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Magnetic anisotropy in density-functional theory

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Magnetic anisotropy is discussed in the context of density-functional theory. A formula for the magnetic torque is derived. This formula includes the effects of the spin part of the exchange-correlation energy. All relativistic effects are taken into account, but assumptions are made for the direction of the spin magnetic moment. The nature of the torque is analyzed by expanding the formula in terms of inverse powers of the speed of light. This analysis shows how to include the effects of the spin-dependent part of the exchange-correlation potential together with the spin-orbit coupling. We find that extra terms exist in addition to the standard spin-orbit coupling. [S0163-1829(99)14803-3]

I. INTRODUCTION

Numerical calculations of the magnetic anisotropy energy are not easy. Early calculations show varying results due to a lack of convergence of the Brillouin-zone integrations. With the availability of fast computers and large disks this limitation has been eliminated. If these calculations are nowadays performed with sufficient care, numerical *precision* should not be an issue.

Density-functional theory[1] is the basis for all current *ab initio* work to calculate the magnetic anisotropy energy. The origin of the magnetic anisotropy energy is a relativistic phenomenon: spin-orbit coupling.[2] There are many ways spin-orbit coupling can be introduced into density-functional calculations. Typically, several approximations are made in this procedure, and often these approximations are not well explained. This leads to questions pertaining to the *accuracy* of the results.

In order to calculate the magnetic anisotropy energy one has to solve the fully relativistic Dirac equation for two different directions of the magnetic field, and compare the values of the total energy. Such a procedure is demanding from a numerical perspective, since it involves subtracting large numbers to obtain the small value of the magnetic anisotropy energy. Therefore, this procedure is often approximated by using second-order perturbation theory for the change in energy and/or by using the Pauli equation, which includes spin-orbit coupling in second-order in an expansion in terms of the inverse speed of light. It is not clear how these approximations affect the accuracy of the results, especially for cubic materials where second order effects cancel due to the high symmetry.

In this paper we systematically derive how one can calculate the magnetic anisotropy energy in density-functional theory. We have discussed the basic theory behind the calculation of magnetic anisotropy before.[3] In this paper we use the general theory to derive an expression for the magnetic torque. We restrict ourselves to a discussion of spin-orbit coupling as a part of the Dirac equation. A discussion of relativistic effects in and other corrections to the exchange-correlation potential used in the calculations (local-density approximation[1]) is outside the scope of this paper.

II. DENSITY-FUNCTIONAL THEORY

The problem we consider is the calculation of the total energy of a system of electrons in the presence of an external Coulomb potential (provided by the nuclei) and an external magnetic field. Although for our discussions it is sufficient to consider a uniform external magnetic field only, we will start with the general case. The interaction with the external fields is of the form

$$\mathcal{L}_i = e : \overline{\psi}(x)\gamma^{\mu}\psi(x)A_{\mu}^{ext}(x) :,$$

which couples the external fields to the conserved four-current

$$\mathcal{J}^{\mu}(x) = -ce : \overline{\psi}(x)\gamma^{\mu}\psi(x) :.$$

For details and the necessary field theory background we refer to Refs. 4 and 5. An overview of density funtional aspects of relativistic field theories was given in Ref. 6. The last paper also has many useful references to older work. Once we know the interaction with the external world we can construct a density-functional theory based on the constrained minimization of Levy[7] and Lieb.[8] Note that this approach is different from Ref. 6. There are formal problems due to renormalization and gauge invariance. For the purpose of this paper these effects are much easier to treat in the constrained minimization approach. These problems have to be treated correctly, of course, when we need to calculate the exchange and correlation energy itself. There are questions about the existence of the minimum in the constrained minimization. We avoid that question, however, since we use the fact that the interacting system has a ground state. Therefore we do not need to address these problems in the current paper.

The result is that we are able to find the total energy of the ground state of this system by minimizing the functional $E[\rho(\vec{r}),\vec{j}(\vec{r})]$ of the charge density $\rho(\vec{r})$ and the current density $\vec{j}(\vec{r})$. This functional is given by

$$E[\rho(\vec{r}),\vec{j}(\vec{r})] = T_{ni}[\rho(\vec{r}),\vec{j}(\vec{r})] + U_H[\rho(\vec{r})] + E_{xc}[\rho(\vec{r}),\vec{j}(\vec{r})] + \int v_{ext}(\vec{r})\rho(\vec{r})d^3r - \frac{1}{c}\int \vec{A}_{ext}(\vec{r})\cdot\vec{j}(\vec{r})d^3r,$$

where T_{ni} is the kinetic energy of a system of noninteracting electrons with the given charge and current density, U_H is the classical Coulomb energy of the charge density, and E_{xc} is the correction term needed to make this a true equality. We will not address the question how to calculate this term which commonly but erroneously is called exchange-correlation energy. The last two terms are the interaction with the external fields.

One important question is which charge and current densities are allowed in this expression. The answer is easy. Once we have stated the set of many-body state vectors used for minimization of the total energy, the allowed charge density and current density are simply in a set derived from the master set of these state vectors. It is clear that we have $\rho(\vec{r})\geqslant 0$ and $\vec{\nabla}\cdot\vec{j}=0$. The last equality is due to the fact that we only consider time-independent external potentials. Of course we could minimize over time-dependent charge densities, but we know that the ground-state density is time independent. Therefore, we restrict ourselves to time-independent densities only.

In our previous paper,[3] we investigated the effects of relativistic corrections to the Coulomb interaction. By including the electromagnetic fields due to the electrons in quantized form, one observes that the electron-electron interaction is modified: in addition to the normal $1/r$ interaction we need to include the Breit interaction, which leads directly to a magnetic dipole-dipole interaction and causes the shape anisotropy. This will also affect the crystalline anisotropy, but in many cases the effects are small.

III. MAGNETIC ANISOTROPY

According to Chikazumi[9] magnetic anisotropy means the dependence of the internal energy on the direction of the spontaneous magnetization. A large contribution to this energy is due to the shape of the sample, as discussed in the same book. Here we are interested only in the interaction of the direction of the magnetization with the crystalline geometry.

Measuring the magnetic anisotropy energy is not without problems. The only way to change the direction of the magnetization is to apply an external field and to rotate the field with respect to the crystalline axes. The field should be strong enough that the magnetization is fully saturated. This does lead, however, to a field dependence of the energy, and one should extrapolate to zero field. This might not be easy. On the other hand, the situation is simple in a theoretical discussion. We force the magnetization density to have a particular direction $\hat{M}_0$ and calculate $E_{gs}(\hat{M}_0)$ with zero external field.

According to the standard treatment in electromagnetism,[10] the current density can be separated in a free density and a magnetic density. Since we have zero external field there is no free current. The magnetic current has zero divergence and hence we can write

$$\vec{j}(\vec{r})=c\vec{\nabla}\times\vec{M},$$

which defines the magnetization density $\vec{M}$. The term describing the interaction with the external field is now simply

$$-\int d^3r\,\vec{B}_{ext}(\vec{r})\cdot\vec{M}(\vec{r})$$

where we assume that the sample is finite. Without this assumption it would be hard to define an external field.

The definition of $\vec{M}$ is not unique. We can always add the gradient of a scalar field $\vec{\nabla}g(\vec{r})$ to obtain the same current density. This does not change the interaction energy, though. Since $\vec{\nabla}\cdot\vec{B}_{\rm ext}=0$, and since the sample is finite, the integral

$$\int d^3r\,\vec{B}_{ext}(\vec{r})\cdot\vec{\nabla}g(\vec{r})$$

is equal to a surface integral at infinity and hence is zero.

The direction of the magnetization is given by the direction of

$$\vec{M}_0=\int d^3r\,\vec{M}(\vec{r})$$

We make the reasonable assumption that the magnetization density decays to zero outside the sample. In that case the fact that the magnetization density is not unique does not alter the overall magnetization $\vec{M}_0$, and the problem of finding the magnetic anisotropy energy is well defined.

We are now able to specify the magnetic anisotropy energy in density functional theory. By definition we have

$$E_{gs}(\hat{M}_0)=\min_{R(\hat{M}_0)}\Big\{T_{ni}[\rho(\vec{r}),\vec{M}(\vec{r})]+U_H[\rho(\vec{r})]+E_{xc}[\rho(\vec{r}),\vec{M}(\vec{r})]+\int v_{ext}(\vec{r})\rho(\vec{r})d^3r\Big\},$$

where the minimization is carried out over all charge densities, and all magnetization densities compatible with $\int d^3r\,\vec{M}(\vec{r})$ parallel to $\hat{M}_0$.

IV. LOCAL-SPIN-DENSITY APPROXIMATION

The exact form of the exchange-correlation functional is not known. Most calculations are performed using the local-spin-density approximation (LSDA). In this approximation we use the exact energy density for a homogeneous electron gas, $\epsilon_{\rm hom}(\rho,s)$, with electron density ρ and spin density s to approximate the exchange-correlation energy by

$$E_{xc}^{LSDA}=\int d^3r\,\epsilon_{\rm hom}(\rho(\vec{r}),s(\vec{r})).$$

The spin density is defined as the expectation value of the operator

$$\vec{\mathcal{S}}(\vec{r})=:\psi^{\dagger}(\vec{r})\frac{1}{2}\vec{\Sigma}\psi(\vec{r}):.$$

The matrix $\vec{\Sigma}$ is very simple in the Pauli-Dirac representation: $1\times\vec{\sigma}$. The magnetization density due to the spins is given by

$$\vec{M}_{spin}(\vec{r})=-2\mu_B\vec{s}(\vec{r}).$$

Even though the local-spin-density approximation is quite a severe approximation, it is remarkable how well calculated results describe experimental data for transition metals. For rare-earth materials the situation is not very good, however.

The definition of the magnetic anisotropy energy in the local-spin-density approximation is simple. We have shown before[3] that the leading terms in the magnetization density are due to spin and orbital angular momentum. Since in the local-spin-density approximation the exchange-correlation energy only depends on the spin density, we have to treat the spin density separately. One solution is to find the functional that relates the ground-state spin and orbital densities. This is hard. The other approach is to vary the spin and orbital (or total) magnetization densities separately. This leads to the following form:

$$E_{gs}(\hat{M}_0)=\min_{R'(\hat{M}_0)}\left\{T'_{ni}[\rho(\vec{r}),\vec{M}_{orb}(\vec{r}),\vec{M}_{spin}(\vec{r})]+U_H[\rho(\vec{r})]\right.$$
$$\left.+E_{xc}[\rho(\vec{r}),s(\vec{r})]+\int v_{ext}(\vec{r})\rho(\vec{r})d^3r\right\},$$

where the noninteracting kinetic energy is now the ground-state kinetic energy of a system on noninteracting electrons with a given charge, spin, and orbital moment density.

We see that in the local-spin-density approximation the orbital magnetization is only present in the noninteracting kinetic energy. Therefore, we can perform the minimization over the orbital moments and redefine the noninteracting kinetic energy as the kinetic energy of a system of noninteracting electrons with spin density $\vec{s}(\vec{r})$ and direction of the total magnetization along $\hat{M}_0$. Hence we have

$$E_{gs}(\hat{M}_0)=\min_{R(\hat{M}_0)}\left\{T_{ni}[\rho(\vec{r}),\vec{s}(\vec{r}),\hat{M}_0]+U_H[\rho(\vec{r})]\right.$$
$$\left.+E_{xc}[\rho(\vec{r}),s(\vec{r})]+\int v_{ext}(\vec{r})\rho(\vec{r})d^3r\right\},$$

where the notation is similar to the one we used before.

We see that in the local-spin-density approximation the energy dependence on the direction of the magnetization is completely within the noninteracting kinetic energy. This is clearly incorrect. In rare-earth materials exchange effects lead to the formation of orbital moments, and obviously the exchange-correlation energy must depend on the direction of the magnetization. Hund's second rule is a direct consequence of this dependence. In transition metals where the orbital angular momentum is almost quenched, one has some hope that this approximation is not too severe. *Ab initio* calculations of the magnetic anisotropy energy, however, fail to reproduce the experimentally observed easy axis in nickel. Most likely, the reason for this is the neglect of the effects leading to Hund's second rule, although it is possible that other commonly made approximations are the cause. These approximations are discussed in the following sections.

V. NONINTERACTING KINETIC ENERGY, SPIN ONLY

In many transition metals the orbital moment is small, typically a few percent of the total moment. In such a case it is reasonable to approximate the direction of the total magnetization by the direction of the spin magnetization. This will only lead to small corrections in the magnetic anisotropy energy. Note that when we need to study rare-earth materials this correction becomes large, and in that case we need to use the correct definition of the direction of the total magnetization density. Replacing $\hat{M}_0$ by the direction of the spin magnetic moment enables us to simplify the calculations. This approximation is used in all density-functional calculations of the magnetic anisotropy energy. It ignores the fact that the total magnetization and the spin magnetization do not have to be parallel.

Our aim is to calculate the noninteracting kinetic energy. This energy follows from

$$T_{ni}[\rho(\vec{r}),\vec{s}(\vec{r})]=\min_{T_\psi}\langle\Psi|\int d^3r\,\mathcal{H}_0(\vec{r})|\Psi\rangle,$$

where the Hamiltonian is defined by

$$\mathcal{H}_0(\vec{r})=:\psi^\dagger(\vec{r})\left[\frac{\hbar c}{i}\vec{\alpha}\cdot\vec{\nabla}+\beta mc^2\right]\psi(\vec{r}):.$$

The minimization is over all state vectors corresponding to the charge and spin densities which are specified. The direction $\hat{M}_0$ now follows directly from the integral of the spin density.

We need to solve the Dirac equation

$$\left[\frac{\hbar c}{i}\vec{\alpha}\cdot\vec{\nabla}+\beta mc^2-ev_{eff}(\vec{r})+\mu_B\vec{B}_{eff}(\vec{r})\cdot\vec{\Sigma}\right]\psi(\vec{r})=\epsilon\psi(\vec{r}),$$

The effective potential is related to the charge and spin density by

$$v_{eff}(\vec{r})=\frac{\delta U_H}{\delta\rho}+\frac{\delta E_{xc}}{\delta\rho}+v_{ext}(\vec{r}),$$

and the effective magnetic induction follows from

$$\vec{B}_{eff}(\vec{r})=+\frac{1}{2\mu_B}\frac{\delta E_{xc}}{\delta\vec{s}}+\vec{B}_{ext}(\vec{r}).$$

In the local-spin-density approximation the exchange-correlation energy only depends on the magnitude of the spin, and we have

$$\vec{B}^{LSDA}_{eff}(\vec{r})=+\frac{1}{2\mu_B}\frac{\delta E^{LSDA}_{xc}}{\delta s}\hat{s}(\vec{r})+\vec{B}_{ext}(\vec{r}).$$

In the local-spin-density approximation all we need to know about the system is the local-spin density. Since the local-spin-density approximation is based on the homogeneous electron gas there is no information about the direction. The natural connection between the exchange-correlation potential and the effective magnetic field is given by the previous formula. The local direction of the effective magnetic field is parallel to the spin direction. This is used in calculations of noncolinear magnetism.

At this point, however, we are still in the same situation as the experimentalists. The only way to point the spin magnetization in a certain direction is when we apply a field large enough to pull it completely into that direction. What we really want to do is to prescribe the net direction of the spin magnetization. One possibility is to use Lagrange multipliers. This is not easy. When one tries to write the forms of the expressions for conserving the direction of the spin density, it requires the norm of the spin density and hence some quadratic expression.

An alternative to using Lagrange multipliers is to make the assumption that the direction of the exchange-correlation field is always along the direction $\hat{B}_0$. Hence we write

$$\vec{B}_{eff}(\vec{r}) = +\frac{1}{2\mu_B}\frac{\delta E_{xc}^{LSDA}}{\delta s}\hat{B}_0 + \vec{B}_{ext}(\vec{r}).$$

This modifies the way we define the exchange-correlation energy. All current *ab initio* density-functional calculations of the magnetic anisotropy energy use this approach. Obviously, this is an approximation. If we now perform our calculations without external magnetic field the only direction in the problem is the direction $\hat{B}_0$. The Dirac equations to solve are

$$\left[\frac{\hbar c}{i}\vec{\alpha}\cdot\vec{\nabla} + \beta mc^2 - ev_{eff}(\vec{r}) + \mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\Sigma}\right]\psi(\vec{r}) = \epsilon\psi(\vec{r})$$

where the effective potential is related to the charge and spin density by

$$v_{eff}(\vec{r}) = \frac{\delta U_H}{\delta\rho} + \frac{\delta E_{xc}}{\delta\rho} + v_{ext}(\vec{r})$$

as before, and the effective magnetic induction is given by

$$B_{eff}(\vec{r}) = +\frac{1}{2\mu_B}\frac{\delta E_{xc}^{LSDA}}{\delta s}.$$

The Dirac equations we have to solve here reduce to the normal spin-dependent Schrödinger equation in the nonrelativistic limit. In that limit the spin is always along $\hat{B}_0$, and for the self-consistent spin density we have $\vec{s}(\vec{r}) = \hat{B}_0 s(\vec{r})$. For the full Dirac equation above the resulting spin density is not necessarely parallel to the direction $\hat{B}_0$ of the exchange-correlation field. Since we have made the assumption, however, that the magnetization is mainly spin, the deviations will be small. This means that we can use $\hat{B}_0$ as a good approximation to the direction of the magnetization, and hence we have achieved our goal of specifying this direction.

The density-functional expression for the magnetic anisotropy energy can now be written in the form

$$E_{gs}(\hat{B}_0) = \min_{\rho,s}\Big\{T_{ni}[\rho(\vec{r}),s(\vec{r}),\hat{B}_0] + U_H[\rho(\vec{r})] + E_{xc}[\rho(\vec{r}),s(\vec{r})] + \int v_{ext}(\vec{r})\rho(\vec{r})d^3r\Big\}.$$

In addition to the previous arguments it is useful to realize that when $\hat{B}_0$ is along a high-symmetry direction (in terms of the crystalline electrostatic potential), the spin and orbital moment will both be parallel to $\hat{B}_0$. This means that $E_{gs}(\hat{B}_0)$ does represent the magnetic energy for those directions. Hence if we want to calculate the energy difference between high-symmetry directions this formula gives the correct differences. We can therefore use $\hat{B}_0$ as a parameter allowing a continuous path between high-symmetry directions. If $\hat{B}_0$ does not correspond to a high-symmetry direction, the energy $E_{gs}(\hat{B}_0)$ is only an approximation to the true magnetic energy.

Once we have found the self-consistent solution it is easy to show that (see Appendix A)

$$\frac{\partial E_{gs}}{\partial\hat{B}_0}(\hat{B}_0) = \frac{\partial T_{ni}}{\partial\hat{B}_0}(\rho_{sc}(\vec{r}),s_{sc}(\vec{r}),\hat{B}_0) = \frac{\partial}{\partial\hat{B}_0}\sum_{occ}\epsilon_n,$$

where the sum over the occupied states may include a Fermi-Dirac or other type of distribution function. If we are not at self-consistency, extra forces play a role. Therefore, we cannot integrate the last equation directly since the self-consistent charge and spin density will change. Also, we do obtain additional forces if our basis for the calculation is incomplete and dependent on the direction of the field.

VI. ROTATIONS IN SPIN SPACE

The analysis of the Dirac equation is easier to follow if we separate the wave function into large and small components L and S. We obtain

$$\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}S + [mc^2 - ev_{eff}(\vec{r}) + \mu_B B_{eff}(\vec{r})\hat{B}\cdot\vec{\sigma}]L = \epsilon L,$$

$$\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}L + [-mc^2 - ev_{eff}(\vec{r}) + \mu_B B_{eff}(\vec{r})\hat{B}\cdot\vec{\sigma}]S = \epsilon S,$$

where the sigma matrices now are the standard two-dimensional Pauli matrices. The effective field is now along an arbitrary direction $\hat{B}$. As shown in Appendix B, we can relate this direction to a reference direction $\hat{B}_0$ by

$$\hat{B}_0\cdot\hat{B} = \cos(\theta) \text{ and } \hat{B}_0\times\hat{B} = \sin(\theta)\hat{n}.$$

Using the result from Appendix B,

$$e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}(\hat{B}_0\cdot\vec{\sigma})e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}} = \hat{B}\cdot\vec{\sigma},$$

we obtain

$$\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}S + [mc^2 - ev_{eff}(\vec{r}) + \mu_B B_{eff}(\vec{r})e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}(\hat{B}_0\cdot\vec{\sigma})e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}]L = \epsilon L,$$

$$\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}L + [-mc^2 - ev_{eff}(\vec{r}) + \mu_B B_{eff}(\vec{r})e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}(\hat{B}_0\cdot\vec{\sigma})e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}]S = \epsilon S.$$

We define the spin-rotated wave functions by

$$L' = e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}L \text{ and } S' = e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}S.$$

For these rotated wave functions we have

$$L'^{\dagger}L' + S'^{\dagger}S' = L^{\dagger}L + S^{\dagger}S,$$

and, using the identities from Appendix B,

$$\begin{aligned}L'^{\dagger}\vec{\sigma}L'+S'^{\dagger}\vec{\sigma}S'=L^{\dagger}\{&\hat{n}(\hat{n}\cdot\vec{\sigma})\\&+\cos(\theta)[\vec{\sigma}-\hat{n}(\hat{n}\cdot\vec{\sigma}])-\sin(\theta)\hat{n}\times\vec{\sigma}L\\&+S^{\dagger}[\hat{n}(\hat{n}\cdot\vec{\sigma})]+\cos(\theta)[\vec{\sigma}-\hat{n}(\hat{n}\cdot\vec{\sigma})]\\&-\sin(\theta)\hat{n}\times\vec{\sigma}\}S.\end{aligned}$$

This shows that the spin-rotated wave functions have the same charge density but a spin density that is rotated in the opposite way from the effective field.

The Dirac equations are now equivalent to

$$\begin{aligned}&\frac{\hbar c}{i}e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}\vec{\sigma}\cdot\vec{\nabla}e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}S'n\\&\quad+[mc^2-ev_{eff}(\vec{r})+\mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\sigma}]L'=\epsilon L',\\&\frac{\hbar c}{i}e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}\vec{\sigma}\cdot\vec{\nabla}e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}L'\\&\quad+[-mc^2-ev_{eff}(\vec{r})+\mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\sigma}]S'=\epsilon S'.\end{aligned}$$

Using the relation from Appendix B, we find

$$\begin{aligned}e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}(\vec{\sigma}\cdot\vec{\nabla})e^{-\frac{i}{2}\theta\hat{n}\cdot\vec{\sigma}}=\vec{\sigma}\cdot\vec{\nabla}+[\cos(\theta)-1][&(\vec{\sigma}\cdot\vec{\nabla})\\&-(\hat{n}\cdot\vec{\nabla})(\hat{n}\cdot\vec{\sigma})]\\&-\sin(\theta)\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla}).\end{aligned}$$

We now define the operator $R(\theta)$ by

$$\begin{aligned}R(\theta)=&[\cos(\theta)-1][(\vec{\sigma}\cdot\vec{\nabla})-(\hat{n}\cdot\vec{\nabla})(\hat{n}\cdot\vec{\sigma})]\\&-\sin(\theta)\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla}),\end{aligned}$$

and find, for the Dirac equations,

$$\begin{aligned}&\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}S'+\frac{\hbar c}{i}R(\theta)S'\\&\quad+[mc^2-ev_{eff}(\vec{r})+\mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\sigma}]L'=\epsilon L',\\&\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}L'+\frac{\hbar c}{i}R(\theta)L'\\&\quad+[-mc^2-ev_{eff}(\vec{r})+\mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\sigma}]S'=\epsilon S'.\end{aligned}$$

This shows that the wave functions for an arbitrary direction of the effective field are related in a simple way to the wave functions for the reference field direction $\hat{B}_0$. The wave functions are given by L and S. The last set of formulas shows that it is more convenient to work with wave functions L' and S' which are rotated back to the original reference direction. Since the Dirac equation is only invariant under simultaneous rotations of spin and space, the back rotation leads to an additional term $R(\theta)$ in the equations. This term represents the spin-orbit interaction. It essentially rotates the gradients back in the same way. If we change our coordinate system to $\vec{r}'$ which is rotated back in the same way as the spin this term disappears, but now we have a rotation in the effective fields, which is much harder to deal with. The physics in the last scenario is very simple, rotating the magnetic field in one direction can also be achieved by rotating the sample in the opposite direction.

For a calculation of the torque we only need a rotation over small angles. In that case we can approximate

$$R(\Delta\theta)\approx-\Delta\theta\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla}).$$

Note that this is not an approximation of the effects of spin-orbit coupling. We are still retaining spin-orbit coupling in all orders. The Dirac equations are now given by

$$\begin{aligned}&\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}S'-\frac{\hbar c}{i}\Delta\theta\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla})S'\\&\quad+[mc^2-ev_{eff}(\vec{r})+\mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\sigma}]L'=\epsilon L',\\&\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}L'-\frac{\hbar c}{i}\Delta\theta\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla})L'\\&\quad+[-mc^2-ev_{eff}(\vec{r})+\mu_B B_{eff}(\vec{r})\hat{B}_0\cdot\vec{\sigma}]S'=\epsilon S'.\end{aligned}$$

First-order perturbation theory gives, for the change in energy of the state,

$$\Delta\epsilon=-\frac{\hbar c}{i}\Delta\theta\int d^3r[L^{0\dagger}\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla})S^0+S^{0\dagger}\vec{\sigma}\cdot(\hat{n}\times\vec{\nabla})L^0],$$

where L^0 and S^0 refer to the solution at the reference field.

At this point we are able to make contact with density-functional theorem via the force theorem (Appendix A) and we find that the change in energy due to a rotation of the magnetic field around a direction $\hat{n}$ is given by

$$\frac{dE_{gs}}{d\theta}=\hat{n}\cdot\vec{\tau},$$

with

$$\vec{\tau}=+\frac{\hbar c}{i}\sum_{occ}\int d^3r[L_k^{0\dagger}(\vec{\sigma}\times\vec{\nabla})S_k^0+S_k^{0\dagger}(\vec{\sigma}\times\vec{\nabla})L_k^0].$$

Note again that in this formula we have not used any form of perturbation expansion in powers of the effective spin-orbit coupling. It is valid in general, under the assumptions explained in the previous sections.

VII. APPROXIMATING THE TORQUE

In Sec. VI, we derived a formula for the magnetic torque on a crystal in density-functional theory. It is clear that the second term in this expression is the complex conjugate of the first, so we only need to consider

$$\vec{\tau}=+2\ \mathrm{Re}\frac{\hbar c}{i}\sum_{occ}\int d^3rL_k^{\dagger}(\vec{\sigma}\times\vec{\nabla})S_k,$$

where Re indicates the real part of the expression. We have dropped the superscript zero and now calculate the torque for an arbitrary direction $\hat{B}$. The small component S can be eliminated by inverting the Dirac equation, which leads to

$$\vec{\tau}=+2\,\mathrm{Re}\frac{\hbar c}{i}\sum_{occ}\int d^3rL_k^\dagger(\vec{\sigma}\times\vec{\nabla})[\epsilon_k+mc^2+ev_{eff}-\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}]^{-1}\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}L_k.$$

It is useful to consider the non-relativistic limit of this equation, which should give zero torque. The energy eigenvalues still contain the rest mass energy, and hence we have

$$\vec{\tau}^0=+2\,\mathrm{Re}\frac{\hbar c}{i}\sum_{occ}\int d^3r\,L_k^\dagger(\vec{\sigma}\times\vec{\nabla})\frac{1}{2mc^2}\frac{\hbar c}{i}\vec{\sigma}\cdot\vec{\nabla}L_k=-2\,\mathrm{Re}\frac{\hbar^2}{2m}\sum_{occ}\int d^3rL_k^\dagger(\vec{\sigma}\times\vec{\nabla})\vec{\sigma}\cdot\vec{\nabla}L_k.$$

Using the relation derived at the end of Appendix B, we find

$$\hat{n}\cdot\vec{\tau}^0=-2\frac{\hbar^2}{2m}\sum_{occ}\mathrm{Re}\int d^3r\,L_k^\dagger\hat{n}\cdot(\vec{\sigma}\times\vec{\nabla})(\vec{\sigma}\cdot\vec{\nabla})L_k=-2\frac{\hbar^2}{2m}\sum_{occ}\mathrm{Re}\,i\int d^3rL_k^\dagger[(\hat{n}\cdot\vec{\sigma})\Delta-(\hat{n}\cdot\vec{\nabla})(\vec{\sigma}\cdot\vec{\nabla})]L_k=0,$$

since the integral is real (all operators are Hermitian) and therefore the prefactor i makes the expression purely imaginary. Note that in this expression we have used the wave functions L_k which are solutions of the Dirac equation. In order to find the order of magnitude of the expression, we subtract a term $\vec{\tau}^0$ from the torque, and after rearranging terms we find

$$\vec{\tau}=-2\,\mathrm{Re}\frac{\hbar^2}{2m}\sum_{occ}\int d^3r\,L_k^\dagger(\vec{\sigma}\times\vec{\nabla})[mc^2-\epsilon_k-ev_{eff}+\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}][\epsilon_k+mc^2+ev_{eff}-\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}]^{-1}\vec{\sigma}\cdot\vec{\nabla}L_k.$$

We can see that this expression scales as $1/2mc^2$, and therefore we obtain a small number without having to subtract large terms. If we now evaluate the leading order of this term in an expansion in the inverse speed of light we obtain

$$\vec{\tau}\approx-2\,\mathrm{Re}\,\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^\dagger(\vec{\sigma}\times\vec{\nabla})[mc^2-\epsilon_k-ev_{eff}+\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}]\vec{\sigma}\cdot\vec{\nabla}L_k.$$

This expression shows how the magnetic effective field has to be included into a spin-orbit coupling calculation. Also, following the same argument that showed that the classical limit of the torque is zero, we can show that the term $mc^2-\epsilon_k$ gives zero for the integral. Therefore we can write

$$\vec{\tau}\approx 2\,\mathrm{Re}\,\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^\dagger(\vec{\sigma}\times\vec{\nabla})[ev_{eff}-\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}]\vec{\sigma}\cdot\vec{\nabla}L_k.$$

The real part is now evaluated by adding the Hermitian conjugate of the expression, taking into account that both derivatives give a minus sign:

$$\vec{\tau}\approx\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^\dagger\{(\vec{\sigma}\times\vec{\nabla})[ev_{eff}-\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}]\vec{\sigma}\cdot\vec{\nabla}+\vec{\sigma}\cdot\vec{\nabla}[ev_{eff}-\mu_B B_{eff}\hat{B}\cdot\vec{\sigma}](\vec{\sigma}\times\vec{\nabla})\}L_k.$$

After some vector algebra we find that the torque splits into three terms. The first of the three integrals, involving the effective potential, simplifies to

$$\vec{\tau}_v=\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^\dagger\{i\vec{\sigma}\times([\vec{\nabla}ev_{eff}]\times\vec{\nabla})\}L_k.$$

The potential energy related to this torque is

$$U_{pot}=-\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^\dagger\{i\vec{\sigma}\cdot([\vec{\nabla}ev_{eff}]\times\vec{\nabla})\}L_k,$$

which can be derived by considering the changes in energy as a function of small changes in the angle between the spin and the lattice. This is the standard expression for the effects of spin-orbit coupling as included in most calculations that do not use the full Dirac equation.[11] The additional terms are generally ignored in such calculations. This casts doubt on many of the density-functional calculations that have been performed to obtain the magnetic anisotropy energy.

The term $\vec{\tau}_v$ is zero if one uses the nonrelativistic form of the wave function in a material with inversion symmetry. In order to evaluate this integral we have to use the wave functions obtained from the full Dirac equation with a magnetic field, as described above. This will be discussed in a following paper.

The second of the three terms in the torque is spin independent. We obtain

$$\vec{\tau}_B=\mu_B\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^\dagger\{i\hat{B}\times([\vec{\nabla}B_{eff}]\times\vec{\nabla})\}L_k.$$

This term represents the fact that there is a torque when the orbital moment and the spin direction are not aligned. The controling parameter is an integral over the derivative of the effective magnetic field, or the difference between spin-up and -down potentials. It represents a correction to the standard implementation of the spin-orbit coupling.

If we assume that the effective fields are spherical symmetric, we obtain

$$\vec{\tau}_v=-\frac{\hbar}{4m^2c^2}\sum_{occ}\int d^3r\frac{1}{r}\frac{\mathrm{dev}_{eff}}{dr}L_k^{\dagger}(\vec{\sigma}\times\vec{L})L_k$$

and

$$\vec{\tau}_B=-\mu_B\frac{\hbar}{4m^2c^2}\sum_{occ}\int d^3r\frac{1}{r}\frac{dB_{eff}}{dr}L_k^{\dagger}(\hat{B}\times\vec{L})L_k\,.$$

Since the spin density is opposite to the effective field, the second term reduces the magnetic anisotropy as calculated in standard investigations. Estimates from atomic calculations show that this reduction can be 10–20 %.

The third term is more complicated:

$$\vec{\tau}_3=\mu_B\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,L_k^{\dagger}\{\vec{\nabla}\times[\vec{\sigma}(B_{eff}\hat{B}\cdot\vec{\nabla})+B_{eff}\hat{B}(\vec{\nabla}\cdot\vec{\sigma})]-[(\vec{\nabla}\cdot B_{eff}\hat{B})\vec{\sigma}+(\vec{\nabla}\cdot\vec{\sigma})B_{eff}\hat{B}]\times\vec{\nabla}\}L_k\,.$$

Integration by parts gives

$$\vec{\tau}_3=\mu_B\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r\,B_{eff}\{[\vec{\sigma}\times(\vec{\nabla}L_k)]^{\dagger}[(\hat{B}\cdot(\vec{\nabla}L_k)]+[\hat{B}\times(\vec{\nabla}L_k{}^{\dagger})][(\vec{\sigma}\cdot(\vec{\nabla}L_k)]$$
$$+[(\hat{B}\cdot(\vec{\nabla}L_k{}^{\dagger})][\vec{\sigma}\times(\vec{\nabla}L_k)]+[(\vec{\sigma}\cdot(\vec{\nabla}L_k)]^{\dagger}[\hat{B}\times(\vec{\nabla}L_k)]\}.$$

The physical origin of this last term is not clear. It is proportional to the effective magnetic field. We can approximate this term when we assume that the exchange splitting is a constant, and that for the spin direction we only take the part parallel to $\hat{B}$. This gives

$$\vec{\tau}_3\approx2\mu_BB_{eff}^{av}\frac{\hbar^2}{4m^2c^2}\sum_{occ}\int d^3r[\hat{B}\times(\vec{\nabla}L_k)]^{\dagger}(\hat{B}\cdot\vec{\sigma})[(\hat{B}\cdot(\vec{\nabla}L_k)]+\text{c.c.}$$

This shows that states with linear momentum parallel or orthogonal to the direction of the effective field do not contribute. It should play a role in cubic materials, where symmetry reduces the effects of the first two terms on the magnetic anisotropy energy difference between high-symmetry directions.

VIII. CONCLUSIONS

In this paper we have investigated the procedure for calculating the magnetic anisotropy energy using density-functional theory. We have defined this energy by

$$E_{gs}(\hat{B}_0)=\min_{\rho,s}\left\{T_{ni}[\rho(\vec{r}),s(\vec{r}),\hat{B}_0]+U_H[\rho(\vec{r})]\right.$$
$$\left.+E_{xc}[\rho(\vec{r}),s(\vec{r})]+\int v_{ext}(\vec{r})\rho(\vec{r})d^3r\right\}.$$

This formula is only valid when the direction $\hat{B}_0$ is a good approximation for the direction of the total magnetization. This requires the orbital magnetic moment to be almost completely quenched, a situation that only arises in transition metals. If, however, the direction $\hat{B}_0$ coincides with a direction of high symmetry in the crystal it will represent the direction of the total magnetization in many cases even when the orbital moment is not quenched. Hence the formula above can be used to calculate differences in magnetic anisotropy energy between high-symmetry directions.

Based on the formula for the magnetic anisotropy energy we evaluated the magnetic torque. We found that the general expression is

$$\vec{\tau}=+2\,\mathrm{Re}\frac{\hbar c}{i}\sum_{occ}\int d^3r\,L_k^{\dagger}(\vec{\sigma}\times\vec{\nabla})S_k\,,$$

where we need the solutions to the Dirac equation. If we expand this expression in terms of powers of the square of the fine-structure constant (which is the inverse of the speed of light) we find that in zeroth order the torque is zero. We analyzed the first-order terms and found that there are three contributions to the magnetic torque. The first one is the standard form of spin-orbit coupling used in all calculations based on Pauli theory. There are two additional terms, however, which are related to the spin-dependent part of the exchange-correlation potential. This is an important development, since it was always unclear how to combine magnetism and spin-orbit coupling in calculations. Our work shows that in the context of density-functional theory such a combination is possible.

Future calculations will have to show how large the contributions of the additional terms are, but a rough estimate based on atomic calculations indicates changes on the order of 10%. The formula for the torque presented above is very useful for theoretical consideration, but is not suitable for practical calculations. In a following paper we will address the issue of how to calculate the torque and magnetic anisotropy efficiently.

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APPENDIX A: FORCE THEOREM

We consider the density-functional expression

$$E[\rho(\vec{r}),s(\vec{r}),\hat{B}_0]=T_{ni}[\rho(\vec{r}),s(\vec{r}),\hat{B}_0] + U_H[\rho(\vec{r})]+E_{xc}[\rho(\vec{r}),s(\vec{r})] + \int v_{ext}(\vec{r})\rho(\vec{r})d^3r.$$

At self-consistency we have

$$0=\frac{\delta E}{\delta\rho}=\frac{\delta T_{ni}}{\delta\rho}+\frac{\delta U_H}{\delta\rho}+\frac{\delta E_{xc}}{\delta\rho}+v_{ext}$$

or

$$\frac{\delta T_{ni}}{\delta\rho}=-v_{eff}.$$

Similarly, at self-consistency we have

$$\frac{\delta T_{ni}}{\delta s}=-2\mu_B B_{eff}.$$

In general we have

$$\Delta E=\frac{\delta E}{\delta\rho}\Delta\rho+\frac{\delta E}{\delta s}\Delta s+\frac{\partial E}{\partial\hat{B}_0}\Delta\hat{B}_0,$$

but at the self-consistent solution the first two terms are zero. Hence

$$\frac{dE_{gs}}{d\hat{B}_0}=\frac{\partial E}{\partial\hat{B}_0}=\frac{\partial T_{ni}}{\partial\hat{B}_0},$$

where the expressions at the right are calculated at self-consistency. The kinetic energy follows from

$$\begin{aligned}T_{ni}[\rho_{sc},s_{sc},\hat{B}_0]&=\sum_{occ}\int d^3r\,\psi_n^{\dagger}(\vec{r})\left(\frac{\hbar c}{i}\vec{\alpha}\cdot\vec{\nabla}+\beta mc^2\right)\psi_n(\vec{r})\\&=\sum_{occ}\int d^3r\,\psi_n^{\dagger}(\vec{r})(\epsilon_n+ev_{eff}-\mu_B B_{eff}\hat{B}_0\cdot\Sigma)\psi_n(\vec{r}).\end{aligned}$$

The sum over occupied states can be weighted by a Fermi-Dirac or other distribution function to include non-zero temperature or some broadening. Using the normalization of the charge of each state and the definitons of charge and spin density, we obtain

$$T_{ni}[\rho_{sc},s_{sc},\hat{B}_0]=\sum_{occ}\epsilon_n-\int d^3r\,v_{eff}(\vec{r})\rho_{sc}(\vec{r}) -2\mu_B\int d^3r\,B_{eff}(\vec{r})\hat{B}_0\cdot\vec{s}(\vec{r}).$$

In general, for the change in kinetic energy we write

$$\Delta T_{ni}=\frac{\delta T_{ni}}{\delta\rho}\Delta\rho+\frac{\delta T_{ni}}{\delta s}\Delta s+\frac{\partial T_{ni}}{\partial\hat{B}_0}\Delta\hat{B}_0,$$

where we have to include the changes in the spin and charge density due to a change in the direction of the magnetization. At self-consistency this reduces to

$$\Delta T_{ni}=-\int v_{eff}\Delta\rho-\int 2\mu_B B_{eff}\Delta s+\frac{\partial T_{ni}}{\partial\hat{B}_0}\Delta\hat{B}_0;$$

from the expression of the kinetic energy in terms of eigenvalues, we find

$$\Delta T_{ni}=\Delta\sum_{occ}\epsilon_n-\int d^3r\,v_{eff}(\vec{r})\Delta\rho_{sc}(\vec{r}) -2\mu_B\int d^3r B_{eff}(\vec{r})\hat{B}_0\cdot\Delta\vec{s}(\vec{r}).$$

At this point again we have to use the assumption that the spin field is approximately parallel to $\hat{B}_0$. As a result we can approximate the change in kinetic energy by

$$\frac{\partial T_{ni}}{\partial\hat{B}_0}=\frac{\partial}{\partial\hat{B}_0}\sum_{occ}\epsilon_n$$

which is the force theorem.

APPENDIX B: SPIN ROTATIONS

Two useful identies with Pauli spin matrices are

$$(\vec{A}\cdot\vec{\sigma})(\vec{C}\cdot\vec{\sigma})=\vec{A}\cdot\vec{C}+i\vec{\sigma}\cdot(\vec{A}\times\vec{C})$$

and

$$U_R=e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}=\cos\left(\frac{1}{2}\theta\right)-i\sin\left(\frac{1}{2}\theta\right)\hat{n}\cdot\vec{\sigma}.$$

These identities are needed to show that

$$e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}(\vec{A}\cdot\vec{\sigma})e^{+(i/2)\theta\hat{n}\cdot\vec{\sigma}}=(\hat{n}\cdot\vec{A})(\hat{n}\cdot\vec{\sigma})+\cos(\theta)[(\vec{A}\cdot\vec{\sigma})-(\hat{n}\cdot\vec{A})(\hat{n}\cdot\vec{\sigma})]+\sin(\theta)\vec{\sigma}\cdot(\hat{n}\times\vec{A}).$$

If the vector $\vec{A}$ is parallel to $\hat{n}$, the second and third terms are zero and $\vec{A}\cdot\vec{\sigma}$ is unchanged. If the vector $\vec{A}$ is orthogonal to $\hat{n}$ we find that $\vec{A}\cdot\vec{\sigma}$ is rotated to $\cos(\theta)(\vec{A}\cdot\vec{\sigma})+\sin(\theta)\vec{\sigma}\cdot(\hat{n}\times\vec{A})$, which corresponds to a rotation of $\vec{A}$ around $\hat{n}$ by an angle θ.

We define the rotation needed to transform the vector $\hat{B}_0$ into an arbitrary vector $\hat{B}$ by the axis of rotation $\hat{n}$ and the angle θ according to

$$\hat{B}_0\cdot\hat{B}=\cos(\theta)\quad\text{and}\quad\hat{B}_0\times\hat{B}=\sin(\theta)\hat{n}.$$

This leads to

$$e^{-(i/2)\theta\hat{n}\cdot\vec{\sigma}}(\vec{B}_0\cdot\vec{\sigma})e^{+(i2)\theta\hat{n}\cdot\vec{\sigma}}=\vec{B}\cdot\vec{\sigma}.$$

Finally, some useful relations are

$$\begin{aligned}(\vec{A}\cdot\vec{\sigma}\times\vec{\nabla})(\vec{\sigma}\cdot\vec{\nabla})&=(\vec{\sigma}\cdot\vec{\nabla}\times\vec{A})(\vec{\sigma}\cdot\vec{\nabla})\\&=(\vec{\nabla}\times\vec{A})\cdot\vec{\nabla}+i\vec{\sigma}\cdot[(\vec{\nabla}\times\vec{A})\times\vec{\nabla}]\\&=i\vec{\sigma}\cdot[\vec{A}\Delta-(\vec{A}\cdot\vec{\nabla})\vec{\nabla}]\end{aligned}$$

$$(\vec{\sigma}\times\vec{A})(\vec{\sigma}\cdot\vec{B})=\vec{B}\times\vec{A}+i(\vec{B}\times\vec{\sigma})\times\vec{A}$$

$$(\vec{\sigma}\cdot\vec{B})(\vec{\sigma}\times\vec{A})=\vec{B}\times\vec{A}-i(\vec{B}\times\vec{\sigma})\times\vec{A}.$$

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