-\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{n,n'}^{\mathrm{occ}}(\epsilon_{n\mathbf{k}}-\mu^{(0)})\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\beta\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n',\mathbf{k}}^{(0)}\rangle\langle\bar{u}_{n',\mathbf{k}}^{(0)}|\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle. \quad (\mathrm{A}29)$$

Combining Eqs. A23, A24, and A29, we obtain the final result,

$$E^{(1)}=\int\frac{d^3k}{(2\pi)^3}\left[\sum_{n}^{\mathrm{occ}}\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\bar{H}_{\mathbf{k}}^{(1)}-\epsilon_{n\mathbf{k}}\bar{S}_{\mathbf{k}}^{(1)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\right.$$

$$+\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}\langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\bar{H}_{\mathbf{k}}^{(0)}+\epsilon_{n\mathbf{k}}\bar{S}_{\mathbf{k}}^{(0)}-2\mu^{(0)}\bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle$$

$$+\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}(\epsilon_{n\mathbf{k}}-\mu^{(0)})\left(\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\beta\bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle+\langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\right)$$

$$\left.-\frac{i}{2}\epsilon_{\alpha\beta\gamma}\sum_{n,n'}^{\mathrm{occ}}(\epsilon_{n\mathbf{k}}-\mu^{(0)})\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\beta\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n',\mathbf{k}}^{(0)}\rangle\langle\bar{u}_{n',\mathbf{k}}^{(0)}|\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\right]. \quad (\mathrm{A}30)$$

Complex though the derivation is, the final result hews closely to the simpler result obtained from a norm-conserving pseudopotential or all-electron treatment. The first term of Eq. A30 is just the energy per unit volume due to the explicit B dependence of the Hamiltonian, after application of magnetic translation symmetry; the second term involves only the unoccupied states and is just what is found in the so-called modern theory of orbital magnetism [6], except for the appearance of $\bar{S}_{\mathbf{k}}^{(0)}$; and terms three and four are present because of the non-trivial overlap operator of a full PAW treatment, and include couplings between the occupied and unoccupied states, and between the zeroth order occupied states.

Finally, the Chern invariant vector can be obtained by differentiating $E^{(1)}$ of Eq. A30 with respect to $\mu^{(0)}$, as described in ref. [6]. We obtain the following:

$$C_\alpha=-(2\pi)^2\frac{dE^{(1)}}{d\mu^{(0)}}=i\int\frac{d^3k}{2\pi}\left[\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}\langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\right.$$

$$\left.+\frac{1}{2}\epsilon_{\alpha\beta\gamma}\sum_{n}^{\mathrm{occ}}\left(\langle\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\beta\bar{S}_{\mathbf{k}}^{(0)}|P_c\partial_\gamma\bar{u}_{n,\mathbf{k}}^{(0)}\rangle+\langle P_c\partial_\beta\bar{u}_{n,\mathbf{k}}^{(0)}|\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)}|\bar{u}_{n,\mathbf{k}}^{(0)}\rangle\right)\right]. \quad (\mathrm{A}31)$$

Note that the derivative with respect to $\mu^{(0)}$ of the final term of $E^{(1)}$ does not appear in C_α, because in that term the matrix elements of $\partial_\beta\bar{S}_{\mathbf{k}}^{(0)}$ and $\partial_\gamma\bar{S}_{\mathbf{k}}^{(0)}$ appear as a symmetric product, and so vanish after contraction with $\epsilon_{\alpha\beta\gamma}$.

Appendix B: Translation invariance of PAW terms

As discussed by Zak [16], the presence of a homogeneous magnetic field breaks the translation symmetry of an electron in a periodic potential. However, a magnetic translation group can be defined which does commute with the Hamiltonian, allowing use of Bloch functions. Accomplishing this requires a proper gauge choice, the

conditions of which are fulfilled by for example the symmetric gauge [16]

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}. \tag{B1}$$

Then, within the symmetric gauge, spatially-dependent operators can be written in terms of a periodic kernel and a magnetic phase factor [16, 17]. For observable O and kernel $\bar{O}$, the relation is

$$O_{\mathbf{r_1},\mathbf{r_2}} = \bar{O}_{\mathbf{r_1},\mathbf{r_2}} e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}\times\mathbf{r_2})}, \tag{B2}$$

where

$$\bar{O}_{\mathbf{r_1}+\mathbf{R},\mathbf{r_2}+\mathbf{R}} = \bar{O}_{\mathbf{r_1},\mathbf{r_2}} \tag{B3}$$

for lattice translations $\mathbf{R}$.

For multiplicative, local operators, this transformation is trivial, because the phase factor becomes $e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r}\times\mathbf{r})} = 0$. For derivative and non-local operators, it is convenient to consider the transformation together with the density operator, as

$$\text{Tr}[A\rho_{\mathbf{r_1},\mathbf{r_2}}] = \text{Tr}[Ae^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}}\bar{\rho}_{\mathbf{r_1},\mathbf{r_2}}]. \tag{B4}$$

This strategy will ultimately yield the energy terms as $\text{Tr}[\bar{H}\bar{\rho}]$, where $\bar{H}$ may have explicit B dependence but will be periodic, as will $\bar{\rho}$, and be compatible with Bloch functions and periodic boundary conditions.

The kinetic energy $T_{\text{KE}} = \frac{1}{2}[-i\nabla + \mathbf{A_0}(\mathbf{r})]^2$, in the symmetric gauge, is transformed as follows. First note that

$$[-i\nabla_{\mathbf{r_1}} + \mathbf{A_0}(\mathbf{r_1})]e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}} =$$
$$[-i\nabla_{\mathbf{r_1}} + \mathbf{A_0}(\mathbf{r_1})]e^{\frac{i}{2}\mathbf{r_1}\cdot\mathbf{r_2}\times\mathbf{B}} =$$
$$e^{\frac{i}{2}\mathbf{r_1}\cdot\mathbf{r_2}\times\mathbf{B}}[-i\nabla_{\mathbf{r_1}} + \mathbf{A_0}(\mathbf{r_1}) - \mathbf{A_0}(\mathbf{r_2})], \tag{B5}$$

so that the effect of $\mathbf{A_0}$ will be canceled once the locality condition $\delta(\mathbf{r_1} - \mathbf{r_2})$ is applied. Then

$$[-i\nabla_{\mathbf{r_1}} + \mathbf{A_0}(\mathbf{r_1})]^2 e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}} =$$
$$e^{\frac{i}{2}\mathbf{r_1}\cdot\mathbf{r_2}\times\mathbf{B}}[-i\nabla_{\mathbf{r_1}} + \mathbf{A_0}(\mathbf{r_1}) - \mathbf{A_0}(\mathbf{r_2})]^2, \tag{B6}$$

and

$$\text{Tr}[\delta(\mathbf{r_1} - \mathbf{r_2})T_{\text{KE}}\rho_{\mathbf{r_1},\mathbf{r_2}}] =$$
$$\text{Tr}[\delta(\mathbf{r_1} - \mathbf{r_2})T_{\text{KE}}e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}}\bar{\rho}_{\mathbf{r_1},\mathbf{r_2}}] = \text{Tr}[\bar{T}_{\text{KE}}\bar{\rho}_{\mathbf{r_1},\mathbf{r_2}}], \tag{B7}$$

with $\bar{T}_{\text{KE}} = \frac{1}{2}(-i\nabla)^2$.

The PAW onsite densities are derived by considering the effect of the magnetic translation invariance on the projectors, as follows. We consider the onsite PAW projector $\sum_{Rij} |\tilde{p}_i\rangle\langle\tilde{p}_j|$, together with $\rho_{\mathbf{r_1},\mathbf{r_2}} = \sum_n^{\text{occ}} |\psi_n(\mathbf{r_1})\rangle\langle\psi_n(\mathbf{r_2})|$. The onsite projector must be transformed with the GIPAW operator $\mathcal{G}$ of Eq. 12 because the $\tilde{p}$ functions are centered at the ion sites [1].

Moreover, $|\tilde{p}_i\rangle$ will be contracted with $\langle\psi(\mathbf{r_2})|$, and hence, written as a spatial function, $\tilde{p}_i = \tilde{p}_i(\mathbf{r_2})$. Similarly, $\tilde{p}_j^* = \tilde{p}_j^*(\mathbf{r_1})$. These considerations lead to the following for the onsite density:

$$\rho_{Rij} = \text{Tr}\left[\bar{\rho}_{\mathbf{r_1},\mathbf{r_2}} e^{\frac{i}{2}\mathbf{B}\cdot\mathbf{r_1}\times\mathbf{r_2}}\right.$$
$$\left. e^{\frac{i}{2}\mathbf{R}\cdot\mathbf{B}\times\mathbf{r_2}}\tilde{p}_i(\bar{\mathbf{r}}_2)\tilde{p}_j^*(\bar{\mathbf{r}}_1)e^{-\frac{i}{2}\mathbf{R}\cdot\mathbf{B}\times\mathbf{r_1}}\right], \tag{B8}$$

where we use the abbreviated notation $\bar{\mathbf{r}} = \mathbf{r} - \mathbf{R}$. Combining the exponentials in Eq. B8 leads to

$$\rho_{Rij} = \text{Tr}\left[\bar{\rho}_{\mathbf{r_1},\mathbf{r_2}} e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2\times\bar{\mathbf{r}}_1}\tilde{p}_i(\bar{\mathbf{r}}_2)\tilde{p}_j^*(\bar{\mathbf{r}}_1)\right], \tag{B9}$$

and allowing us to identify the translationally invariant projector kernel

$$\bar{p}_{ij,\bar{\mathbf{r}}_1,\bar{\mathbf{r}}_2} = e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2\times\bar{\mathbf{r}}_1}\tilde{p}_i(\bar{\mathbf{r}}_2)\tilde{p}_j^*(\bar{\mathbf{r}}_1). \tag{B10}$$

The projector kernel can be used with other on-site operators to find their translationally invariant PAW forms. For example, the overlap S becomes

$$\bar{S} = \delta(\mathbf{r_2} - \mathbf{r_1}) + \sum_{Rij} e^{-\frac{i}{2}\mathbf{B}\cdot\bar{\mathbf{r}}_2\times\bar{\mathbf{r}}_1}\tilde{p}_i(\bar{\mathbf{r}}_2)\tilde{p}_j^*(\bar{\mathbf{r}}_1)s_{ij}. \tag{B11}$$

Appendix C: Operator products under magnetic field

This appendix focuses on how products of operators, characterized by a wavevector, behave when a non-zero magnetic field is present, the kernels of such operators transforming in real space according to Eq. (B2). As in Appendix B, the symmetric gauge is assumed.

First, the appendix provides a simple proof of the first-order Taylor expansion in term of magnetic field for such products, based on the iterative usage of the result for the product of two operators. The products of three operators and of four operators are deduced. Then, a more general approach for the product of three operators is described, where the Taylor expansion is delayed as much as possible, in the same way that a formula valid for all magnetic field strengths had been provided by Gonze and Zwanziger (GZ) [10].

The case of a product of two operators has been proven earlier [10]:

$$(\overline{UV})_{\mathbf{k}} = \bar{U}_{\mathbf{k}}\bar{V}_{\mathbf{k}} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha(\partial_\beta\bar{U}_{\mathbf{k}})(\partial_\gamma\bar{V}_{\mathbf{k}}) + O(B^2). \tag{C1}$$

The totally antisymmetric unit tensor is noted $\epsilon_{\alpha\beta\gamma}$ and summation over repeated indices is implied. For use in the present paper, the goal is to derive the three-operator generalization:

$$(\overline{UVW})_{\mathbf{k}} = \bar{U}_{\mathbf{k}}\bar{V}_{\mathbf{k}}\bar{W}_{\mathbf{k}} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha.$$
$$\left[(\partial_\beta\bar{U}_{\mathbf{k}})(\partial_\gamma\bar{V}_{\mathbf{k}})\bar{W}_{\mathbf{k}} + (\partial_\beta\bar{U}_{\mathbf{k}})\bar{V}_{\mathbf{k}}(\partial_\gamma\bar{W}_{\mathbf{k}}) + \bar{U}_{\mathbf{k}}(\partial_\beta\bar{V}_{\mathbf{k}})(\partial_\gamma\bar{W}_{\mathbf{k}})\right]$$
$$+ O(B^2). \tag{C2}$$

Note that some conventions for the present article differ from those of GZ [10]. Indeed, the speed of light c mentioned in Eqs. (1), (6), (7), of GZ is absorbed in B in the present article, that also includes a change of sign

because in the present article atomic units are used, with electron charge $q = -1$.

Using twice Eq. (C1), first for the product of UV and W, then for the product of U and V, gives

$$(\overline{UVW})_\mathbf{k} = (\overline{UV})_\mathbf{k}\bar{W}_\mathbf{k} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha(\partial_\beta(\overline{UV})_\mathbf{k})(\partial_\gamma\bar{W}_\mathbf{k}) + O(B^2)$$

$$= \left(\bar{U}_\mathbf{k}\bar{V}_\mathbf{k} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha(\partial_\beta\bar{U}_\mathbf{k})(\partial_\gamma\bar{V}_\mathbf{k})\right)\bar{W}_\mathbf{k} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha(\partial_\beta(\bar{U}_\mathbf{k}\bar{V}_\mathbf{k}))(\partial_\gamma\bar{W}_\mathbf{k}) + O(B^2)$$

$$= \bar{U}_\mathbf{k}\bar{V}_\mathbf{k}\bar{W}_\mathbf{k} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha\left[(\partial_\beta\bar{U}_\mathbf{k})(\partial_\gamma\bar{V}_\mathbf{k})\bar{W}_\mathbf{k} + (\partial_\beta\bar{U}_\mathbf{k})\bar{V}_\mathbf{k}(\partial_\gamma\bar{W}_\mathbf{k}) + \bar{U}_\mathbf{k}(\partial_\beta\bar{V}_\mathbf{k})(\partial_\gamma\bar{W}_\mathbf{k})\right] + O(B^2), \quad \text{(C3)}$$

that is the expected result. Similarly, the product of four operators is

$$(\overline{UVWX})_\mathbf{k} = \bar{U}_\mathbf{k}\bar{V}_\mathbf{k}\bar{W}_\mathbf{k}\bar{X}_\mathbf{k} - \frac{i}{2}\epsilon_{\alpha\beta\gamma}B_\alpha\ \big[\ (\partial_\beta\bar{U}_\mathbf{k})(\partial_\gamma\bar{V}_\mathbf{k})\bar{W}_\mathbf{k}\bar{X}_\mathbf{k} + (\partial_\beta\bar{U}_\mathbf{k})\bar{V}_\mathbf{k}(\partial_\gamma\bar{W}_\mathbf{k})\bar{X}_\mathbf{k} + (\partial_\beta\bar{U}_\mathbf{k})\bar{V}_\mathbf{k}\bar{W}_\mathbf{k}(\partial_\gamma\bar{X}_\mathbf{k})$$

$$\bar{U}_\mathbf{k}(\partial_\beta\bar{V}_\mathbf{k})(\partial_\gamma\bar{W}_\mathbf{k})\bar{X}_\mathbf{k} + \bar{U}_\mathbf{k}(\partial_\beta\bar{V}_\mathbf{k})\bar{W}_\mathbf{k}(\partial_\gamma\bar{X}_\mathbf{k}) + \bar{U}_\mathbf{k}\bar{W}_\mathbf{k}(\partial_\beta\bar{X}_\mathbf{k})(\partial_\gamma\bar{X}_\mathbf{k})\big]$$

$$+ O(B^2). \quad \text{(C4)}$$

Coming now to the treatment of the product of three operator without resorting to a Taylor series, in real space, the kernel of the triple product of operators $T = UVW$ under non-zero magnetic field becomes

$$\bar{T}(\mathbf{r_1}, \mathbf{r_4}) = \int d\mathbf{r_2} \int d\mathbf{r_3}\bar{U}(\mathbf{r_1}, \mathbf{r_2})\bar{V}(\mathbf{r_2}, \mathbf{r_3})\bar{W}(\mathbf{r_3}, \mathbf{r_4})e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}\times\mathbf{r_2}+\mathbf{r_2}\times\mathbf{r_3}+\mathbf{r_3}\times\mathbf{r_4}+\mathbf{r_4}\times\mathbf{r_1})}. \quad \text{(C5)}$$

The operators $\bar{T}$, $\bar{U}$, $\bar{V}$ and $\bar{W}$ are periodic in real space, with kernel behavior

$$\bar{\mathcal{O}}(\mathbf{r_1} + \mathbf{R}, \mathbf{r_2} + \mathbf{R}) = \bar{\mathcal{O}}(\mathbf{r_1}, \mathbf{r_2}). \quad \text{(C6)}$$

where $\mathbf{R}$ is a lattice vector. Note the typographical error after Eq.(1) of GZ. They are decomposed into operators $\bar{\mathcal{O}}_\mathbf{k}$ that are periodic in each argument separately, and characterized by a wavevector:

$$\bar{\mathcal{O}}(\mathbf{r_1}, \mathbf{r_2}) = \int_{BZ} \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r_1}}\bar{\mathcal{O}}_\mathbf{k}(\mathbf{r_1}, \mathbf{r_2})e^{-i\mathbf{k}\cdot\mathbf{r_2}}, \quad \text{(C7)}$$

with

$$\bar{\mathcal{O}}_\mathbf{k}(\mathbf{r_1} + \mathbf{R}, \mathbf{r_2}) = \bar{\mathcal{O}}_\mathbf{k}(\mathbf{r_1}, \mathbf{r_2} + \mathbf{R}) = \bar{\mathcal{O}}_\mathbf{k}(\mathbf{r_1}, \mathbf{r_2}), \quad \text{(C8)}$$

Note the typographical error after Eq.(5) of GZ. In order to avoid ambiguity, the notation $\tilde{\mathcal{O}}_\mathbf{k}$ (note the tilde)

adopted by GZ is replaced by $\bar{\mathcal{O}}_\mathbf{k}$ (note the bar), as the tilde is already used, with an other meaning, in the PAW framework, see Eq. (11).

One can obtain $\bar{\mathcal{O}}_\mathbf{k}$ from $\bar{\mathcal{O}}$ by the backwards formula

$$\bar{\mathcal{O}}_\mathbf{k}(\mathbf{r_1}, \mathbf{r_2}) = \sum_\mathbf{R} e^{-i\mathbf{k}\cdot\mathbf{r_1}}\bar{\mathcal{O}}(\mathbf{r_1}, \mathbf{r_2} + \mathbf{R})e^{i\mathbf{k}\cdot(\mathbf{r_2}+\mathbf{R})}. \quad \text{(C9)}$$

In order to establish the latter equation, the following identity has been used,

$$\sum_\mathbf{R} e^{i\mathbf{k}\cdot\mathbf{R}} = (2\pi)^3 \sum_\mathbf{G} \delta(\mathbf{k} + \mathbf{G}), \quad \text{(C10)}$$

where $\mathbf{G}$ are the reciprocal lattice vectors, and δ is the Dirac delta distribution. The use of Eq. (C9) for $\bar{T}$, Eq. (C7) for $\bar{U}$, $\bar{V}$ and $\bar{W}$, and right-argument periodicity of the kernel of $\bar{W}_\mathbf{k}$ yields

$$\bar{T}_\mathbf{k}(\mathbf{r_1}, \mathbf{r_4}) = \sum_\mathbf{R} e^{-i\mathbf{k}\cdot\mathbf{r_1}}e^{i\mathbf{k}\cdot(\mathbf{r_4}+\mathbf{R})} \int d\mathbf{r_2} \int d\mathbf{r_3}\bar{U}(\mathbf{r_1}, \mathbf{r_2})\bar{V}(\mathbf{r_2}, \mathbf{r_3})\bar{W}(\mathbf{r_3}, \mathbf{r_4} + \mathbf{R})e^{\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}\times\mathbf{r_2}+\mathbf{r_2}\times\mathbf{r_3}+\mathbf{r_3}\times(\mathbf{r_4}+\mathbf{R})+(\mathbf{r_4}+\mathbf{R})\times\mathbf{r_1})}$$

$$= \sum_\mathbf{R} \int d\mathbf{r_2} \int d\mathbf{r_3} \int \frac{d\mathbf{k}_U}{(2\pi)^3} \int \frac{d\mathbf{k}_V}{(2\pi)^3} \int \frac{d\mathbf{k}_W}{(2\pi)^3} \bar{U}_{\mathbf{k}_U}(\mathbf{r_1}, \mathbf{r_2})\bar{V}_{\mathbf{k}_V}(\mathbf{r_2}, \mathbf{r_3})\bar{W}_{\mathbf{k}_W}(\mathbf{r_3}, \mathbf{r_4})$$

$$\exp\left(i(\mathbf{k}_U - \mathbf{k})\cdot\mathbf{r_1} + (\mathbf{k}_V - \mathbf{k}_U)\cdot\mathbf{r_2} + (\mathbf{k}_W - \mathbf{k}_V)\cdot\mathbf{r_3} + (\mathbf{k} - \mathbf{k}_W)\cdot(\mathbf{r_4} + \mathbf{R})\right)$$

$$\exp\left(\frac{i}{2}\mathbf{B}\cdot(\mathbf{r_1}\times\mathbf{r_2} + \mathbf{r_2}\times\mathbf{r_3} + \mathbf{r_3}\times(\mathbf{r_4}+\mathbf{R}) + (\mathbf{r_4}+\mathbf{R})\times\mathbf{r_1})\right). \quad \text{(C11)}$$

Continuing, the summation over $\mathbf{R}$ is eliminated thanks

to Eq. (C10), with the resulting sum over $\mathbf{G}$ and Brillouin

Zone integration over $\mathbf{k}_W$ jointly eliminated thanks to the Dirac delta. Further progress involves splitting the integral over $\mathbf{r_2}$ in the full tridimensional space into an integral over $\mathbf{r_{20}}$ belonging to the primitive cell Ω_0 and summation over real space lattice vectors $\mathbf{R_2}$, with $\mathbf{r_2} = \mathbf{r_{20}} + \mathbf{R_2}$,

$$\int d\mathbf{r_2} f(\mathbf{r_2}) = \int_{\Omega_0} d\mathbf{r_{20}} \sum_{\mathbf{R_2}} f(\mathbf{r_{20}} + \mathbf{R_2}), \qquad (C12)$$

then again, using Eq. (C10) to eliminate the sum over

$\mathbf{R_2}$, with the appearance of a Dirac delta and summation over reciprocal space lattice. The integral over $\mathbf{k}_U$ and this reciprocal space lattice summation are eliminated thanks to the Dirac delta as well as thanks to

$$\hat{\mathcal{O}}_{\mathbf{k}+\mathbf{G}}(\mathbf{r_1}, \mathbf{r_2}) = e^{i\mathbf{G}\cdot(\mathbf{r_2}-\mathbf{r_1})} \hat{\mathcal{O}}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_2}), \qquad (C13)$$

deduced from Eq. (C9). The resulting equation is

$$\bar{T}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_4}) = \int_{\Omega_0} d\mathbf{r_{20}} \int d\mathbf{r_3} \int \frac{d\mathbf{k}_V}{(2\pi)^3} \exp\left(i(\mathbf{k}_V - \mathbf{k})\cdot(\mathbf{r_1} - \mathbf{r_3})\right)$$
$$\bar{U}_{\mathbf{k}_V + \frac{1}{2}\mathbf{B}\times(\mathbf{r_1}-\mathbf{r_3})}(\mathbf{r_1}, \mathbf{r_{20}}) \bar{V}_{\mathbf{k}_V}(\mathbf{r_{20}}, \mathbf{r_3}) \bar{W}_{\mathbf{k}_V - \frac{1}{2}\mathbf{B}\times(\mathbf{r_1}-\mathbf{r_3})}(\mathbf{r_3}, \mathbf{r_4}). \qquad (C14)$$

This is the farthest that one can go for a magnetic field of arbitrary strength : this result is valid irrespective of the size of $\mathbf{B}$.

To show that this formula indeed reduces to the first-order formula Eq. (C2), one proceeds then with a Taylor series expansion in $\mathbf{B}$,

$$\bar{T}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_4}) = \bar{T}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} + B_\alpha \frac{\partial \bar{T}_{\mathbf{k}}}{\partial B_\alpha}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} + \frac{1}{2} B_\alpha B_{\alpha'} \frac{\partial^2 \bar{T}_{\mathbf{k}}}{\partial B_\alpha \partial B_{\alpha'}}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} + O(B^3), \qquad (C15)$$

where the first-order coefficient is

$$\frac{\partial \bar{T}_{\mathbf{k}}}{\partial B_\alpha}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} = \int_{\Omega_0} d\mathbf{r_{20}} \int d\mathbf{r_3} \int \frac{d\mathbf{k}_V}{(2\pi)^3} \frac{1}{2} \epsilon_{\alpha\beta\gamma}(r_{1\gamma} - r_{3\gamma}) \exp\left(i(\mathbf{k}_V - \mathbf{k})\cdot(\mathbf{r_1} - \mathbf{r_3})\right)$$
$$\bar{V}_{\mathbf{k}_V}(\mathbf{r_{20}}, \mathbf{r_3})\left[\left(-\frac{\partial}{\partial k_{V\beta}}\bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\right)\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4}) + \bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\left(\frac{\partial}{\partial k_{V\beta}}\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4})\right)\right]. \qquad (C16)$$

The $(r_{1\gamma} - r_{3\gamma})$ factor can be obtained by differentiating the exponential with respect to $k_{V\gamma}$. Then one integrates the derivative $\frac{\partial}{\partial k_{V\gamma}}$ by parts, to obtain

$$\frac{\partial \bar{T}_{\mathbf{k}}}{\partial B_\alpha}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} = \int_{\Omega_0} d\mathbf{r_{20}} \int d\mathbf{r_3} \int \frac{d\mathbf{k}_V}{(2\pi)^3} \frac{i}{2} \exp\left(i(\mathbf{k}_V - \mathbf{k})\cdot(\mathbf{r_1} - \mathbf{r_3})\right)$$
$$\epsilon_{\alpha\beta\gamma} \frac{\partial}{\partial k_{V\gamma}} \left(\bar{V}_{\mathbf{k}_V}(\mathbf{r_{20}}, \mathbf{r_3})\left[\left(-\frac{\partial}{\partial k_{V\beta}}\bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\right)\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4}) + \bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\left(\frac{\partial}{\partial k_{V\beta}}\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4})\right)\right]\right). \qquad (C17)$$

Then, in the second line, the derivative $\frac{\partial}{\partial k_{V\gamma}}$ is applied and the antisymmetry property of the $\epsilon_{\alpha\beta\gamma}$ tensor allows one to deduce

$$\frac{\partial \bar{T}_{\mathbf{k}}}{\partial B_\alpha}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} = \int_{\Omega_0} d\mathbf{r_{20}} \int d\mathbf{r_3} \int \frac{d\mathbf{k}_V}{(2\pi)^3} \frac{i}{2} \exp\left(i(\mathbf{k}_V - \mathbf{k})\cdot(\mathbf{r_1} - \mathbf{r_3})\right)$$
$$(-\epsilon_{\alpha\beta\gamma})\left(\left(\frac{\partial}{\partial k_{V\beta}}\bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\right)\left(\frac{\partial}{\partial k_{V\gamma}}\bar{V}_{\mathbf{k}_V}(\mathbf{r_{20}}, \mathbf{r_3})\right)\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4}) + \right.$$
$$\left(\frac{\partial}{\partial k_{V\beta}}\bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\right)\bar{V}_{\mathbf{k}_V}(\mathbf{r_{20}}, \mathbf{r_3})\left(\frac{\partial}{\partial k_{V\gamma}}\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4})\right) +$$
$$\left.\bar{U}_{\mathbf{k}_V}(\mathbf{r_1}, \mathbf{r_{20}})\left(\frac{\partial}{\partial k_{V\beta}}\bar{V}_{\mathbf{k}_V}(\mathbf{r_{20}}, \mathbf{r_3})\right)\left(\frac{\partial}{\partial k_{V\gamma}}\bar{W}_{\mathbf{k}_V}(\mathbf{r_3}, \mathbf{r_4})\right)\right). \qquad (C18)$$

The function contained in big parentheses after the antisymmetric tensor is periodic in $\mathbf{r_3}$. As previously for $\mathbf{r_2}$, the integral over $\mathbf{r_3}$ in the full tridimensional space is split into an integral over $\mathbf{r_{30}}$ belonging to the primitive cell Ω_0 and summation over real space lattice vectors $\mathbf{R_3}$, with $\mathbf{r_3} = \mathbf{r_{30}} + \mathbf{R_3}$. Then again, using Eq. (C10), the sum over $\mathbf{R_3}$ is eliminated, with the appearance of a Dirac delta and summation over reciprocal space lattice. The integral over $\mathbf{k}_V$ and this reciprocal space lattice summation are both eliminated than to the Dirac delta, leaving

$$
\frac{\partial \bar{T}_{\mathbf{k}}}{\partial B_\alpha}(\mathbf{r_1}, \mathbf{r_4})\Big|_{\mathbf{B}=0} = \int_{\Omega_0} d\mathbf{r_{20}} \int_{\Omega_0} d\mathbf{r_{30}} \frac{-i}{2} \epsilon_{\alpha\beta\gamma}
$$

$$
\left(\left(\frac{\partial}{\partial k_\beta} \bar{U}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_{20}})\right) \left(\frac{\partial}{\partial k_\gamma} \bar{V}_{\mathbf{k}}(\mathbf{r_{20}}, \mathbf{r_{30}})\right) \bar{W}_{\mathbf{k}}(\mathbf{r_{30}}, \mathbf{r_4}) + \right.
$$

$$
\left(\frac{\partial}{\partial k_\beta} \bar{U}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_{20}})\right) \bar{V}_{\mathbf{k}}(\mathbf{r_{20}}, \mathbf{r_{30}}) \left(\frac{\partial}{\partial k_\gamma} \bar{W}_{\mathbf{k}}(\mathbf{r_{30}}, \mathbf{r_4})\right) +
$$

$$
\left. \bar{U}_{\mathbf{k}}(\mathbf{r_1}, \mathbf{r_{20}}) \left(\frac{\partial}{\partial k_\beta} \bar{V}_{\mathbf{k}}(\mathbf{r_{20}}, \mathbf{r_{30}})\right) \left(\frac{\partial}{\partial k_\gamma} \bar{W}_{\mathbf{k}}(\mathbf{r_{30}}, \mathbf{r_4})\right) \right). \tag{C19}
$$

This result, combined with Eq. (C15) gives Eq. (C2), as announced at the beginning of this appendix.

The next order can be similarly obtained, delivering

$$
\frac{\partial^2 \bar{T}_{\mathbf{k}}}{\partial B_\alpha \partial B_{\alpha'}} = -\frac{1}{4} \epsilon_{\alpha\beta\gamma} \epsilon_{\alpha'\beta'\gamma'} \left[(\partial_\beta \partial_{\beta'} \bar{U}_{\mathbf{k}})(\partial_\gamma \partial_{\gamma'} \bar{V}_{\mathbf{k}}) \bar{W}_{\mathbf{k}} + (\partial_\beta \partial_{\beta'} \bar{U}_{\mathbf{k}}) \bar{V}_{\mathbf{k}} (\partial_\gamma \partial_{\gamma'} \bar{W}_{\mathbf{k}}) + \bar{U}_{\mathbf{k}} (\partial_\beta \partial_{\beta'} \bar{V}_{\mathbf{k}})(\partial_\gamma \partial_{\gamma'} \bar{W}_{\mathbf{k}}) \right.
$$

$$
\left. + (\partial_\beta \partial_{\beta'} \bar{U}_{\mathbf{k}})(\partial_\gamma \bar{V}_{\mathbf{k}})(\partial_{\gamma'} \bar{W}_{\mathbf{k}}) + (\partial_\beta \bar{U}_{\mathbf{k}})(\partial_{\beta'} \partial_\gamma \bar{V}_{\mathbf{k}})(\partial_{\gamma'} \bar{W}_{\mathbf{k}}) + (\partial_\beta \bar{U}_{\mathbf{k}})(\partial_{\beta'} \bar{V}_{\mathbf{k}})(\partial_\gamma \partial_{\gamma'} \bar{W}_{\mathbf{k}}) \right]. \tag{C20}
$$

This result can alternatively be obtained from the iterative usage of the expansion of the two-operator product, Eq. (7) of GZ [10].

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