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Formal valence, charge distribution and chemical bond in a compound with a high oxidation state: $KMnO_4$

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Transition metals compounds with high oxidation state often reveal anomalous properties with a rich phase diagram, like for example in trivalent nickel in $RNiO_3$ [1] and tetravalent iron in $CaFeO_3$ [2]. There one observes metal-insulator transitions, charge ordering and unusual types of antiferromagnetic ordering. Charge disproportionation in charge ordered states formally corresponds to appearance of even higher oxidation states Ni^{+4} and Fe^{+5}. All those anomalies are usually ascribed to significant contribution of oxygen orbitals to formally d-states of transition metals.

Chemically those high oxidation compounds are also very unusual. They are often unstable and can be used as strong oxidizers. The high formal metal ionic charge looks strange because it requires very large energy to create such ions. The most interesting example of this class is $KMnO_4$ where formal valency of manganese ion is Mn^{+7}. To make such highly charged ion one needs ~ 119 eV [3], while energies of chemical bonds are below ~ 10 eV.

In this paper we present electronic structure calculations for this compound and analyze it using formalism of Wannier function (WF). Our conclusion is that the chemical bond in MnO_4^- complex is strongly covalent and charge transfer between d-states of manganese to p-states of oxygen is rather small in spite of very large formal valence. Also, our calculations give the number of d-electrons on Mn ion 5.25 that is more appropriate to ionic charge +2 rather than +7.

Electronic structure calculations were performed using Quantum ESPRESSO package. Wannier functions (WF) used for its results analysis are the most general and natural choice for definition a set of localized atomic orbitals as electronic states that are formally equivalent to the set of itinerant Bloch functions set. The transition between them can be considered as unitary transformation in Hilbert functional space. The localization degree and the symmetry of such wave functions could be controlled in the projection procedure. We used the procedure [4–6], that constraint symmetry of the WF to be the same as the symmetry of pure atomic d-orbitals.

WFs were generated as projections of the pseudoatomic orbitals $|\phi_n^{\mathbf{k}}\rangle = \sum_{\mathbf{T}} e^{i\mathbf{kT}}|\phi_n^{\mathbf{T}}\rangle$ onto a subspace of the Bloch functions $|\Psi_\mu^{\mathbf{k}}\rangle$ (the detailed description of WFs construction procedure is given in [7]):

$$|W_n^{\mathbf{T}}\rangle = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{k}} |W_n^{\mathbf{k}}\rangle e^{-i\mathbf{kT}}, \tag{1}$$

where

$$|W_n^{\mathbf{k}}\rangle \equiv \sum_{\mu=N_1}^{N_2} |\Psi_\mu^{\mathbf{k}}\rangle\langle\Psi_\mu^{\mathbf{k}}|\phi_n^{\mathbf{k}}\rangle. \tag{2}$$

Here $\mathbf{T}$ is the lattice translation vector. The resulting WFs $|W_n^{\mathbf{T}}\rangle$ have symmetry of the atomic orbitals ϕ_n positioned at the unit cell defined by $\mathbf{T}$ and describe electronic states that form energy bands numbered from N_1 to N_2. Within this new basis of WFs one can calculate energies, occupation numbers for every WF and also get contribution of atomic orbitals to the specific WF. All these data are used below for the analysis of electronic configuration of Mn ion in potassium permanganate.

$KMnO_4$ crystallizes in the orthorhombic Pmmn space group with unit cell parameters $a = 5.93$ Å, $b = 7.58$ Å, $c = 9.23$ Å [8]. The manganese ion is surrounded by four oxygens ions with a tetrahedral environment corresponding to the T_d point group symmetry. Obtained energy bands dispersion and density of states show rather narrow bands in agreement with well separated MnO_4^- ions in the structure.

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In order to analyze spatial distribution of electronic states in this material we have calculated squared modulus of WF for the unoccupied bands. The results are presented in Fig. 1. The figure shows spatial distribution of holes for various symmetry states of MnO_4^- ion. As one can easily see, nearly half of the hole density for every WF is situated on the neighboring oxygen ions. The Table 1 shows percentage of Mn d and O p contributions to the WF charge representing holes in formally d^0 shell of manganese ion. It is clear that in fact more than half of each ten formally d holes in reality belong to the oxygen states. The total number of d-holes from this Table gives 4.54 which corresponds to the number of d-electrons 5.46. That agrees well with the occupancy of manganese d-shell 5.25 obtained in full DFT calculations. So while formal valence of Mn in this compound is seven the occupancy of d-shell corresponds rather to Mn^{+2} with admixture of Mn^{+}.

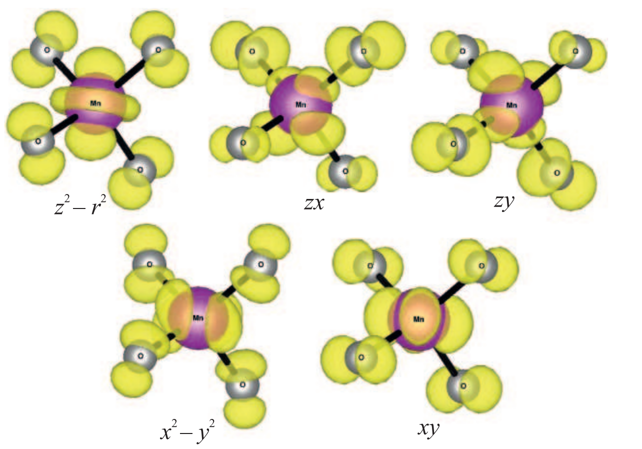

Fig. 1. (Color online) WF (isosurface of the squared moduli) with the symmetry of manganese d-orbitals

Таблица 1. Contribution of atomic states to WF of $KMnO_4$

	z^2-r^2	zx	zy	x^2-y^2	xy
Mn d	46 %	45 %	45 %	45 %	46 %
O p	50 %	49 %	48 %	47 %	50 %

Using the WF formalism, we calculated the contribution of covalent and ionic parts to the chemical bond within the MnO_4^- complex. The obtained values $E^{\text{cov}}_{\text{bond}} = -38.2$ eV and $E^{\text{ion}}_{\text{bond}} = 0.07$ eV confirm that MnO_4^- ion in $KMnO_4$ is a totally covalent complex.

To summarize, we have calculated electronic structure for $KMnO_4$ compound with formally seven valency Mn ion and analyzed the results with WF formalism. We have found the chemical bond in MnO_4^- complex being nearly of perfectly covalent type with practically no presence of ionic contribution. The d-electors charge distribution for Mn atom corresponds to rather Mn^{+2} ionic state then to formal valency Mn^{+7}.

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1. M. L. Medarde, J. Phys.: Condens. Matter **9**, 1679 (1997).
2. P. M. Woodward, D. E. Cox, E. Moshopoulou, A. W. Sleight, and S. Morimoto, Phys. Rev. B **62**, 844 (2000).
3. https://en.wikipedia.org/wiki/Ionization_energies_of_the_elements_(data_page).
4. V. Anisimov, D. Kondakov, A. Kozhevnikov, I. Nekrasov, Z. Pchelkina, J. Allen, S.-K. Mo, H.-D. Kim, P. Metcalf, S. Suga, A. Sekiyama, G. Keller, I. Leonov, X. Ren, and D. Vollhardt, Phys. Rev. B **71**, 125119 (2005).
5. A. O. Shorikov, M. A. Korotin, S. V. Streltsov, S. L. Skornyakov, D. M. Korotin, and V. I. Anisimov, JETP **108**, 121 (2009).
6. A. O. Shorikov, D. Y. Novoselov, D. M. Korotin, and V. I. Anisimov, JETP Lett. **116**, 798(2022).
7. D. Korotin, A. V. Kozhevnikov, S. L. Skornyakov, I. Leonov, N. Binggeli, V. I. Anisimov, and G. Trimarchi, Eur. Phys. J. B **65**, 91 (2008).
8. D. Marabello, R. Bianchi, G. Gervasio, and F. Cargnoni, Acta Crystallogr. A **60**, 5 (2004).