Research articles

Can the correspondence principle lead to improper relations between the uniaxial magnetic anisotropy constant *K* and the axial zero-field splitting parameter *D* for adatoms on surfaces?

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ABSTRACT

Studies of magnetic adatoms on surfaces utilize experimental techniques (scanning tunneling microscopy (STM), inelastic tunneling spectroscopy (ITS) and *ab-initio* modeling methods. Several fundamental issues involved in these studies, being of utmost importance in view of potential technological applications, are critically examined and elucidated. This includes applications of the correspondence principle and relationships between the notions: magnetic anisotropy (MA), magnetic anisotropy energy (MAE), single-ion anisotropy (SIA), zero-field splitting (ZFS) as well as spin-flip energy of tunneling electrons and energy barrier to magnetization reversal. Proper quantum–mechanical relations between the uniaxial SIA constant *K* and the axial ZFS parameter *D* valid for the cases $D > 0$ and $D < 0$, as well as integer and half-integer spins, including $S = 1/2$, are derived. These considerations show that direct equating SIA with ZFS is unwarranted, whereas usage of the correspondence principle to justify such equating proves redundant. So-derived improper relations bear detrimentally on interpretation of STM/ITS and *ab-initio* results, e.g. for Co($S = 1$) and Fe($S = 3/2$) on Pt(111) yielding *K* (*aka* 'MAE') values differing from those obtained from the proper relations by 100 and 50 percent, respectively. Implications of confusion concerning the basic tenets for $S = 1/2$ systems, classical versus quantum spin approaches, and applicability of the crucial notions for magnetic adatoms are also discussed.

1. Introduction

Transition-metal (TM) and rare-earth (RE) adatoms on surfaces [1,2] provide examples of the atomic scale and low-dimensional magnets, which have attracted huge interest in view of potential applications for data storage with high-bit density [3–5]. Recent advances in nanotechnology and developments in experimental characterization techniques, e.g. scanning tunneling microscopy (STM) and inelastic tunneling spectroscopy (ITS), have enabled building magnetic lattices using vertical atom manipulation and to probe them locally. This has opened a way to realize quantum–mechanical systems with controlable magnetic anisotropy and study their transitions to the classical limit. Theoretical modeling using semiempirical or *ab-initio* calculations have enabled prediction and verification of experimentally measurable quantities for adatoms on surfaces. However, interpretation of experimental STM, ITS, and/or related data and their meaningful correlation with theoretical results may be detrimentally affected, since imprecise definitions of crucial notions are often employed in optical and electron

magnetic (paramagnetic) resonance (EMR/EPR) spectroscopy [6–12] as well as magnetism [13–18].

The interrelated notions often being confused are embedded in the *physical* Hamiltonians, H_{phys}, which describe the actual physical interactions within a quantum system, and the *effective* spin Hamiltonians (SH), $\widetilde{H}_{spin}$, which describe *effectively* the lowest subsets of the spin energy levels of H_{phys}; for succinct definitions, see, e.g., Refs. [19–22]. To facilitate clarification of the terminological confusions existing in magnetism, optical and EMR spectroscopy, the notions underlying these areas have been systematically defined and their logical interrelationships clarified in the reviews [19–22] with focus on TM and RE ions in crystals and exchange coupled systems, including single molecule magnets. The notions that are most crucial also for description of properties of adatoms on surfaces are: (i) the crystal field (CF) [the ligand field (LF)] Hamiltonians, which are included in the full H_{phys}, (ii) the zero-field splitting (ZFS) [the fine structure] Hamiltonians, $\widetilde{H}_{spin}$, which are included in $\widetilde{H}_{spin}$ for TM and RE with an orbital singlet ground state, and (iii) the notion of magnetic anisotropy (MA)

describing the phenomenon of the dependence of the various magnetic properties of the TM- or RE-based systems on the directions in a crystal or molecule. The latter notion includes, as one of its specific sources, the single-ion anisotropy (SIA) [or *synonymously* the magnetocrystalline anisotropy (MCA)]. The SIA/MCA and other MA sources, e.g. anisotropic exchange interactions, give rise to the magnetic anisotropy energy (MAE). This macroscopic quantity, MAE, is expressed in terms of the magnetic anisotropy constants K_i. The quantities: spin-flip energy of tunneling electrons, E_{sf}, and the energy barrier to magnetization reversal, $U = U_{eff}$, which are also important in studies of magnetic adatoms, are quantitatively defined in Section 3.

To distinguish inappropriate terminology from appropriate one, a generic definition of confusion between any two distinct notions (A and B) is adopted. The confusion of the type A = B pertains to the cases of incorrect referral to the quantities (QB) associated with the notion B (e.g., ZFS) by the names of the quantities (QA) associated with the notion A (e.g. CF). The quantities may comprise Hamiltonians, eigenfunctions, energy level splitting, or associated parameters. Such terminological confusion arises due to disregarding the well-accepted meaning of the given notions: A and B. The MA = ZFS confusion, dominant in adatoms' studies, is defined [19,23,24,25] as referring to the actual ZFS quantities [6–12,19–22] as the "MA (MAE, SIA/MCA)" quantities [13–19]. This confusion arises from direct equating the notion MA (MAE, SIA/MCA) with the ZFS notion, which is unwarranted. Specific cases of the MA = ZFS confusion in adatoms' studies [26–29] have been discussed [30] in the context of the non-standard ZFS parameter sets [31]. To a lesser extent, also the CF = ZFS confusion (i.e. referring to the ZFS quantities as the "CF/LF" quantities [19–25]) and the inverse ZFS = CF confusion (i.e. referring to the CF/LF quantities as the "ZFS" quantities [22]) have occurred in adatoms' studies [32]. The clarifications [30,32] illustrate that clear distinction between the ZFS quantities and the MA (MAE, SIA/MCA) quantities as well as the CF/LF quantities is indispensable for proper interpretation of experimental and theoretical data on magnetic properties of the TM- or RE-based systems.

In this paper, we attempt to solve the dilemma posed by the title question. To this end, several fundamental issues involved in recent studies of magnetic adatoms on surfaces [33–38] are revisited based on the definitions of the crucial notions [6–25]. Keeping in mind the *Caveat* [39], it is shown that the MA = ZFS confusion occurring in Refs. [33–38] creates not only an ambiguity concerning the actually measured or calculated quantities, but may also lead to incorrect numerical results. The organization of this paper is as follows. Theoretical background, including the correspondence principle, methods of estimation of: (i) the uniaxial SIA constant K from the knowledge of the axial ZFS parameter D and (ii) D from the measured E_{sf} values, are discussed in Section 2. Results of the quantum–mechanical derivations of proper relations between SIA constants and ZFS parameters are presented in Section 3, together with implications of these relations. In Section 4 pertinent aspects concerning the classical spin approach versus quantum spin approach are considered as well as interpretation and applicability of the crucial notions in magnetic adatoms' studies are discussed. Summary and conclusions are given in Section 5.

2. Theoretical background

Recent descriptions of adatoms [33–38] in terms of MA (MAE, SIA/MCA) and ZFS have been strongly influenced by the pioneering work [40]. An inspection of Ref. [40] reveals that the hard axis magnetization curve of the sizable clusters of magnetic impurities was fitted using a classical Hamiltonian. The MAE constant K (9.3 $\pm$ 1.6 meV/Co atom) [40] was determined by measuring the cluster magnetization parallel to the magnetic field $\boldsymbol{B}$ assuming uniaxial MAE term $-nK(sin\theta_0 sin\theta cos\phi + cos\theta_0 cos\theta)^2$. Later it has become clear that the magnetization curve will not follow the simple classical theory but has to be described by the partition function of the quantum system in a

magnetic field, see, e.g., Ref. [41]. Since the finite-sized magnetic nanoparticles were considered, application of the notion of MAE for their description in [40] was justified. Following the approach [40], several authors observing single impurities by ITS used a quantum–mechanical description based on the measured values of E_{sf} (see, Section 3). However, to make connection to the results [40], a classical MA was estimated using the correspondence principle [33–38]. This procedure invoked specific relations between the MA constant K (defined in, e.g., Refs. [13–19]) and the ZFS parameters D (defined in, e.g., Refs. [6–12,19–23]).

For the sake of clarify let's recall two aspects. (i) In general, the phenomenon of MA in bulk magnets may be due to either the anisotropic exchange interactions and/or the single-ion contributions [13–19]. The latter originate for the TM ions and the S-state RE ions (Gd^{3+}, Eu^{2+}) from the single-ion ZFS terms ($\tilde{H}_{ZFS}$), whereas for other RE ions from the CF/LF effects within a given ground $J(f^N)$-multiplet. The MA of this origin is known as SIA or MCA. (ii) The correspondence principle [42] states that behavior of physical systems described by quantum mechanics reproduces classical physics in the limits of large quantum numbers, i.e. for large orbits and energies classical theory has to be recovered.

The correspondence principle has first been invoked to estimate K using D and E_{sf} values for Fe and Co adatoms and their small clusters on Pt(111) surface [33] and later for other systems [34–38]. However, estimation [33–38] of K using the measured values of E_{sf} and D involving this principle requires reconsideration. To illustrate the problem, let's quote [33]: *'the uniaxial anisotropy energy DS_z^2 (D < 0 for easy axis out of plane)'*, arising *'in the quantum limit,* i.e. *for an isolated magnetic object with spin S'*, was linked with MAE, i.e. *'the classical uniaxial MAE $Kcos^2 \theta$ by the correspondence principle $cos\theta = S_z/S$ (θ is the angle of the magnetization with respect to the surface normal)'*. The relations were derived: *'For known S, K can be estimated as $E_{sf} \times S^2/(2S-1)$ and $|D|(2S-1) = E_{sf}$'*. The name *'anisotropy energy '* [33] may be misleading, since the operator DS_z^2, representing the axial term in $\tilde{H}_{ZFS}$, accounts for SIA and hence shall not be directly equated with SIA [13–19,23–25]. The relation [33]: $|D|(2S-1) = E_{sf}$ is valid for integer and half-integer spin S, and arises from the energy levels within an S-multiplet assuming $D < 0$ (see, Fig. 1 in Section 3). To obtain the $K \propto E_{sf}$ relation, one must assume: $K = |D|S^2$, then putting $|D| = E_{sf}/(2S-1)$ yields: $K = E_{sf}S^2/(2S-1)$. This relation was used to obtain K values (referred to as 'MAE') from experimental E_{sf} values and to compare with DFT/*ab-initio* calculations [33]. It turns out that the relation [33]: $K = |D|S^2$ neither arises directly from the correspondence principle nor can be justified by this principle. In fact, the classical MA energy (MAE) was first equated [33] with its quantifying constant (K), which is unwarranted since MAE $\neq K$, then "MAE = K" was equated with the maximal ZFS energy within the S-multiplet (S) (see, Fig. 1). The relation: (S) = $|D|S^2$ is valid for $D > 0$ and $D < 0$ but only for integer spins.

Survey of papers citing Ref. [33] reveals no criticism of the above relations, while the correspondence principle was similarly invoked [34–36] to equate SIA with the ZFS. Specific problems identified in Refs. [34–36] are as follows. Assuming a ferromagnetic coupling for Fe ($S = 3/2$) and Co($S = 1$) clusters, the classical MAE was extracted [34] from the observed energies E_{sf}. The approach [33] was used to interpret the MAE of Gd atoms determined by detecting the inelastic spin-flip excitation with ITS [35]. The relationship [33] between MAE and ZFS was expressed using the total angular momentum $\boldsymbol{J}$ for the S-state Gd^{3+} atoms [35] exhibiting no orbital momentum $\boldsymbol{L}$ ($\boldsymbol{J} \equiv \boldsymbol{S}$). Invoking the correspondence principle, the relation [36]: $K = -DS^2$ was explicitly stated, then the energy of threshold voltage given as: $eV_{sf} = D((S-1)^2 - S^2)$ yielded *'the classical uniaxial anisotropy'*: $K = eV_{sf}S^2/(2S-1)$.

Other distinct cases of invoking the correspondence principle, identified in magnetic adatoms' studies, are also worth mentioning. To compare spectra and the *'model anisotropy parameter D'* to DFT results, E_a(MAE) was connected with D by the correspondence principle as