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On the site-decomposition of magnetocrystalline anisotropy energy using one-electron eigenstates

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We discuss two different schemes for decomposing the magnetocrystalline anisotropy energy into atomic site-specific contributions, and show that one of these, which uses projected single-particle states, is inherently ill-defined in practical applications. We therefore argue that the other decomposition scheme, involving ground state matrix elements of the spin-orbit operator, is preferable for the numerical prediction of one-site contributions to the anisotropy.

One of the important quantities of interest for permanent magnets is the magnetocrystalline anisotropy energy (MAE), which is defined at $T = 0$ to be the difference in ground state energies:

$$\kappa \equiv U^i - U^j, \quad (1)$$

where i and j denote spin polarization directions for which the absolute value of this difference is maximized (i.e., hard and easy axes, respectively). For typical magnetic materials, a nonzero value of MAE is due to the interplay between the spin-orbit (SO) term in the Hamiltonian and the crystal field effect, which causes electronic eigenstates to be preferentially oriented with respect to the crystallographic axes [1]. Because the effective potential corresponding to the SO term is quite local in nature and concentrated near each ion, it is natural to assume that the MAE itself can be decomposed into site-specific contributions [2–4]. This could then in principle aid researchers in predicting how various atomic substitutions might affect the MAE in a material of interest.

Two different schemes for affecting a site-decomposition of the MAE have been discussed and applied. The first uses ground state expectation values of the SO term, and arises naturally from the so-called torque method [5], in which the continuous variation of energy with respect to spin polarization direction, $U(\theta)$, is considered. We will refer to this as the λ -integration scheme, for reasons that will become clear. The second uses site-specific projection operators applied to one-electron states (Kohn-Sham eigenstates in a typical DFT picture). In Ref.[4], it was pointed out that these two approaches (or at least approaches similar to what we describe here) produce qualitatively different predictions for the relative contributions of Fe and Pt to the MAE of FePt. We aim to clarify this difference in this report.

A. λ -integration decomposition scheme

Let us write the Hamiltonian as

$$H_\lambda = H_0 + \lambda H_{\text{SO}}, \quad (2)$$

where H_0 is the Hamiltonian in the absence of spin-orbit and H_{SO} is the spin-orbit term. $H_{\lambda=1}$ is the true Hamiltonian for the physical value of SO. Considering two different spin polarization directions, i and j , the MAE is:

$$\kappa_\lambda = U_\lambda^i - U_\lambda^j = \langle \Psi_\lambda^i | H_\lambda | \Psi_\lambda^i \rangle - \langle \Psi_\lambda^j | H_\lambda | \Psi_\lambda^j \rangle, \quad (3)$$

where $|\Psi_\lambda^i\rangle$ and $|\Psi_\lambda^j\rangle$ are ground state wave functions for these different polarizations. From the Hellman-Feynman theorem [6],

$$\frac{dU_\lambda^{i,j}}{d\lambda} = \langle \Psi_\lambda^{i,j} | H_{\text{SO}} | \Psi_\lambda^{i,j} \rangle. \quad (4)$$

Since H_{SO} is strictly local [7], these SO matrix elements can be decomposed into site-specific terms:

$$\begin{aligned} \langle \Psi_\lambda^{i,j} | H_{\text{SO}} | \Psi_\lambda^{i,j} \rangle &= \sum_{s,\nu,\nu'} \langle \Psi_\lambda^{i,j} | s, \nu \rangle \langle s, \nu | H_{\text{SO}} | s, \nu' \rangle \langle s, \nu' | \Psi_\lambda^{i,j} \rangle \\ &\equiv \sum_s E_{\text{SO}}^{i,j}(s; \lambda), \end{aligned} \quad (5)$$

where the states $|s, \nu\rangle$ are localized orbitals centered on site s , with quantum numbers indicated by the composite index ν ($= p_x, d_{x^2-y^2}, \dots$). We have made two assumptions in Eq.5:

1. $\langle s, \nu | H_{\text{SO}} | s', \nu' \rangle \propto \delta_{s,s'}$: The locality of H_{SO} , which arises from its proportionality to $\frac{1}{r} \frac{dV}{dr}$.
2. $\sum_{s,\nu} |s, \nu\rangle \langle s, \nu| = 1$: Here, "1" refers specifically to the identity operator for vectors in the Hilbert space spanned by the states in the underlying electronic structure calculation, whatever they may be (i.e., even a small collection of localized orbitals for each site).

Using Eqs.4 and 5, the site-decomposed MAE is then:

$$\begin{aligned} \kappa &= U_{\lambda=1}^i - U_{\lambda=1}^j = \int_0^1 d\lambda \left[\frac{dU_\lambda^i}{d\lambda} - \frac{dU_\lambda^j}{d\lambda} \right] \\ &= \sum_s \left\{ \int_0^1 d\lambda \left[E_{\text{SO}}^i(s; \lambda) - E_{\text{SO}}^j(s; \lambda) \right] \right\}. \end{aligned} \quad (6)$$

The quantity in curly brackets in Eq.6 is the contribution to the MAE from the ion at site s . Detailed DFT calculations of this decomposition using the VASP code [8] (see below) show that Pt contributes far more than Fe to the MAE of FePt, which is expected since the SO term is large for Pt but small for Fe [3, 4]. Note that the λ -integration scheme requires that $|\Psi_\lambda^i\rangle$ be determined self-consistently for each direction i and for every λ , since the Hellman-Feynman theorem is invoked. However, the general strategy of relating the MAE to sums of site-specific SO matrix elements is also possible using perturbation theory, wherein H_{SO} is assumed to be small and the $E_{\text{SO}}^i(s; \lambda)$ are expanded in powers of λ [3].

B. one-electron decomposition scheme

As an alternative scheme, we consider the computation of MAE from one-electron states. Since H_{SO} is indeed small relative to H_0 in most cases, an accurate rendering of MAE can often be obtained within DFT by determining the self-consistent electronic charge density, ρ , in the *absence* of H_{SO} , and then adding on H_{SO} as a perturbation (without updating ρ) for each of the two polarizations. In this procedure, both U^i and U^j are built from the same ρ , and the force theorem [9] then mandates that their difference is equal to the difference of occupied one-electron eigenvalues:

$$\kappa = U^i - U^j \approx \sum_{n\mathbf{k}} \left[f_{n\mathbf{k}}^i \varepsilon_{n\mathbf{k}}^i - f_{n\mathbf{k}}^j \varepsilon_{n\mathbf{k}}^j \right] \equiv E_{\text{band}}^i - E_{\text{band}}^j. \quad (7)$$

It might seem at first that a sensible site decomposition could now be accomplished by including the appropriate projectors onto localized one-electron states, in a similar spirit to that discussed above,

$$E_{\text{band}}^i \approx \sum_s E_{\text{band}}^{is} = \sum_s \sum_{n\mathbf{k}\nu} f_{n\mathbf{k}}^i \varepsilon_{n\mathbf{k}}^i |\langle \psi_{n\mathbf{k}}^i | s, \nu \rangle|^2. \quad (8)$$

The \approx sign directly above indicates that E_{band}^i contains contributions outside the atom-centered regions defined by the $|s, \nu\rangle$; but these contributions are largely cancelled in the difference $E_{\text{band}}^i - E_{\text{band}}^j$, as we will demonstrate below in a concrete example.

However there is a larger problem, which we illustrate by adding the same arbitrary constant to both U^i and U^j , leaving κ unchanged. We write this constant as Nx , where N ($= \sum_{n\mathbf{k}} f_{n\mathbf{k}}^i = \sum_{n\mathbf{k}} f_{n\mathbf{k}}^j$) is the total number of electrons, and x is an energy per electron which can take on any value. For the total MAE, we have,

$$\begin{aligned} \kappa &= \left(\sum_{n\mathbf{k}} f_{n\mathbf{k}}^i \varepsilon_{n\mathbf{k}}^i + Nx \right) - \left(\sum_{n\mathbf{k}} f_{n\mathbf{k}}^j \varepsilon_{n\mathbf{k}}^j + Nx \right) \\ &= \sum_{n\mathbf{k}} f_{n\mathbf{k}}^i (\varepsilon_{n\mathbf{k}}^i + x) - \sum_{n\mathbf{k}} f_{n\mathbf{k}}^j (\varepsilon_{n\mathbf{k}}^j + x) \end{aligned}$$

$$\equiv E_{\text{band}}^i(x) - E_{\text{band}}^j(x)$$

$$= \sum_{n\mathbf{k}} \left[f_{n\mathbf{k}}^i \varepsilon_{n\mathbf{k}}^i - f_{n\mathbf{k}}^j \varepsilon_{n\mathbf{k}}^j \right] + x \sum_{n\mathbf{k}} \left[f_{n\mathbf{k}}^i - f_{n\mathbf{k}}^j \right]. \quad (9)$$

Since $\sum_{n\mathbf{k}} f_{n\mathbf{k}}^i = N$, the second term on the last line vanishes and the arbitrary constant, x , has no effect on the MAE, as mandated by the cancellation in the first line. The site-projected band energy with the added constant is

$$\begin{aligned} E_{\text{band}}^i(x) &= \sum_{n\mathbf{k}} f_{n\mathbf{k}}^i (\varepsilon_{n\mathbf{k}}^i + x) \\ &= \sum_{n\mathbf{k}s\nu} f_{n\mathbf{k}}^i (\varepsilon_{n\mathbf{k}}^i + x) \underbrace{\langle \psi_{n\mathbf{k}}^i | s, \nu \rangle \langle s, \nu | \psi_{n\mathbf{k}}^i \rangle}_{P_{n\mathbf{k}}^{is\nu}} \\ &\equiv \sum_s E_{\text{band}}^{is}(x), \end{aligned} \quad (10)$$

where s again denotes the site, and

$$E_{\text{band}}^{is}(x) = \sum_{n\mathbf{k}\nu} f_{n\mathbf{k}}^i (\varepsilon_{n\mathbf{k}}^i + x) P_{n\mathbf{k}}^{is\nu}. \quad (11)$$

The site-projected MAE from the force theorem is now:

$$\begin{aligned} E_{\text{band}}^{is}(x) - E_{\text{band}}^{js}(x) &= \sum_{n\mathbf{k}\nu} \left[f_{n\mathbf{k}}^i \varepsilon_{n\mathbf{k}}^i P_{n\mathbf{k}}^{is\nu} - f_{n\mathbf{k}}^j \varepsilon_{n\mathbf{k}}^j P_{n\mathbf{k}}^{js\nu} \right] \\ &\quad + x \sum_{n\mathbf{k}\nu} \left[f_{n\mathbf{k}}^i P_{n\mathbf{k}}^{is\nu} - f_{n\mathbf{k}}^j P_{n\mathbf{k}}^{js\nu} \right]. \end{aligned} \quad (12)$$

Unlike in Eq.9, the site-projected MAE for each individual site s *does* depend on x , because $\sum_{n\mathbf{k}\nu} \left[f_{n\mathbf{k}}^i P_{n\mathbf{k}}^{is\nu} - f_{n\mathbf{k}}^j P_{n\mathbf{k}}^{js\nu} \right]$ does not sum to zero in practice. Thus, while the total MAE is always well defined upon adding an arbitrary constant to the energy, the relative contributions from each site computed in this way are generally not.

We present a concrete example in Fig.1, which shows the computed MAE for FePt as a function of the arbitrary constant, x . Calculations were performed within density functional theory using the projector augmented wave method [10] as implemented in the Vienna ab-initio simulation package [8]; the exchange-correlation functional was taken to be the Perdew-Burke-Ernzerhof GGA form [11]. For Brillouin-zone integrations we used a Γ -centered $53 \times 53 \times 39$ \mathbf{k} -point mesh; the tetrahedron integration scheme [12] was employed to determine the occupation numbers. We used a plane-wave cutoff energy of 350 eV. The SO integration was included using the second-variation approach. Solid and long-dashed lines show the results of the one-electron decomposition method, while dotted lines (horizontal, independent of x) show the results of the λ -integration decomposition scheme. Several points are worth noting: 1. While the sum of the individual Fe and Pt components determined by the one-electron scheme (blue solid and long-dashed

lines) is *roughly* independent of x , the individual components (red and green solid and long-dashed lines) vary wildly. For small x , $\kappa_{\text{Pt}} > \kappa_{\text{Fe}}$, while the opposite is true for large x . 2. In addition to the variation with x , the one-electron decomposition scheme is somewhat sensitive to the sizes of the integration spheres around each ion within which the projectors, $p_{nk}^{i\alpha}$, are applied. This is a result of the contribution from the interstitial region neglected in Eq.8. Long-dashed lines indicate results for larger sphere sizes, and solid lines show values for smaller spheres. Clearly, the larger of the two is the more appropriate choice here, since the total contribution (long-dashed blue), $\kappa_{\text{Pt}} + \kappa_{\text{Fe}}$, is less dependent on x . However, we see that increasing the sphere size does nothing to reduce the ambiguity of the relative contributions, $\kappa_{\text{Pt}}/(\kappa_{\text{Pt}} + \kappa_{\text{Fe}})$ and $\kappa_{\text{Fe}}/(\kappa_{\text{Pt}} + \kappa_{\text{Fe}})$. 3. The results of the λ -integration scheme (red and green horizontal dotted lines) confirm the expectation that Pt is the major contributor to the MAE of FePt. Note as well that the total contribution ($\kappa_{\text{Fe}} + \kappa_{\text{Pt}}$) from λ -integration (blue horizontal dotted line) agrees quite well with the total contribution from the one-electron decomposition scheme when the larger sphere sizes are used.

In summary, we have discussed two different schemes for decomposing the magnetocrystalline anisotropy energy into site-specific contributions. While we believe the λ -integration scheme to be robust, the site-projected one-electron scheme suffers from an inherent ambiguity that produces wild swings in the relative contributions, depending on the degree of completeness of the localized orbitals on which the projections are defined. This sheds

light on the origin of the conundrum outlined in Ref.[4], and reiterates the view that the decomposition of the MAE using matrix elements of the spin-orbit operator is a more robust means for obtaining one-site contributions to the MAE [3].

In closing, we note that during the later stages of the preparation of this manuscript, we became aware of the work described in Refs.[13] and [14], which also clarify the inefficacy of the one-electron decomposition scheme for MAE using very similar arguments to those presented here. For this reason, we elected not to submit this work for publication in a journal.

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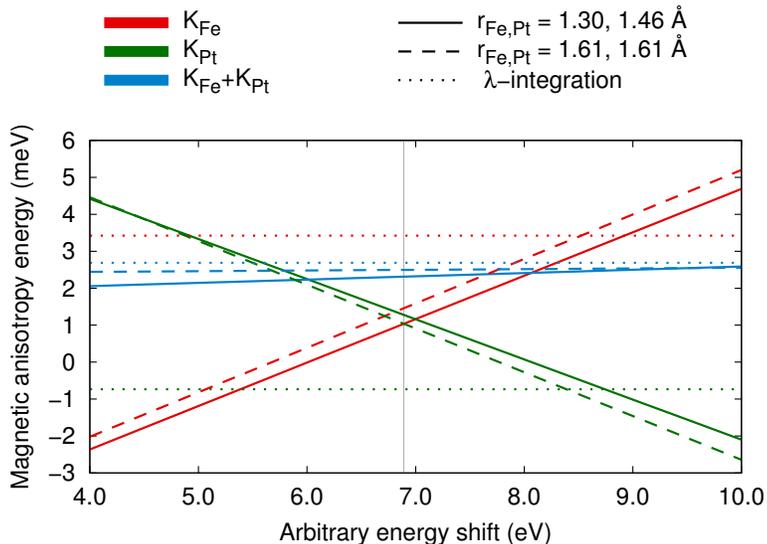


FIG. 1: MAE of FePt as decomposed into contributions from Pt and Fe using the one-electron scheme (invoking the force theorem), as a function of arbitrary energy shift. The vertical gray line corresponds to the Fermi level in the 100 direction, and the horizontal dotted lines indicate the decompositions determined by the λ -integration scheme. See text for details.

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