



# Electronic and magnetic properties of semiconducting nanoclusters and large organic molecules: Features interesting for spintronics

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## ABSTRACT

Spin properties of single-doped and single-electron charged nano-systems having an odd number of electrons are studied. Starting from an expression for quasiparticle energies in the GW approximation, a simple analytical expression for the spin-splitting of an electron spectrum in such system is derived. First-principles calculations by the DFT–GGA, Hartree-Fock, GW- and hybrid functional methods, which were performed for the silicon clusters and metal phthalocyanine molecules of 1 nm diameter, support this analytical consideration. They show that the spin-splitting energy calculated by the DFT–GGA method is about one order lower, than the results obtained with the methods based on the many-electron theory. A large value of spin-splitting in investigated nano-systems, which is typically of several eV, has an origin in strong localization of electrons and weak screening of exchange interaction. A possible use of this effect in spintronic applications is discussed.

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## 1. Introduction

Progress in nanotechnology offers us possibility to operate semiconductor systems of several nanometers in size (quantum dots, nanoclusters, and colloidal nanocrystals). Even a few doping atoms essentially modify properties of such small systems. For an example, one impurity atom introduced into the silicon cluster of 3 nm in size provides the carrier concentration of  $7 \times 10^{19} \text{ cm}^{-3}$  that corresponds to a heavily doped semiconductor. The same carrier concentration can be provided by charging the semiconductor cluster by an electron or a hole. Such semiconducting systems often display properties promising for applications. For example, the InAs quantum dots of 2.8 nm in size, which were charged by one electron, show a doublet splitting of 0.25 eV in the tunneling conductance spectrum [1]. The optical spin orientation experiments performed on a single Mn atom imbedded into a CdSe quantum dot, demonstrated an anomalously long spin lifetime of  $\mu\text{s}$  time scale [2]. These facts indicate that single-doped and single charged semiconductor nanosystems can be of significant interest for spintronics and optoelectronics. Their development has a solid technological ground, as several well controlled fabrication methods for nanostructures with single dopants have

been described (see as examples [3,4]). In this paper we focus on the theoretical study of single-dopant and single charged semiconductor nanosystems and large organic molecules, which have an odd number of electrons. These nanosystems and molecules have a spin moment (of  $1 \mu_B$ , as a rule), even if magnetic atoms are absent in their composition. We show that the presence of the spin moment splits the electron spectrum of small nanosystems very significantly and this effect can be of practical interest.

## 2. Theory

The density functional theory (DFT) reproduces correctly the ground state properties of solids (the total energy, elastic properties, electron density, etc), but fails in predicting the quasiparticle energy spectrum of semiconductors and dielectrics, in particular, the gap width (see, for an example, [5,6]). Both the ground state properties and the quasiparticle spectrum can be successfully described with the GW approximation to the many-electron theory. In this approximation the energies of non-relativistic quasi-particles  $E_{n,\sigma}$  ( $\sigma$  is the index of spin-projection) are the eigenvalues of an integro-differential equation:

$$\left[ \frac{\hat{p}^2}{2m} + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) \right] \psi_{n,\sigma}(\mathbf{r}) + \int d\mathbf{r}' \Sigma_{\sigma}(\mathbf{r}, \mathbf{r}', E_{n,\sigma}) \psi_{n,\sigma}(\mathbf{r}') = E_{n,\sigma} \psi_{n,\sigma}(\mathbf{r}) \quad (1)$$

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Here  $V_{\text{ext}}(\mathbf{r})$  and  $V_H(\mathbf{r})$  are the external and Hartree potentials, respectively and  $\Sigma_\sigma(\mathbf{r}, \mathbf{r}', E)$  is the self-energy operator, which is given by an expression [7]:

$$\Sigma_\sigma(\mathbf{r}, \mathbf{r}', E_{n,\sigma}) = -\sum_i f_{i,\sigma} \psi_{i,\sigma}(\mathbf{r}) \psi_{i,\sigma}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}', E_{i,\sigma} - E_{n,\sigma}) + \sum_i \psi_{i,\sigma}(\mathbf{r}) \psi_{i,\sigma}^*(\mathbf{r}') \int dE' \frac{\text{Im}\{W(\mathbf{r}, \mathbf{r}', E')\}}{E_{i,\sigma} - E_{n,\sigma} - E'} \quad (2)$$

where  $f_{i,\sigma}$  are electron occupation numbers and  $W(\mathbf{r}, \mathbf{r}', E)$  is the dynamically screened Coulomb interaction. In Eq. (2) the main dependence on a spin index  $\sigma$  goes from the electron occupation numbers  $f_{i,\sigma}$ , while the wave functions  $\psi_{i,\sigma}(\mathbf{r})$  (we speak here about the spatial part of  $\psi_{i,\sigma}(\mathbf{r})$ , but not its spinor part) and the energy differences  $E_{i,\sigma} - E_{n,\sigma}$  depends on  $\sigma$  much more weakly. Taking this into account, it is possible to estimate the spin-splitting of the quasiparticle spectrum  $\Delta_j$  from Eqs. (1) and (2) as

$$\Delta_j = E_{j,\downarrow} - E_{j,\uparrow} \approx \sum_i \iint d\mathbf{r} d\mathbf{r}' \psi_j^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_j(\mathbf{r}') W(\mathbf{r}, \mathbf{r}', E_{i,\uparrow} - E_{j,\uparrow}) (f_{i,\uparrow} - f_{i,\downarrow}) \quad (3)$$

Here we ignored a weak spin-dependence of the spatial part of wave functions  $\psi_{i,\sigma}(\mathbf{r})$  and of the energy differences  $E_{i,\sigma} - E_{j,\sigma}$ . For this reason the first contribution to l.h.s. of (1), which is proportional to  $[p^2/2m + V_{\text{ext}} + V_H]$ , and the second contribution to r.h.s. of (2) drops out of the Eq. (3) for  $\Delta_j$ . At this stage the special feature of our system, namely, an odd number of electrons becomes important. If the total spin moment of a system is  $1 \mu_B$ , all occupied states  $i$ , excepting one, are occupied by electron pairs and have  $f_{i,\uparrow} = f_{i,\downarrow} = 1$ . If one unpaired electron occupies the state  $i=s$ , then the electron occupation numbers of this state are  $f_{s,\uparrow} = 1$  and  $f_{s,\downarrow} = 0$ . Substituting these occupation numbers in (3), we obtain a simple formula for the spin-splitting energy of the  $s$ -th state:

$$\Delta_s \approx \iint d\mathbf{r} d\mathbf{r}' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') W(\mathbf{r}, \mathbf{r}', 0) \quad (4)$$

where  $\rho_s(\mathbf{r}) = |\psi_s(\mathbf{r})|^2$ . The spin-splitting of other electron states is much weaker, because of the orthogonality between the wave functions  $\psi_{i \neq s}(\mathbf{r})$  and  $\psi_s(\mathbf{r})$ .

As has been noted by several authors [8–11], the averaged dielectric function of small quantum dots is significantly reduced comparing to its bulk value. This reduction greatly affects the spin-splitting  $\Delta_s$ , therefore this effect should be considered in details. The static screened Coulomb interaction  $W(\mathbf{r}, \mathbf{r}', 0)$  contains two contributions: the bare Coulomb interaction  $V_0(\mathbf{r}) = e^2/r$  and an indirect Coulomb interaction caused by electron response:

$$W(\mathbf{r}, \mathbf{r}', 0) = V_0(\mathbf{r} - \mathbf{r}') + \iint d\mathbf{r}_1 d\mathbf{r}_2 V_0(\mathbf{r} - \mathbf{r}_1) \chi(\mathbf{r}_1, \mathbf{r}_2) V_0(\mathbf{r}_2 - \mathbf{r}') \quad (5)$$

Here the integral operator  $\chi(\mathbf{r}, \mathbf{r}') = \delta\rho(\mathbf{r})/\delta V_{\text{ext}}(\mathbf{r}')$  denotes the electron density–density response. This operator is negative definite, as just the operator  $-\chi^{-1}(\mathbf{r}, \mathbf{r}')$  determines the total energy increase produced by the deviation of electron density from its ground state distribution. The GW-approximation suggests that the screened Coulomb interaction  $W(\mathbf{r}, \mathbf{r}', E)$  is described within the random-phase approximation (RPA). In the RPA, the operator  $\chi(\mathbf{r}, \mathbf{r}')$  has a general form:

$$\chi(\mathbf{r}, \mathbf{r}') = \sum_{n,n'} \varphi_n^*(\mathbf{r}) \chi_{n,n'} \varphi_n(\mathbf{r}') \quad (6)$$

where  $n = \{i, f\}$  is a composite index, which combines the indexes of one occupied ( $i$ ) and one unoccupied ( $f$ ) states. Because of the orthogonality between the  $i$ -th and  $f$ -th wave functions, the functions  $\varphi_n(\mathbf{r}) = \psi_i^*(\mathbf{r}) \psi_f(\mathbf{r})$  obey the condition:

$$\int_\Omega d\mathbf{r} \psi_{i,\sigma}^*(\mathbf{r}) \psi_{f,\sigma}(\mathbf{r}) f_{i,\sigma} (1 - f_{f,\sigma}) = \int_\Omega d\mathbf{r} \varphi_n(\mathbf{r}) = 0 \quad (7)$$

where  $\Omega$  is the nano-system volume. Condition (7) assures that electron response conserves electron charge in a nano-system. Using this condition, Eq. (4) can be rewritten as

$$\Delta_s \approx \int_\Omega d\mathbf{r} \rho_s(\mathbf{r}) V_s(\mathbf{r}) + \iint_\Omega d\mathbf{r} d\mathbf{r}' (V_s(\mathbf{r}) - V_s^{av}) \chi(\mathbf{r}, \mathbf{r}') (V_s(\mathbf{r}') - V_s^{av}) \quad (8)$$

where  $V_s(\mathbf{r})$  is a potential generated by the density  $\rho_s(\mathbf{r})$ :

$$V_s(\mathbf{r}) = \int_\Omega d\mathbf{r}' V_0(\mathbf{r} - \mathbf{r}') \rho_s(\mathbf{r}') \quad (9)$$

and  $V_s^{av}$  is its value averaged over  $\Omega$ . The first integral in (8) is the spin-splitting energy corresponding to the Hartree-Fock approximation (the contribution of exchange interaction). The second integral in (8) is the contribution of electronic correlations relating to the screening of exchange interaction. This integral, which describes the effect of electronic response in a nano-system, has the negative sign, as  $\chi(\mathbf{r}, \mathbf{r}')$  which is a negative definite integral operator. A special feature of Eq. (8), which stems from (7), is the substitution of  $\delta V_s(\mathbf{r}) = V_s(\mathbf{r}) - V_s^{av}$  for  $V_s(\mathbf{r})$  in the electronic response term. In large systems this substitution changes nearly nothing, as  $V_s^{av} \rightarrow 0$  at  $\Omega \rightarrow \infty$ . In nano-size systems the averaging over small volume  $\Omega$  provides  $V_s^{av}$ , which is close to  $V_s(\mathbf{r})$ , therefore the absolute value of the response term in (8) is decreased by the factor  $(\delta V_s/V_s)^2 \ll 1$  comparing to the bulk case. This decrease expresses the fact that electronic response in small-size systems is strictly restricted by the charge conservation requirement: the decrease of electronic density in one part of  $\Omega$  should be compensated by its increase in other parts, so the screening of  $V_s(\mathbf{r})$  in one region of  $\Omega$  leads to the anti-screening of  $V_s(\mathbf{r})$  in others.

### 3. Calculation

Eqs. (4) and (8) show that the spin-splitting energy  $\Delta_s$  depends essentially on the spatial distribution of spin density  $\rho_s(\mathbf{r}) = |\psi_s(\mathbf{r})|^2$  and electronic response in a nano-system. To estimate its value numerically, we performed the first-principles studies of the objects of two types: (1) single-charged and phosphorus-doped silicon nanoclusters and (2) single-charged and neutral metal phthalocyanine (MPc) molecules. Our initial nanocluster  $\text{Si}_{35}\text{H}_{36}$  was of 1.1 nm diameter and close to a sphere in shape (Fig. 1a). To gain an odd number of electrons, this cluster was charged by a single electron or doped by a single P atom, which substituted for the central atom of Si in  $\text{Si}_{35}\text{H}_{36}$ . The molecule of metal phthalocyanine has a flat, cross-like shape with a metal atom in the center and the diameter of 1.3 nm (Fig. 1b). The molecule MPc has an odd number of electrons, if the molecule is neutral and a metal atom has it. In the case of an even number of electrons on a metal atom, an odd number of electrons is obtained, if a single electron is added to the molecule or removed from it.

Our first-principles calculations of nanoclusters were performed by the supercell method using the ABINIT code [12] with

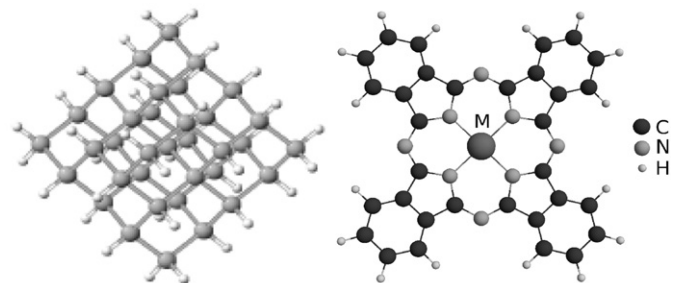


Fig. 1. The atomic structure of two studied nano-size systems: (a) the nanocluster  $\text{Si}_{35}\text{H}_{36}$  (on left) and (b) the molecule of metal phthalocyanine (on right).

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