Electronic quasiparticle spectrum in semiconductor nano-objects

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Contents.

1. Introduction.

✓ At present there is the consensus: the DFT is inadequate for the description of electronic quasiparticle spectrum in semiconductor nano-objects (nanoclusters and large organic molecules).

✓ The GW approximation predicts well the quasiparticle spectra of nano-objects. This approximation provides a simple analytical expression for the self-energy operator, which is simplified further by the discrete character of an electron spectrum in nano-objects.

✓ In this presentation the GW method is used to consider analytically: (i) the effect of electron occupation on the spectrum, (ii) correction to the HOMO-LUMO gap, and (iii) the spin-splitting of the spectrum in magnetic nano-objects.

✓ Our numerical studies (the GW approximation, hybrid functionals, and the DFT-GGA method) were performed for:

(a) charged and doped silicon nanoclusters $Si_{35}H_{36}$,

(b) metal phthalocyanine molecules (MPc).

These calculations support analytical results and provides information which is interesting for nano-electronic and spintronic applications.

1. Basic theory

The Dyson equation for electronic quasiparticle energies is:

$$\left[\frac{\hat{p}^2}{2m} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\psi_n(\mathbf{r}) + \int \mathbf{dr}'\Sigma(\mathbf{r},\mathbf{r}',E_n)\psi_n(\mathbf{r}') = E_n\psi_n(\mathbf{r}) \qquad (1)$$

(a) The self-energy operator *Σ(r,r',E)* in the GW approximation:

$$\Sigma(\mathbf{r},\mathbf{r}',E) = \frac{i}{2\pi}\int dE' G(\mathbf{r},\mathbf{r}',E+E')W(\mathbf{r},\mathbf{r}',E') \qquad (2)$$

It is convenient to write the dynamically screened Coulomb interaction *W(***r**,**r'**,*E)* in the spectral representation:

$$W(\mathbf{r},\mathbf{r}',E) = V_{Coul}(\mathbf{r}-\mathbf{r}') + \int_0^{+\infty} d\Omega \frac{2\Omega B(\mathbf{r},\mathbf{r}',\Omega)}{E^2-\Omega^2+i\delta},$$

$$B(\mathbf{r},\mathbf{r}',E) = -\mathrm{Im}\{W(\mathbf{r},\mathbf{r}',E\} \qquad (3)$$

The Green function *G(***r**,**r'**,*E)* is taken in the quasiparticle form:

$$G(r,r',E) = \sum_m \frac{\psi_m(r)\psi_m^*(r')}{E-E_m+i\delta\cdot\mathrm{sgn}(E_m-\mu)} \qquad (4)$$

After integration over *E'* the matrix element of (1) obtains the form:

$$\Sigma_n \equiv \int \mathbf{dr dr'}\,\psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')\Sigma(\mathbf{r},\mathbf{r}',E_n) = \Sigma_n^{(HF)} + \Sigma_n^{(corr)} \qquad (5)$$

$$\Sigma_n^{(HF)} = -\sum_m f_{m\cdot} \cdot V_{nm}^{Coul}, \quad \text{where} \quad V_{nm}^{Coul} \equiv < m,n \,|\, V_{Coul}(\mathbf{r}-\mathbf{r}') \,|\, n,m >$$

$$\Sigma_n^{(corr)} = -\sum_m \int_0^{+\infty} d\Omega\, B_{nm}(\Omega)\left[\frac{f_m}{E_{mn}-\Omega+i\delta} + \frac{1-f_m}{E_{mn}+\Omega-i\delta}\right] \qquad (6)$$

Here f_m is the occupation number of the m-th electron level ,

$$B_{nm}(\Omega) = < m,n \,|\, B(\mathbf{r},\mathbf{r}',\Omega) \,|\, n,m > \quad \text{and} \quad E_{mn} = E_m - E_n$$

Eq. (6) is the standard expression for a matrix element of the self-energy operator caused by electron-boson interaction. It is simplified further if the features of matrix elements and electronic screening is taken into account.

We note that the matrix elements V_{nm}^{Coul} (and $B_{nm}(\Omega)$) contains the terms of two types:

(i) n=m "charge-charge" interaction:

$$V_{nn}^{Coul} = \int_V \mathbf{dr dr'}\rho_n(\mathbf{r})V_{Coul}(\mathbf{r}-\mathbf{r}')\rho_n(\mathbf{r}'), \quad \text{where } \rho_n(\mathbf{r}) = |\psi_n(\mathbf{r})|^2, \quad \int_V \mathbf{dr}\,\rho_n(\mathbf{r}) = 1 \qquad (7a)$$

(ii) n≠m "dipole-dipole" interaction:

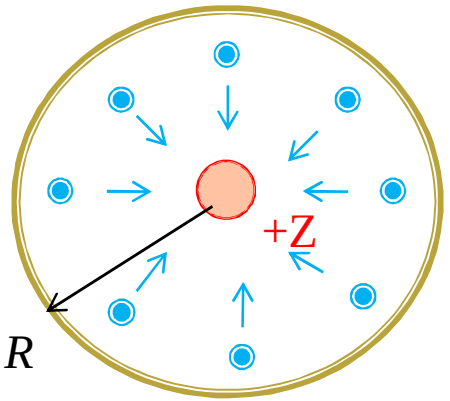
$$V_{nm}^{Coul} = \int \mathbf{dr dr'} d_{nm}^*(\mathbf{r})V_{Coul}(\mathbf{r}-\mathbf{r}')d_{nm}(\mathbf{r}'), \quad \text{where } d_{nm}(\mathbf{r}) = \psi_n(\mathbf{r})\psi_m^*(\mathbf{r}), \quad \int_V \mathbf{dr}\, d_{nm}(\mathbf{r}) = 0 \qquad (7b)$$

In the following, we show that the terms of these two types are very different in value.

(b) Screened Coulomb interaction in nano-objects

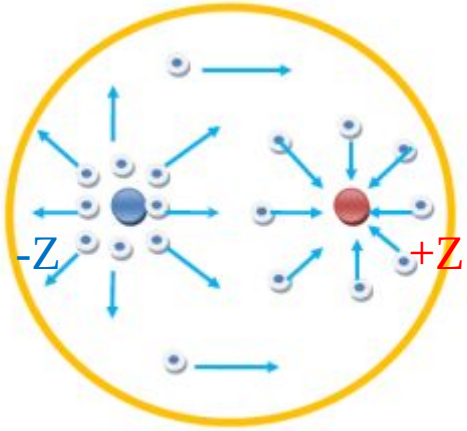
Screening in nano-objects has important features, arising from the conservation of charge in a small spatial region (see *Delerue 2003*, *Ogut 2003*, *Franceschetti 2005*, *Cartoixa 2005*, and *Ninno 2006*). Simple examples are:

Screening of the charge +Z



(a) Near +Z there is electron gain (screening)
(b) Near the boundary there is electron deficit (anti-screening)
(c) Out of the cluster electric field is $+Z/r$ (zero screening)

Screening of the dipole (+Z,-Z)



Electrons move from –Z to +Z and screen dipole field efficiently

In nano-objects, the field of “dipoles” is screened much better than the field of “charges”.

The screened Coulomb interaction *W(**r**,**r**',0)* is given by a general equation:

$$W(\mathbf{r},\mathbf{r}',E) = V_{Coul}(\mathbf{r}-\mathbf{r}') + \iint \mathbf{dr_1 dr}_2 V_{Coul}(\mathbf{r}-\mathbf{r_1})\chi(\mathbf{r_1},\mathbf{r_2},E)V_{Coul}(\mathbf{r_2}-\mathbf{r}') \qquad (8)$$

Here $\chi(\mathbf{r},\mathbf{r}',E) = \dfrac{\delta\rho(\mathbf{r})}{\delta \mathrm{V}_{\mathrm{ext}}(\mathbf{r}',E)}$ is the density-density response function.

The use of the GW approximation implies that the response function $\chi(\mathbf{r},\mathbf{r}',E)$ is calculated by the RPA method. In this method $\chi(\mathbf{r},\mathbf{r}',E)$ has the structure:

$$\chi(\mathbf{r},\mathbf{r}',E) = \sum_{i,i'} \varphi_n^*(\mathbf{r})\chi_{i,i'}(E)\varphi_{i'}(\mathbf{r}') \quad \text{with} \quad i = \{n,m\} \qquad (9)$$

This structure maintains electron charge conservation, because of the orthogonality condition: $\int_V \mathbf{dr}\,\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\,f_n(1-f_m) = \int_V \mathbf{dr}\varphi_i(\mathbf{r}) = 0$

The use of this condition modifies integrals important for matrix elements of the self-energy operator.

$$\int_V \mathbf{drdr}'\rho(\mathbf{r})W(\mathbf{r},\mathbf{r}',E)\rho(\mathbf{r}') = \int_V \mathbf{drdr}'\rho(\mathbf{r})V_{Coul}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + \iint_\Omega \mathbf{drdr}'\delta V_C(\mathbf{r})\chi(\mathbf{r},\mathbf{r}',E)\delta V_C(\mathbf{r}'),$$

where $\delta V_C(\mathbf{r}) = V_C(\mathbf{r}) - \dfrac{1}{V}\int_V \mathbf{dr}V_C(\mathbf{r})$ and $V_C(\mathbf{r}) = \int_V \mathbf{dr}'V_{Coul}(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')$ (10)

For "charge-charge" interaction there exists an inequality $\delta V_C(\mathbf{r}) << V_C(\mathbf{r})$, while for "dipole-dipole" interaction approximate equality $\delta V_C(\mathbf{r}) \approx V_C(\mathbf{r})$ is the case. This fact provides significant difference in screening. For an example, in the cluster of 1 nm in diameter the efficient dielectric function is:

$\varepsilon_{eff} \approx 1.4$ for the "charge-charge" interaction

$\varepsilon_{eff} \approx \varepsilon_{bulk} >> 1$ for the "dipole-dipole" interaction

This difference in the screening of charges and dipoles is the feature of nano-objects.

(c) A small parameter in the GW calculations of nano-objects

We shall show that in nano-objects the matrix elements of the dynamically screened Coulomb interaction obey an inequality $W_{n \neq m}(E) << W_{nn}(E)$, where $E < \hbar \Omega_{plasm}$. This inequality has two origins:

(i) The bare Coulomb interaction of "charges" is much stronger in general than the interaction of "dipoles". Several example demonstrating this statement are:

(a) The spherical model cluster of 1.6 nm in diameter (the zero boundary condition, $\psi_n(\mathbf{r}) = i^l j_l(kr) Y_L(\mathbf{r}/r)$).

$V_{00}^{Coul} = 3.2$ eV and $V_{01}^{Coul} = 0.6$ eV.

(b) The nanocluster $Si_{35}H_{36}$.

$V_{nn}^{Coul} \approx 3.5$ eV and $V_{n \neq m}^{Coul} \approx 0.05\text{-}0.1$ eV

(c) Organic molecule CuPc.

$V_{nn}^{Coul} \approx 4\text{-}15$ eV and $V_{n \neq m}^{Coul} \approx 0.1$ eV

(ii) Non-diagonal matrix elements are further suppressed by a much better screening of Coulomb interaction.

These examples show that in semiconductor nano-objects the ratio $W_{n\neq m}/W_{nn}$ is as small as 0.01-0.05. This ratio can be considered as a small parameter of GW calculation in nanoclusters and large organic molecules. It is probable that this ratio remains small even in the case of bulk semiconductors. We note that *L. Hedin* made a similar assumption for a uniform electron gas model in 1965. However in the case of metallic screening, when the interaction $W(\mathbf{r},\mathbf{r}',E)$ has short-range behavior, the inequality $W_{n\neq m}/W_{nn} << 1$ is hardly justified. It can be used only for rough qualitative estimates.

(d) The HOMO-LUMO gap and the spin-splitting of a quasiparticle spectrum

The formulas of the GW method are greatly simplified in the zero order over $W_{n\neq m}/W_{nn}$. In particular, equations (5) and (6) take the form:

$$\Sigma_n \approx -\frac{1}{2}V_{nn}^{Coul} + \frac{1}{2}\left[(1-f_n)W_{nn}(0) - f_n W_{nn}(0)\right] \qquad (11)$$

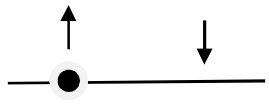
Using (11), it is easy to find that the contribution of exchange-correlation processes to the HOMO-LUMO gap width is:

$$\Delta E_g = \Sigma_{n=LUMO} - \Sigma_{n=HOMO} \approx \frac{1}{2}\left[W_{nn=LUMO}(0) + W_{nn=HOMO}(0)\right] \qquad (12)$$

A similar equation was suggested for bulk semiconductors by E. Maksimov, I. Mazin, S. Savrasov, and Yu. Uspenskii in 1987.

The spin splitting of the electron levels depends on their occupation. There are two different situations:

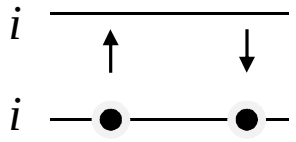
(1) The electron state $s\uparrow$ is occupied and $s\downarrow$ is unoccupied.



$$\Delta_s = \Sigma_{s\downarrow} - \Sigma_{s\uparrow} \approx \frac{1}{2}\left[W_{ss\downarrow}(0) + W_{ss\uparrow}(0)\right] \qquad (13)$$

(Yu. Uspenskii, E. Kulatov, A. Titov, E. Tikhonov et al, 2011)

(2) Both electron states $i\uparrow$ and $i\downarrow$ are occupied or unoccupied.



or

In the zero order over $W_{n\neq s}/W_{ss}$ the answer is:

$$\Delta_{n\neq s} = \Sigma_{n\downarrow} - \Sigma_{n\uparrow} \approx 0 \qquad (14)$$

In the first order over $W_{n\neq s}/W_{ss}$ the spin splitting of fully occupied or fully empty electron states is:

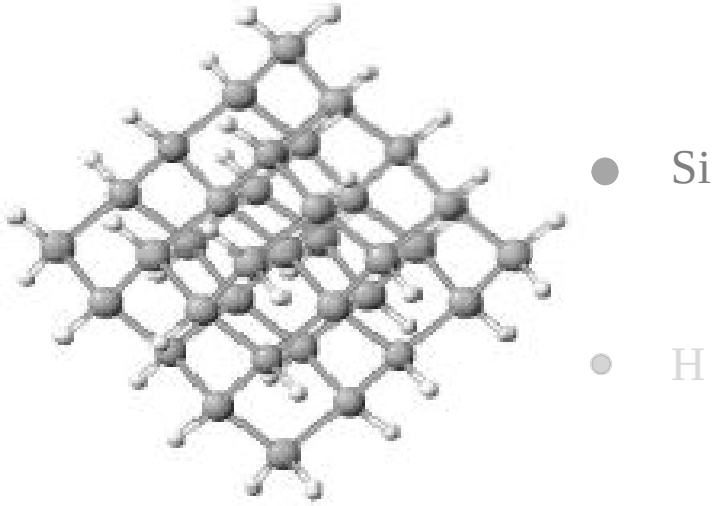
$$\Delta_{n\neq s} = \Sigma_{n\downarrow} - \Sigma_{n\uparrow}$$

$$= \sum_s W_{ns\uparrow}(E_{sn\uparrow}) - \sum_s \int_0^{+\infty} d\Omega \left[\frac{B_{ns\downarrow}(\Omega)}{E_{sn\downarrow} + \Omega - i\delta} - \frac{B_{ns\uparrow}}{E_{sn\uparrow} + \Omega - i\delta} \right]$$

$$\approx \sum_s W_{ns\uparrow}(E_{sn\uparrow}), \quad \text{if} \quad E_{sn\uparrow} \equiv E_{s\uparrow} - E_{n\uparrow} \geq 0 \qquad (15)$$

A large increase of $\Delta_{n\neq s}$ at $E_{sn\uparrow} \approx \hbar\Omega_{plasm}$ may provide a satellite = spin excitation + plasmon, which is analogous to "plasmaron"= one-electron excitation + plasmon.

3. Gap-narrowing in charged and doped silicon nanoclusters



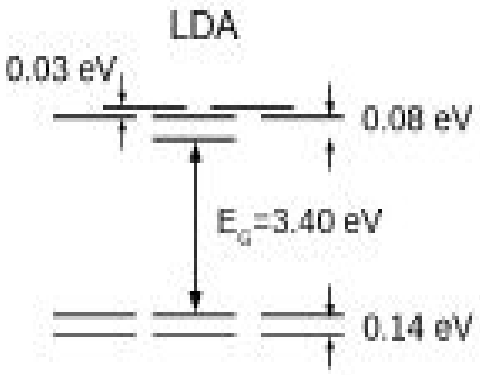
Initial $Si_{35}H_{36}$ cluster

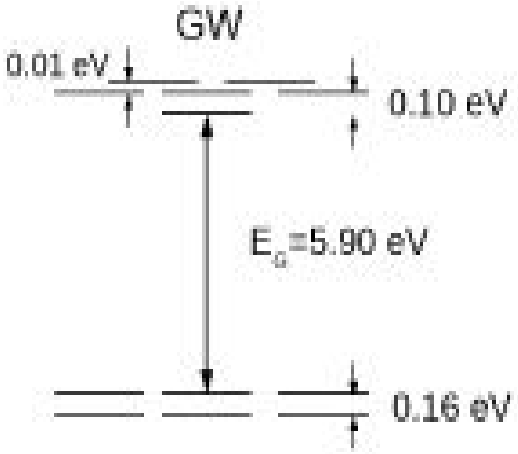
We studied the nanocluster $Si_{35}H_{36}$ doped by a single atom P or charged by a single electron.

Computational details

The calculations were performed with the GGA and GW methods using the ABINIT code. The Troullier-Martin norm-conserving pseudopotentials were used for atoms. The cluster was modelled with the supercell approach and periodic boundary conditions.

A simple estimate: $\Delta Eg \approx V_{nn}^{Coul}/\varepsilon_{eff} = 3.5\text{eV}/1.4 = 2.5$ eV





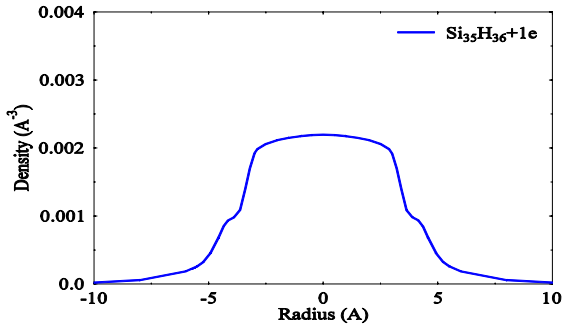
The electronic structures calculated by the GGA and GW methods are very different, as it has been observed for semiconductors and insulators

Table 1. Spin-splitting of several electron levels in $Si_{34}PH_{36}$ (in the HF approximation)

N	86-88	89	90-92
$E\uparrow$ (eV)	-7.00	-0.98	+2.85
$E\downarrow$ (eV)	-6.95	+2.56	+2.96

Spin density distribution $\rho_{s\uparrow}(\mathbf{r})=|\psi_{s\uparrow}(\mathbf{r})|^2$.

$Si_{35}H_{36}$+1e



$Si_{34}PH_{36}$

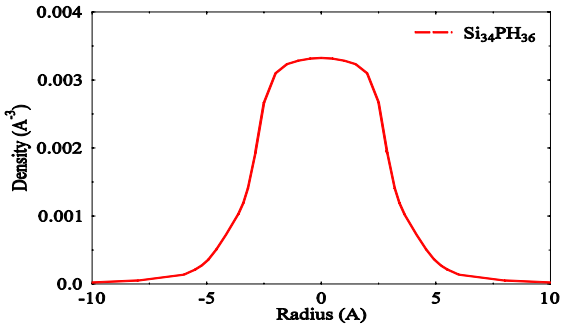


Table 2. Spin splitting in silicon nanoclusters.

Nano-system	ε_{eff}	Δ_s^{DFT}	Δ_s	$\Delta_s^{HF}/\varepsilon_{eff}$
$Si_{35}H_{36}$+1e	**1.38**	**0.08**	**2.27**	**2.15**
$Si_{34}PH_{36}$	**1.32**	**0.11**	**2.59**	**2.68**

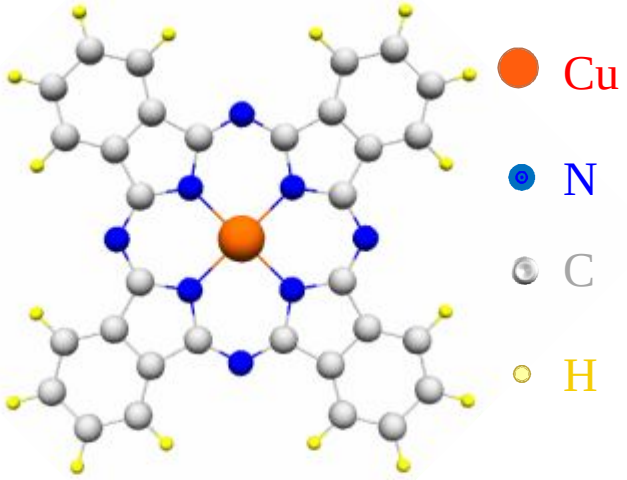
The effect of gap-narrowing caused by one electron added to the cluster by charging or doping is seen from the analytical formula:

$$\Sigma_n^{(0)} = -\frac{1}{2}V_{nn}^{Coul} + \frac{1}{2}(1-2f_n)W_{nn}(0)$$

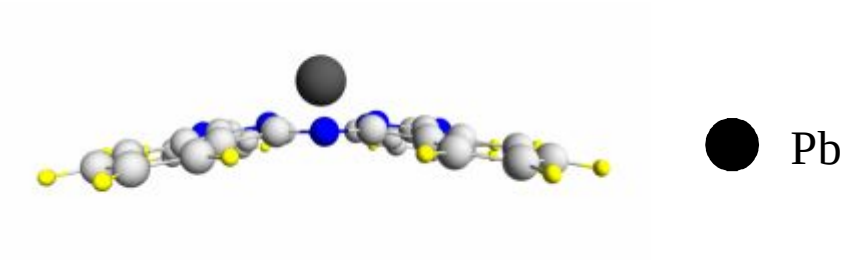
Predicted values ΔE_g are: 2.2 eV (for charging) 2.7 eV(for P-doping). They agree reasonably with direct numerical calculation by the GW method: 2.7 eV and 3.1 eV.

4. Photoemission spectra of metal phthalocyanine molecules (MPc).

CuPc has planar structure.



PbPc, as an example of non-planar MPc .

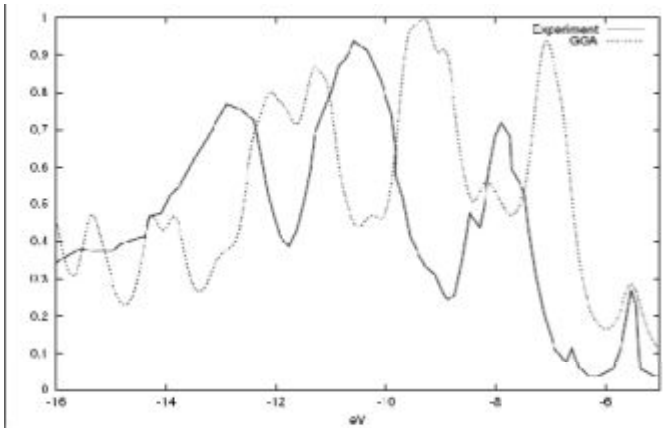


Properties of MPc

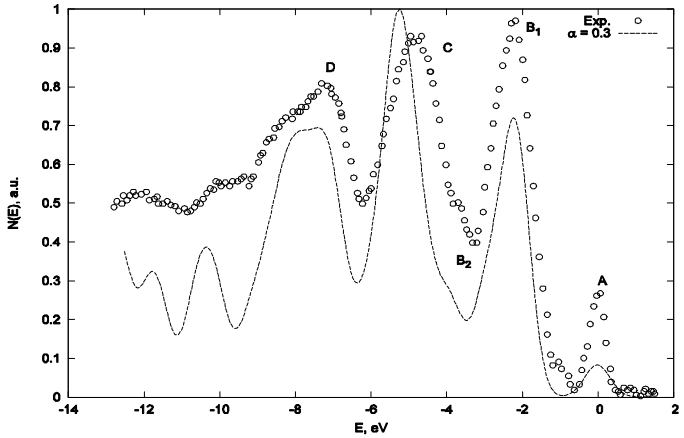
- MPc can be synthesized with the pureness of 10^{14}-10^{16} impurity atoms in 1 cm^3, which is record for organic materials.
- MPc are thermally and chemically resistive. They are stable up to 400-600 C in air and up to 900 C in vacuum.
- MPc form a wide class of organic molecules, as the most of chemical elements can play a role of M atoms.

The analysis of photoemission spectra provides information about the electron quasiparticle spectrum. In rough approximation one can assume that $I_{photoemiss}(E) \approx const \cdot N(E)$. We calculated the quasiparticle spectra of several MPc by the hybrid functional method with a varied parameter $\alpha \approx 1/\varepsilon_{eff}$ and compared the density of state $N(E)$ with the experimental spectra of $I_{photoemiss}(E)$.

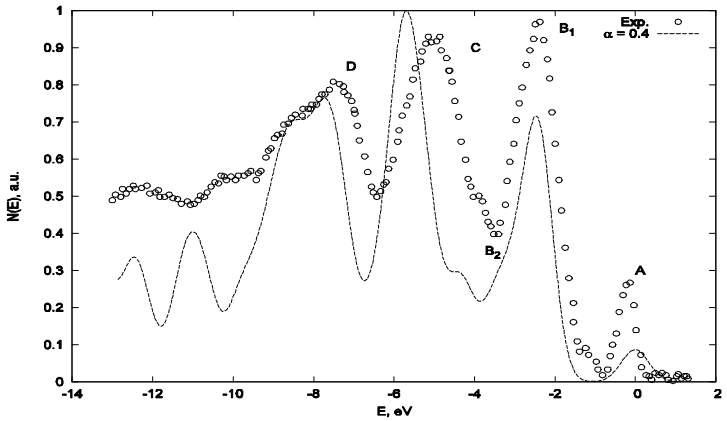
CuPc $\alpha=0$ (DFT-GGA)



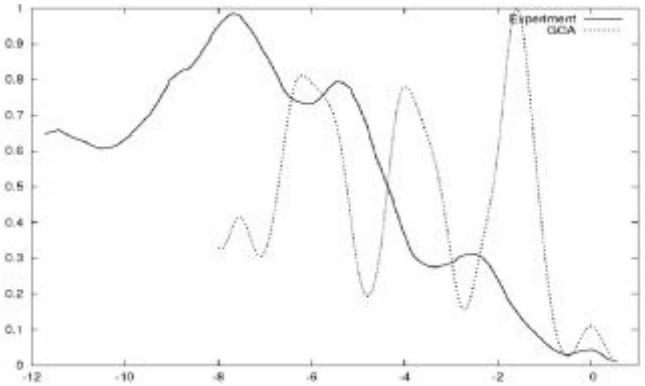
CuPc $\alpha=0.3$



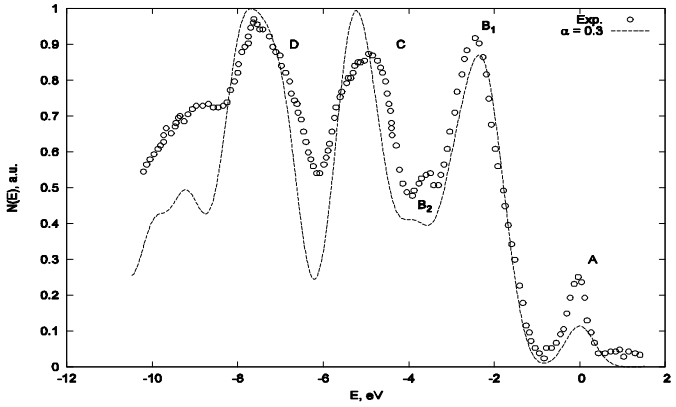
CuPc $\alpha=0.4$



H_2Pc $\alpha=0$ (DFT-GGA)



H_2Pc $\alpha=0.3$



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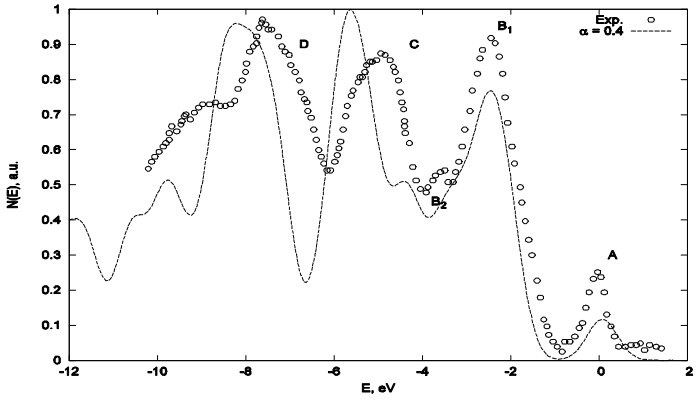
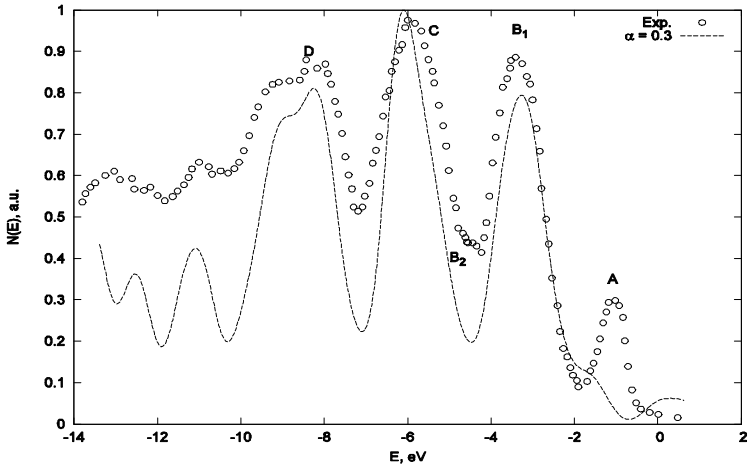
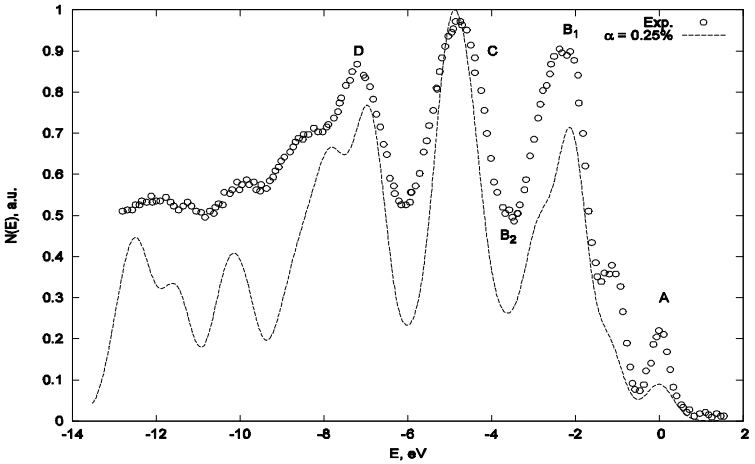


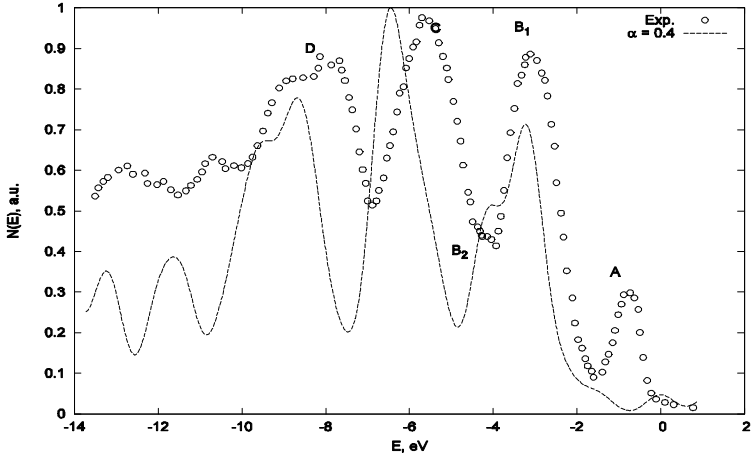
FePc $\alpha=0.3$



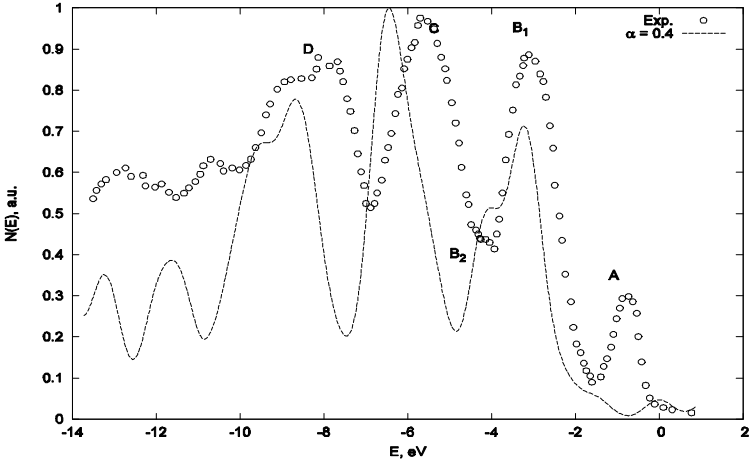
PtPc $\alpha=0.3$



FePc $\alpha=0.4$



PtPc $\alpha=0.4$



4. Spin effects in metal phthalocyanines (MPc).

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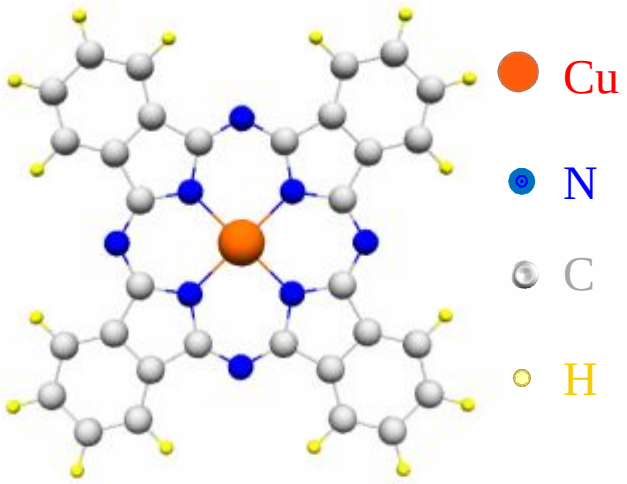

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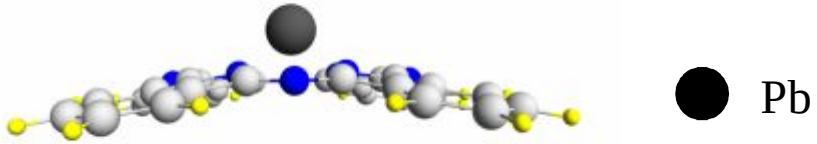

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4. Spin effects in metal phthalocyanines (MPc).

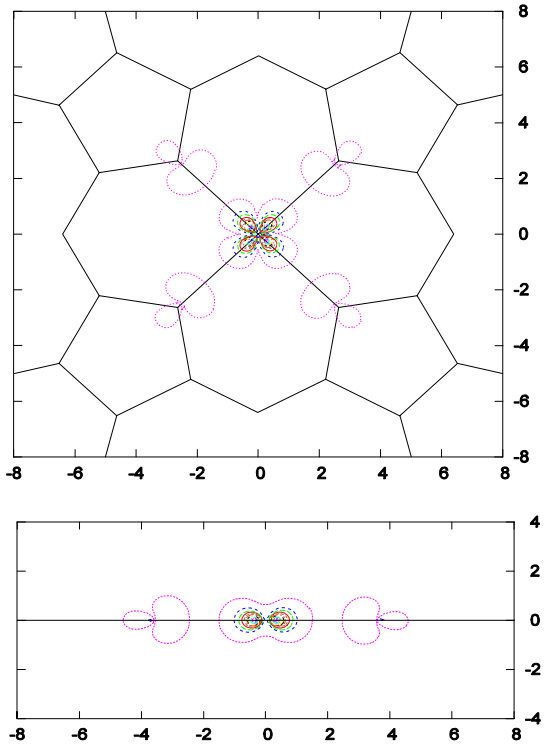
Table 1. Several quasiparticle energies in CuPc (from N. Maron, X. Ren, J. Moussa, J. Chelikowsky, and L. Kronik

GW	b_{1g}	a_{1u}	e_g
E↑ (eV)	-7.49	-6.20	-2.22
E↓ (eV)	-0.92	-6.21	-2.19

Our calculation provides: $V_{b1g\uparrow}^{Coul} = 8.4$ eV and $V_{b1g\downarrow}^{Coul} = 19.9$ eV. For $\alpha = 0.4$ ($\varepsilon_{eff} = 2.5$) the spin splitting is $\Delta_s^{(0)} = 5.7$ eV. Large difference between the values of $V_{b1g\uparrow}^{Coul}$ and $V_{b1g\downarrow}^{Coul}$ is caused by their spatial localization: the state $b1g\uparrow$ has a significant contribution from N atoms, while the state $b1g\downarrow$ is localized on Cu.

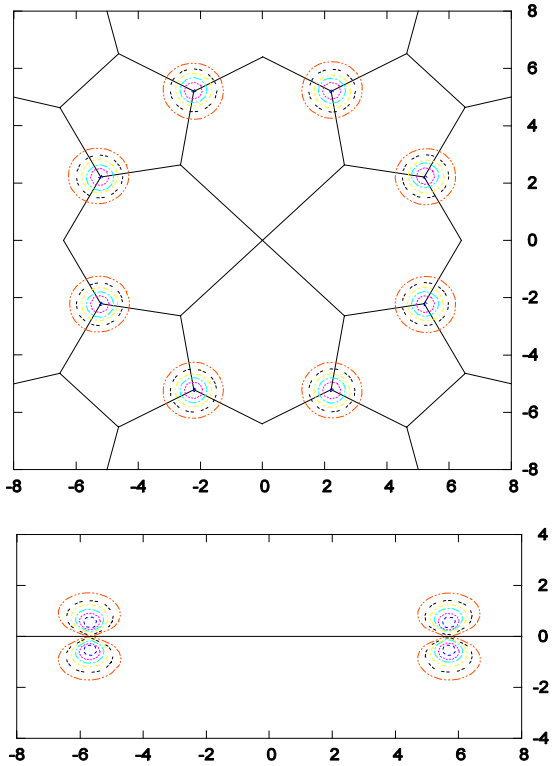
Spatial spin density distribution in MPc

CuPc



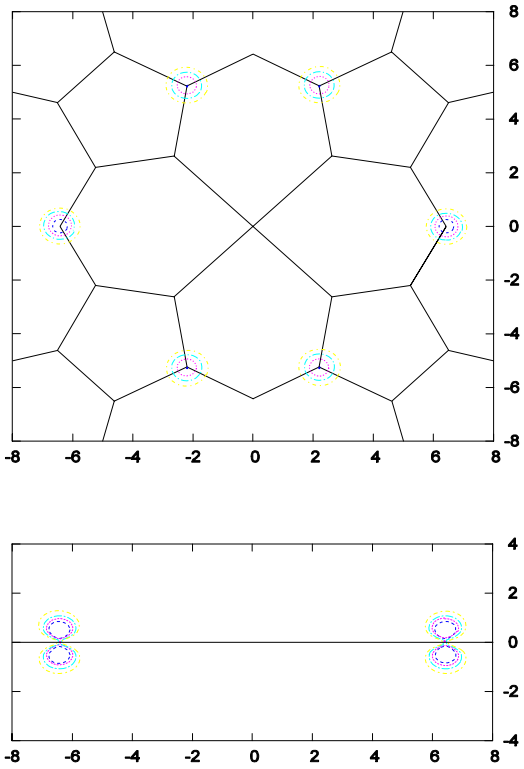
Δ^{GGA}=1.1 eV, Δ_s=5.7 eV, Δ^{hybrid}=7.5 eV

ZnPc-1e

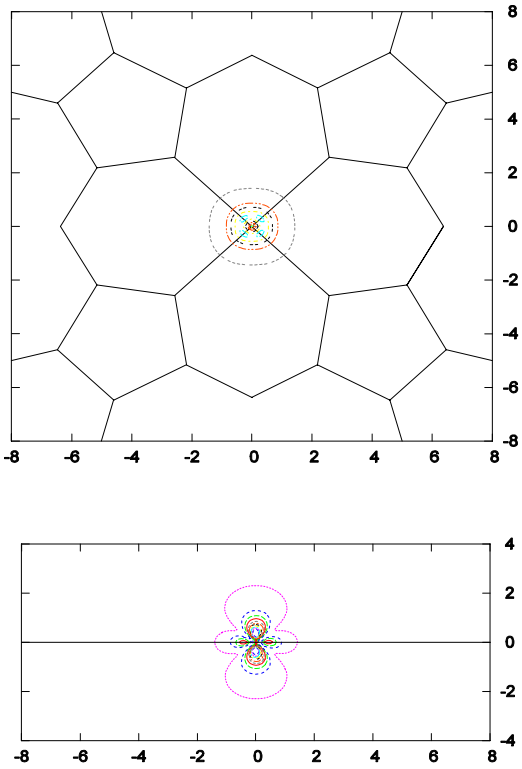


Δ^{GGA}=0.25 eV, Δ_s=2.0 eV, Δ^{hybrid}=2.2 eV

GaPc



CoPc

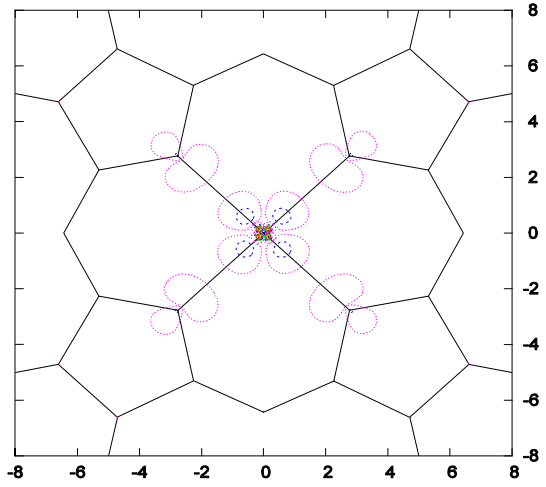


The symmetry of GaPc is reduced by the Jahn-Teller effect.

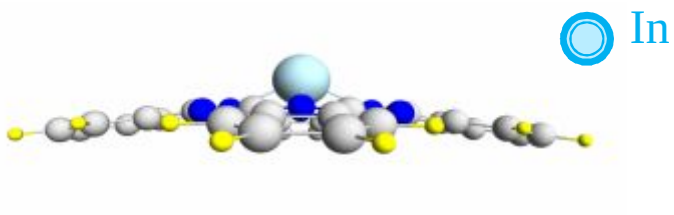
Δ^{GGA}=0.27 eV, Δ_s=1.5eV, Δ^{hybrid}=1.8 eV

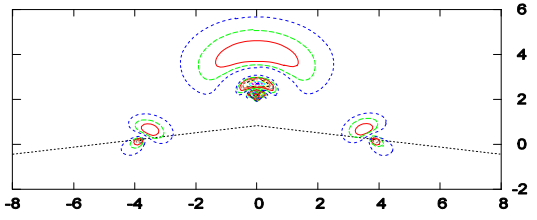
Δ^{GGA}=2.4 eV, Δ_s=11.0 eV, Δ^{hybrid}=9.2 eV

AgPc



InPc



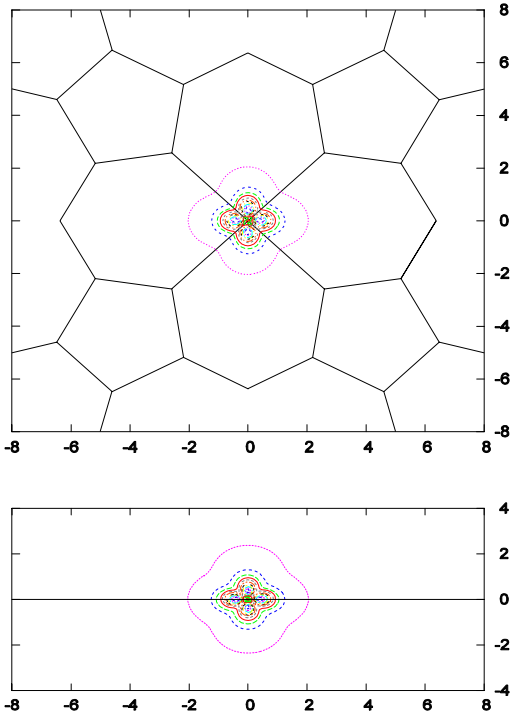


The geometry of InPc is not planar.

Δ^{GGA}=0.65 eV, Δ_s=5.2 eV, Δ^{hybrid}=4.9 eV

Δ^{GGA}=1.0 eV, Δ_s=3.1 eV, Δ^{hybrid}=2.9 eV

FePc

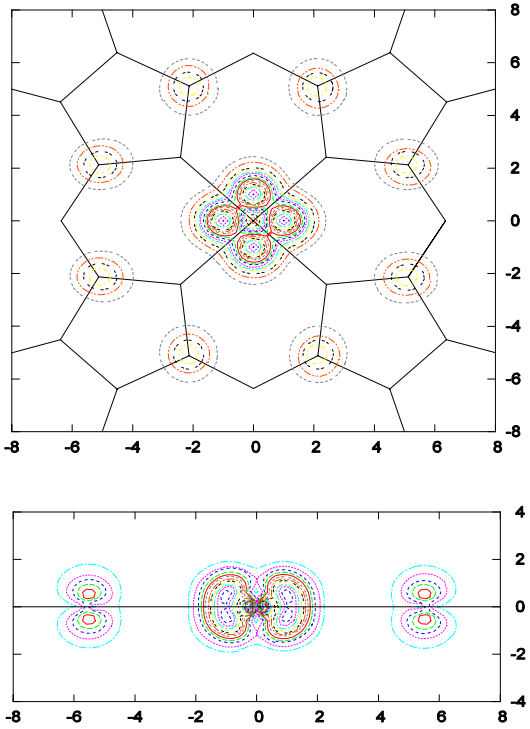


Spin moment $2\mu_B$

Δ^{GGA}=2.8 eV, Δ_s=7.6 eV, Δ^{hybrid}=8.7 eV

Δ^{GGA}=1.4 eV, Δ_s=3.7 eV, Δ^{hybrid}=3.9 eV

MnPc



Spin moment $3\mu_B$

Δ^{GGA}=1.7 eV, Δ_s=5.1eV, Δ^{hybrid}=5.7 eV

Δ^{GGA}=0.5 eV, Δ_s=2.1 eV, Δ^{hybrid}=2.82eV

5. Conclusions.

- In semiconductor nano-objects the GW method has a small parameter $W_{n\neq m}/W_{nn} \approx 0.01\text{-}0.05$.
- In the zero order over $W_{n\neq m}/W_{nn}$ the formulas of the GW method are greatly simplified and become physically transparent.
- Analytical formulas correctly predict gap correction and gap-narrowing in neutral, charged and doped silicon nanoclusters.
- The density of quasiparticle states of MPc molecules, which was calculated by the hybrid functional method with $\alpha=0.3$, agrees well with experimental photoemission spectra.
- The spin-splitting of quasiparticle spectrum in MPc molecules is described rather well by analytical formulas with $\alpha=0.4$ ($\varepsilon_{eff}=2.5$). Its value is large (of 3-10 eV) and greatly depends on the spatial localization of an unpaired electrons.
- Considered effects are of interest for nano-electronics and nano-spintronics.