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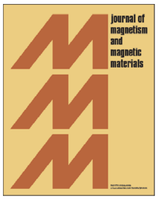

The criterion of magnetism in semiconductor nanoobjects

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ABSTRACT

The Stoner criterion is known as a useful tool predicting the ferromagnetic state (FM) in metals. This criterion is not applied to nanoobjects, because of their discrete electron spectrum. In our paper we consider a generalization of this criterion, which can be applied to magnetism in semiconductor nanoobjects. To derive it, we compare total energies of the FM and non-magnetic states using many-body perturbation theory. The derived criterion has compact form and may be useful for prediction of ferromagnetism in nanoobjects. To check its precision, we performed first-principle calculations of several semiconductor nanoobjects in the FM and non-magnetic states and compared their results with predicted ones.

1. Introduction

Engineering of nanomaterials possessing both semiconductor and magnetic properties is of great importance for spintronics, nanoelectronics, medicine and other applications. Since the atomic structure and properties of small nanoobjects are commonly different from the structure and properties of related solids, characteristics of bulk materials are not reliable guidelines for nanomaterial design. Experimental information about nanoparticles and other artificial nanoobjects frequently is scarce, so pure empirical approach to the design of magnetic nanosemiconductors is not efficient. In this situation, first-principles calculations based on density functional theory (DFT) are among most practical instruments of design. They provide specific and rather reliable results for the characteristics of nanoobjects. For the high efficiency of material quest it is desirable to have the criterion of magnetism in nanosemiconductors, which permits a fast evaluation of promising materials. An example of this type is the famous Stoner criterion widely used for the prediction of magnetism in metallic alloys and compounds [1–4]. The Stoner criterion says that a metal is instable relative to spontaneous magnetization, when $N(E_F)I_m > 1$, where $N(E_F)$ is the electron density of states at the Fermi level and I_m is the Stoner parameter describing exchange–correlation interaction of spins. This criterion does not apply to nanosemiconductors, as for them $N(E_F)=0$, because of the HOMO–LUMO gap and a discrete electron spectrum. Furthermore, the standard derivation of Stoner's criterion from the response to infinitesimally small magnetization is not suitable to nanosystems, where only finite magnetization caused by spin flipping of one electron can be generated. For these reasons the derivation of the magnetism criterion for semiconductor nanoobjects should be based on different approach, which takes into account the features of electronic structure in nanosystems. The present paper contains the derivation of such criterion and its numerical testing by the example of several magnetic and non-magnetic nanoobjects.

2. Theory

In our consideration we deal with a finite semiconductor system having an even number of electrons $N=2n$. The case of an odd number of electrons is not discussed, as it always gives nonzero magnetization. To derive the magnetism criterion, we compare the total energies of states with magnetic moments $M=0\,\mu_B$ and $M=2\,\mu_B$, that is, evaluate energy gain caused by the spin-flipping of one electron. The DFT equation for the total energy of such system at zero temperature is

$$E_{tot} = \sum_{i,\sigma} \varepsilon_{i\sigma} f_{i\sigma} - \sum_{\sigma} \int \mathrm{d}\mathbf{r}\, V_{eff}(\mathbf{r},\sigma)\rho_\sigma(\mathbf{r}) + \int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\rho(\mathbf{r})V_C(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + E_{xc}[\rho, m] \tag{1}$$

Here $\varepsilon_{i\sigma}$ and $V_{eff}(\mathbf{r},\sigma)$ are, respectively, the eigenvalues and efficient potential of the Kohn–Sham equation for electrons with a spin projection σ, $V_C(\mathbf{r}-\mathbf{r}')=e^2/|\mathbf{r}-\mathbf{r}'|$ is the bare Coulomb interaction,

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$\rho(r)=\rho_\uparrow(\mathrm{r})+\rho_\downarrow(\mathrm{r})$ and $m(r)=\rho_\uparrow(\mathrm{r})-\rho_\downarrow(\mathrm{r})$ are electron and spin densities, respectively, and $E_{xc}[\rho,m]$ is the exchange–correlation energy functional. The efficient potential $V_{eff}(r,\sigma)$ is determined by the extremum condition $\delta E_{tot}/\delta\rho_\sigma(r)=0$, which provides $V_{eff}(r,\sigma)=V_{ext}(r)+V_H(r)+V_{xc}(r,\sigma)$, where $V_{ext}(r)$ is the external potential from Eq. (1) (the potential of atomic nuclei), $V_H(r)=\int \mathrm{d}r' V_C(r-r')\rho(r')$ is the Hartree potential, and $V_{xc}(r,\sigma)=\delta E_{xc}[\rho,m]/\delta\rho_\sigma(r)$ is the exchange–correlation potential for electrons with the spin projection σ. In Eq. (1), the sum of the first two terms is the kinetic energy, while the rest terms represent the potential energy (its electron–nuclei, Hartree and exchange–correlation contributions).

The main difference between the nonmagnetic and magnetic states of a system arises from different electron occupation numbers $f_{i\sigma}$. In the nonmagnetic state ($M=0\ \mu_\mathrm{B}$) they are $f_{i\uparrow}=f_{i\downarrow}=1$ for $1\le i\le n$ and $f_{i\uparrow}=f_{i\downarrow}=0$ otherwise, while in the magnetic state with $M=2\ \mu_\mathrm{B}$ there are $f_{i\uparrow}=1$ for $1\le i\le n+1$, $f_{i\downarrow}=1$ for $1\le i\le n-1$ and $f_{i\uparrow}=f_{i\downarrow}=0$ otherwise. This change in occupation numbers causes the change of electron and spin densities and, as a result, changes in the efficient potential $V_{eff}(r,\sigma)$ and the eigenvalues $\varepsilon_{i\sigma}$. We introduce following notations for changes in the spin-components of density $\Delta\rho_\sigma(r)=\tilde{\rho}_\sigma(r)-\rho(r)/2$ (quantities related to the magnetic state are marked by a wave at the top):

$$\Delta\rho_\uparrow(r)=\Delta\rho_{ext\uparrow}(r)+\delta\rho_\uparrow(r)=|\psi_{n+1}(r)|^2+\delta\rho_\uparrow(r)$$
$$\Delta\rho_\downarrow(r)=\Delta\rho_{ext\downarrow}(r)+\delta\rho_\downarrow(r)=-|\psi_n(r)|^2+\delta\rho_\downarrow(r) \tag{2}$$

Here $\Delta\rho_{ext,\sigma}(r)$ are changes in density spin-components caused by the reoccupation of n-th and $n+1$-th electron states, which act as an external perturbation, while $\delta\rho_\sigma(r)$ are changes caused by electron response to $\Delta\rho_{ext,\sigma}(r)$, that is, electronic correlations. In a similar manner, introducing $\Delta\rho(r)=\Delta\rho_\uparrow(r)+\Delta\rho_\downarrow(r)=\Delta\rho_{ext}(r)+\delta\rho(r)$ and $m(r)=\Delta\rho_\uparrow(r)-\Delta\rho_\downarrow(r)=m_{ext}(r)+\mu(r)$, it is easy to express changes in $V_{eff}(r,\sigma)$ in the terms of Coulomb and exchange–correlation interactions:

$$\Delta V_{eff}(\mathrm{r},\ \sigma)=\int \mathrm{d}\mathrm{r}'\ V_c(\mathrm{r},\mathrm{r}')\ \ \Delta\rho_\sigma(\mathrm{r}')-I_{xc}(r)\,\Delta\rho(r)-I_m(r)m(r) \tag{3}$$

where the exchange–correlation interactions are of both charge–charge and spin–spin types: $-I_{xc}(r,r')=\delta^2E_{xc}/\delta\rho(r)\delta\rho(r')$ and $-I_m(r,r')=\delta^2E_{xc}/\delta m(r)\delta m(r')$.

Our derivation assumes that changes in electronic structure caused by transition from the state $M=0\ \mu_\mathrm{B}$ to the state $M=2\ \mu_\mathrm{B}$ are rather small and their effect can be estimated with perturbation theory. Using expansion to the second order in $\Delta\rho_\sigma(r)$ and $\Delta V_{eff}(r,\sigma)$, we obtain for changes in the kinetic energy of the system:

$$\Delta E_{kin}=(\varepsilon_{n+1}-\varepsilon_n)$$
$$-\tfrac{1}{2}\sum_\sigma\int \mathrm{d}r\ \Delta V_{eff}(r,\sigma)\,\delta\rho_\sigma(r)-\int \mathrm{d}r\Delta\rho(r)V_{eff}(r) \tag{4}$$

This equation was obtained by expanding the sum of one-electron energies $\tilde{\varepsilon}_{i\sigma}$ in powers of $\Delta V_{eff}(r,\sigma)$ (to the second order) and combining result with $\int \mathrm{d}r\tilde{\rho}_\sigma(r)\tilde{V}_{eff}(r,\sigma)$ expressed through $\Delta\rho_\sigma(r)$ and $\Delta V_{eff}(r,\sigma)$. Similar expansion of the potential energy contribution provides:

$$\Delta E_{pot}=\int \mathrm{d}r\ \Delta\rho(r)\ \ V_{eff}(r)+\frac{1}{2}\int \mathrm{d}r\mathrm{d}r'\Delta\rho(r)\ \left[V_C(r-r')-I_{xc}(r,r')\right]$$
$$\Delta\rho(r')-\frac{1}{2}\int \mathrm{d}r\mathrm{d}r' m(r)I_m(r,r')m(r') \tag{5}$$

The last term in Eq. (4) and the first term in Eq. (5) are of the first order in $\Delta\rho(r)$. These terms are identical and have opposite signs. In the total energy they cancel each other, so ΔE_{tot} contains only the eigenvalue difference of reoccupied electron states $(\varepsilon_{n+1}-\varepsilon_n)$ and the terms of the second order:

$$\Delta E_{tot}=(\varepsilon_{n+1}-\varepsilon_n)-\frac{1}{2}\sum_\sigma\int \mathrm{d}r\Delta V_{eff}(r,\sigma)\,\delta\rho_\sigma(r)$$
$$+\frac{1}{2}\int \mathrm{d}r\mathrm{d}r'\Delta\rho(r)\left[V_C(r-r')-I_{xc}(r,r')\right]\Delta\rho(r')$$
$$-\frac{1}{2}\int \mathrm{d}r\mathrm{d}r' m(r)I_m(r,r')m(r') \tag{6}$$

The total cancellation of first order terms in Eq. (6) is an expected result of the extremum condition $\delta E_{tot}/\delta\rho_\sigma(r)=0$. For practical use it is convenient to express $\Delta V_{eff}(r,\sigma)$, $\delta\rho_\sigma(r)$, $\Delta\rho(r)$ and $m(r)$ in terms of “external” perturbations $\Delta\rho_{ext}(r)=|\psi_{n+1}(r)|^2-|\psi_n(r)|^2$ and $m_{ext}(r)=|\psi_{n+1}(r)|^2+|\psi_n(r)|^2$:

$$\Delta\rho(r)=\hat{\varepsilon}^{-1}\,\Delta\rho_{ext}(r)$$
$$=\int \mathrm{d}r'\left\{\delta(r-r')+\int \mathrm{d}r''\pi_0(r,r'')\left[V_C(r''-r')-I_{xc}(r'',r')\right\}^{-1}\Delta\rho_{ext}(r')\right.$$
$$m(r)=\hat{f}_m\ m_{ext}(r)$$
$$=\int \mathrm{d}r'\left\{\delta(r-r')-\int \mathrm{d}r''\pi_0(r,r'')I_{xc}(r'',r')\right\}^{-1}m_{ext}(r') \tag{7}$$

Here ε is the dielectric function operator, f_m is an operator causing spatial redistribution of spin moment, and $-\pi_0(r,r')$ is the susceptibility of non-interacting electrons. Using these equations, we obtain from Eq. (6) the final formula for ΔE_{tot}:

$$\Delta E_{tot}=(\varepsilon_{n+1}-\varepsilon_n)+\int \mathrm{d}r\mathrm{d}r'\Delta\rho_{ext}(r)\hat{\varepsilon}^{-1}\left[V_C(r-r')-I_{xc}(r,r')\right]$$
$$\times\,\Delta\rho_{ext}(r')-\tfrac{1}{2}\int \mathrm{d}r\mathrm{d}r' m_{ext}(r)\hat{f}_m\ I_m(r,r')\,m_{ext}(r') \tag{8}$$

Considering this equation, we see that transition to the magnetic state reduces the total energy of a system $\Delta E_{tot}<0$, if its non-magnetic state has a narrow HOMO–LUMO gap $\Delta_{HOMO-LUMO}=\varepsilon_{n+1}-\varepsilon_n$, the spatial redistribution of electron charge $\Delta\rho_{ext}(r)$ does not increase significantly Coulomb energy, and the spin–spin interaction provides a large energy gain. These are qualitative requirements to a nanoobject for its spontaneous transition to the magnetic state.

It is of interest to compare Eq. (8) with the Stoner criterion. One may note that Eq. (8) contains the contribution arising from spatial charge redistribution $\Delta\rho_{ext}(r)$. This contribution is absent in the Stoner criterion related to metals, as for them only small magnetization with $\psi_{n+1}(r)\approx\psi_n(r)$ is considered, so for metals $\Delta\rho_{ext}(r)\approx 0$ and $m_{ext}(r)\approx 2|\psi_n(r)|^2$. With this refinement and considering inverse energy difference $2/(\varepsilon_{n+1}-\varepsilon_n)$ as a discrete analog of $N(E_F)$, we get the conclusion that for metals the present criterion transforms exactly to Stoner's one.

3. Calculations

To check the derived criterion, we calculated the electronic structure and spin polarization of four semiconductor organic molecules: the phthalocyanines of nickel, iron and chromium (NiPc, FePc, and CrPc), as well as the bis(benzene)chromium molecule Cr(Bz)$_2$. These molecules containing magnetic atoms have the planar (MPc, M=Ni, Fe, and Cr) or sandwich-type (Cr(Bz)$_2$) structure with the diameter of 1.0–1.5 nm (Fig. 1) and their magnetic properties (or nonmagnetic behavior) are known from experiment [5,6].

Our first-principles calculations were made by the ORCA code [7] with effective core potential basis sets from EMSL basis set library [8–10]. The Stuttgart–Dresden–Bonn pseudopotentials [9,10] and DFT approach with the exchange–correlation functional PWLDA [11] were used. The relaxation of atoms to their equilibrium positions was conducted until forces acting on atoms

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