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HYBRID FUNCTIONAL ANALYSIS OF ELECTRONIC PROPERTIES OF TRANSITION-METAL PHTHALOCYANINES

This work presents the ab initio study of transition-metal phthalocyanines within a PBE0 hybrid functional. The list of metal impurities includes manganese, iron, cobalt, nickel, copper, and zinc. All calculations of isolated molecules have been performed with the use of the projector augment-wave method. For iron phthalocyanine, we have performed four calculations with different values of the mixing parameter α (the value of the exact exchange) – 0, 1/4, 1/3, and 1/2. For all other molecules, the calculations have been performed for $\alpha = 1/4$ and 1/3. The electronic structure parameters including the HOMO-LUMO energy gap, Fermi level, magnetization, and imaginary part of the dielectric function are presented and compared with available theoretical and experimental data. Manganese, iron, and cobalt phthalocyanines show a strong dependence of electronic properties on the value of the exact exchange interaction. In other molecules with nickel, copper, and zinc, this dependence is not significant.

Keywords: organometallic materials, hybrid functionals.

1. Introduction

Metal phthalocyanine complexes is a group of metal-organic materials. Each complex is a planar molecule of phthalocyanine with a metal atom inside the inner C–N ring including 18 π -electrons. Metal-phthalocyanines are widely investigated for electronics purposes and for organic photovoltaics especially. Some phthalocyanines are already well-known dyes. It is worth to note that, during the last decades, organic dyes were intensively studied for electronics purposes. The cause is in the processability and/or some unique characteristics of some agents. In addition to perylene-based dyes which are to be small molecule acceptors in organic photovoltaics (OPV) heterostructures, phthalocyanines are explored as small molecule donor materials [1–5] and organic-inorganic interfaces [6–9]. Phthalocyanines are also

attractive for OPV due the possibility to convert light into electricity in the near-infrared (NIR) region [10–12].

Beside the light conversation and light emitting devices [13–15] including the photodynamic therapy [16, 17], phthalocyanine are widely studied in the field of organic field transistors [18], gas sensors [19], and biosensors [20, 21].

In the case of transition-metal phthalocyanines, researchers explore the behavior of d -electrons and the interaction with different substrates (graphene, gold, etc.) in order to get the possibility to use these materials in spintronics [22–26].

This work is supposed to consider the electronic properties of a number of transition-metal-phthalocyanines (Fig. 1) within a PBE0 hybrid functional and to analyze the impact of the exact exchange and self-interaction of d -electrons in metal-organic systems.

2. Methods

The hybrid functional is a mixing of an implicit exact-correlation potential with the exact Hartree–Fock (exchange) potential. This trick is supposed to solve the band-gap problem in density functional theory (DFT). Both local (LDA) and semilocal (GGA) approximations of DFT underestimate the value of the electron energy gap in solids, as well as in molecules or other bounded systems [27–29]. As the cause for this fact, we consider the self-interaction which is canceled in the Hartree–Fock theory. The influence of the self-interaction rises with the orbital angular momen-

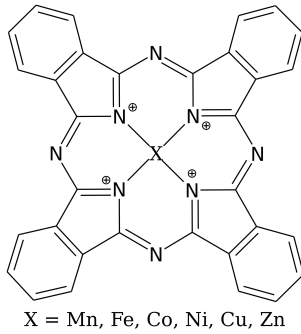


Fig. 1. Chemical structure of the phthalocyanines under study

Table 1. The initial options for the PAW generation: the cut-off radii r_c and valence basis states

Atom	r_c, r_{Bohr}	Valence states
H	0.9	$1s^1$
C	1.3	$2s^2 2p^2$
Mn	2.1	$3s^2 3p^6 3d^6 4s^1$
Fe	2.1	$3s^2 3p^6 3d^7 4s^1$
Co	2.1	$3s^2 3p^6 3d^8 4s^1$
Ni	1.8	$3s^2 3p^6 3d^8 4s^2$
Cu	2.0	$3s^2 3p^6 3d^{10} 4s^1$
Zn	2.3	$3d^{10} 4s^2$

Table 2. PBE0 electronic structure parameters of FePc obtained with four different mixing parameters α

α	$E_g, \text{ eV}$	$E_f, \text{ eV}$	m, μ_B
0	1.45/0.06	-1.68	2.05
1/4	1.43/1.31	-1.71	2.00
1/3	1.38/0.91	-1.52	2.29
1/2	1.37/0.96	-1.48	4.35

tum. The reduction of the self-interaction for d -states is essential in order to obtain accurate results. Here, we are going to use a PBE0 functional in order to describe metal-organic complexes by the example of metal-phthalocyanines.

The general formula describing the PBE0 formalism is as follows:

$$E_{xc}^{\text{PBE0}} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{PBE}} + E_c^{\text{PBE}}, \quad (1)$$

where E_{xc}^{PBE0} is the hybrid PBE0 exchange-correlation potential, E_x^{HF} is the exact Hartree–Fock exchange, and E_x^{PBE} and E_c^{PBE} are the approximated exchange and correlation potentials proposed in [30]. The coefficient α determines the value of the exact exchange.

We have carried out calculations of the ground state within the Projector Augmented Wave (PAW) method [31]. This method combines pseudopotentials with the linearized augmented plane waves (LAPW) method. In this case, we can get an auxiliary wave function $\tilde{\psi}_n$ from the exact all-electron Kohn–Sham wave function ψ_n , using the transformation operator as follows:

$$|\psi_n\rangle = \hat{T} |\tilde{\psi}_n\rangle, \quad (2)$$

where index n includes \mathbf{k} index, band index, and spin index. This expression results in a new form of the Kohn–Sham equation:

$$\hat{T}^\dagger \hat{H} \hat{T} |\tilde{\psi}_n\rangle = \epsilon_n \hat{T}^\dagger \hat{T} |\tilde{\psi}_n\rangle. \quad (3)$$

The transformation operator \hat{T} can be atom-centered transformed into the following form:

$$\hat{T} = 1 + \sum_a \hat{T}^a = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|, \quad (4)$$

where \hat{T}^a is non-zero only inside a sphere centered at an atom a with a radius r_c . The quantities ϕ_i^a and $\tilde{\phi}_i^a$ present the true and smooth partial waves, respectively, and \tilde{p}_i^a is the smooth projector satisfying the relation

$$\langle \tilde{p}_i^a | \tilde{\phi}_j^a \rangle = \delta_{i,j}, \quad r < r_c^a. \quad (5)$$

The summary of PAW options is presented in Table 1. All calculations have been performed, by using the ABINIT code [32]. Molecular geometries have been optimized by a simple relaxation of the ionic

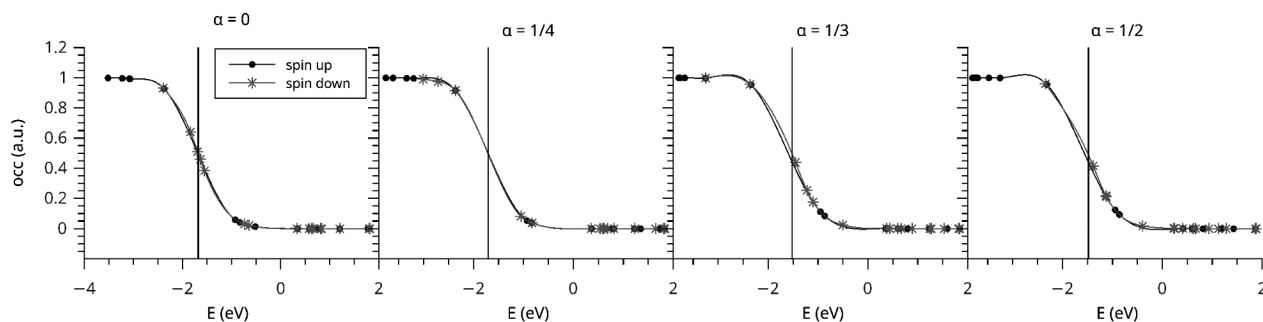


Fig. 2. Occupation of spin-polarized electrons in FePc obtained with different mixing parameters α . Drop black line represents the Fermi level

Table 3. PBE0 electronic structure parameters of transition-metal phthalocyanines obtained with two mixing parameters, α . The column “other” contains the information about other *ab initio* studies with several hybrid functionals (noted in scopes) and experimental data on the magnetic state

	PBE0 ($\alpha = 1/4$)			PBE0 ($\alpha = 1/3$)			Other	
	E_g , eV	E_f , eV	E_g , eV	m , μ_B	E_f , eV	m , μ_B	E_g , eV	Spin
MnPc	1.38/1.04	-1.42	3.41	1.37/1.07	-1.40	3.45	0.9 (HSE06) [33] 1.4 (B3LYP) [33] 0.4 (DFT + U, U = 5 eV) [33] 1.4 (PBE0) [37] 1.4 (HSE) [37]	3/2 [34–36]
FePc	1.43/1.31	-1.71	2.00	1.38/0.91	-1.52	2.29	1.38 (VNW+UHF) [38] 1.5 (HSE06) [33] 1.9 (B3LYP) [33] 1.3 (DFT + U, U = 5 eV) [33] 1.8 (B3LYP) [41]	1 [39, 40]
CoPc	1.39/0.08	-1.61	1.09	1.41/1.30	-1.64	2.91	1.96 (VNW+UHF) [38] 1.8 (HSE06) [33] 2.2 (B3LYP) [33] 1.5 (DFT + U, U = 5 eV) [33]	1/2 [36, 42, 43]
NiPc	1.41/1.41	-1.72	0.00	1.41/1.41	-1.72	0.00	1.47 (VNW+UHF) [38] 1.8 (HSE06) [33] 2.2 (B3LYP) [33] 1.5 (DFT + U, U = 5 eV) [33]	0 [42]
CuPc	0.76/0.76	-1.63	0.00	0.82/0.82	-1.59	0.00	1.42 (VNW+UHF) [38] 1.8 (HSE06) [33] 2.2 (B3LYP) [33] 1.4 (DFT + U, U = 5 eV) [33] 2.3 (PBE0) [44]	1/2 [35, 36]
ZnPc	1.35/1.35	-1.63	0.00	1.35/1.35	-1.64	0.00	1.91 (VNW+UHF) [38] 2.2 (B3LYP) [41] 2.0 (B3LYP) [45]	

positions according to the force convergence. Having performed the convergence study, we have defined the optimal plane wave cutoff energies: 30 Ha for the wave function, 140 Ha for the electron density and

potentials, and 3 Ha for RPA dielectric matrix. All molecules have been calculated, by using the set consisting of 190 bands with metallic occupation described by the Fermi–Dirac smearing.

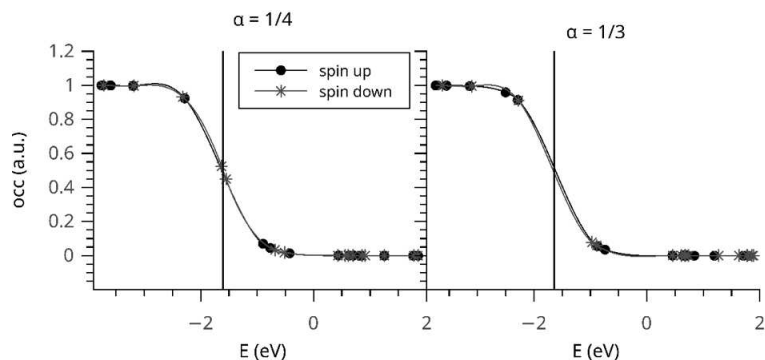


Fig. 3. Occupation of spin-polarized electrons in CoPc obtained within different mixing parameters α . Drop black line represents the Fermi level

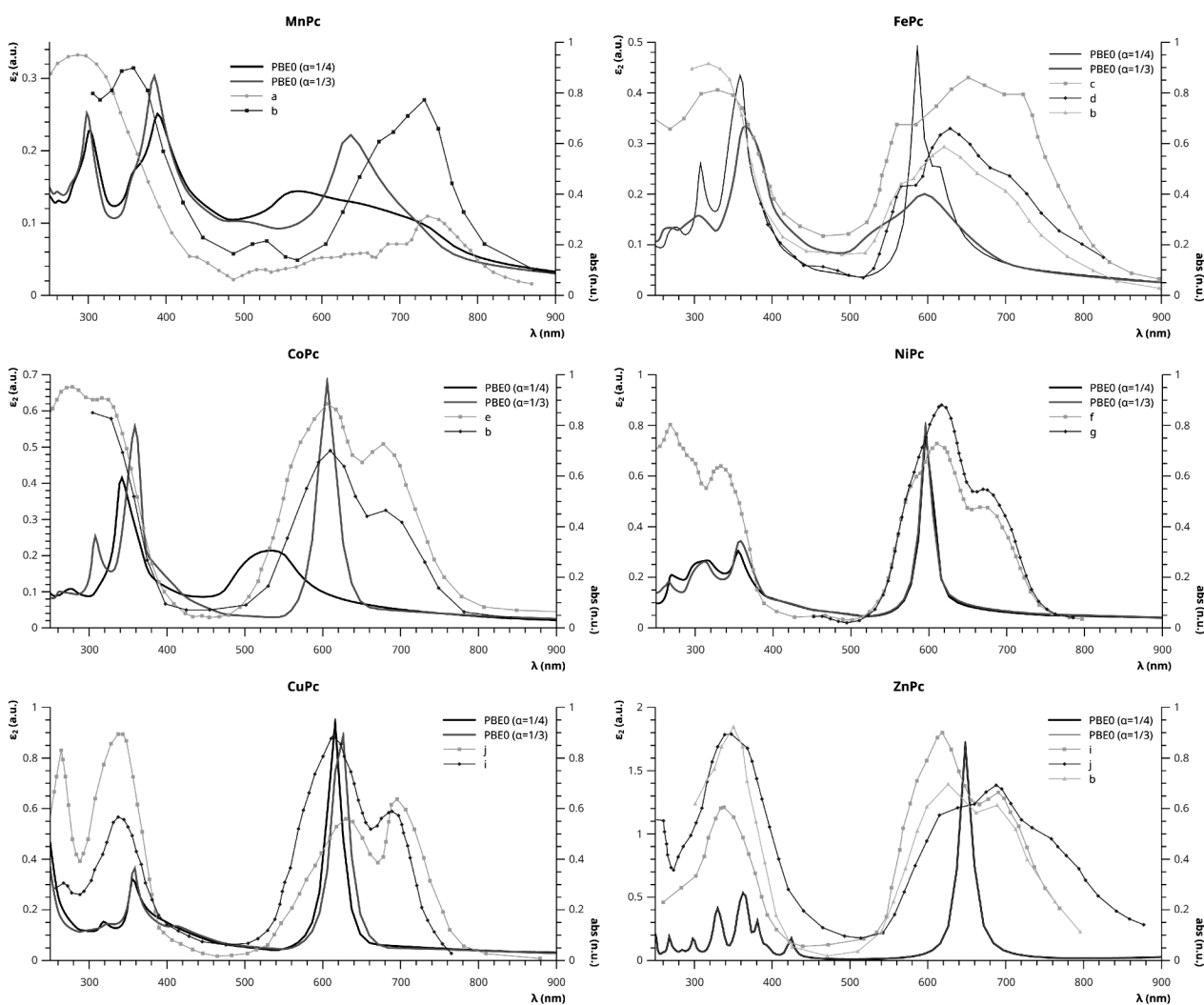


Fig. 4. Imaginary part of DF obtained in RPA on the base of PBE0 with $\alpha = 1/4$ and $1/3$ in comparison with experimental absorption spectra. *a* – [46], *b* – [47], *c* – [48], *d* – [49], *e* – [50], *f* – [51], *g* – [52], *h* – [53], *i* – [54], *j* – [55]

3. Results and Discussion

For iron (II) phthalocyanine (FePc), we have performed four calculations with different mixing factors: the pure PBE with $\alpha = 0$, and the hybrid ones with $\alpha = 1/4, 1/3$, and $1/2$. The main results for FePc are presented in Table 2. We can admit a slight dependence of the energy band gap E_g for a spin-up electron. Meanwhile, a significant diversity of E_g is observed in the case of a spin-down one. Spin-polarized electron occupations are presented in Fig. 2. In the case of a non-hybrid functional ($\alpha = 0$), we can observe a smearing of spin-down electrons around the Fermi level E_f caused by using the Fermi–Dirac distribution. In the case of $\alpha = 1/4$, we observe a slight difference between spin-up and spin-down electron levels with the Fermi level E_f close to the middle of E_g . In the cases where $\alpha = 1/3$ and $1/2$, the electronic parameters (E_g and E_f) and occupations are quite similar, but the magnetization m is almost twice higher (Table 2).

We have performed PBE0 calculations for the list of materials (Fig. 1) with $\alpha = 1/4$ and $1/3$ (Table 3). We also have obtained the frequency-dependent dielectric function (DF) in the Random Phase Approximation (RPA). The imaginary part of DF ϵ_2 is presented in Fig. 4.

Considering MnPc, we can note a slight dependence of both electronic (E_g and E_f) and magnetic (m) properties on the parameter α (Table 3). MePc has magnetization m around $3.4 \mu_B$.

Similarly to FePc, a strong impact of the mixing factor α have been found in CoPc with a smeared spin-down electron is observed in CoPc with $\alpha = 1/4$ (Fig. 3). In addition to the difference in electronic parameters, we have noticed a high difference in magnetic properties: the total magnetization in CoPc with $\alpha = 1/3$ is almost three times higher than in in CoPc with $\alpha = 1/4$. Comparing ϵ_2 with experimental absorption spectra in CoPc, we can say that PBE0 ($\alpha = 1/3$) shows a better agreement.

4. Conclusions

The values of $1/4$ and $1/3$ of the coefficient α formally mean a smaller and larger admixture of the exact Hartree–Fock exchange in the exchange–correlation functional. It is worth analyzing how the choice of the exchange–correlation functional influences the results of calculations of the dielectric function shown in

Fig. 4. From Fig. 4, it can be seen that the dielectric functions corresponding to the functionals are different over the entire spectrum of the photon energy only for the MnPc, FePc, and CoPc. Why does the NiPc fall out of this row? The answer to this question is sought in Table 3. It turns out that the magnetic moment of the entire molecule NiPc is zero. Therefore, it becomes clear why dielectric functions for both values of the mixing coefficient are almost identical. From Fig. 4, we see that the dielectric functions of the NiPc and CoPc, corresponding to different values of the mixing factor, are close to each of these materials. For ZnPc, the dielectric functions, corresponding to different values of the mixing parameter, are identical throughout the spectrum of the photon energies under consideration. The dielectric constants depicted in Fig. 4 allow us to draw the following conclusions. Significant differences in the dielectric functions of the MnPc, FePc, and CoPc, corresponding to different mixing parameters, are due to the strong hybridization of the 3d states of the transition elements with the states in the valence and conduction bands. In the materials of NiPc and CuPc, this hybridization is less pronounced. For the CuPc material, it is even weaker.

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ДОСЛІДЖЕННЯ ЕЛЕКТРОННИХ ВЛАСТИВОСТЕЙ МЕТАЛО-ФТАЛОЦІАНІНІВ ЗА ДОПОМОГОЮ ГІБРИДНОГО ФУНКЦІОНАЛА

В даній роботі представлено дослідження метало-фталоціанінів з використанням гібридного функціонала. Досліджені фталоціаніни містили атоми перехідних металів, а саме марганець, залізо, кобальт, нікель, мідь та цинк. Проведено розрахунок ізольованих молекул. Для фталоціаніну з атомом заліза було проведено розрахунки з чотирма параметрами змішування: 0, 1/4, 1/3 та 1/2. Для всіх інших молекул ми провели розрахунки з двома значеннями: 1/4 та 1/3. В роботі наведено основні параметри електронної структури, такі як енергетична щільність між заселеними та незаселеними рівнями, намагніченість, а також графіки залежності уявної частини діелектричної функції від енергії фотона в порівнянні з експериментальними спектрами поглинання. Фталоціаніни із марганцем, залізом та кобальтом мають сильну залежність електронних властивостей від величини доданої точної обмінної взаємодії. Тоді як в молекулах з нікелем, міддю та цинком зміна цієї величини суттєво не впливає на отримані результати.

Ключові слова: металоорганічні матеріали, гібридний функціонал.