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Validity of the force theorem for magnetocrystalline anisotropy

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Abstract

The validity of the so-called force theorem is critical for the computational/theoretical determination of the magnetocrystalline anisotropy (MCA) in the framework of local density theory. This theorem states that the spin–orbit coupling induced MCA energy is given by the difference in the fully relativistic band energies between two magnetization directions calculated with the same self-consistent scalar-relativistic potential. We show that the charge- and spin-density variations caused by spin–orbit coupling vanish to first order in the spin–orbit coupling strength. By the stationary property of the total energy functional, we establish rigorously the validity of the force theorem for surface/interface MCA. We show that our arguments also apply to a variant of the MCA force theorem and discuss problems of applying the force theorem for MCA in bulk systems with cubic crystalline symmetry.

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It has long been an outstanding challenge to determine the magnetocrystalline anisotropy (MCA) from first principles. It is well known that spin–orbit coupling coupled with magnetism is the underlying physical mechanism for the MCA. The magnetocrystalline anisotropy energy (MAE) is the fully relativistic total energy difference between two different magnetization directions. In this paper, we only discuss the spin–orbit coupling induced MAE. In almost all first principles calculations of MAE within the local spin density approximation (LSDA) [1] to density functional theory [2], the so-called force theorem is applied: i.e. the MAE is taken to be the difference in band energies of the two magnetization directions with spin–orbit coupling included in the Kohn–Sham equation while using the same self-consistent scalar-relativistic potential [3]. There are some variants of the form of this theorem: e.g., Ref. [4] calculates MAE by taking the difference in band energies of the two magnetization directions using the fully relativistic self-consistent potential of one magnetization direction. The force theorem greatly reduces the complexities of calculating MAE to such a point that current LSDA methods are most promising for first principles determinations of MCA. Due to its growing importance, the validity of the MCA force theorem is investigated here.

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In the following, we first point out a defect in the usual proof of the MCA force theorem, and then show that such a defect can be corrected by showing that the charge- and spin-density variations caused by spin–orbit coupling vanish to first order in the spin–orbit coupling strength. Finally, we address the problems of applying the MCA force theorem to bulk systems with cubic crystalline symmetry.

For the sake of completeness and clarity, we outline the usual proof of the force theorem for MAE following Ref. [3]. We start from a complete self-consistent spin-polarized scalar-relativistic (SR) calculation and let the resulting charge and spin density be $\rho_0(\boldsymbol{r})$ and $\boldsymbol{m}_0(\boldsymbol{r})$, respectively [5]. The LDA total energy can then be written as

$$E^{\mathrm{SR}}[\rho_0,\boldsymbol{m}_0] = T^{\mathrm{SR}}[\rho_0,\boldsymbol{m}_0] + U[\rho_0] + E_{\mathrm{xc}}[\rho_0,|\boldsymbol{m}_0|] + E_{\mathrm{ext}}[\rho_0]. \tag{1}$$

Now, assume that the complete self-consistent scalar-relativistic plus spin–orbit coupling (SR + SO) calculation will yield charge and spin densities $\rho(\boldsymbol{r})$ and $\boldsymbol{m}(\boldsymbol{r})$, respectively; the total energy is then

$$E^{\mathrm{SR+SO}}[\rho,\boldsymbol{m}] = T^{\mathrm{SR+SO}}[\rho,\boldsymbol{m}] + U[\rho] + E_{\mathrm{xc}}[\rho,|\boldsymbol{m}|] + E_{\mathrm{ext}}[\rho]. \tag{2}$$

In both cases, T, U, E_{xc} and E_{ext} are the kinetic energy, electron–electron Coulomb energy, exchange-correlation energy, and the 'external' contribution written for the sum of the electron–ion and ion–ion Coulomb energies, respectively. Specifically,

$$T[\rho,\boldsymbol{m}] = \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon_i(\boldsymbol{k}) - 2U[\rho] - \sum_{\alpha} \int \mathrm{d}\boldsymbol{r}\, \rho_\alpha(\boldsymbol{r})\,\mu_\alpha(\boldsymbol{r}) - \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, v_{\mathrm{ext}}(\boldsymbol{r}), \tag{3}$$

where, without loss of generality, we have taken the density matrix to be diagonal in spin space (α is the spin index $\pm$), and

$$\mu_\alpha(\boldsymbol{r}) = \frac{\delta E_{\mathrm{xc}}[\rho,|\boldsymbol{m}|]}{\delta \rho_\alpha}, \tag{4}$$

with $\rho_\pm = \rho \pm \frac{|\boldsymbol{m}|}{2}$,

$$U[\rho] = \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\, \frac{\rho(\boldsymbol{r})\,\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{5}$$

$$E_{\mathrm{xc}}[\rho,|\boldsymbol{m}|] = \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, \epsilon_{\mathrm{xc}}(\rho,|\boldsymbol{m}|), \tag{6}$$

and

$$E_{\mathrm{ext}}[\rho] = \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, v_{\mathrm{ext}}(\boldsymbol{r}) + E_{\mathrm{ion-ion}}. \tag{7}$$

The spin–orbit coupling induced energy is then

$$E^{\mathrm{SR+SO}}[\rho,\boldsymbol{m}] - E^{\mathrm{SR}}[\rho_0,\boldsymbol{m}_0], \tag{8}$$

which can be reorganized as

$$\left\{E^{\mathrm{SR+SO}}[\rho,\boldsymbol{m}] - E^{\mathrm{SR+SO}}[\rho_0,\boldsymbol{m}_0]\right\} + \left\{E^{\mathrm{SR+SO}}[\rho_0,\boldsymbol{m}_0] - E^{\mathrm{SR}}[\rho_0,\boldsymbol{m}_0]\right\}. \tag{9}$$

We now define

$$\delta\rho = \rho - \rho_0 \tag{10}$$

and

$$\delta \boldsymbol{m} = \boldsymbol{m} - \boldsymbol{m}_0. \tag{11}$$

By the variational character of the LDA total energy, the first bracketed term in Eq. (9) is

$$E^{\mathrm{SR+SO}}[\rho,\boldsymbol{m}] - E^{\mathrm{SR+SO}}[\rho_0,\boldsymbol{m}_0] = \mathrm{O}\left[(\delta\rho)^2,(\delta\boldsymbol{m})^2\right], \tag{12}$$

and the second term in Eq. (9) is simply the difference in band energies with and without spin–orbit coupling

$$E^{\mathrm{SR+SO}}[\rho_0, \boldsymbol{m}_0] - E^{\mathrm{SR}}[\rho_0, \boldsymbol{m}_0] = \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon_i^0(\hat{\boldsymbol{m}}, \boldsymbol{k}) - \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon_i^0(\boldsymbol{k}), \tag{13}$$

where the superscript 0 denotes the band energies calculated under the scalar-relativistic self-consistent potential and $\hat{\boldsymbol{m}}$ is the direction of the magnetization.

At this point, it was argued in Ref. [3] that the correction term expressed in Eq. (12) is much smaller than the band energy difference term in Eq. (13), and the MAE between two different magnetization directions $\hat{\boldsymbol{m}}_1$ and $\hat{\boldsymbol{m}}_2$ is then

$$\mathrm{MAE} = \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon_i^0(\hat{\boldsymbol{m}}_1, \boldsymbol{k}) - \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon_i^0(\hat{\boldsymbol{m}}_2, \boldsymbol{k}). \tag{14}$$

However, we note that the first order contribution with respect to the spin–orbit coupling strength ξ in Eq. (13) is zero and in general the spin–orbit coupling induced energy from Eq. (13) is at least of the order of ξ^2; therefore, the MAE is at least of the order of ξ^2. Hence, a complete proof of the force theorem has to show that $\delta\rho$ and $\delta\boldsymbol{m}$ are of the order of ξ^2, i.e. $\delta\rho = 0$ and $\delta\boldsymbol{m} = 0$ to first order in ξ. (Note that if $\xi = 0$, Eq. (12) vanishes completely.) We show this in the following.

Within LDA, the charge and/or spin density is given by

$$\rho_\sigma(\boldsymbol{r}) = \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \rho_{i,\sigma}(\boldsymbol{k}; \boldsymbol{r}). \tag{15}$$

Since the energy level shift after turning on the spin–orbit coupling is at least of order ξ^2, the change of Fermi volume/area due to spin–orbit coupling is also of the order of ξ^2, and can be neglected if we are only interested in *first order* variations in the charge/spin density. Therefore, we have

$$\delta\rho_\sigma = \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \delta\rho_{1,\sigma}(\boldsymbol{k}). \tag{16}$$

From now on, ρ is understood to be a function of the real space position $\boldsymbol{r}$.

Using first order perturbation theory, to first order in ξ the wavefunctions are

$$\psi_{i,\sigma}(\boldsymbol{k}) = \psi_{i,\sigma}^0(\boldsymbol{k}) + \sum_{j,\sigma} \frac{\psi_{j,\sigma}^0(\boldsymbol{k}) \langle \psi_{j,\sigma}^0(\boldsymbol{k}) | H_{\mathrm{so}}^{\sigma,\sigma} | \psi_{i,\sigma}^0(\boldsymbol{k}) \rangle}{\epsilon_{i,\sigma}^0(\boldsymbol{k}) - \epsilon_{j,\sigma}^0(\boldsymbol{k})}, \tag{17}$$

where the spin–orbit coupling Hamiltonian is

$$H_{\mathrm{so}}^{\sigma,\sigma} = c^{-2} \tau^{\sigma,\sigma} \cdot \{\nabla V \times \hat{\boldsymbol{p}}\}, \tag{18}$$

τ is the Pauli matrix and for spherical V, Eq. (18) gives the usual $\tau \cdot \hat{\boldsymbol{l}}$ form. Therefore, to first order in ξ, we have

$$\delta\rho_{i,\sigma}(\boldsymbol{k}) = \sum_j \psi_{i,\sigma}^0(\boldsymbol{k})^* \psi_{j,\sigma}^0(\boldsymbol{k}) \frac{\langle \psi_{j,\sigma}^0(\boldsymbol{k}) | H_{\mathrm{so}}^{\sigma,\sigma} | \psi_{i,\sigma}^0(\boldsymbol{k}) \rangle}{\epsilon_{i,\sigma}^0(\boldsymbol{k}) - \epsilon_{j,\sigma}^0(\boldsymbol{k})} + \mathrm{c.c.} \tag{19}$$

Now, without spin–orbit coupling, we have for the zeroth order wavefunctions

$$\psi_{i,\sigma}^0(-\boldsymbol{k}) = \{\psi_{i,\sigma}^0(\boldsymbol{k})\}^*, \tag{20}$$

where the superscript $*$ denotes complex conjugation. Summing $\delta\rho_{i,\sigma}(\boldsymbol{k})$ and $\delta\rho_{i,\sigma}(-\boldsymbol{k})$ yields

$$\sum_j \psi_{i,\sigma}^0(\boldsymbol{k})^* \psi_{j,\sigma}^0(\boldsymbol{k}) \frac{\langle \psi_{j,\sigma}^0(\boldsymbol{k}) | H_{\mathrm{so}}^{\sigma,\sigma} | \psi_{i,\sigma}^0(\boldsymbol{k}) \rangle + \langle \psi_{i,\sigma}^0(\boldsymbol{k})^* | H_{\mathrm{so}}^{\sigma,\sigma} | \psi_{j,\sigma}^0(\boldsymbol{k})^* \rangle}{\epsilon_{i,\sigma}^0(\boldsymbol{k}) - \epsilon_{j,\sigma}^0(\boldsymbol{k})} + \mathrm{c.c.}, \tag{21}$$

where we have repeatedly used Eq. (20).

We also have

$$\langle \psi^0_{j,\sigma}(\boldsymbol{k})|H^{\sigma,\sigma}_{\mathrm{so}}|\psi^0_{i,\sigma}(\boldsymbol{k})\rangle + \langle \psi^0_{i,\sigma}(\boldsymbol{k})^*|H^{\sigma,\sigma}_{\mathrm{so}}|\psi^0_{j,\sigma}(\boldsymbol{k})^*\rangle = c^{-2}\tau^{\sigma,\sigma}\cdot\boldsymbol{I}, \tag{22}$$

where

$$\begin{aligned}\boldsymbol{I} &= -i\int \mathrm{d}\boldsymbol{r}\left\{\psi^0_{j,\sigma}(\boldsymbol{k})^*\nabla V\times\nabla\psi^0_{i,\sigma}(\boldsymbol{k}) + \psi^0_{i,\sigma}(\boldsymbol{k})\nabla V\times\nabla\psi^0_{j,\sigma}(\boldsymbol{k})^*\right\}\\ &= -i\int \mathrm{d}\boldsymbol{r}\left\{\nabla V\times\nabla\left[\psi^0_{i,\sigma}(\boldsymbol{k})\psi^0_{j,\sigma}(\boldsymbol{k})^*\right]\right\}\\ &= -i\int \mathrm{d}\boldsymbol{r}\nabla\times\left\{V\nabla\left[\psi^0_{i,\sigma}(\boldsymbol{k})\psi^0_{j,\sigma}(\boldsymbol{k})^*\right]\right\}\\ &= -i\oint \mathrm{d}\boldsymbol{S}\times\left\{V\nabla\left[\psi^0_{i,\sigma}(\boldsymbol{k})\psi^0_{j,\sigma}(\boldsymbol{k})^*\right]\right\}\\ &= 0.\end{aligned} \tag{23}$$

The last equality of Eq. (23) follows from periodic boundary conditions for crystalline systems or the vanishing of both potential and wavefunction at infinity for finite clusters. It follows from Eq. (23) that Eq. (21) is zero and therefore our conclusion

$$\delta\rho_\sigma = \mathrm{O}\left[\xi^2\right], \tag{24}$$

where, again, ξ is the spin–orbit coupling strength.

We have demonstrated above that corrections coming from $\delta\rho$ and δm are at least of order ξ^4 due to the variational character of Eq. (12). Thus we have proved rigorously the validity of the MCA force theorem for surfaces/interfaces; that is, for most surface or interface MAE, the band energy difference given by Eq. (14) gives the leading order contribution. We note that, in Ref. [4], the authors used the force theorem in a somewhat different way; there, the MAE is calculated by

$$\mathrm{MAE} = \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon^1_i(\hat{\boldsymbol{m}}_1,\boldsymbol{k}) - \sum_{i,\boldsymbol{k}}^{\mathrm{occ}} \epsilon^1_i(\hat{\boldsymbol{m}}_2,\boldsymbol{k}), \tag{25}$$

where the superscript 1 denotes the band energies calculated using the fully relativistic charge/spin density of magnetization $\hat{\boldsymbol{m}}_1$. It is clear that, for the same argument as given above, Eq. (25) holds only when the difference of charge/spin density between the two magnetization directions vanishes to first order in ξ. It is easy to see that this is a corollary of our proof, since

$$\rho^1_\sigma - \rho^2_\sigma = \delta\rho^1_\sigma - \delta\rho^2_\sigma \sim \xi^2, \tag{26}$$

where ρ^i_σ is the fully relativistic self-consistent charge/spin density and $\delta\rho$ is given in Eq. (10).

Having proved the validity of the MCA force theorem for surfaces/interfaces, we now turn to discuss bulk systems, specifically those with cubic crystalline symmetry. It has been shown that the MAE between (001) and (111) directions for bulk systems with cubic crystalline symmetry is of order ξ^4 [6]. This means that the above result does not warrant that Eq. (14) gives the correct anisotropic MAE. We will argue in the following that Eq. (14) is not likely to hold for these systems.

It is well known that spin–orbit coupling generally lowers the symmetry of a magnetic system compared to its crystalline symmetry. As a consequence of this lowered symmetry, the fully relativistic self-consistent charge/spin density will have a symmetry breaking component that is not present in the scalar-relativistic self-consistent charge/spin density. These symmetry breaking components of the charge/spin density are, in general, of the order of ξ^2 and, more importantly, they are distinctly different between systems with

magnetization direction along say (100) and (111). By *distinctly different* we mean that no symmetry operation can transfer one into the other. According to Eq. (12), in addition to the band energy difference, there is another term that will also give rise to the anisotropic MAE of order ξ^4. These symmetry arguments also suggest that if one puts spin–orbit coupling in the self-consistent loop, it is important to retain those symmetry breaking terms for MCA determinations.

In conclusion, we have proved the validity of the MCA force theorem for surface/interface systems where the leading order (ξ^2) part of MAE dominates.

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