

**Multiband  $d - p$  model and self-doping in the electronic structure of  $\text{Ba}_2\text{IrO}_4$** Krzysztof Rościszewski<sup>1</sup> and Andrzej M. Oleś<sup>1,2</sup><sup>1</sup>*Marian Smoluchowski Institute of Physics, Jagiellonian University, prof. S. Łojasiewicza 11, PL-30348 Kraków, Poland*<sup>2</sup>*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

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We introduce and investigate the multiband  $d - p$  model describing a  $\text{IrO}_4$  layer (such as realized in  $\text{Ba}_2\text{IrO}_4$ ) where all 34 orbitals per unit cell are partly occupied, i.e.,  $t_{2g}$  and  $e_g$  orbitals at iridium and  $2p$  orbitals at oxygen ions. The model takes into account anisotropic iridium-oxygen  $d - p$  and oxygen-oxygen  $p - p$  hopping processes, crystal-field splittings, spin-orbit coupling, and the on-site Coulomb interactions, both at iridium and at oxygen ions. We show that the predictions based on assumed idealized ionic configuration (with  $n_0 = 5 + 4 \times 6 = 29$  electrons per  $\text{IrO}_4$  unit) do not explain well the independent *ab initio* data and the experimental data for  $\text{Ba}_2\text{IrO}_4$ . Instead we find that the total electron density in the  $d - p$  states is smaller,  $n = 29 - x < n_0$  ( $x > 0$ ). When we fix  $x = 1$ , the predictions for the  $d - p$  model become more realistic and weakly insulating antiferromagnetic ground state with the moments lying within  $\text{IrO}_2$  planes along (110) direction is found, in agreement with experiment and *ab initio* data. We also show that (i) holes delocalize over the oxygen orbitals and the electron density at iridium ions is enhanced; hence (ii) their  $e_g$  orbitals are occupied by more than one electron and have to be included in the multiband  $d - p$  model describing iridates.

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Iridates such as  $\text{Sr}_2\text{IrO}_4$  and  $\text{Ba}_2\text{IrO}_4$  are transition metal oxides with partly occupied, spatially extended  $5d$  orbitals. They belong to strongly correlated systems and are weak antiferromagnetic (AF) insulators, with a complex competition of local Coulomb interactions, Hund's exchange coupling, crystal-field effects, and very strong spin-orbit interactions. The debate continues about whether these systems are better viewed as a realization of (i) spin-orbit Mott insulators [1], or (ii) an old idea of a Slater insulator with insulating behavior resulting from long-range AF order in a correlated electronic band [2] is also at work in iridates [3,4], or finally (iii) a mixture of both above scenarios interrelated with each other and contributing almost equally [5].

The electronic structure of  $\text{Sr}_2\text{IrO}_4$  (and to a lesser extent of  $\text{Ba}_2\text{IrO}_4$ ) was a subject of numerous investigations [3,6–8] on a different level of sophistication. The interest in  $\text{Sr}_2\text{IrO}_4$  is motivated by its structural similarity to cuprates [9], and indeed  $d$ -wave superconductivity was predicted in electron doped  $\text{Sr}_2\text{IrO}_4$  by numerical studies [10]. Recently mapping of the three-band ( $d - p$ ) model to a single band was presented and it was shown that further neighbor hopping is necessary to describe the difference between hole and electron doped iridates [11]. The recent experimental evidence seems to support the scenario that  $\text{Ba}_2\text{IrO}_4$  is a close realization of spin-orbit Mott insulator rather than a Slater system [12,13], similar to  $\text{Sr}_2\text{IrO}_4$  investigated using angle-resolved photoemission [14], optical conductivity, x-ray absorption measurements, and first-principles band calculations [15]. Recently it has been shown that strong spin-orbit coupling changes radically the electronic states in Mott insulators [16,17]. Within this limit of an insulator, strong spin-orbit interaction accompanied by large crystal-field effects split  $t_{2g}$  orbitals of  $\text{Ir}^{4+}$  ions into fully filled manifold with effective total angular momentum  $J_{\text{eff}} = 3/2$  and singly occupied manifold  $J_{\text{eff}} = 1/2$  (half-filled ground state) [18,19]. Consequently, tight-binding model calculations were performed using a model for  $t_{2g}$  orbitals

which includes the above effects. It gives results in agreement with the angle-resolved photoemission data for the occupied electronic bands [13].

The origin of AF order in the ground state is more subtle. It was shown by *ab initio* calculations that the Heisenberg superexchange is the largest low-energy scale but also Ising-like compass interactions contribute [20]. Therefore, individual  $\text{Ba}_2\text{IrO}_4$  layers provide a close realization of the quantum spin-1/2 compass-Heisenberg model [21]. We note that similarly complex structure of the superexchange was established for the honeycomb lattice compound  $\text{Na}_2\text{TiO}_3$ , where it takes the form of Kitaev-Heisenberg model which is under intense discussion at present [22].

However, there remain some serious doubts (supported by experimental data) whether such a simplified scenario focused on  $t_{2g}$  orbitals is indeed fully realistic [23]. One has to admit that a simple picture and a model as simple as possible are useful tools when it comes to interpretation of rather complicated experimental data. However, this is only one level of physical description. On the second level one requires much better understanding of what is going on. This is the aim of the present paper—we wish to verify to what extent the charge transfer from Ba ions to  $\text{IrO}_4$  units is complete and whether the ionic model could be used to describe the electronic structure of  $\text{Ba}_2\text{IrO}_4$ . We are not satisfied with an idealistic picture of  $\text{Ir}^{4+}$  (with  $e_g$  orbitals being empty) surrounded by  $\text{O}^{2-}$  ions and we want to investigate the true charge densities and the magnetic order parameters realized in this system. To this end we constructed a multiband  $d - p$  model and performed unrestricted Hartree-Fock (HF) computations on a finite  $\text{IrO}_4$  cluster which contains  $4 \times 4$  Ir ions and the accompanying  $4 \times 4 \times 4$  oxygen ions—half of them located within the same plane as Ir ions, while the second half being in out-of-plane (apical) positions. The model involves (per a single  $\text{IrO}_4$  unit) five  $5d$  orbitals at each Ir and  $4 \times 3$  oxygen  $2p$  orbitals per unit cell, and these orbitals are occupied by (i)  $n_0 = 5 + 4 \times 6$  electrons, according to the formal and idealized ionic model, or (ii) a lower electron number by

one electron, i.e.,  $n = 4 + 4 \times 6$  electrons, according to the realistic *ab initio* computations [24].

The paper is organized as follows. In Sec. II we introduce the multiband model which includes all  $5d$  states at iridium ions and  $2p$  states at oxygen ions. The parameters of the model are specified in Sec. III. The Hartree-Fock approximation for the Coulomb interactions is explained in Sec. IV, while in Sec. V we present the results of numerical calculations: for the formal ionic model in Sec. V A, and for the model with self-doping in Sec. V B. Here we also discuss the justification of finite self-doping (with respect to the electron densities in the ionic model) and the possible effect of electronic correlations. The paper is concluded with a short discussion and summary of the main results in Sec. VI.

## II. MODEL HAMILTONIAN

The  $d - p$  Hamiltonian for  $\text{IrO}_4$  plane reads

$$\mathcal{H} = H_{\text{kin}} + H_{\text{diag}} + H_{\text{so}} + H_{\text{int}}. \quad (2.1)$$

It consists of several parts—the different terms in Eq. (2.1) stand for the kinetic energy ( $H_{\text{kin}}$ ), spin-orbit coupling ( $H_{\text{so}}$ ), crystal-field splittings ( $H_{\text{diag}}$ ), and the intra-atomic Coulomb interactions ( $H_{\text{int}}$ ).

In Sec. V we report a study of charge space-homogeneous solutions. All symmetry-equivalent occupation numbers, i.e., HF primary order parameters, are assumed to be the same in different parts of the cluster. When studying the possibility of antiferromagnetism there are two sublattices and the number of order parameters doubles. Looking for charge space-homogeneous ground states can be considered to be a consequence of strong long-range interionic electrostatic interactions. These interactions are not explicitly included in the model (2.1) but to some extent they are accounted for by the homogeneity assumption.

### A. Kinetic energy

The kinetic part is

$$H_{\text{kin}} = \sum_{\{i\mu;mv\},\sigma} (t_{i\mu;mv} c_{i\mu,\sigma}^\dagger c_{mv,\sigma} + \text{H.c.}), \quad (2.2)$$

where  $c_{i\nu,\sigma}^\dagger$  stands for the creation of an electron at site  $i$  in an orbital  $\nu$  with spin  $\sigma = \uparrow, \downarrow$ . The model includes all  $5d$  orbital states  $\nu \in \{xy, yz, zx, x^2 - y^2, 3z^2 - r^2\}$  per Ir atom at site  $m$  (in this order), and three  $2p$  orbitals  $\nu \in \{p_x, p_y, p_z\}$  per oxygen atom at site  $i$ . When choosing an alternative and more intuitive notation, one can write creation operators  $d_{m\nu,\sigma}^\dagger$  for electron creation in  $d$  orbitals and  $p_{i\nu,\sigma}^\dagger$  for  $p$  orbitals, as used in Sec. IID.

The matrix elements  $t_{i,\mu;m,\nu}$  are assumed to be nonzero only for nearest neighbor iridium-oxygen  $p - d$  pairs, and a similar formula stands for nearest neighbor oxygen-oxygen  $p - p$  pairs (i.e., next nearest hopping elements are neglected). The geometry of the cluster is identical to that for  $\text{RuO}_4$  layer (as realized in  $\text{Sr}_2\text{RuO}_4$ ); thus the matrix elements  $t_{i,\mu;j,\nu}$  can be directly adapted from the Appendix of Ref. [25].

### B. Crystal-field splittings

Let us now present the diagonal part  $H_{\text{diag}}$  of the  $d - p$  Hamiltonian (2.1). It depends only on electron number operators, and takes into account the effects of crystal field and the difference of reference orbital energies (here we employ the electron notation),

$$\Delta = \varepsilon_d - \varepsilon_p, \quad (2.3)$$

between  $d$  and  $p$  orbitals, both for empty states (i.e., when neglecting the interaction terms from  $H_{\text{int}}$ , see below). We remark that in principle  $\varepsilon_p$  might be different for apical oxygens and for in-plane oxygens. A large difference  $\sim 1$  eV between these level positions was considered in ruthenate perovskites [26] as a possibility. We have found within the present  $d - p$  model (also in a ruthenate [25]) that such a difference is definitely too large and would overestimate the difference between charge densities. Qualitatively, the main factor responsible for the charge anisotropy between  $2p$  orbitals at these nonequivalent oxygen position is their weaker hybridization with  $5d$  orbitals, while the difference between the corresponding level energies is of secondary importance.

We put the reference orbital energy  $\varepsilon_d$  for  $\text{Ir}(5d)$  states to be zero; hence we use only  $\varepsilon_p$  as a parameter and write

$$H_{\text{diag}} = \sum_{i,\mu=x,y,z;\sigma} \varepsilon_p p_{i,\mu,\sigma}^\dagger p_{i,\mu,\sigma} + \sum_{m,\mu=xy,yz,\dots;\sigma} f_{\mu,\sigma} d_{m,\mu,\sigma}^\dagger d_{m,\mu,\sigma}. \quad (2.4)$$

Here the first sum is restricted to oxygen sites, while the second one runs over iridium sites. The vector containing the elements of  $\{f_{\mu,\sigma}\}$  is

$$f = \frac{1}{3} D_1 \begin{bmatrix} 2 \\ -1 \\ -1 \\ 0 \\ 0 \\ 2 \\ -1 \\ -1 \\ 0 \\ 0 \end{bmatrix} + D_2 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} + D_3 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \quad (2.5)$$

It includes the orbital splittings of  $5d$  orbitals at Ir ions in the tetragonal crystal field. The constant  $D_1$  serves as a crude estimate of the splitting between the orbital  $xy$  and the orbital doublet  $\{yz, zx\}$ . The  $\{D_2, D_3\}$  parameters refer to splitting between  $t_{2g}$  and  $e_g$  orbitals at iridium and are much larger than  $D_1$ ; see below.

Jahn-Teller part will be neglected in the Hamiltonian (2.1). The exception is the elongation of bonds between iridium and apical oxygens which could be considered as static and global  $Q_3$  Jahn-Teller distortion, but it is simpler to include it by a proper renormalization of the crystal-field splittings. Note that in  $\text{Sr}_2\text{IrO}_4$  Jahn-Teller effects are not negligible due to distortions of octahedra, while they vanish for  $\text{Ba}_2\text{IrO}_4$  (see Fig. 1 in Ref. [13]).

### C. Spin-orbit coupling

Formally, spin-orbit part  $H_{\text{so}}$  of the Hamiltonian Eq. (2.1) has similar mathematical structure to the kinetic part  $H_{\text{kin}}$  [25,27,28], with  $t_{\mu,\sigma;v,\sigma'}^{\text{so}}$  elements restricted to single iridium sites,

$$H_{\text{so}} = \sum_m H_{\text{so}}^{(m)} = \sum_m \left\{ \sum_{\mu \neq v; \sigma, \sigma'} t_{\mu,\sigma;v,\sigma'}^{\text{so}} d_{m\mu,\sigma}^\dagger d_{mv,\sigma'} + \text{H.c.} \right\}, \quad (2.6)$$

where the summation runs only over iridium sites. The matrix elements are all proportional to spin-orbit coupling strength  $\zeta$  which is large on Ir sites and usually assumed to be about  $\zeta = 0.4$  eV [8]. Just like the hopping elements also the elements  $t_{\mu,\sigma;v,\sigma'}^{\text{so}}$  can be directly adapted from Ref. [25] [for the explicit entries for  $t_{\mu,\sigma;v,\sigma'}^{\text{so}}$  see Eq. (2.4) in Ref. [25]]. As we use the basis of real  $5d$  orbitals (and not the spherical harmonics) several spin-orbit elements turn out to be imaginary [thus our Hamiltonian (2.1) is complex]. Note that the consequence of finite spin-orbit coupling is that the total spin of the system and total  $z$ th spin component are not conserved quantities.

### D. Local Coulomb interactions

The last part of the multiband  $d - p$  Hamiltonian,  $H_{\text{int}} \equiv H_{\text{int}}^d + H_{\text{int}}^p$ , stands for strong local on-site interactions. For the  $d$  orbitals at iridium sites it reads

$$H_{\text{int}}^d = U_d \sum_{m,\mu} n_{m,\mu,\uparrow} n_{m,\mu,\downarrow} + \frac{1}{2} \sum_{i,\mu \neq v} \left( U_d - \frac{5}{2} J_{d,\mu\nu} \right) n_{m,\mu} n_{m,v} - \sum_{i,\mu \neq v} J_{d,\mu\nu} \mathbf{S}_{m,\mu} \cdot \mathbf{S}_{m,v} + \sum_{m,\mu \neq v} J_{d,\mu\nu} d_{m,\mu,\uparrow}^\dagger d_{m,\mu,\downarrow}^\dagger d_{m,v,\downarrow} d_{m,v,\uparrow}, \quad (2.7)$$

where  $J_{d,\mu\nu}$  is the tensor of on-site interorbital exchange elements for  $d$  orbitals which can be expressed using Racah parameters  $B$  and  $C$  [29,30] (see also Table I given by Horsch in Ref. [31]). The anisotropy between different Hund's exchange elements  $\{J_{d,\mu\nu}\}$  vanishes only for orbitals of the same symmetry, i.e., either in pure  $t_{2g}$  system or in pure  $e_g$  system [32]). For convenience, we rewrite Eq. (2.7) to separate it into the diagonal terms in electron densities (first line) and the quantum fluctuating part (the last two lines) as follows:

$$H_{\text{int}}^d = U_d \sum_{m,\mu} n_{m\mu,\uparrow} n_{m\mu,\downarrow} + \frac{1}{2} \sum_{m\mu \neq v,\sigma} (U_d - 3J_{d,\mu\nu}) n_{m\mu,\sigma} n_{mv,\sigma} + \frac{1}{2} \sum_{m\mu \neq v,\sigma} (U_d - 2J_{d,\mu\nu}) n_{m\mu,\sigma} n_{mv,-\sigma} - \sum_{m,\mu \neq v} J_{d,\mu\nu} d_{m\mu,\uparrow}^\dagger d_{m\mu,\downarrow}^\dagger d_{mv,\downarrow} d_{mv,\uparrow} + \sum_{i,\mu \neq v} J_{d,\mu\nu} d_{m\mu,\uparrow}^\dagger d_{m\mu,\downarrow}^\dagger d_{mv,\downarrow} d_{mv,\uparrow}. \quad (2.8)$$

The formula for local Coulomb interactions  $2p$  orbitals at oxygen sites,  $H_{\text{int}}^p$ , is analogous,

$$H_{\text{int}}^p = U_p \sum_{i,\mu} n_{i\mu,\uparrow} n_{i\mu,\downarrow} + \frac{1}{2} (U_p - 3J_p) \sum_{i,\mu \neq v,\sigma} n_{i\mu,\sigma} n_{iv,\sigma} + \frac{1}{2} (U_p - 2J_p) \sum_{i,\mu \neq v,\sigma} n_{i\mu,\sigma} n_{iv,-\sigma} - \sum_{i,\mu \neq v} J_p p_{i\mu,\uparrow}^\dagger p_{i\mu,\downarrow}^\dagger p_{iv,\downarrow} p_{iv,\uparrow} + \sum_{i,\mu \neq v} J_p p_{i\mu,\uparrow}^\dagger p_{i\mu,\downarrow}^\dagger p_{iv,\downarrow} p_{iv,\uparrow}, \quad (2.9)$$

and is defined by the intraatomic Coulomb element  $U_p$  and Hund's exchange  $J_p$ , as the tensor  $J_{p,\mu\nu}$  has identical elements  $J_p$  for all off-diagonal pair of the orbitals of the same symmetry. Here  $n_{i\mu,\sigma} \equiv p_{iv,\sigma}^\dagger p_{iv,\sigma}$  and  $p_{i\mu,\sigma}^\dagger$  operators refer to the density and electron creation within  $(\mu, \sigma)$  spin-orbital at site  $i$ .

## III. HAMILTONIAN PARAMETERS

### A. Previous studies and deducing the parameters

The effective  $d - p$  model (2.1) requires a choice of a number of explicitly included parameters. They may be to a large extent deduced from the previous *ab initio* studies. We have adopted the values of in-plane hopping elements ( $pd\sigma$ ) and ( $pd\pi$ ) used in Ref. [8] for  $\text{Sr}_2\text{IrO}_4$ , and rescaled them (both for in-plane and out-of-plane bonds) using Harrison formulas [33] to fit the bond lengths in the structure of  $\text{Ba}_2\text{IrO}_4$  (reported by Moser *et al.* [13]). The elements ( $pp\sigma$ ) and ( $pp\pi$ ) were taken directly from Ref. [25] and were rescaled in a similar way.

The choice of the Coulomb elements is rather difficult due to their unknown screening. There are many reliable estimations for  $U_d$  in effective models featuring only  $5d$  Wannier orbitals at iridium ions ( $2p$  oxygen orbitals are absent, but effective iridium  $5d$  orbitals are then renormalized by hybridization with oxygen  $2p$  orbitals). No need to say that such parameters would have to be completely different in the framework of the multiband  $d - p$  model. A rather low value of  $U_d \in [1.0, 2.0]$  eV was first suggested by Mazin *et al.* [34], but we argue that a more probable value is  $U_d = 3.0$  eV. This value (and  $J_d = 0.6$  eV) were used in local density approximation (LDA+ $U$ ) computations for  $\text{Na}_2\text{IrO}_3$  [35,36] and also for  $\text{Ba}_2\text{IrO}_4$  [13]. A similar value of  $U_d = 2.72$  eV was obtained by constrained random phase approximation in  $\text{Na}_2\text{IrO}_3$  [37]. Other estimates include  $U_d \simeq 1.9$  eV [3] and  $U_d = 2.5$  eV [4,23]. Following this discussion and arguments presented in Ref. [4], we decided to fix  $U_d = 2.5$  eV.

Hund's exchange elements are less screened than intraorbital Coulomb elements and are closer to their atomic values. For Hund's exchange  $J_d$  between two  $t_{2g}$  electrons we selected the value 0.5 eV, in agreement with the old semiempirical prescription ( $J_d/U_d \simeq 0.2$ ) [38]. The same value was used in Refs. [8,34], while slightly smaller ( $J_d = 0.4$  eV [13]), very small ( $J_d = 0.14$  eV [3]), or larger ( $J_d = 0.6$  eV [35,36]) values were also considered. For the sake of fixing precisely Hund's coupling tensor elements  $J_{d,\mu\nu}$  we use Table I from

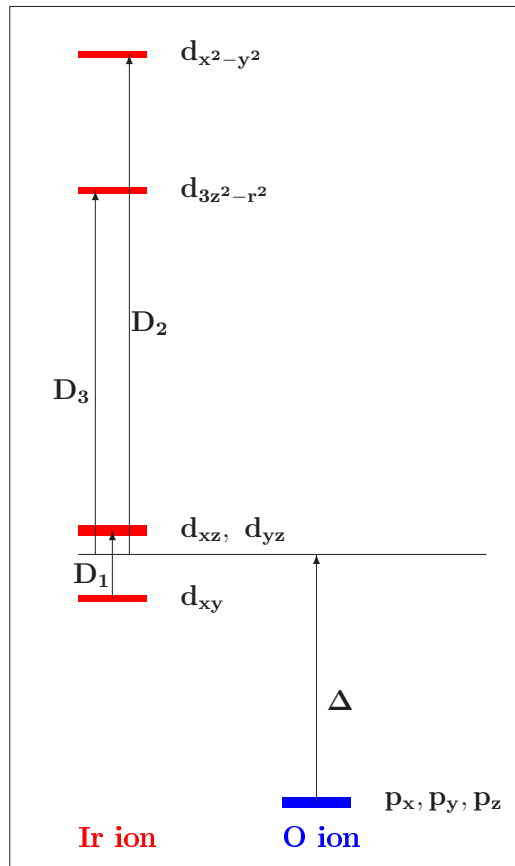


FIG. 1. Artist's view of the 5d orbital energies split by the elements  $\{D_1, D_2, D_3\}$  at Ir ions in the absence of spin-orbit coupling ( $\zeta = 0$ ) (left), and the  $d - p$  splitting  $\Delta$  Eq. (2.3) and O( $2p$ ) orbitals (right).

Ref. [31] and in addition we use a semiempirical formula  $C \simeq 4B$  for Racah parameters. With this *Ansatz* one finds  $J_d = 3B + C \approx 7B$  for a pure  $t_{2g}$  system [32]. The  $J_{d,\mu\nu}$  elements concerning  $e_g$  orbitals are finite and fixed again using the entries from Table I in Ref. [31].

Unfortunately, not much is known about the intraorbital Coulomb repulsion  $U_p$  at oxygen ions (in iridates). In Ref. [39] this parameter is estimated to be within  $U_p \in [4.0, 6.0]$  eV. We recall that in cuprates the values  $U_p = 4.5$  eV [40] and  $U_p \simeq 4.0$  eV [41,42] were considered; note that several other values were also suggested (all in the range 3–8 eV), while 6.0 eV was indicated by some experimental data [43]. We use below  $U_p = 4.4$  eV. For Hund's coupling  $J_p$  at oxygen ions the values  $J_p = 0.6$ – $0.8$  eV were suggested [39], while Grant and McMahan computations in cuprates yield  $J_p = 0.8$  eV [42]. Following these estimates we use below as well  $J_p = 0.8$  eV.

To complete the set of the Hamiltonian parameters we must provide estimates for the crystal-field splittings of Sec. II B. These are  $D_1 = -0.07$  eV,  $D_2 = 2.6$  eV, and  $D_3 = 2.0$  eV, and we adopted them from *ab initio* computations [24]. The 5d orbital degeneracy is lifted by these terms and the orbital states at Ir ions for  $\zeta = 0$  are shown in Fig. 1. The  $e_g$  orbitals are much higher than  $t_{2g}$  ones, and the highest orbital energy is found for  $x^2 - y^2$  orbital, similar to the situation in cuprates for the corresponding 3d orbital [41,42].

TABLE I. Parameters of the Hamiltonian (2.1) (all in eV) used in the HF calculations. For the hopping integrals we present only representative in-plane Slater integrals ( $pd\pi$ ) and ( $pp\pi$ ). Out-of-plane integrals are obtained by applying Harrison scaling [33]. The charge-transfer gap,  $\Delta = \varepsilon_d - \varepsilon_p$ , is examined in the range  $\Delta \in [1.0, 5.0]$  eV.

$U_d$	$J_d$	$U_p$	$J_p$	$\zeta$	$D_1$
2.5	0.5	4.4	0.8	0.43	-0.07
$D_2$	$D_3$	( $pd\sigma$ )	( $pd\pi$ )	( $pp\sigma$ )	( $pp\pi$ )
2.6	2.0	-1.69	0.78	0.55	-0.14

The charge-transfer gap  $\Delta$  (2.3) will be examined as a continuous parameter in the range from 1.0 eV up to 5.0 eV, and the representative situation is shown in Fig. 1. Indeed, oxygen  $2p$  orbital energies are below the Fermi energy, but hybridization with  $5d$  orbitals is responsible for partial electron transfer towards Ir( $5d$ ) orbitals analyzed below in Sec. V. We have taken  $\Delta$  as a free parameter as its precise value is unknown. There are only a few values for  $\Delta$  in the literature, and these data are inconclusive. In Refs. [6,8]  $\Delta = 3.3$  eV was used. According to *ab initio* computations [24] of charge-transfer excitations, the value of  $\Delta$  is about 2.0 eV or slightly larger—this value however is not a bare parameter but includes spin-orbit coupling plus strong correlation effects; thus the bare value could be significantly larger. In Ref. [44] the value of  $\Delta = 2.0$  eV is given for  $\text{Na}_2\text{IrO}_3$ .

Finally, the spin-orbit coupling strength  $\zeta$  on Ir sites is large—it modifies the orbital states and mixes the spin states at iridium ions [16]. It is usually assumed to be 0.4 eV [8]. A more accurate value is 0.43 eV [19,24] and we use it in the present study.

All the parameters we use in the calculations below are collected in Table I. Note that during computations we are setting the value of  $\varepsilon_d$  to be zero as the reference energy. Note that the value of parameter ( $pd\sigma$ ) which is involved in hopping processes from  $t_{2g}$  to  $e_g$  orbitals is  $-1.69$  eV, see Appendix in Ref. [25], and the splitting between  $t_{2g}$  and  $e_g$  orbitals is 2.0–2.6 eV. This suggests that the expectation that  $e_g$  levels are empty is unrealistic.

## B. Previous views and *ab initio* studies

There are several views on the electronic structure of  $\text{Ba}_2\text{IrO}_4$  in the literature. Frequently it is being assumed that  $e_g$  orbitals are empty in  $\text{Ba}_2\text{IrO}_4$ . In the present paper we make an attempt to find the electron densities in  $e_g$  orbitals and in  $2p$  oxygen orbitals. We are motivated by the *ab initio* computations performed on a small cluster with embedding [24]. According to Mullikan population analysis the 5d-shell charge on Ir ions is about  $6.5e$ ; the effective ionic charge within  $2p$  orbitals is about  $5.2e$  on in-plane oxygens and about  $5.6e$  on apical oxygens [45]. Note however that the direct mapping of these entries to the  $d - p$  model cannot be perfect as *ab initio* computations include in addition oxygen valence  $s$  orbitals, and also  $s$ ,  $p$ , and  $f$  orbitals at iridium ions (absent in the  $d - p$  model).

Nonetheless, it seems clear that the formal idealized ionic model with six electrons occupying  $2p$  levels of each oxygen

and five electrons occupying  $5d$  levels of each Ir ion can serve only as a rather crude starting view for the electronic structure of  $\text{Ba}_2\text{IrO}_4$ . For the sake of convenience let us introduce the notion of *self-doping*  $x$  for a single  $\text{IrO}_4$  unit: with respect to the idealized formal ionic model where we have  $x = 0$ ; instead for the real compound we shall consider finite self-doping value  $x = 1.0$ , i.e., one electron less per  $\text{IrO}_4$  (according to Katukuri [24]  $x \sim 0.8$ ; however, we shall use  $x = 1$  instead because our cluster is rather small and while the self-doping  $x = 1$  translates well into integer total electron number in the cluster, other fractional values of  $x$  would not.)

#### IV. UNRESTRICTED HARTREE-FOCK APPROXIMATION

##### A. Self-consistent Hartree-Fock problem

We use the unrestricted HF approximation to investigate the  $\text{IrO}_4$  cluster (with cyclic boundary conditions). The technical implementation is the same as described in Refs. [25,27,46]. Namely, the local Coulomb interaction Hamiltonian  $H_{\text{int}}$  is replaced by mean field terms derived in HF approximation. The averages  $\langle d_{i\mu,\sigma}^\dagger d_{iv,\sigma'} \rangle$  (which appear within this treatment) can be treated as order parameters (there is a similar set of order parameters for oxygens). For the numerical calculations some initial values (some educated guess) have to be assigned to them to start the search for a self-consistent solution of the HF equations. During HF iterations the order parameters are recalculated self-consistently until convergence.

##### B. Hartree-Fock calculations

We are interested in charge-homogeneous solutions, in particular homogeneity concerns primary order parameters,  $\langle d_{i\mu,\sigma}^\dagger d_{iv,\sigma'} \rangle$ , with  $\mu = v$ , i.e., the electron densities (occupations). To obtain unbiased results, we have studied several different types of order, and compared the energies of the self-consistently found solutions to establish the ground state. Consequently, during the computations the following scenarios were studied: nonmagnetic phase, the  $x, y, z$  spin components at all atoms were set to be zero; ferromagnetic (FM) phase with spins aligned along (1,1,0) direction; FM phase with spins aligned along (1,0,0) direction (parallel to the  $a$  axis); FM phase with spins (at all atoms) aligned along (0,0,1) direction (parallel to the  $c$  axis); AF phase with spins (at all atoms) aligned along (1,1,0) direction according to the pattern shown in Fig. 2; AF phase with spins (at all atoms) aligned along (1,0,0) direction (like in Fig. 2 but with spins rotated by  $45^\circ$ ); AF phase with spins (at all atoms) aligned along (0,0,1) direction. In addition, all the magnetic phases were studied again with an additional constraint that the magnetic moments at oxygen ions vanish, i.e., for nonmagnetic oxygens.

Let us immediately comment on the the last scenario (magnetic iridiums and nonmagnetic oxygens): surprisingly, it yields too high HF energies and therefore it is never realized in the ground state. Therefore, we conclude that also oxygen ions contribute to the magnetic order by double exchange mechanism.

The total number of different order parameters is large and results in a rather slow convergence of the HF procedure. The standard remedy for poor convergence is so-called dumping technique or a more sophisticated (possibly better) quantum

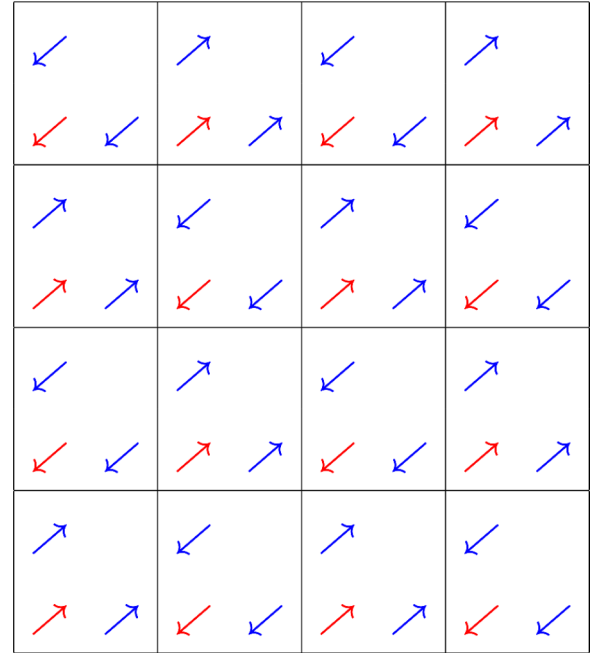


FIG. 2. Antiferromagnetic spin alignment along (1,1,0) direction in a  $4 \times 4$   $\text{IrO}_4$  cluster. The arrows represent magnetic moments within an  $\text{IrO}_2$  plane with the structure of  $\text{CuO}_2$  plane in cuprates (apical oxygens are not shown), with red arrows for iridium ions, and blue arrows for in-plane oxygen ions; the spin magnitudes are arbitrary and only the directions are relevant. Vertical and horizontal lines are only guides to the eye—they indicate  $\text{IrO}_4$  units for a better visibility of individual symmetry and unit cells within the cluster.

chemistry technique called level shifting [47] (more details on the level-shifting technique as applied to the  $d - p$  multiband model may be found in Ref. [25]). We have used both techniques in the present calculations. HF convergence criteria were the following conditions fulfilled simultaneously for the two consecutive iterations: (i) relative energy change should be smaller than  $0.2 \times 10^{-6}$ ; (ii) absolute charge change should be smaller than  $0.5 \times 10^{-3}e$ ; (iii) absolute magnetization change (per ion) should be smaller than  $0.5 \times 10^{-3}$ . Performing computations with dumping or with different level shifts, also with different starting conditions (initial charge and magnetic densities) we completed many runs for each set of Hamiltonian parameters. The comparisons done afterwards lead us to believe that a practical accuracy of our HF solutions (on convergence) is about 1–2 meV.

#### V. NUMERICAL RESULTS

Numerical studies of the multiband  $d - p$  model (2.1) require not only the parameters which were fixed in Sec. III, but also an assumption concerning the total electron number per unit cell. We consider below two different scenarios: (i) the idealistic formal ionic model with  $n_0 = 5 + 4 \times 6 = 29$  electrons per  $\text{IrO}_4$  unit, and (ii) the realistic model with a smaller total number of  $n = 29 - x$  electrons, where we consider only one *self-doping* namely  $x = 1.0$  [24]. Thereby we concentrate on the most important results obtained for

realistic values of Coulomb interactions within the framework of these two different scenarios.

### A. Formal ionic model (self-doping $x = 0$ )

Taking the formal ionic model as a starting configuration for the HF iterations, we assume that each  $\text{IrO}_4$  unit has a negative charge  $Q = 29e$  (the two  $\text{Ba}^{2+}$  ions are considered only as donors of  $4e$  to the  $\text{IrO}_4$  unit). The initial charge distribution assumed on start of HF iterations quickly redistributes to reach the uniform and stable distribution during the iteration process (this is achieved due to finite  $d - p$  hybridization). The emerging ground states are shown in Table II: for the ionic model with  $x = 0$  in the top part, and for the realistic model with self-doping  $x = 1$  (for the discussion see the next subsection) in the bottom part. From the data in the top part of Table II it follows that strong magnetic degeneracy occurs for the resulting magnetic ground states obtained in HF approximation. It is remarkable that the values of charge densities as well as average magnetic moments and average angular momenta are almost the same for degenerate FM and AF HF states. On the one hand, the experimentally observed antiferromagnet with moments aligned along  $(1,1,0)$  direction is confirmed, but on the other hand its energy is degenerated with other magnetic phases.

Finally, we present charge and magnetization densities obtained for the ionic model; see Fig. 3. As expected, increasing  $\Delta$  reduces the charge density within  $5d$  Ir orbitals due to weaker hybridization. Notably, there is a considerable electron transfer to  $e_g$  orbitals which contain typically more

than one  $e_g$  electron per Ir ion. More precisely, the  $e_g$  electron density decreases with increasing  $\Delta$  from  $\sim 1.7$  to  $\sim 1.0$  in the investigated range of  $\Delta$ . Also charge transfer between  $5d$  and  $2p$  orbitals is found for increasing  $\Delta$ , and the charge densities increase for both nonequivalent oxygen positions, in-plane and apical. The density is closer to  $\langle n_p \rangle = 6$  obtained in the ionic picture for apical positions, where the hybridization plays a minor role. However, the most important feature is the observed disagreement of the results of Fig. 3. with the available *ab initio* data [24]. The charge occupations and the magnetization densities for AF [aligned along  $(1,1,0)$  direction] HF ground state are shown in Fig. 3.

### B. Realistic model with self-doping $x = 1.0$

In the second scenario we follow the *ab initio* results of Katukuri *et al.* [24] and we assume a reduced total number of electrons per  $\text{IrO}_4$  unit. Taking the total electron number  $n = 29 - x$  with  $x = 1.0$  this corresponds to *self-doping* by one hole. The obtained ground states and their characteristics are shown in the bottom part of Table II while the corresponding charge and magnetization densities are displayed in Fig. 4. Altogether, taking a representative value of  $\Delta = 3.0$  eV one finds enhanced electron density in  $e_g$  orbitals and all magnetic moments larger by a factor close to 2 than those obtained in the ionic model; cf. Figs. 3 and 4.

From the lower part of Table II we conclude that AF1 is the true ground state for a broad range of  $\Delta \in [1.0, 3.5]$  eV. For higher values of  $\Delta$  the identification of the true ground state is difficult due to strong degeneracy of the lowest energy

TABLE II. Results of the HF calculations for the  $d - p$  model (2.1) concerning the magnetic order and degeneracy of HF ground state for ionic model without self-doping ( $x = 0$ ) (top), and realistic model at self-doping  $x = 1.0$  (bottom), as obtained for increasing charge-transfer gap,  $\Delta$  (2.3). The quantities presented are HOMO-LUMO gap  $G$ , the average energy of spin-orbit term (2.6) per a single iridium ion  $\langle SO \rangle$ , and HF energy per one  $\text{IrO}_4$  unit  $E_{\text{HF}}$ . The obtained states are as follows: AF1—AF state with moment alignment along  $(1,1,0)$  direction; AF2—AF state with moment alignment along  $(1,0,0)$  direction, i.e., along the  $a$  axis; FM1 and FM2 are FM states with the numbers 1 and 2 having the same meaning like for AF states. The numbers in brackets (last column) are in (meV) and denote the energetic distance to the true (best) HF ground state. Note that some low-energy states with a different magnetic order could not be detected during computations (denoted by ? in the last column). Note also that all these states are well insulating due to sizable HOMO-LUMO gaps  $G$ . In contrast, the ground states obtained for the realistic model ( $x = 1.0$ ) have very small or small HOMO-LUMO gaps  $G$ , and are weakly insulating or even close to conducting.

Model	$x$	$\Delta$ (eV)	$G$ (eV)	$\langle SO \rangle$ (eV)	$E_{\text{HF}}$ (eV)	Ground state	Excited states
Ionic model	0.0	1.0	0.12	-0.36	141.675	AF1	?
		1.5	0.29	-0.41	130.964	AF2	AF1 (2); FM1 (2); FM2 (2)
		2.0	0.36	-0.43	120.093	AF1	AF2 (0); FM1 (2); FM2 (2)
		2.5	0.41	-0.46	109.159	AF1	AF2 (0); FM1 (0); FM2 (0)
		3.0	0.45	-0.49	98.162	AF1	FM1 (0); AF2 (1); ?
		3.5	0.46	-0.54	87.094	AF1	FM1 (4); FM2 (3); ?
		4.0	0.40	-0.59	75.952	AF1	AF2 (5); FM1 (5); FM2 (5)
		4.5	0.31	-0.64	64.731	AF1	FM1 (3); FM2 (3); AF2 (5)
		5.0	0.29	-0.68	53.436	AF1	FM1 (0); FM2 (7); AF2 (7)
Realistic model	1.0	1.0	0.028	-0.41	128.974	AF1	AF2 (0); FM1 (1)
		1.5	0.032	-0.43	118.613	AF1	AF2 (2); ?
		2.0	0.042	-0.45	108.197	AF1	AF2 (0); FM1 (0); FM2 (0)
		2.5	0.064	-0.48	97.723	AF1	FM1 (30); ?
		3.0	0.154	-0.58	87.134	AF1	FM1 (1); ?
		3.5	0.091	-0.61	76.444	AF1	FM1 (0); ?
		4.0	0.019	-0.62	65.663	FM1	AF1 (3); ?
		4.5	0.129	-0.67	54.846	AF2	FM2 (0); AF1 (2)
		5.0	0.231	-0.68	43.852	AF2	FM1 (4.5); AF1 (4.5)

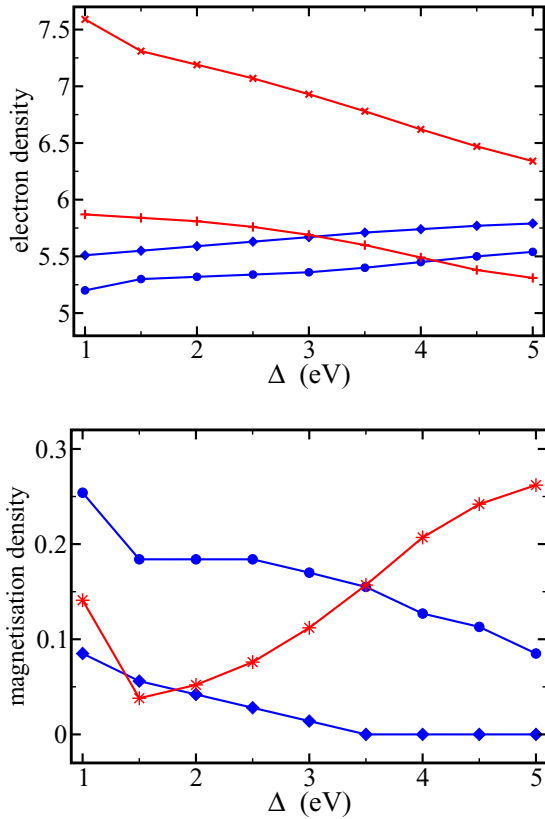


FIG. 3. Electron occupation and spins in the multiband model for increasing  $\Delta \equiv -\varepsilon_p$  obtained in the formal ionic model without self-doping ( $x = 0$ ). The investigated ground state is insulating with AF order aligned along (1,1,0) direction. No significant orbital order was detected. Legend: data for Ir ions are represented by red lines; data for O ions are represented by blue lines; data points show electron occupation numbers in  $t_{2g}$  orbitals (pluses), all  $5d$  orbitals ( $\times$ ),  $2p$  orbitals at in-plane oxygens (circles), and  $2p$  orbitals at apical oxygens (diamonds).

states obtained from HF iterations for various magnetization distributions. Moreover, very small HOMO-LUMO gaps obtained frequently are direct evidence that multiconfiguration HF computations would be necessary to establish the ground state and its magnetic order in a reliable way. However, such multiconfiguration HF computations are prohibitively costly for the considered cluster, both in terms of computer power and computation time. Therefore, we present rather qualitative evidence which suggests that the magnetic order obtained in this range of  $\Delta$  may compete with other magnetic states.

Thus both for idealistic ionic ( $x = 0$ ) and for realistic model with  $x = 1$  it is difficult to reach definite conclusions about the nature of the true ground state. However one bright point are computations for  $x = 1$  and  $\Delta = 3.0$  eV. Here the HOMO-LUMO gap  $G$  of 0.154 eV is large enough to believe that HF (without correlations) performs satisfactorily. Moreover, this value is close to that reported in Ref. [13], and the electron occupation numbers are quite close to the values reported in *ab initio* calculations [24]. The magnetization magnitude at iridium ions is also roughly that which was found in the experiment [48].

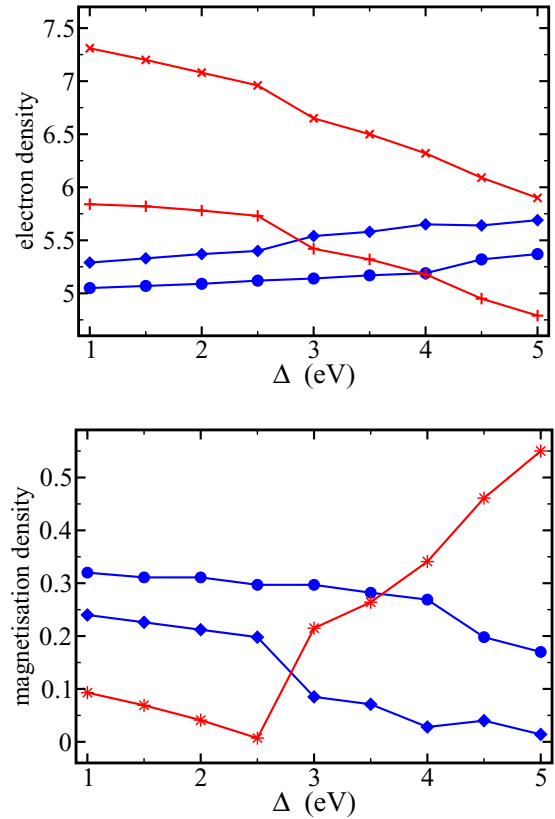


FIG. 4. Electron occupations and magnetic moments in the multiband model for increasing  $\Delta \equiv -\varepsilon_p$ , obtained in the realistic model with self-doping  $x = 1$ . The investigated ground state is weakly insulating with AF order aligned along (1,1,0) direction. No significant orbital order was detected. Legend: data for Ir ions are represented by red lines; data for O ions are represented by blue lines; data points show electron occupation numbers in  $t_{2g}$  orbitals (pluses), all  $5d$  orbitals ( $\times$ ),  $2p$  orbitals at in-plane oxygens (circles), and  $2p$  orbitals at apical oxygens (diamonds).

### C. Sensitivity of the results to variation of Hubbard repulsion $U_d$

Consider first the electron distribution obtained for the self-doping model; see Table III. First of all, one finds almost one hole per ion for  $O_1$  oxygen positions in the  $IrO_2$  planes,

TABLE III. Average electron densities  $\langle n \rangle$ , average magnetization densities  $\langle S^\alpha \rangle$ , and average orbital momenta  $\langle L^\alpha \rangle$ , with  $\alpha = x, y, z$ , as obtained for  $x = 1$  and  $\Delta = 3.0$  eV for AF1 ground state. Average charge densities are close to those reported by *ab initio* studies [24]. HOMO-LUMO gap  $G = 0.154$  eV (weak insulator). Altogether the obtained data agree quite well with the experimental results. Legend:  $O_1$ —in plane oxygen;  $O_3$ —apical oxygen; Ir—iridium ion. Note that for AF1 state the signs of the  $\langle S^\alpha \rangle$  and  $\langle L^\alpha \rangle$  components alternate between sublattices.

Atom	$\langle n \rangle$	$\langle S^x \rangle$	$\langle S^y \rangle$	$\langle S^z \rangle$	$\langle L^x \rangle$	$\langle L^y \rangle$	$\langle L^z \rangle$
Ir	6.65	0.152	0.152	0.0	-0.18	0.22	0.0
$O_1$	5.14	0.21	0.21	0.0	0.03	0.03	0.0
$O_3$	5.54	0.06	0.06	0.0	-0.01	-0.01	0.0

and roughly half of the hole at apical O<sub>3</sub> positions. This demonstrates a considerable hole delocalization over oxygen orbitals in the IrO<sub>2</sub> plane. Furthermore, also  $e_g$  orbitals are partly filled, as one finds the electron numbers:  $n_{t_{2g}} = 5.42$  and  $n_{e_g} = 1.24$  per one Ir ion. Large electron density in  $e_g$  orbitals may be explained by a stronger  $\sigma$  bond between  $x^2 - y^2$  orbitals and O( $2p_\sigma$ ) orbitals within the IrO<sub>2</sub> planes. These numbers suggest that even in the effective models which feature only Ir( $5d$ ) orbitals also  $e_g$  orbitals have to be included.

The order parameters presented in Table III suggest that physical description of the IrO<sub>4</sub> plane in the framework of the realistic model (with self-doping  $x = 1$ ), with charge occupations close to the *ab initio* data, and with Hamiltonian parameters from Table I fits the experimental data reasonably well. However, a natural question arises: was this achieved by accident or are the obtained results generic (at least in some limited sense)? To get a better insight into the problem we performed numerous additional computations for different sets of Hamiltonian parameters (we could not afford the full study of the phase diagram as the number of parameters involved and already discussed technical issues make the computations rather expensive).

The results of these computations indicate that the obtained results are indeed generic and the selection of the parameters is quite representative. To give an explicit example let us consider two additional sets of Hamiltonian parameters: the first set with  $U_d = 2.0$  eV and  $J_d = 0.4$  eV with weaker correlations at iridium ions, and the second set with stronger correlations for  $U_d = 3.0$  eV and  $J_d = 0.6$  eV. All other Hamiltonian parameters remain unchanged (note that we keep the ratio  $J_d/U_d = 0.2$ ). We make scans varying  $\Delta$  for realistic scenario when self-doping  $x = 1$  is selected. We made a search for and accepted results which give the occupation numbers close to *ab initio* results, i.e., the  $n_{t_{2g}} + n_{e_g}$  electron occupation on Ir close to 6.5. The collected results are presented in Table IV (compare with Table III).

TABLE IV. Average electron densities  $\langle n \rangle$ , average magnetization densities  $\langle S^\alpha \rangle$ , and average orbital momenta  $\langle L^\alpha \rangle$ , with  $\alpha = x, y, z$ , as obtained for different atoms at self-doping  $x = 1$  and for two different sets of Hamiltonian parameters as follows. Top part: for large  $\Delta = 5.0$  eV,  $E_{\text{HF}} = 38.7174$  eV and HOMO-LUMO gap  $G = 0.138$  eV; the values of order parameters are almost the same for both (energy degenerate) FM and AF ground states (for AF1 phase they alternate between the two sublattices); parameters:  $U_d = 2.0$  eV;  $J_d = 0.4$  eV. Lower part: for small  $\Delta = 1.5$  eV,  $E_{\text{HF}} = 124.8861$  eV and HOMO-LUMO gap  $G = 0.124$  eV; the ground state is FM (FM1) but the energy of nearly degenerate AF1 state is only by 50 meV higher; parameters:  $U_d = 3.0$  eV;  $J_d = 0.6$  eV.

Atom	$\langle n \rangle$	$\langle S^x \rangle$	$\langle S^y \rangle$	$\langle S^z \rangle$	$\langle L^x \rangle$	$\langle L^y \rangle$	$\langle L^z \rangle$
AF1 ground state							
Ir	6.59	0.162	0.162	0.0	-0.20	-0.22	0.0
O <sub>1</sub>	5.16	0.20	0.20	0.0	0.03	0.03	0.0
O <sub>3</sub>	5.54	0.06	0.06	0.0	0.0	0.0	0.0
FM1 ground state							
Ir	6.58	0.169	0.169	0.0	-0.20	-0.25	0.0
O <sub>1</sub>	5.18	0.19	0.19	0.0	0.03	0.03	0.0
O <sub>3</sub>	5.53	0.07	0.07	0.0	0.0	0.0	0.0

We emphasize that not only the electron densities and magnetic moments are similar for the two sets of parameters used in Table IV, but also the populations of  $t_g$  and  $e_g$  orbitals at Ir ions are. For the first choice with  $U_d = 2.0$  eV, one finds  $n_{t_{2g}} = 5.38$  and  $n_{e_g} = 1.22$ . In the case of larger  $U_d = 3.0$  eV, one finds  $n_{t_{2g}} = 5.40$  and  $n_{e_g} = 1.18$ . Note that these densities are also quite close to the ones obtained for the parameters given in Table I.

To summarize, we remark that FM and AF ground states with magnetic moments aligned along (1,1,0) direction are energetically very close to each other. Nonmagnetic ground state and states with the moments aligned along (0,0,1) direction are much higher in energy; thus they can be safely excluded.

#### D. Can magnetic moments in IrO<sub>4</sub> plane be aligned along $z$ axis?

The next question one should try to answer is the magnetic anisotropy. Why almost all magnetic states are aligned parallel to the plane, and what about alignments (if any) along the  $z$  axis? In fact, there are also ground states with magnetic moments aligned along the  $z$  axis (perpendicular to the iridiums-oxygen plane). They occur both for the idealistic ionic model (i.e., for  $x = 0$ ) and for the realistic model (with self-doping  $x = 1$ ). The conditions for them to appear are the following: large  $U_d$  and large  $\Delta$  (and what follows large charge occupations on oxygens, close to  $6e$ ). Here we also present an example in Table V.

The electron densities obtained for large values of  $\Delta$  and the magnetic states with magnetic oriented along the  $z$  spin axis show a much better hole localization at Ir ions. The hole densities at O<sub>1</sub> and O<sub>3</sub> oxygen positions are reduced by more than half with respect to their values obtained for the states presented in Tables III and IV. With more holes within  $5d$  orbitals, also electron densities are reduced to  $n_{t_{2g}} = 4.41$  and  $n_{e_g} = 1.00$ , but again the density of  $e_g$  electrons is large and also in this case it is necessary to include all five  $5d$  orbitals at Ir ions.

It might be tempting to speculate that for a ground state antiferromagnetism aligned along (1,1,0) or (1,0,0) direction results from the optimization of kinetic hoppings parallel to the iridium-oxygen plane and this happens only for substantial hole occupations on oxygen orbitals. On the other hand, when charge densities within  $2p$  oxygen orbitals become much closer to six (no holes), this blocks effective long-range hopping and only then the possibility of magnetization along the  $z$  axis may become an option.

TABLE V. Average charge occupations  $\langle n \rangle$ , average magnetic spin components  $\langle S^\alpha \rangle$ , and average orbital momenta  $\langle L^\alpha \rangle$ , with  $\alpha = x, y, z$ , obtained for different ions the AF ground state with magnetic moments *aligned along the  $z$  axis*. Note that the energy of this AF state is degenerate with that of FM state (with moments also aligned along the  $z$  axis). The Hamiltonian parameters are  $U_d = 3.0$  eV,  $J_d = 0.6$  eV,  $\Delta = 5.0$  eV, and  $x = 1.0$ .

Atom	$\langle n \rangle$	$\langle S^x \rangle$	$\langle S^y \rangle$	$\langle S^z \rangle$	$\langle L^x \rangle$	$\langle L^y \rangle$	$\langle L^z \rangle$
Ir	5.41	0.0	0.0	0.78	0.0	0.0	0.43
O <sub>1</sub>	5.52	0.0	0.0	0.01	0.0	0.0	0.04
O <sub>3</sub>	5.72	0.0	0.0	0.00	0.0	0.0	0.03



### E. Do correlations favor antiferromagnetic over ferromagnetic order?

The energy-degenerate ground states, FM and AF (see Table II), are a puzzle. The question arises of which one is the true ground state. On the HF level this cannot be answered, but after one includes electronic correlation one can get the final answer. In general the task to compute the correlations is very difficult and costly. There is however a simple (though not rigorous) intuitive approach which suggests that the AF order should be favored in the ground state.

Namely let us consider configuration-interaction computations used in quantum chemistry to derive the correlation energy, as defined for instance in Refs. [49,50]. Let us limit ourselves only to double-excitations from the occupied to virtual states. For the Hamiltonian (2.1) with the parameters from Table I (i.e., with large  $U_d$  in the interaction part of the Hamiltonian) it is expected that singlet excitations are dominant and the triplet excitations are probably much less important.

Now consider intra-atomic correlations (each of the double excitations is coming out from occupied levels on some single ion [49]). These are strictly local, i.e., for AF or FM ground state they look the same and most probably give the same contribution to the total correlation energy. (Thus they do not differentiate between AF and FM order).

In contrast, interatomic correlations only involve excitations from *different* pairs of ions [49]. The consequence is that, naively speaking, the number of the occupied electron pairs of the singlet-type (and located on different ions) is much bigger for AF ground state. Each such occupied singlet pair (in AF) during CI computations is annihilated (while the virtual singlet pair is created at the same time) giving substantial contribution to the total singlet correlation energy. The number of occupied triplet pairs of the electrons is smaller and the triplet excitations give much smaller correlation contribution anyway [we recall that for the Hamiltonian (2.1) singlet excitations are probably dominant].

For the FM ground state we can apply a similar reasoning. Now, the number of occupied triplet pairs of the electrons (on different ions) is bigger. However, the annihilation of each such pair gives rise to a much smaller triplet contribution to the total correlation energy.

In summary, one can expect that the total correlations contribution to the total ground state energy is mainly of the singlet type and that the correlations contribution to the total energy is enhanced for AF ground state while being weaker for FM ground state. Thus one expects that AF order should win in the ground state.

## VI. DISCUSSION AND SUMMARY

We have shown that the HF computational results for the assumed idealized ionic configuration do not describe properly the experimental data for  $\text{Ba}_2\text{IrO}_4$  for almost all studied values of  $\Delta$ . Namely, the charge on iridium ions is  $7e - 7.5e$ , i.e., it is significantly higher than  $6.5e$  (as suggested by *ab initio* [24]) and the HOMO-LUMO gap  $G$  is also too large, so the system is a good insulator. Only for very large  $\Delta = 5.0$  eV the agreement with *ab initio* calculations (charges on iridium and

also on oxygens) improves but still the HOMO-LUMO gap is twice larger than 0.14 eV expected from the experimental data for  $\text{BaIrO}_4$  [12,13]. Note that large insulating gap was found instead in  $\text{Na}_2\text{IrO}_3$  [35].

In contrast, the realistic model with self-doping  $x = 1$  is doing much better. The charges on iridium are generally smaller (in comparison to the  $x = 0$  case) and in particular for  $\Delta = 3.0$  eV the charge occupations on both iridium and oxygens are very close to those indicated by *ab initio* [24] and the ground state: (i) is antiferromagnetic aligned along (1,1,0); (ii) is weakly insulating (not far from being metal;  $G = 0.15$  eV, i.e., the value indicated by experimental data [12,13]); (iii) has magnetic moments with magnitude being close to the experimental findings [12,13]; (iv) is characterized by some traces of weak orbital order.

We emphasize that the present treatment of the spin-orbit interaction is sufficient to break the SU(2) symmetry in the spin space and to realize the experimentally observed type of antiferromagnetic phase. Further justification to the self-doping concept comes from the hole delocalization over oxygen orbitals, found practically for all considered parameter sets. This delocalization implies that also Ba ions cannot be considered as  $\text{Ba}^{2+}$  which would be the case of the idealistic ionic model. Furthermore, using the analogy to cuprates, we suggest that also  $\text{CuO}_2$  planes in the undoped high- $T_c$  materials [40,51–53] cannot be considered as charged formally in the same way as predicted in the ionic model, i.e.,  $\text{Cu}^{2+}\text{O}_2^{2-}$ , but in agreement with recent results [54], self-doping is also here an important effect to include.

Notably, in the Hartree-Fock analysis quantum fluctuations are neglected and thus both ferromagnetic and antiferromagnetic phases are energetically degenerate. But by a simple reasoning one can come to the conclusion that when including these effects and correlations beyond Hartree-Fock, the antiferromagnetic order observed in experiment should become more stable.

There are other important messages. Namely when describing  $\text{IrO}_4$  plane in the framework of  $d - p$  model numerous interesting physical facts and electronic mechanisms become visible. In this respect the  $d - p$  model is a very good supplement to the simpler but more widely used five-band model (featuring only Ir ions with five  $5d$ -type occupied Wannier orbitals which are coming from hybridization of iridium  $5d$  and oxygen  $2p$  orbitals). Our results serve as a guideline that effective models such as the five-band model have to be constructed including their proper electron densities and thus indicate the importance of self-doping. In other words, the formal ionic picture (with zero self-doping) most probably does not describe faithfully the electronic states, and to introduce self-doping is a must. Unfortunately, in order to do it properly some preliminary *ab initio* investigations (in a small cluster) are necessary.

After completing this paper, we became aware of a very recent paper which presents a complete study of the superexchange model [55]. The AF phase obtained by us from the multiband model captures the interplay between the spin-orbit coupling and charge excitations in a charge-transfer insulator and agrees well with the one which follows from the low-energy superexchange model.

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