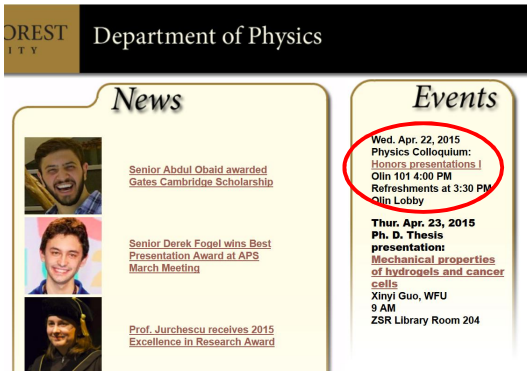
PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 35:

- The Hubbard model
  - LDA+U methods

21	Wed: 03/18/2015	Chap. 16	Electron Transport	#20	03/20/2015
22	Fri: 03/20/2015	Chap. 16	Electron Transport	#21	03/23/2015
23	Mon: 03/23/2015	Chap. 17	Electron Transport	#22	03/25/2015
24	Wed: 03/25/2015	Chap. 17 & 18	Electron Transport		
25	Fri: 03/27/2015	Chap. 18	Microscopic picture of transport	#23	03/30/2015
26	Mon: 03/30/2015	Chap. 19	Semiconductor devices	#24	04/01/2015
27	Wed: 04/01/2015	Chap. 20	Models of dielectric functions	#25	04/06/2015
	Fri: 04/03/2015	Good Friday	No class		
28	Mon: 04/06/2015	Chap. 21	Optical properties of solids	#26	04/08/2015
29	Wed: 04/08/2015	Chap. 22	Modern theory of polorization	#27	04/10/2015
30	Fri: 04/10/2015		Surface properties of solids	#28	04/13/2015
31	Mon: 04/13/2015		X-ray and neutron diffraction in solids	#29	04/15/2015
32	Wed: 04/15/2015	Chap. 26	The Hubbard model	#30	04/17/2015
33	Fri: 04/17/2015	Chap. 26	The Hubbard Model		
34	Mon: 04/20/2015	Chap. 26	The Hubbard Model		
35	Wed: 04/22/2015	Chap. 26	The Hubbard Model		
36	Fri: 04/24/2015		Review		
	Mon: 04/27/2015		Presentations I		
	Wed: 04/29/2015		Presentations II		
	Fri: 05/01/2015		Presentations III & Take home exam		



WFU Physics Colloquium

TITLE: Physics Honors Theses Presentations I

SPEAKERS: Five Undergraduate Thesis Students

TIME: Wednesday April 22, 2015 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

PROGRAM

- Jay Einhorn & Andy Lundeen -- "Effects of Conformally invariant Quantum Fields on Future Singularities"
- Erica Freund -- "Long-term Storage Conditions of Nanoparticle Encapsulated Orlistat to Maintain Cytotoxicity"
- Billy Nicholson -- "Quantifying the Stability of Acridness to Putative Ribosomal DNA G-Quadruplexes"
- Kelli Simms --"TBA"

Schedule for PHY 752 Presentations

Monday 4/27/2015

	Presenter	Topic
11:00 -11:25 AM	David Montgomery	Phonon models
11:25-11:50 AM	Ahmad Al Qawasmeh	Electronic and structural properties of graphite and graphene

Wednesday 4/29/2015

	Presenter	Topic
11:00 -11:25 AM	Drew Onken	"Treating Crystal Defects and Dislocations"
11:25-11:50 AM	Calvin Arter	Van der Waals density exchange functionals with spin effects

Friday 5/1/2015

	Presenter	Topic
11:00 -11:25 AM	Evan Welchman	"How and why structure searches work"
11:25-11:50 AM	Jason Howard	"Using C++ to translate and compare lattice coordinates"

Motivation for the LDA+U approach

Self-interaction problem

Within Kohn-Sham theory, the total electronic energy is a functional of the electron density $\rho(\mathbf{r})$ having the form:

$$E_{tot}(\rho) = \underbrace{E_K(\rho)}_{\text{Kinetic}} + \underbrace{E_N(\rho)}_{\text{Nuclear}} + \underbrace{E_H(\rho)}_{\text{Hartree}} + \underbrace{E_x(\rho)}_{\text{Exchange}} + \underbrace{E_c(\rho)}_{\text{Correlation}} \quad . \tag{1}$$

Here,

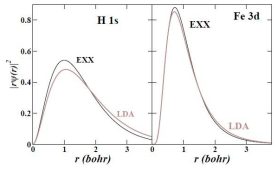
$$E_H(\rho) \equiv \frac{e^2}{2} \int \int d^3r \, d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{2}$$

representing the Coulomb interaction between electrons, including the self-interaction. **Only for E_x chosen to have the form of Fock exchange, can this self-interaction be completely removed from the formalism.**

Fock exchange form

$$E_x(\{\Psi_p(\mathbf{r})\}) = -\frac{e^2}{2}\sum_{pq(occ)}\delta_{\sigma_p\sigma_q}\int d^3r\int d^3r'\ \frac{\Psi_p^*(\mathbf{r})\Psi_q(\mathbf{r})\Psi_p(\mathbf{r}')\Psi_q^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \quad (3)$$

where the summation over all occupied states includes the the self-interaction correction for $p \equiv q$ and $\sigma_p \equiv \sigma_q$. For wavefunctions $\Psi_p(\mathbf{r})$ representing extended states, the self-interaction energy is not large. Two notable exceptions are:



For a H atom:

$E_{tot}^{\mathrm{LDA}} = -0.9$ Ry

$E_{tot}^{\mathrm{EXX}} = -1.0$ Ry.

For a Fe atom:

$\epsilon_{4s}^{\mathrm{LDA}} - \epsilon_{3d}^{\mathrm{LDA}} = 0.2$ Ry

$\epsilon_{4s}^{\mathrm{EXX}} - \epsilon_{3d}^{\mathrm{EXX}} = 0.3$ Ry.

Details of the self-interaction problem

Assuming all states occupied equally with up and down spins:

$$E_H = 2e^2\sum_{p,q(occ)}\int d^3r\int d^3r'\frac{\Psi_p^*(\mathbf{r})\Psi_p(\mathbf{r})\Psi_q^*(\mathbf{r}')\Psi_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_x = -e^2\sum_{p,q(occ)}\int d^3r\int d^3r'\frac{\Psi_p^*(\mathbf{r})\Psi_q(\mathbf{r})\Psi_q^*(\mathbf{r}')\Psi_p(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Form of exchange energy used in LDA (local density approximation)

$$E_x^{LDA} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}e^2\int d^3r\left(\rho(\mathbf{r})\right)^{4/3}$$

- Hartree-Fock formalism removes self-interaction error
- LDA+U approximately removes self-interaction error and can possibly add some additional physics

PHYSICAL REVIEW B **71**, 035105 (2005)

Linear response approach to the calculation of the effective interaction parameters in the LDA+U method

Matteo Cococcioni* and Stefano de Gironcoli
SISSA-Scuola Internazionale Superiore di Studi Avanzati and INFM-DEMOCRITOS National Simulation Center, via Beirut 2-4, I-34014 Trieste, Italy
(Received 5 May 2004; published 18 January 2005)

In this work we reexamine the LDA+U method of Anisimov and co-workers in the framework of a plane-wave pseudopotential approach. A simplified rotational-invariant formulation is adopted. The calculation of the Hubbard U entering the expression of the functional is discussed and a linear response approach is proposed that is internally consistent with the chosen definition for the occupation matrix of the relevant localized orbitals. In this way we obtain a scheme whose functionality should not depend strongly on the particular implementation of the model in *ab initio* calculations. We demonstrate the accuracy of the method, computing structural and electronic properties of a few systems including transition and rare-earth correlated metals, transition metal monoxides, and iron silicate.

DOI: 10.1103/PhysRevB.71.035105 PACS number(s): 71.15.Mb, 71.15.Nc, 71.20.−b

Total energy expression for LDA+U used by Cococcioni and de Gironcoli for all atomic sites *I*:

$$E_{\mathrm{LDA+U}}[n(\mathbf{r})] = E_{\mathrm{LDA}}[n(\mathbf{r})] + E_{\mathrm{Hub}}[\{n_{mm'}^{I\sigma}\}] - E_{\mathrm{DC}}[\{n^{I\sigma}\}],$$

Coulomb and exchange interactions on atomic sites corrected for "double counting"

In principle the atomic site contributions could be calculated using atomic basis functions. Alternatively they can be introduced as model parameters or determined consistently from the modified equations.

LDA+U – continued

Approach is particularly important for describing *d* and *f* electrons where spin and orbital degeneracies also appear. Cococcioni and de Gironcoli use dominating spherically symmetric contribution and allow site occupancies n_I to vary consistently.

Simplified LDA+U Hamiltonian

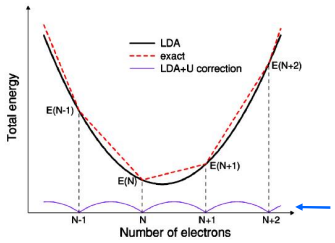
$$\begin{aligned} E_U[\{n_{mm'}^{I\sigma}\}] &= E_{\mathrm{Hub}}[\{n_{mm'}^{I}\}] - E_{\mathrm{DC}}[\{n^{I}\}] \\ &= \frac{U}{2}\sum_{I}\sum_{m,\sigma}\left\{n_{mm}^{I\sigma} - \sum_{m'} n_{mm'}^{I\sigma} n_{m'm}^{I\sigma}\right\} \\ &= \frac{U}{2}\sum_{I,\sigma}\mathrm{Tr}[\mathbf{n}^{I\sigma}(1-\mathbf{n}^{I\sigma})]. \end{aligned}$$

Atomic site occupations $n^{I\sigma}$ depend on choice of basis functions, but net result should be robust.

Behavior of energy with expectation value.

For statistical ensemble of atoms with N or $N+1$ electrons, we expect the average energy to be

$$\langle E \rangle = (1-\nu)E_N + \nu E_{N+1}$$



Needed correction to be provided by U term.

FIG. 1. (Color online) Sketch of the total energy profile as a function of number of electrons in a generic atomic system in contact with a reservoir. The bottom curve is simply the difference between the other two (the LDA energy and the "exact" result for an open system).

Cococcioni and de Girancoli proposal for calculating U:

Introduce new variables q_I representing local orbital occupations

$$E(n(\mathbf{r}),\{q_I\}) = E^{LDA}(n(\mathbf{r})) + \sum_I \alpha_I (n_I - q_I)$$

$$U = \frac{\partial^2 E[\{q_I\}]}{\partial q_I^2} - \frac{\partial^2 E^{KS}[\{q_I\}]}{\partial q_I^2}.$$

Cococioni & de Gironcoli

Example for FeO

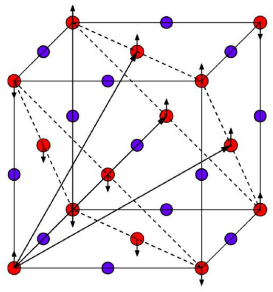


FIG. 6. (Color online) The unit cell of FeO: blue spheres represent oxygen ions, red ones are Fe ions, with arrows showing the orientation of their magnetic moments. Ferromagnetic (111) planes of iron ions alternate with opposite spins producing type-II antiferromagnetic order and rhombohedral symmetry.

Cococioni & de Gironcoli

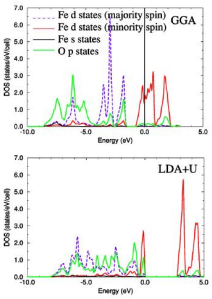


FIG. 9. (Color online) Projected density of states of FeO in the undistorted (cubic) AF configuration at the experimental lattice spacing obtained within GGA (top panel) and LDA+U using the computed Hubbard U of 4.3 eV (bottom panel).

Application of LDA+U to phase stability of Li_xFeO_4

PHYSICAL REVIEW B **69**, 201101(R) (2004)

Phase separation in Li_xFePO_4 induced by correlation effects

F. Zhou*
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

C. A. Marianetti, M. Cococcioni, D. Morgan, and G. Ceder†
Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 10 March 2004; published 12 May 2004)

We report on a significant failure of the local density approximation (LDA) and the generalized gradient approximation (GGA) to reproduce the phase stability and thermodynamics of mixed-valence Li_xFePO_4 compounds. Experimentally, Li_xFePO_4 compositions ($0 \leqslant x \leqslant 1$) are known to be unstable and phase separate into $LiFePO_4$ and $FePO_4$. However, first-principles calculations with LDA/GGA yield energetically favorable intermediate compounds and hence no phase separation. This qualitative failure of LDA/GGA seems to have its origin in the LDA/GGA self-interaction which delocalizes charge over the mixed-valence Fe ions, and is corrected by explicitly considering correlation effects in this material. This is demonstrated with LDA+U calculations which correctly predict phase separation in Li_xFePO_4 for $U-J \geq 3.5$ eV. The origin of the destabilization of intermediate compounds is identified as electron localization and charge ordering at different iron sites. Introduction of correlation also yields more accurate electrochemical reaction energies between $FePO_4/Li_xFePO_4$ and Li/Li^+ electrodes.

DOI: 10.1103/PhysRevB.69.201101 PACS number(s): 71.15.Mb, 71.27.+a, 91.60.Ed

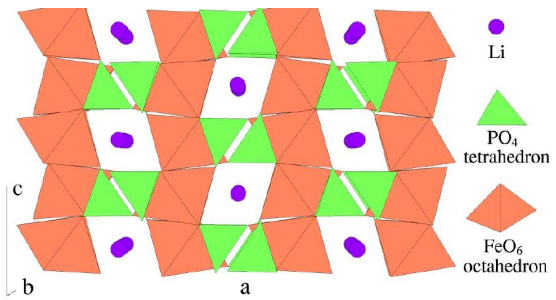


FIG. 1. Structure of $LiFePO_4$ with cation polyhedra.

Experimentally, $Li_{0.5}FePO_4$ is unstable wrt to $FePO_4$ and $LiFePO_4$.

Simplified LDA+U

$$E(n^I) = E_{LDA} + \frac{U_{eff}}{2} Tr(n^I(1-n^I))$$

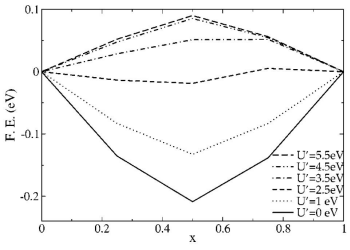


FIG. 2. Formation energy of Li_xFePO_4 at different x and U' values. Points at $x = 0.5$ correspond to structure 0.5a.