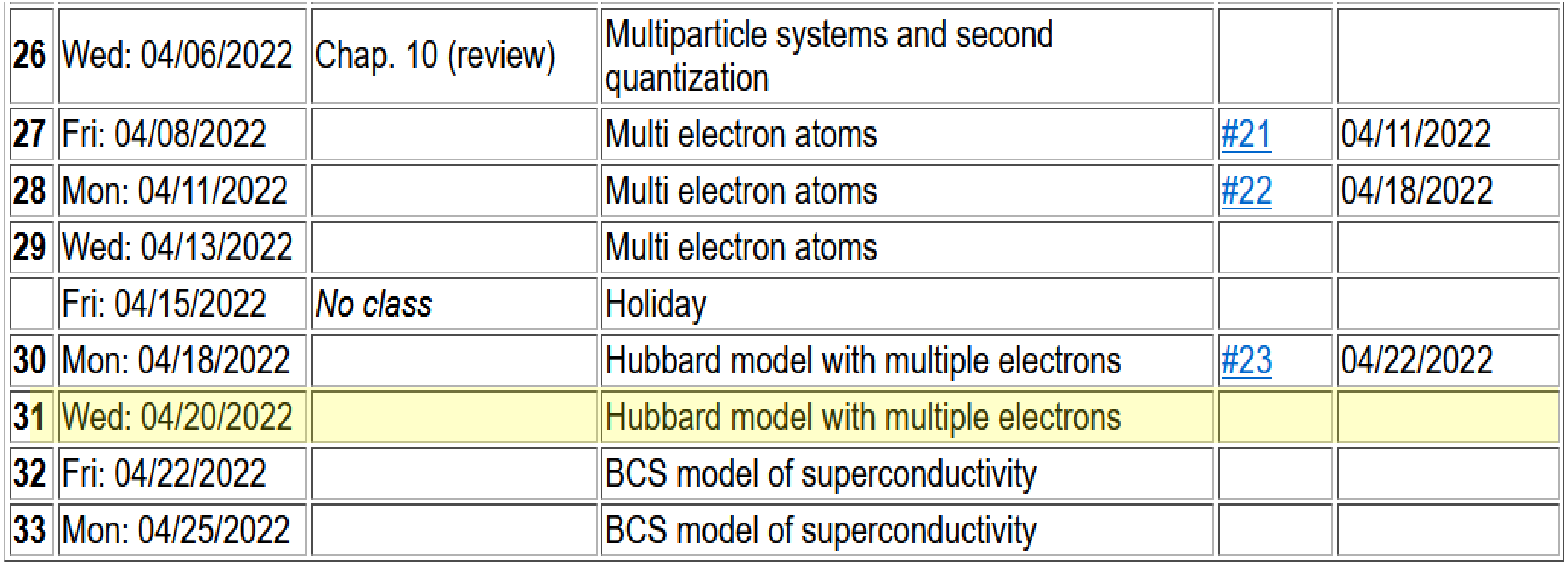
PHY 742 Quantum Mechanics II
12-12:50 PM MWF Olin 103

Plan for Lecture 31

Quantum Mechanics of the Hubbard Model

1. Summary of results for one-dimensional periodic system
2. Simple Hartree-Fock solution
3. More complicated Hartree-Fock solutions
4. Comment about solutions in higher dimensions
5. LDA+U formalism



26	Wed: 04/06/2022	Chap. 10 (review)	Multiparticle systems and second quantization		
27	Fri: 04/08/2022		Multi electron atoms	#21	04/11/2022
28	Mon: 04/11/2022		Multi electron atoms	#22	04/18/2022
29	Wed: 04/13/2022		Multi electron atoms		
	Fri: 04/15/2022	*No class*	Holiday		
30	Mon: 04/18/2022		Hubbard model with multiple electrons	#23	04/22/2022
31	Wed: 04/20/2022		Hubbard model with multiple electrons		
32	Fri: 04/22/2022		BCS model of superconductivity		
33	Mon: 04/25/2022		BCS model of superconductivity		

The Hubbard Hamiltonian:

Using Fermi particle second quantization operators

$c_{l\sigma}$ and $c^{\dagger}_{l\sigma}$

$$\hat{\mathcal{H}} = \sum_{\substack{\langle ll' \rangle \\ \sigma}} -\mathrm{t}\left[\hat{c}^{\dagger}_{l\sigma}\hat{c}_{l'\sigma} + \hat{c}^{\dagger}_{l'\sigma}\hat{c}_{l\sigma}\right] + U\sum_{l}\hat{c}^{\dagger}_{l\uparrow}\hat{c}_{l\uparrow}\hat{c}^{\dagger}_{l\downarrow}\hat{c}_{l\downarrow},$$

single particle contribution

two particle contribution

$$\{c_{l\sigma}, c_{l'\sigma'}\} = 0$$

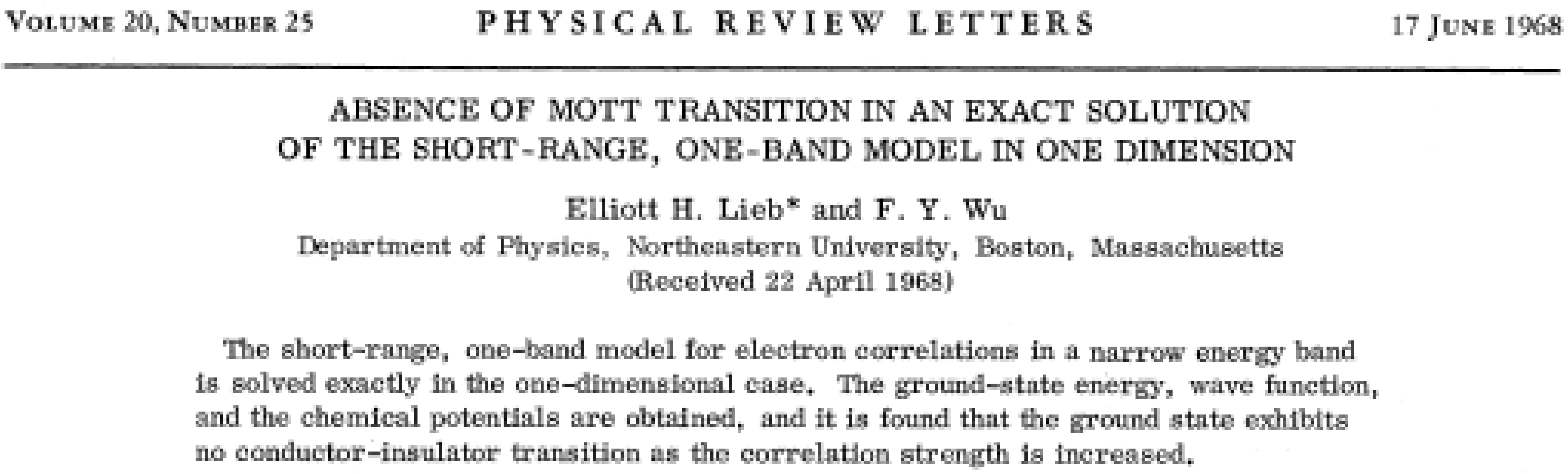
$$\{c^{\dagger}{}_{l\sigma}, c^{\dagger}{}_{l'\sigma'}\} = 0$$

$$\{c_{l\sigma}, c^{\dagger}{}_{l'\sigma'}\} = \delta_{ll'}\delta_{\sigma\sigma'}$$

N-site system in one dimension

$$H = -t \sum_{n=1}^{N-1} \sum_{\sigma=\uparrow}^{\downarrow} \left(c^{\dagger}_{n\sigma} c_{n+1\sigma} + c^{\dagger}_{n+1\sigma} c_{n\sigma} \right) + U \sum_{n=1}^{N} c^{\dagger}_{n\uparrow} c_{n\uparrow} c^{\dagger}_{n\downarrow} c_{n\downarrow}$$

Solved analytically in 1968 **Extension to 2 and 3 dimensions has remained elusive…..**



VOLUME 20, NUMBER 25 PHYSICAL REVIEW LETTERS 17 JUNE 1968

ABSENCE OF MOTT TRANSITION IN AN EXACT SOLUTION
OF THE SHORT-RANGE, ONE-BAND MODEL IN ONE DIMENSION

Elliott H. Lieb* and F. Y. Wu
Department of Physics, Northeastern University, Boston, Massachusetts

(Received 22 April 1968)

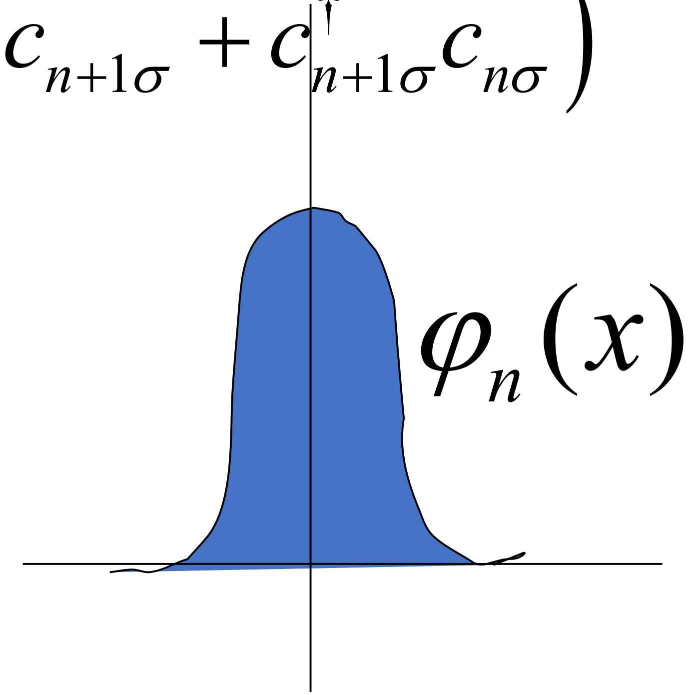
The short-range, one-band model for electron correlations in a narrow energy band is solved exactly in the one-dimensional case. The ground-state energy, wave function, and the chemical potentials are obtained, and it is found that the ground state exhibits no conductor-insulator transition as the correlation strength is increased.

https://doi.org/10.1103/PhysRevLett.20.1445 https://doi.org/10.1103/PhysRevLett.21.192.2
https://doi.org/10.1016/S0378-4371(02)01785-5 reminiscence and proofs

Consider the single particle term --

$$H_{SP} = -t\sum_{n=1}^{N-1}\sum_{\sigma=\uparrow}^{\downarrow}\left(c^{\dagger}_{n\sigma}c_{n+1\sigma} + c^{\dagger}_{n+1\sigma}c_{n\sigma}\right)$$

Here we imagine that the basis functions for a site *n* are localized on that site – Wannier functions --



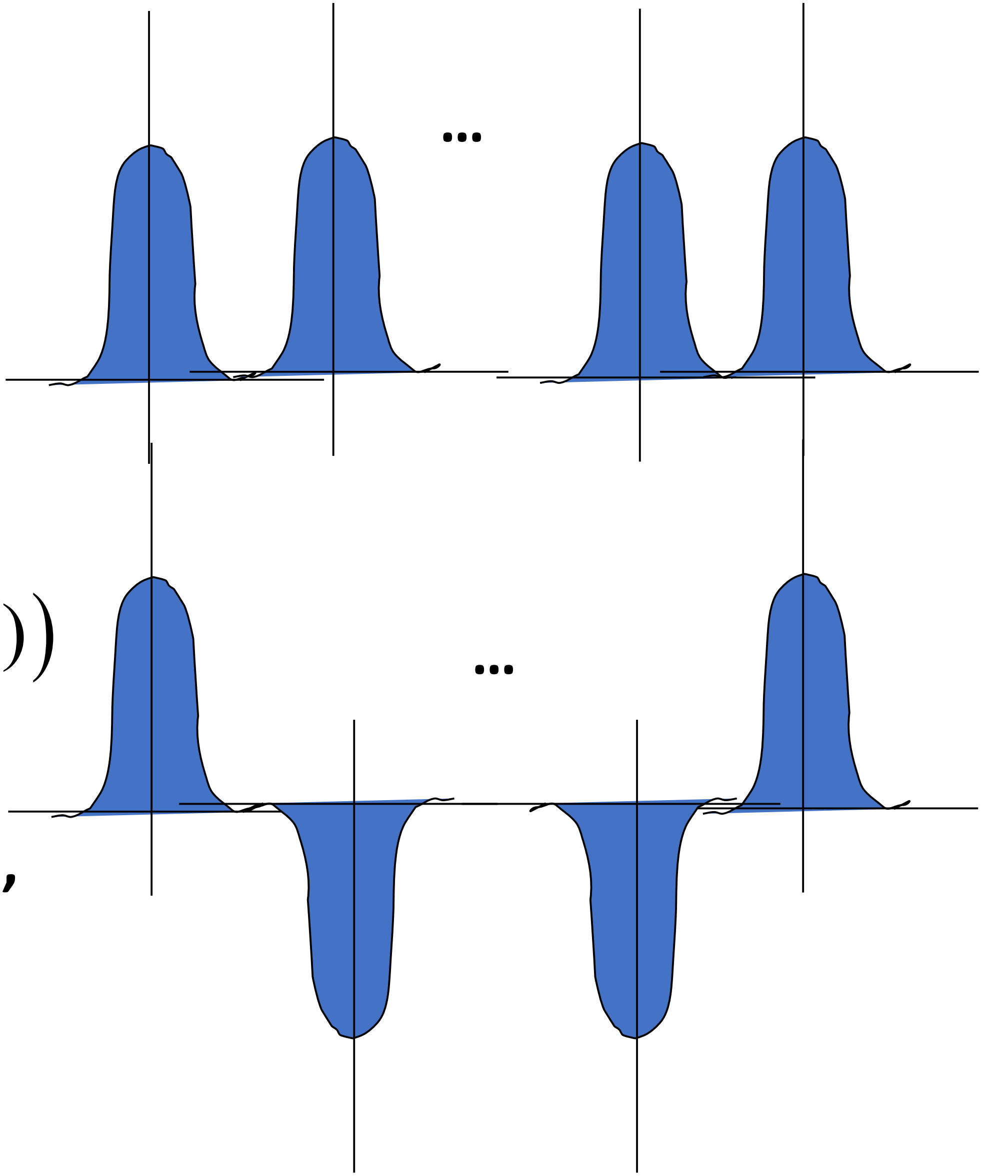
Now we assume that we have *N* electrons (*N* →∞) and that all of the states have equal probability of being on any of the sites.

Example N-particle wavefunction:

$$\Psi_N^a = \frac{1}{\sqrt{N}}\left(\varphi_1(x) + \varphi_2(x) + \ldots\varphi_n(x) + \ldots\varphi_N(x)\right)$$

Another example N-particle wavefunction:

$$\Psi_N^z = \frac{1}{\sqrt{N}}\left(\varphi_1(x) - \varphi_2(x) + \ldots - \varphi_{N-1}(x) + \varphi_N(x)\right)$$



These are only two examples of possible wavefunctions, all of which have have different energies

Systematic approach using Bloch symmetry --

Systematic approach using Bloch symmetry

$$\Psi^{k}_{N\sigma} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikan} \varphi_{n\sigma}(x)$$

Here we assume that the Wannier functions $\varphi_{n\sigma}(x)$ are centered at the position na and have the extent

$-\frac{a}{2} \leq x \leq \frac{a}{2}$. There are N distinct values of k:

$-\frac{\pi}{a} \leq k < \frac{\pi}{a}$, which becomes a continuum as $N \rightarrow \infty$.

Analysis within second-quantized framework:

$$H_{SP} = -t\sum_{n=1}^{N-1}\sum_{\sigma=\uparrow}^{\downarrow}\left(c_{n\sigma}^{\dagger}c_{n+1\sigma} + c_{n+1\sigma}^{\dagger}c_{n\sigma}\right)$$

Define new operators in the Bloch basis:

$$A_{k\sigma} = \frac{1}{\sqrt{N}}\sum_{n=1}^{N}e^{ikan}c_{n\sigma}$$

$$\{A_{k\sigma}, A_{k'\sigma'}\} = 0$$

$$\{A^{\dagger}{}_{k\sigma}, A^{\dagger}{}_{k'\sigma'}\} = 0$$

$$\{A_{k\sigma}, A^{\dagger}{}_{k'\sigma'}\} = \delta_{kk'}\delta_{\sigma\sigma'}$$

$$H_{SP} = -2t\sum_{k}\sum_{\sigma=\uparrow}^{\downarrow}\left(\cos(ka)\,A_{k\sigma}^{\dagger}A_{k\sigma}\right)$$

Single particle eigenstates --

Note that we are considering the case were there are N sites and N electrons (called "half-filling" case)

$$H_{SP} = -2t\sum_{k}\sum_{\sigma=\uparrow}^{\downarrow}\left(\cos(ka)\ A^{\dagger}_{k\sigma}A_{k\sigma}\right)$$

$$\psi_{k\sigma} = A^{\dagger}_{k\sigma}\left|0\right\rangle$$

$$H_{SP}\psi_{k\sigma} = \varepsilon_k\psi_{k\sigma} \qquad \varepsilon_k = -2t\cos(ka)$$

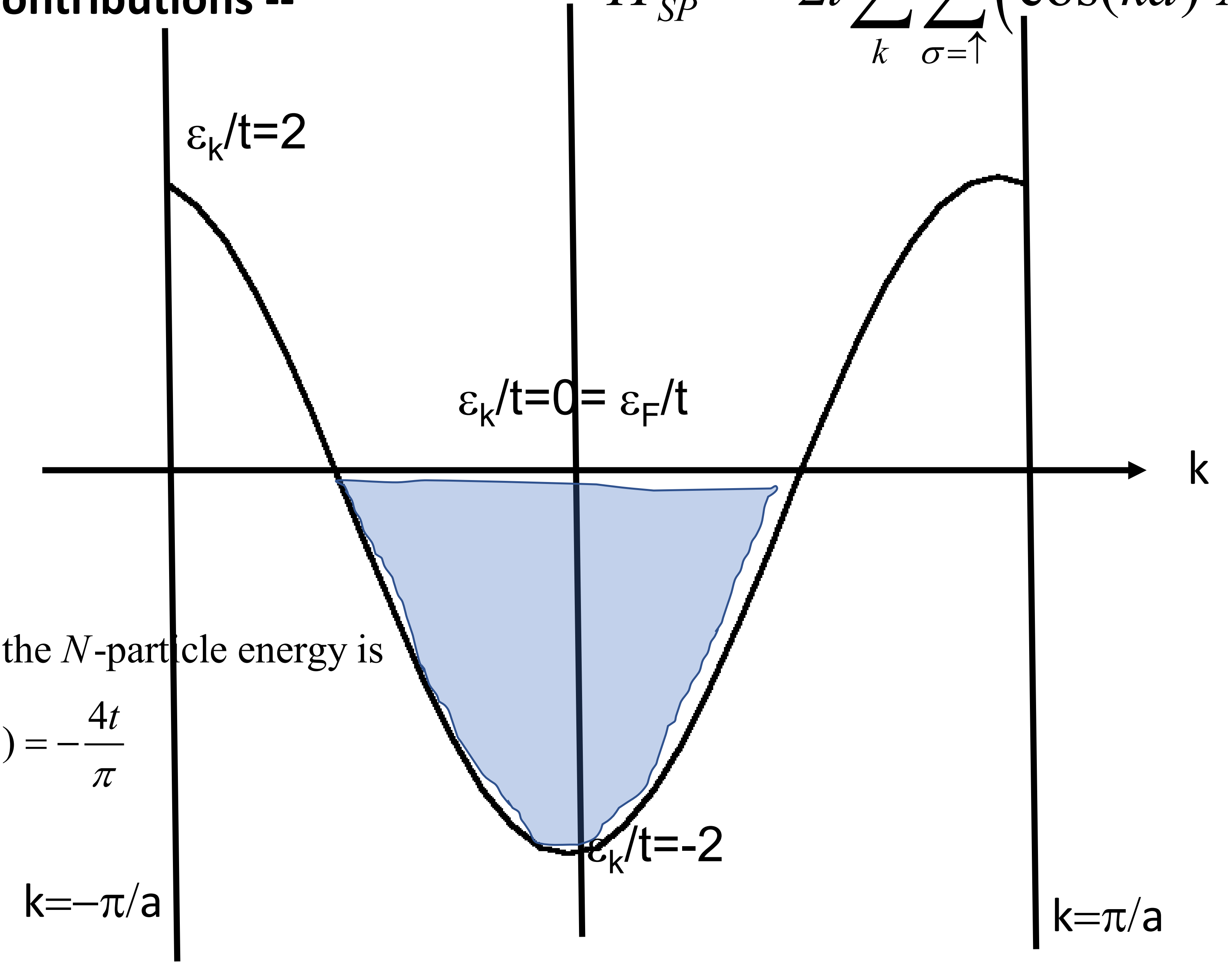
N particle state: $\Psi_N = \prod_{k\sigma} A^{\dagger}_{k\sigma}\left|0\right\rangle$

The range of k is $-k_F \leq k \leq k_F$ where $2\sum_{k} = N$

It can be shown that: $k_F = \dfrac{\pi}{2a}$

Single particle contributions --

$$H_{SP} = -2t\sum_{k}\sum_{\sigma=\uparrow}^{\downarrow}\left(\cos(ka)\ A^{\dagger}_{k\sigma}A_{k\sigma}\right)$$



It can be shown that the N-particle energy is

$$\frac{E_N}{N} = -4t\sum_{k=-k_F}^{k_F}\cos(ka) = -\frac{4t}{\pi}$$

Treatment of the full one-dimensional Hubbard model -- using the Bloch basis --

$$H = -2t \sum_{k\sigma} \cos\left(ka\right) A^{\dagger}_{k\sigma} A_{k\sigma} + \frac{U}{2N} \sum_{kq\sigma k'q'\sigma'} A^{\dagger}_{k\sigma} A^{\dagger}_{k'\sigma'} A_{q'\sigma'} A_{q\sigma} \delta(-k-k'+q+q')$$

where the delta function must be satisfied modulo a reciprocal lattice vector $\frac{2\pi}{a}$

Hartree-Fock solution for N-particle system; assuming double occupancy for each Bloch state:

N particle state: $\Psi_N = \prod_{-k_F \leq k \leq k_F} A^{\dagger}_{k\uparrow} A^{\dagger}_{k\downarrow} \left|0\right\rangle$

The range of k is $-k_F \leq k \leq k_F$ where $2\sum_k = N \quad \Rightarrow k_F = \frac{\pi}{2a}$

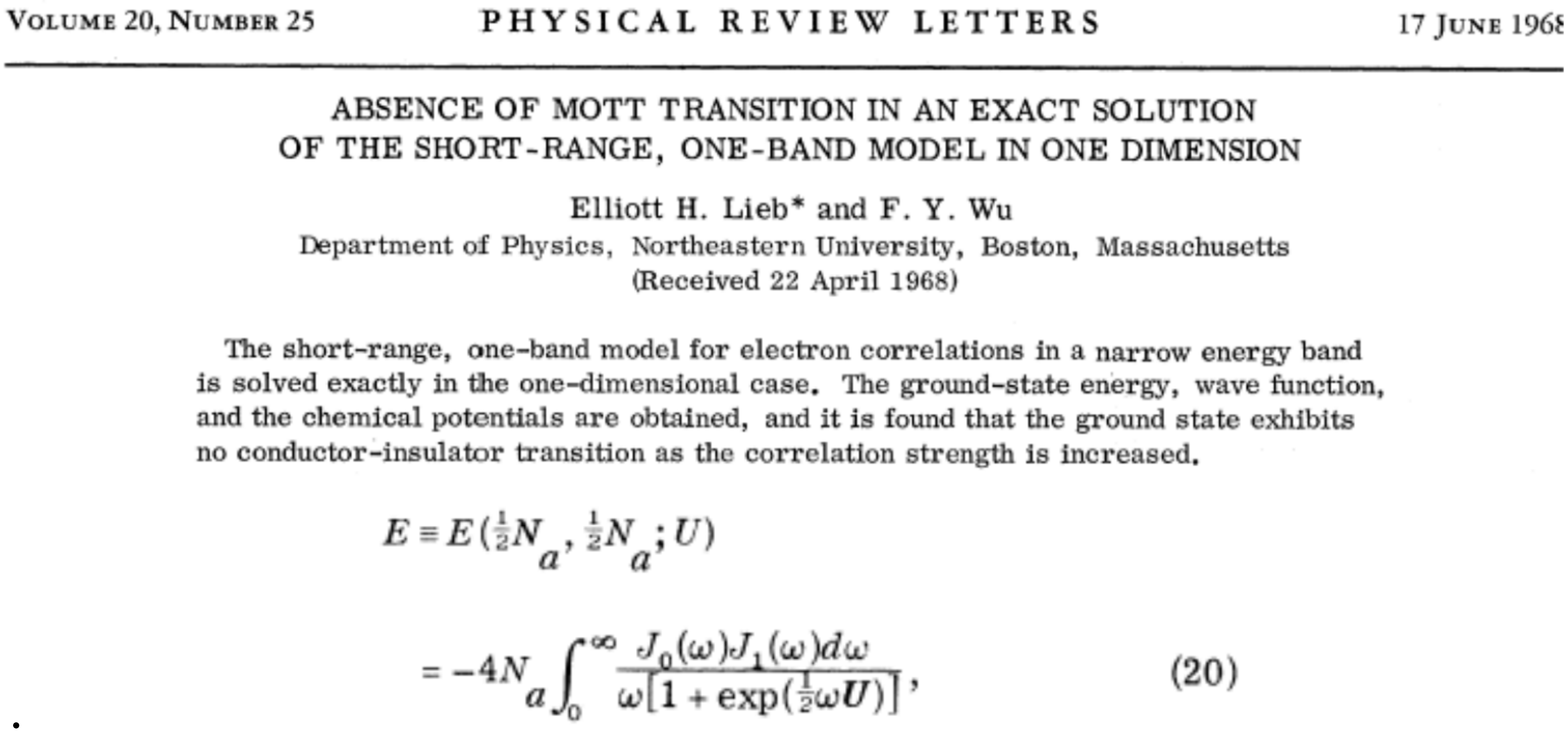
Evaluating the ground state energy in this simple Hartree Fock approximation, we find that

N particle state: $$\Psi_N = \prod_{-k_F \le k \le k_F} A^\dagger_{k\uparrow} A^\dagger_{k\downarrow} \left|0\right\rangle$$

The range of k is $-k_F \le k \le k_F$ where $2\sum_k = N \quad \Rightarrow k_F = \frac{\pi}{2a}$

$$\left\langle \Psi_N \middle| H \middle| \Psi_N \right\rangle = -4t \sum_{-k_F \le k \le k_F} \cos(ka) + U\left(\frac{1}{2}\right)^2 = -\frac{4t}{\pi} + \frac{U}{4}$$

Exact solution --



VOLUME 20, NUMBER 25 PHYSICAL REVIEW LETTERS 17 JUNE 196

ABSENCE OF MOTT TRANSITION IN AN EXACT SOLUTION OF THE SHORT-RANGE, ONE-BAND MODEL IN ONE DIMENSION

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$$E \equiv E(\tfrac{1}{2}N_a, \tfrac{1}{2}N_a; U)$$

$$= -4N_a \int_0^\infty \frac{J_0(\omega)J_1(\omega)d\omega}{\omega[1+\exp(\frac{1}{2}\omega U)]}, \qquad (20)$$

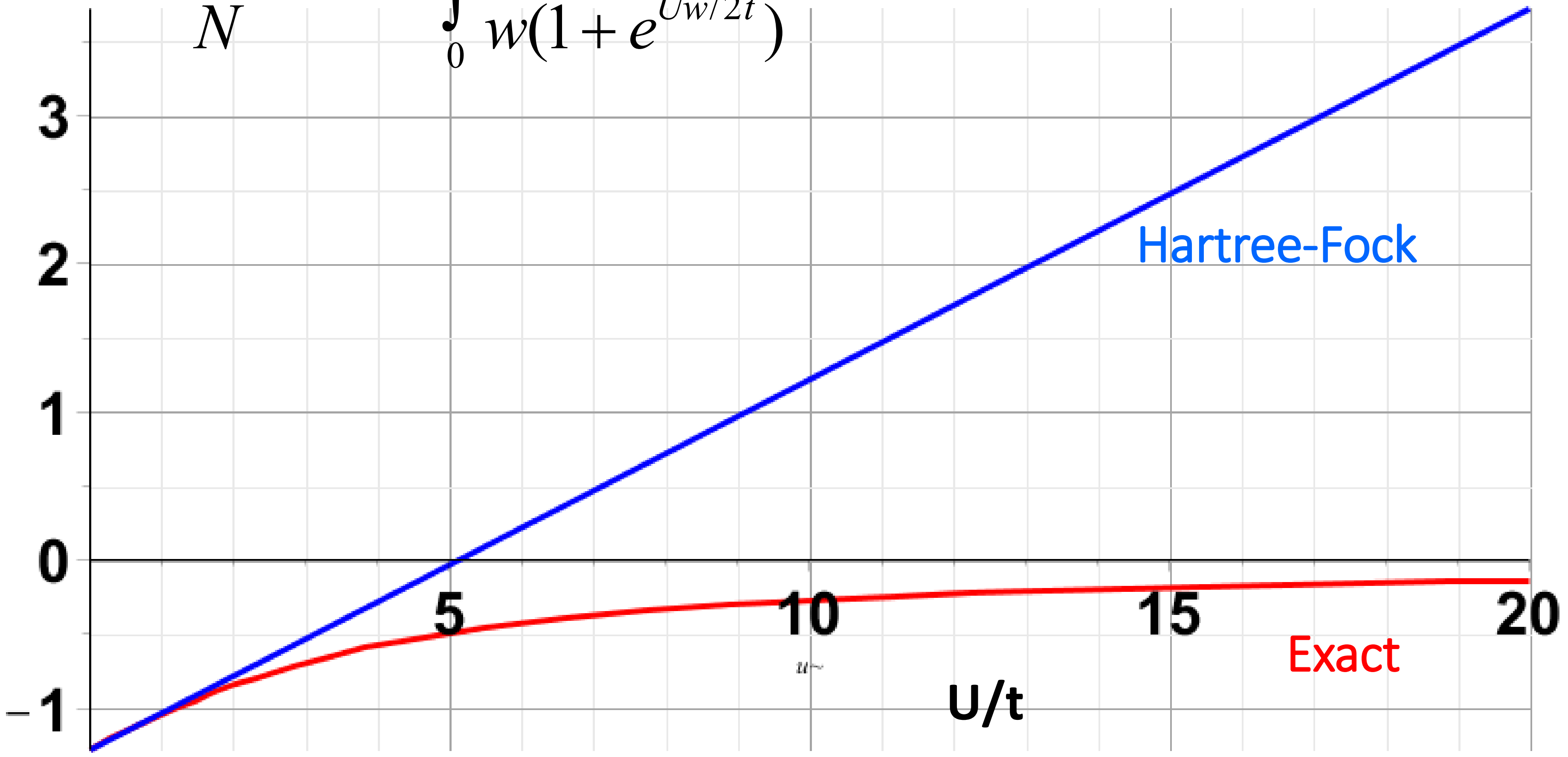
In our notation:

$$\frac{E_{exact}}{N} = -4t \int_0^\infty \frac{J_0(w)J_1(w)}{w(1+e^{Uw/2t})} dw$$

Evaluation of exact model in comparison with Hartree-Fock approximation

Lieb-Wu solution:

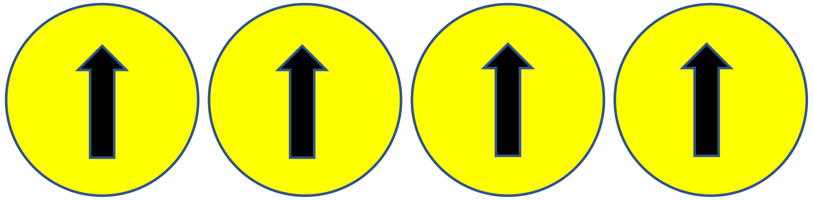
$$\frac{E_{exact}}{N} = -4t \int_0^{\infty} \frac{J_0(w)J_1(w)}{w(1+e^{Uw/2t})}\,dw$$



Can we improve the Hartree-Fock analysis?

What if we populate all N sites with with spin up electrons – "ferromagnetic" solution

$$\left|\Psi_{NF}\right\rangle =$$



$$H = -t\sum_{n=1}^{N-1}\sum_{\sigma=\uparrow}^{\downarrow}\left(c_{n\sigma}^{\dagger}c_{n+1\sigma} + c_{n+1\sigma}^{\dagger}c_{n\sigma}\right) + U\sum_{n=1}^{N}c_{n\uparrow}^{\dagger}c_{n\uparrow}c_{n\downarrow}^{\dagger}c_{n\downarrow}$$

$$\left\langle\Psi_{NF}\right|H\left|\Psi_{NF}\right\rangle = 0$$

Note that in the Bloch basis, this corresponds to filling all of the single particle states with spin up electrons

Digression – we can define a magnetization --

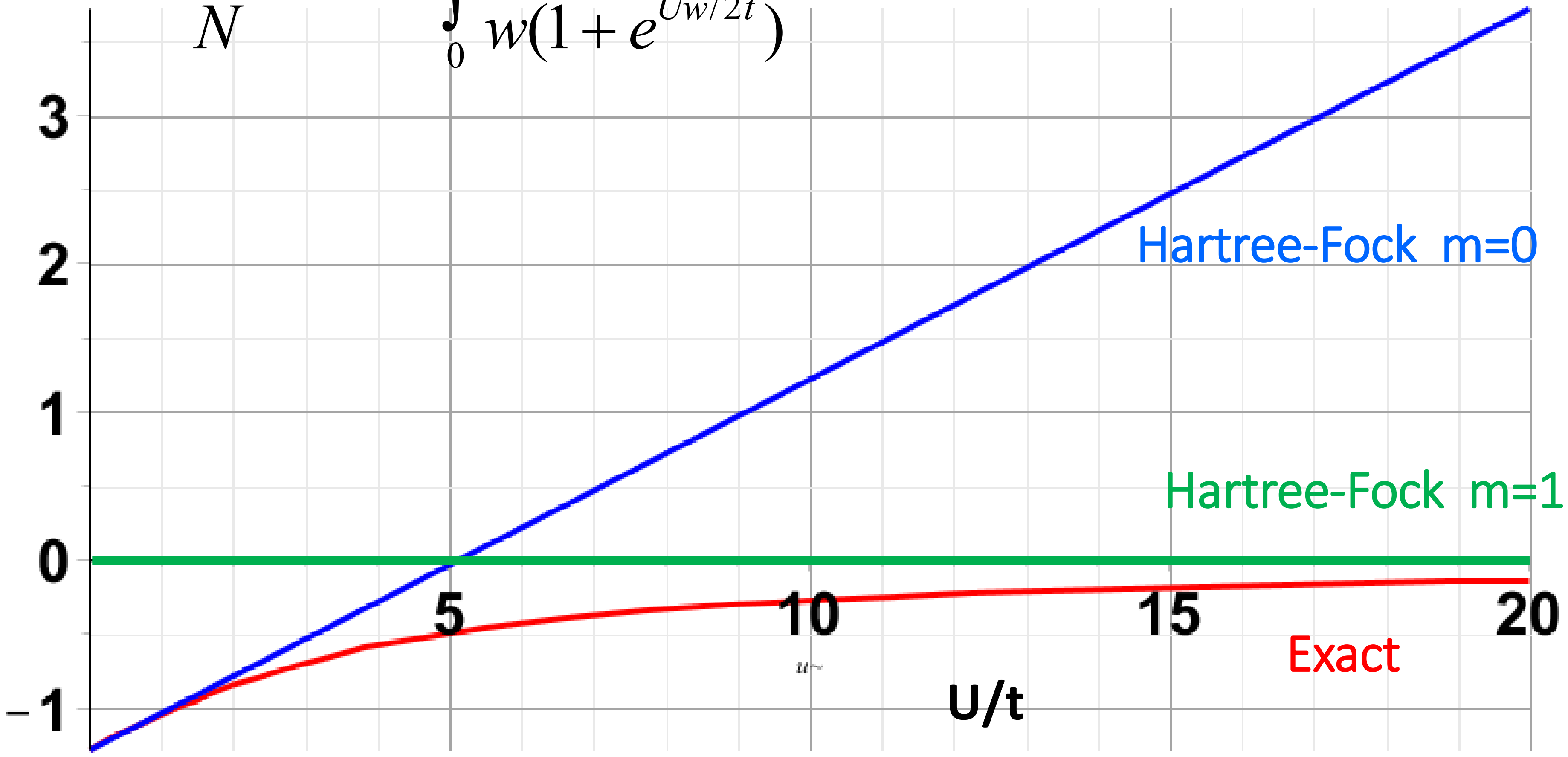
$$\frac{\langle N_{n\uparrow}\rangle - \langle N_{n\downarrow}\rangle}{\langle N_{n\uparrow}\rangle + \langle N_{n\downarrow}\rangle} \equiv m.$$

m=1 for the Ferromagnetic case
m=0 for the simple case

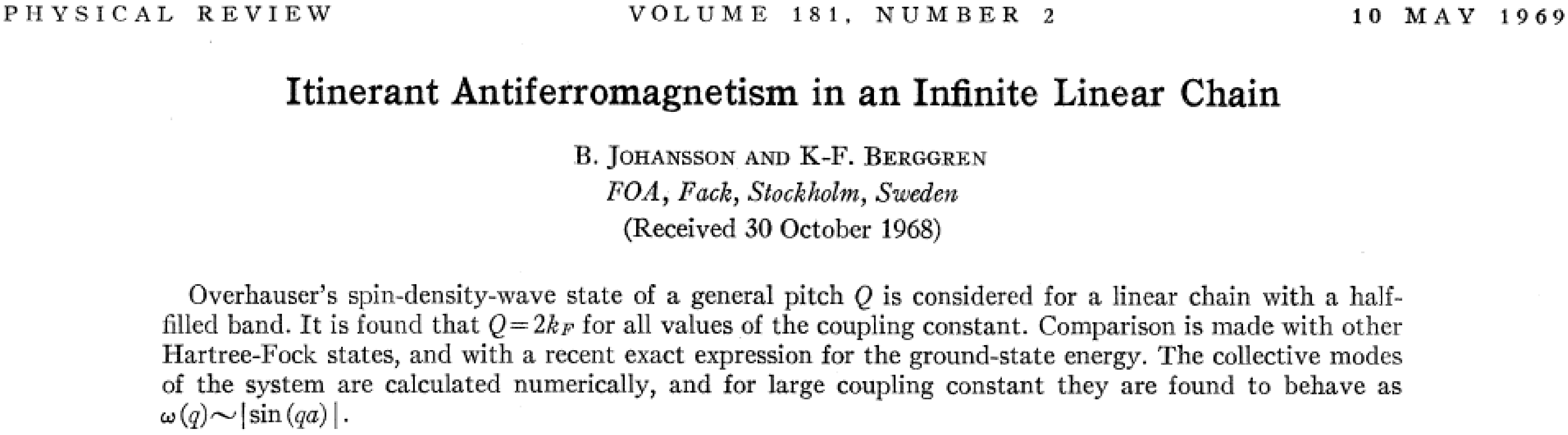
Evaluation of exact model in comparison with Hartree-Fock approximation

Lieb-Wu solution:

$$\frac{E_{exact}}{N} = -4t\int_0^\infty \frac{J_0(w)J_1(w)}{w(1+e^{Uw/2t})}dw$$



Approximate solutions in terms of single particle states; "broken symmetry" Hartree-Fock type solutions



PHYSICAL REVIEW VOLUME 181, NUMBER 2 10 MAY 1969

Itinerant Antiferromagnetism in an Infinite Linear Chain

B. JOHANSSON AND K-F. BERGGREN
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(Received 30 October 1968)

Overhauser's spin-density-wave state of a general pitch Q is considered for a linear chain with a half-filled band. It is found that $Q=2k_F$ for all values of the coupling constant. Comparison is made with other Hartree-Fock states, and with a recent exact expression for the ground-state energy. The collective modes of the system are calculated numerically, and for large coupling constant they are found to behave as $\omega(q) \sim |\sin(qa)|$.

Spin density wave Hartree Fock approximation

An alternative composite Bloch wave can be defined:

$$S_{k\uparrow} \equiv \cos\theta_k A_{k\uparrow} + \sin\theta_k A_{k+Q\downarrow}. \qquad (26)$$

Here, Q will be determined; for example $Q = \pi / a$ corresponds to a doubled unit cell. (It can be shown that the orthogonal linear combination state does not contribute to the ground state wavefunction.)

$$\left|\Psi_{SDW}\right\rangle = \prod_k S_k^\dagger \left|0\right\rangle$$

$$E_{SDW} = \left\langle \Psi_{SDW} \right| H \left| \Psi_{SDW} \right\rangle = \sum_k E_k^S$$

where $E_k^S = \frac{1}{2}\left(\varepsilon_k + \varepsilon_{k+Q}\right) - \frac{1}{2}\left(\left(\varepsilon_k - \varepsilon_{k+Q}\right)^2 + \Delta^2\right)^{1/2}$

Here $\varepsilon_k = -2\cos(ka)$

Spin density wave solution -- continued

Using slightly different notation ---

Consistency conditions on Δ:

$$\frac{1}{\mathcal{N}}\sum_k \frac{1}{\left(\left(\varepsilon_k-\varepsilon_{k+Q}\right)^2+\Delta^2\right)^{1/2}}=\frac{1}{u}$$

$$\tan(2\theta_k)=\frac{\Delta}{\varepsilon_k-\varepsilon_{k+Q}}$$

Expression for energy:

$$\frac{E_{SDW}}{\mathcal{N}}=\frac{1}{2\mathcal{N}}\sum_k\left\{\left(\varepsilon_k+\varepsilon_{k+Q}\right)+\left(\varepsilon_k-\varepsilon_{k+Q}\right)\cos(2\theta_k)\right\}+\frac{u}{4}\left(1-\frac{1}{\mathcal{N}^2}\sum_{kq}\sin(2\theta_k)\sin(2\theta_q)\right)$$

Johannson and Berggren show that:

$$\eta K(\eta)=\frac{2\pi}{u}\sin(Qa/2)$$

where $\quad \eta=\dfrac{1}{\left(1+\dfrac{\Delta^2}{16}\sin^2\left(Qa/2\right)\right)^{1/2}}$

Elliptic integral:

$$K(m)\equiv\int_0^{\pi/2}\frac{d\phi}{\left(1-m\sin^2\phi\right)^{1/2}}$$

Spin density wave solution -- continued

Expression for energy:

$$\frac{E_{SDW}}{\mathcal{N}} = -\frac{4}{\pi}\sin(Qa/2)\frac{E(\eta)}{\eta} + \frac{u}{4}\left(1+\frac{\Delta^2}{u^2}\right)$$

Elliptic integral:

$$E(m) \equiv \int_0^{\pi/2}\left(1-m\sin^2\phi\right)^{1/2} d\phi$$

Optimal solution obtained for $Qa/2 = \pi/2$:

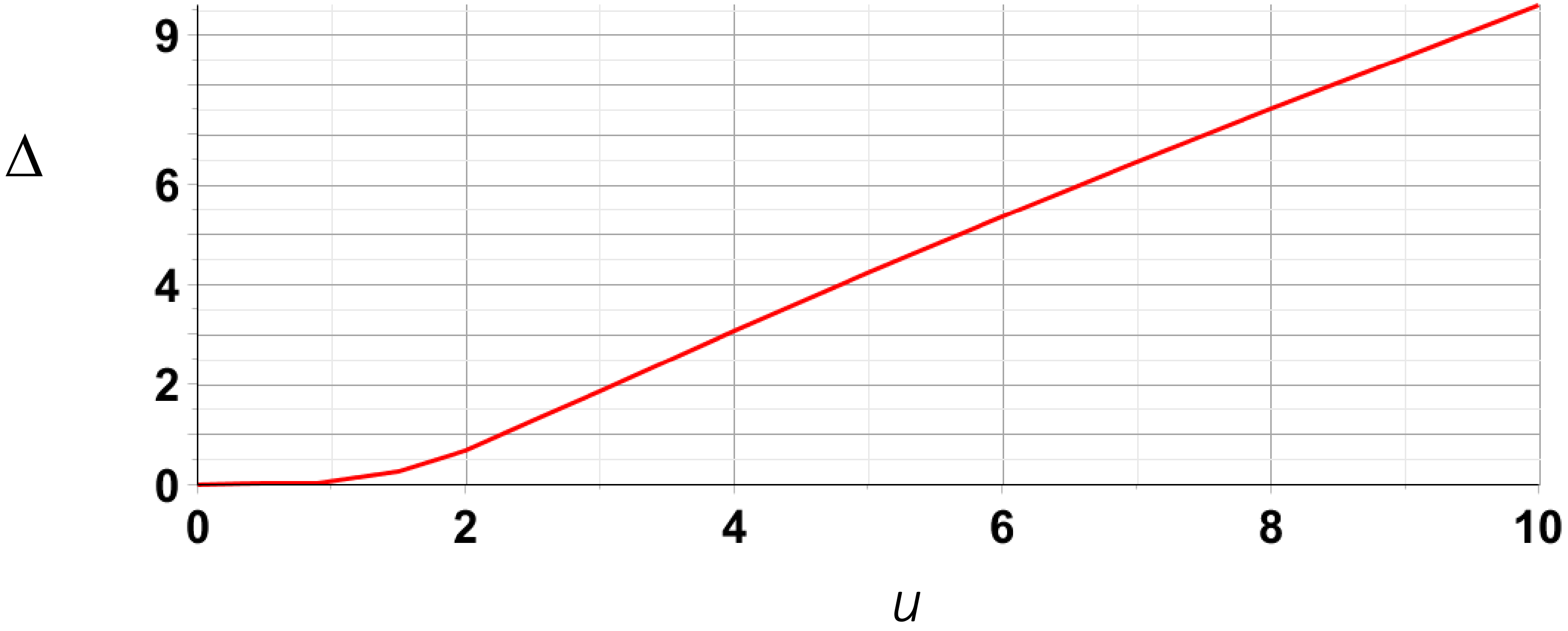
$$\eta K(\eta) = \frac{2\pi}{u} \qquad \text{where} \quad \eta = \frac{1}{\left(1+\frac{\Delta^2}{16}\right)^{1/2}}$$

$$\frac{E_{SDW}}{\mathcal{N}} = -\frac{4}{\pi}\frac{E(\eta)}{\eta} + \frac{u}{4}\left(1+\frac{\Delta^2}{u^2}\right)$$

Spin density wave solution -- continued

Numerical solutions for Δ:

$$\frac{2\pi}{\eta K(\eta)} = u \qquad \text{where} \quad \eta = \frac{1}{\left(1+\frac{\Delta^2}{16}\right)^{1/2}}$$

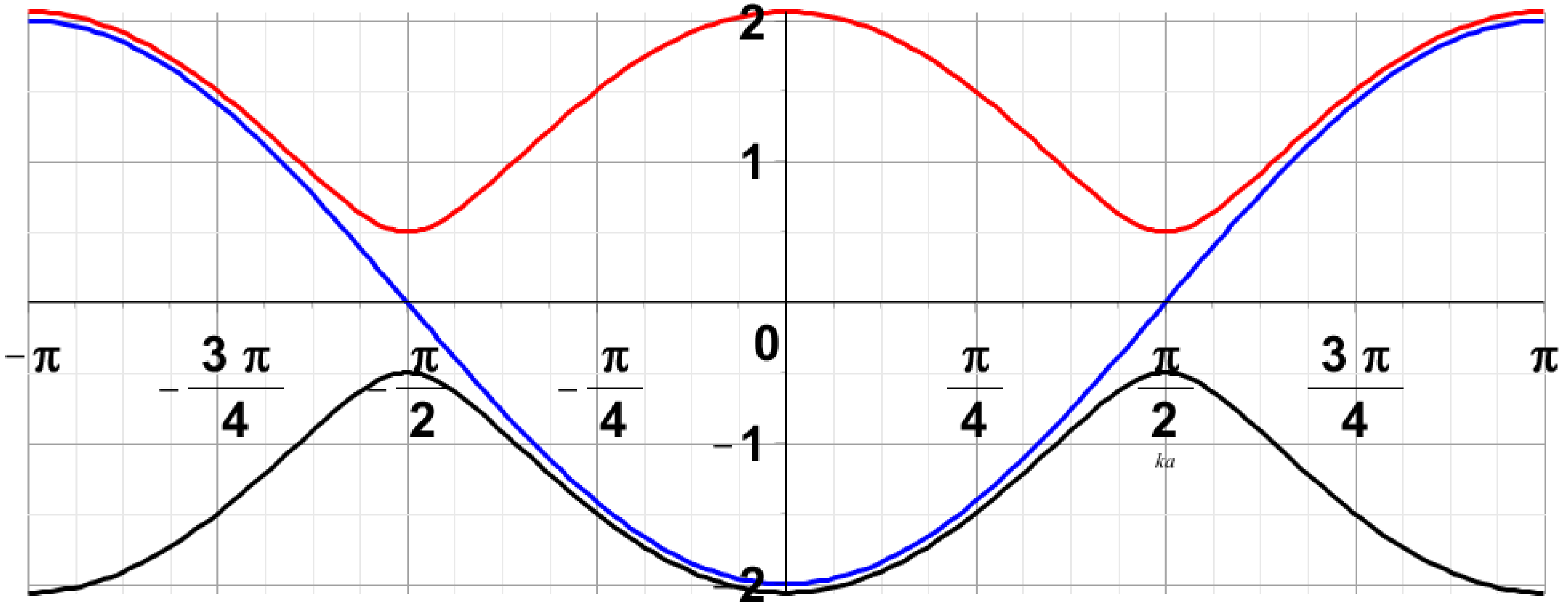


Spin density wave solution -- continued

Effects on single particle states

Non-interacting states: $\varepsilon_k = -2\cos(ka)$

Spin density wave states: $E_k^S = \pm\frac{1}{2}\left(\left(4\cos(ka)\right)^2 + \Delta^2\right)^{1/2}$

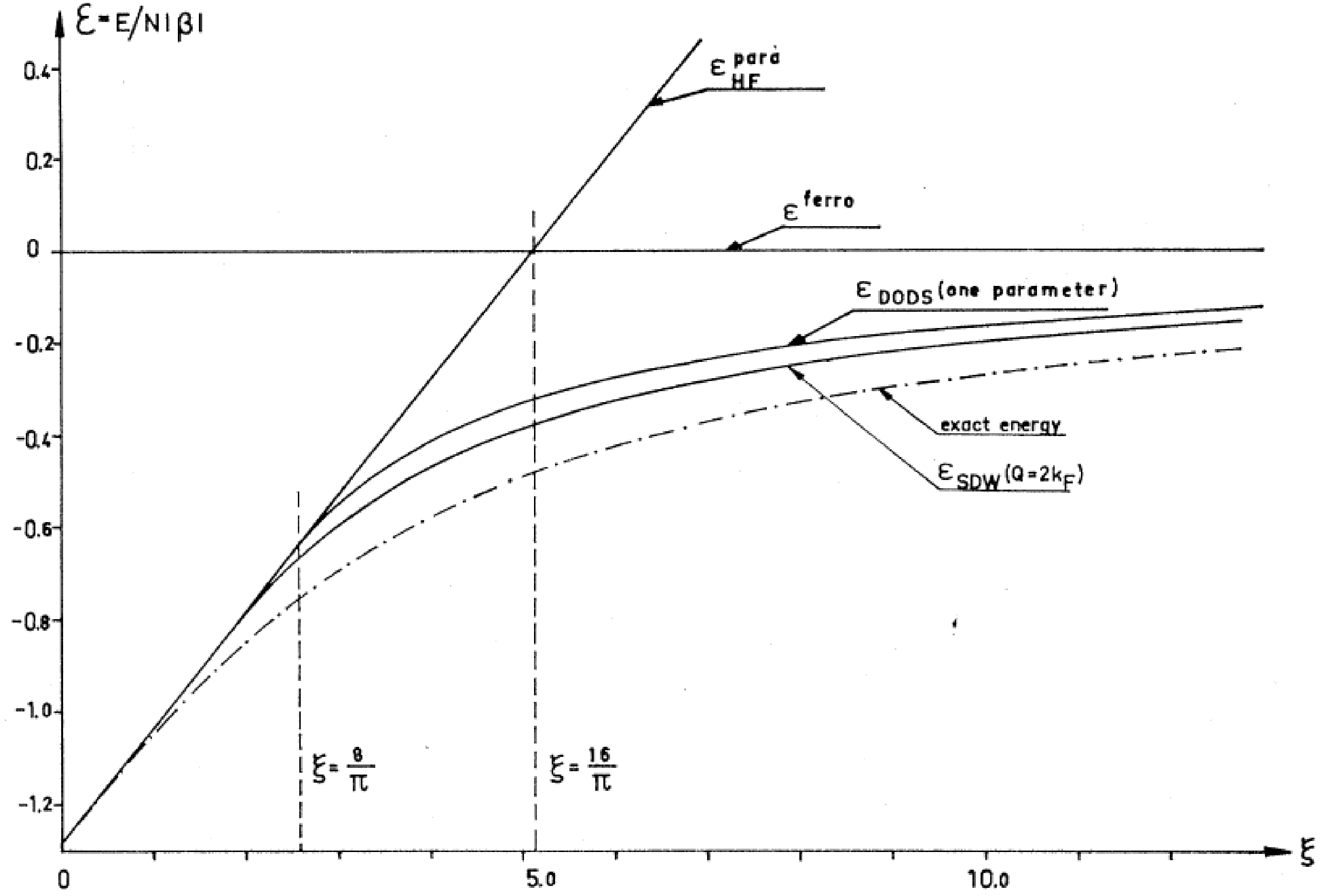


Spin density wave solution -- continued

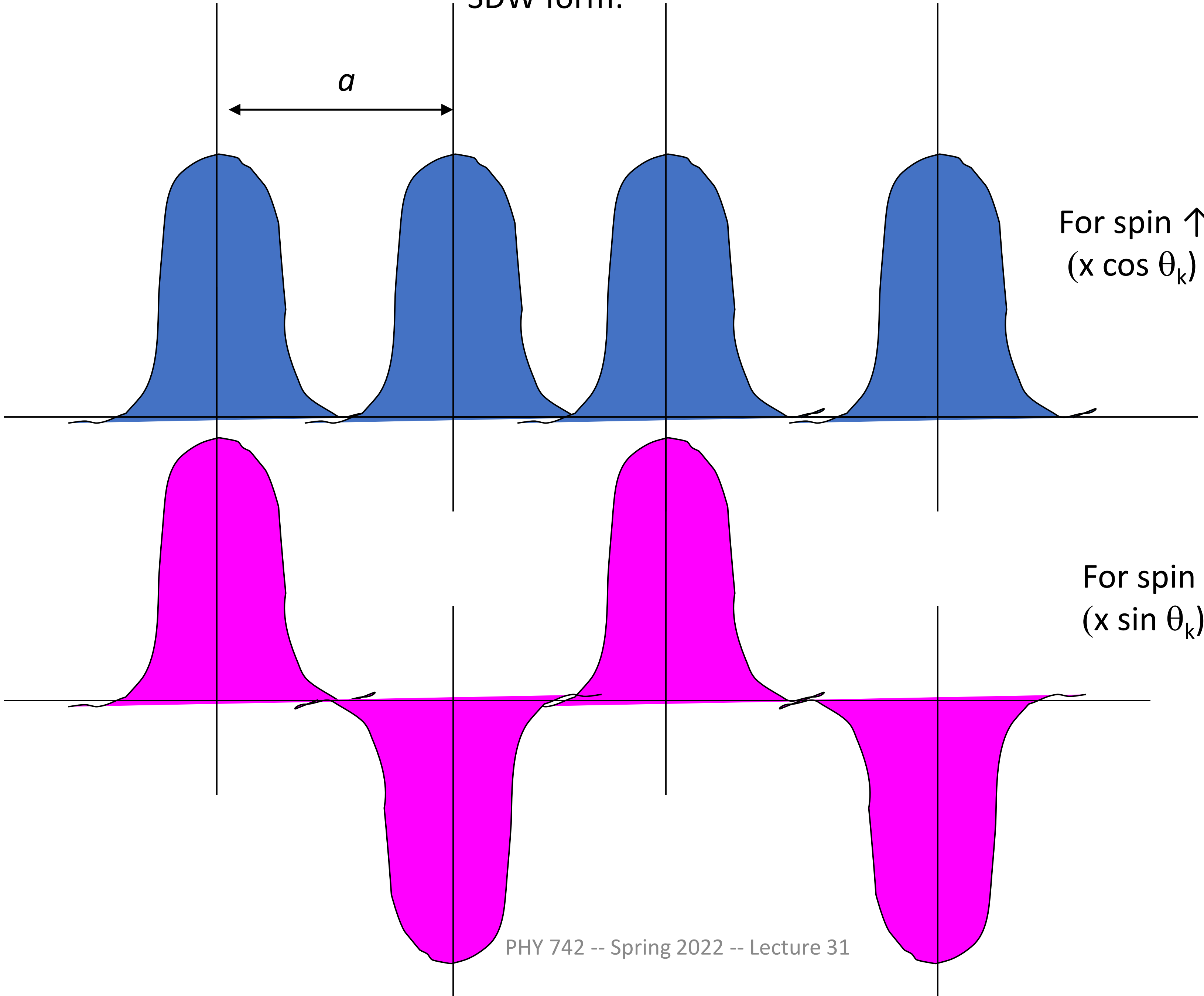
Nature of spin density wave state:

$$S_k = \cos\theta_k A_{k\uparrow} + \sin\theta_k A_{k+\frac{\pi}{a}\downarrow}$$

$$\tan(2\theta_k) = \frac{\Delta}{\varepsilon_k - \varepsilon_{k+Q}} = -\frac{\Delta}{4\cos(ka)}$$

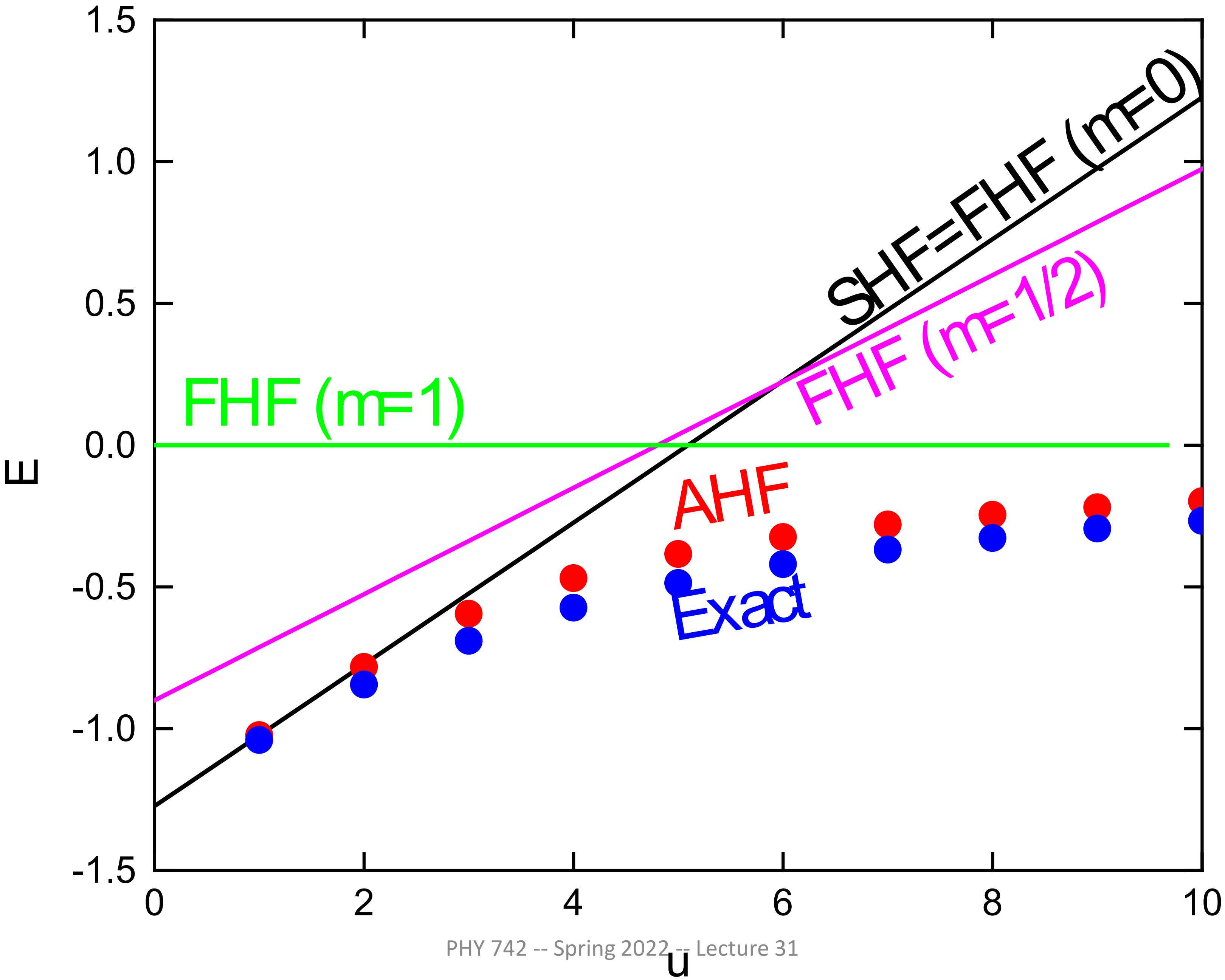


SDW form:



For spin ↑
(x cos θ_k)

For spin ↓
(x sin θ_k)


1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
E
0
2
4
6
8
10
u
SHF=FHF (m=0)
FHF (m=1/2)
FHF (m=1)
AHF
Exact

Comment on Hubbard model in higher dimensions –

Used to study model systems of finite size with exact diagonalization

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:

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

Here,

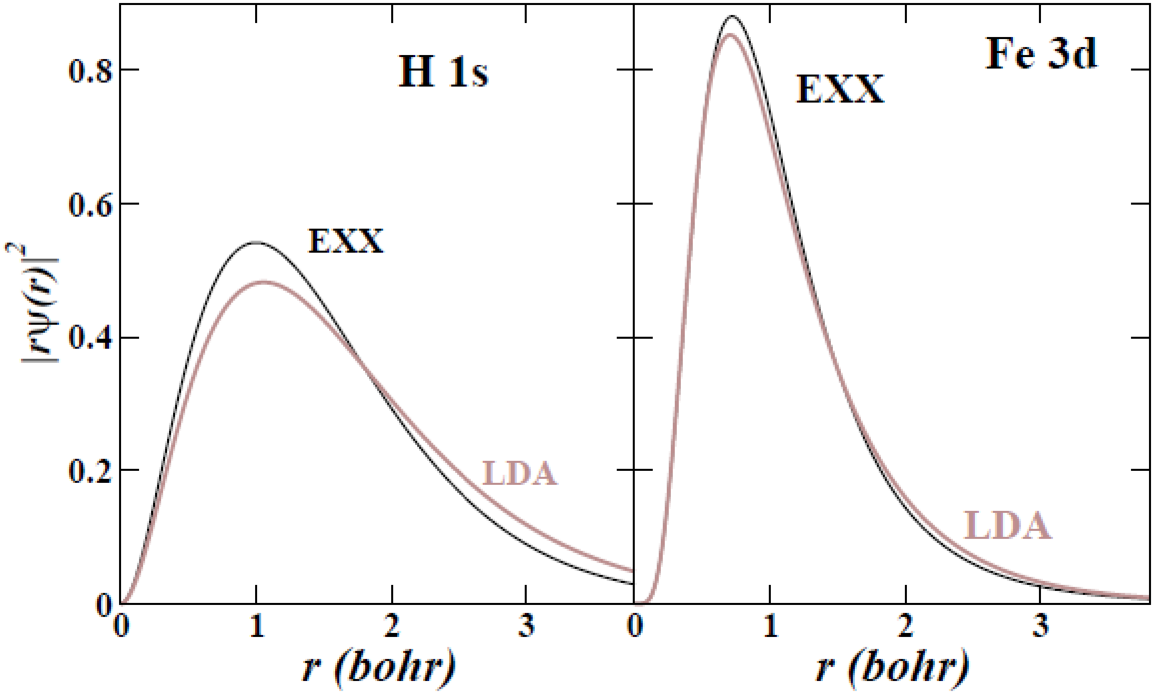
$$E_H(\rho) \equiv \frac{e^2}{2} \int \int d^3r \, d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \qquad (2)$$

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

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

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:

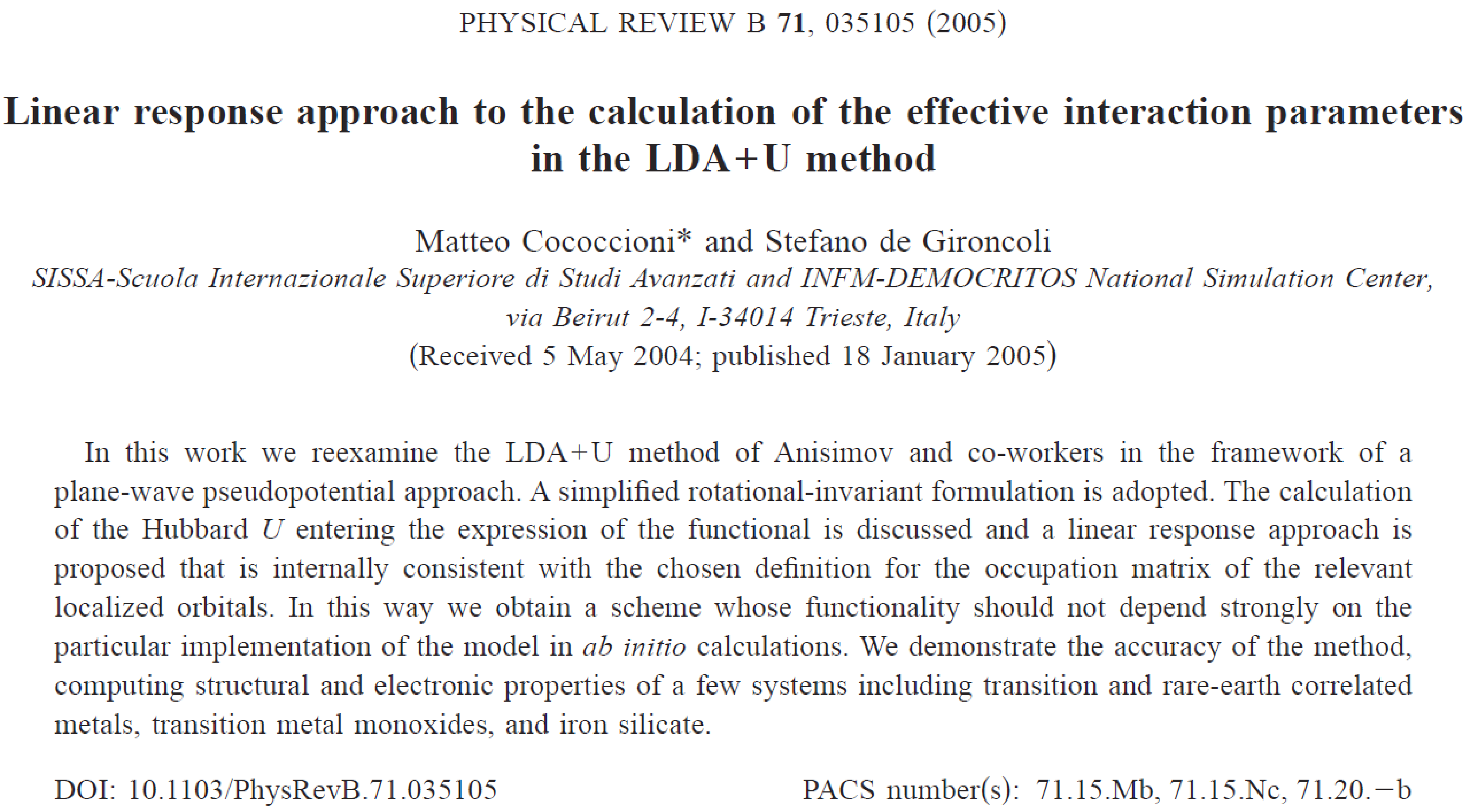
$$E_H = 2e^2 \sum_{p,q(occ)} \int d^3r \int d^3r' \frac{\Psi_p^*(\mathbf{r})\Psi_p(\mathbf{r})\Psi_q^*(\mathbf{r}')\Psi_q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

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

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
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(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*:

$$E_{\mathrm{LDA+U}}[n(\mathbf{r})] = E_{\mathrm{LDA}}[n(\mathbf{r})] + \underbrace{E_{\mathrm{Hub}}[\{n_m^{I\sigma}\}] - E_{\mathrm{DC}}[\{n^{I\sigma}\}]}_{\text{Coulomb and exchange interactions on atomic sites corrected for “double counting”}},$$

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_l to vary consistently.

Simplified LDA+U Hamiltonian

$$E_U[\{n_{mm'}^{I\sigma}\}] = E_{\text{Hub}}[\{n_{mm'}^{I}\}] - E_{\text{DC}}[\{n^I\}]$$

$$= \frac{U}{2}\sum_I \sum_{m,\sigma} \left\{ n_{mm}^{I\sigma} - \sum_{m'} n_{mm'}^{I\sigma} n_{m'm}^{I\sigma} \right\}$$

$$= \frac{U}{2}\sum_{I,\sigma} \mathrm{Tr}[\mathbf{n}^{I\sigma}(1-\mathbf{n}^{I\sigma})].$$

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

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

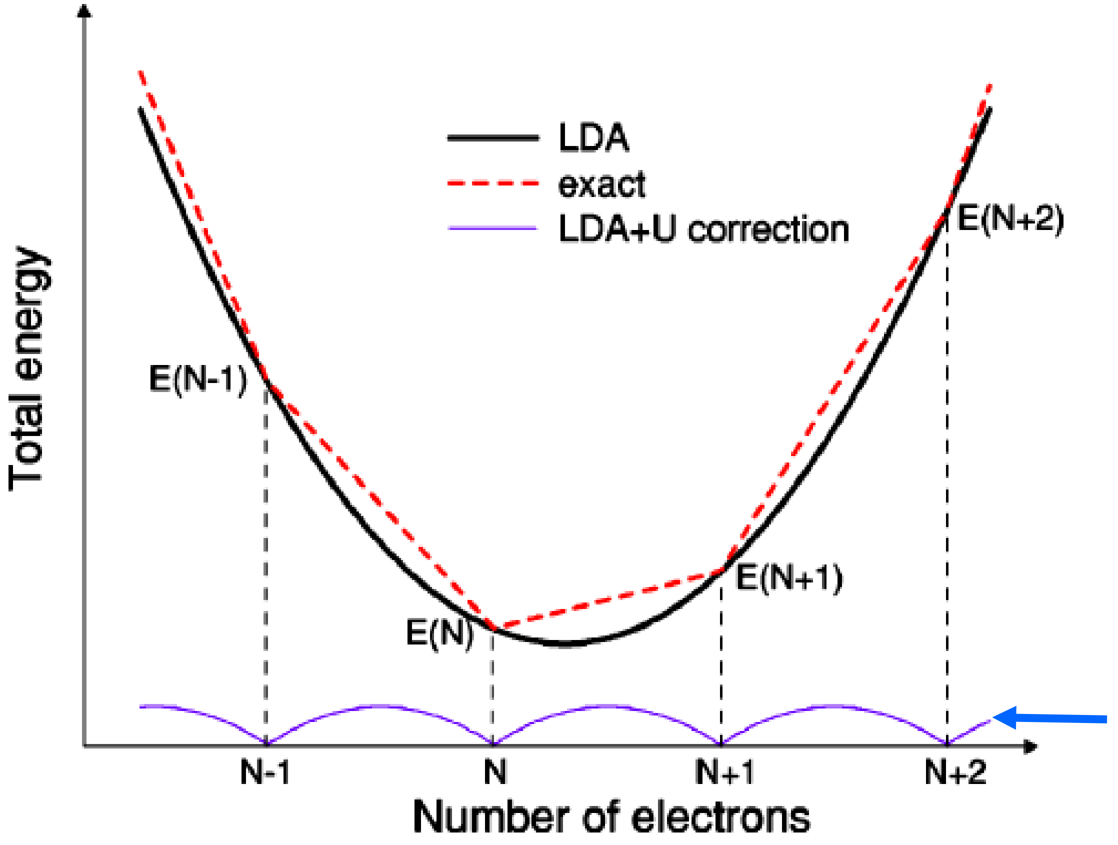


FIG. 1. (Color online) Sketch of the total energy profile as a function of number of electrons in a generic atomic system in contact with a reservoir. The bottom curve is simply the difference between the other two (the LDA energy and the "exact" result for an open system).

Needed correction to be provided by U term.

Cococcioni and de Girancoli proposal for calculating U:

Introduce new variables q_I representing local orbital occupations

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

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

Cococioni & de Gironcoli

Example for FeO

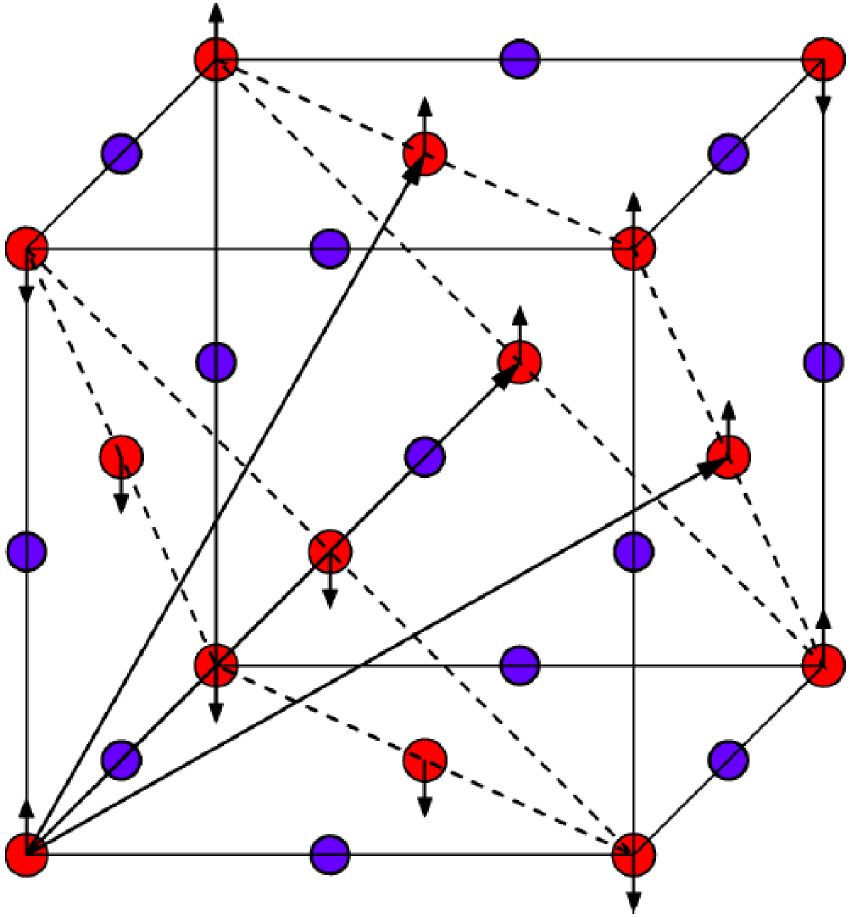


FIG. 6. (Color online) The unit cell of FeO: blue spheres represent oxygen ions, red ones are Fe ions, with arrows showing the orientation of their magnetic moments. Ferromagnetic (111) planes of iron ions alternate with opposite spins producing type-II antiferromagnetic order and rhombohedral symmetry.

Cococioni & de Gironcoli

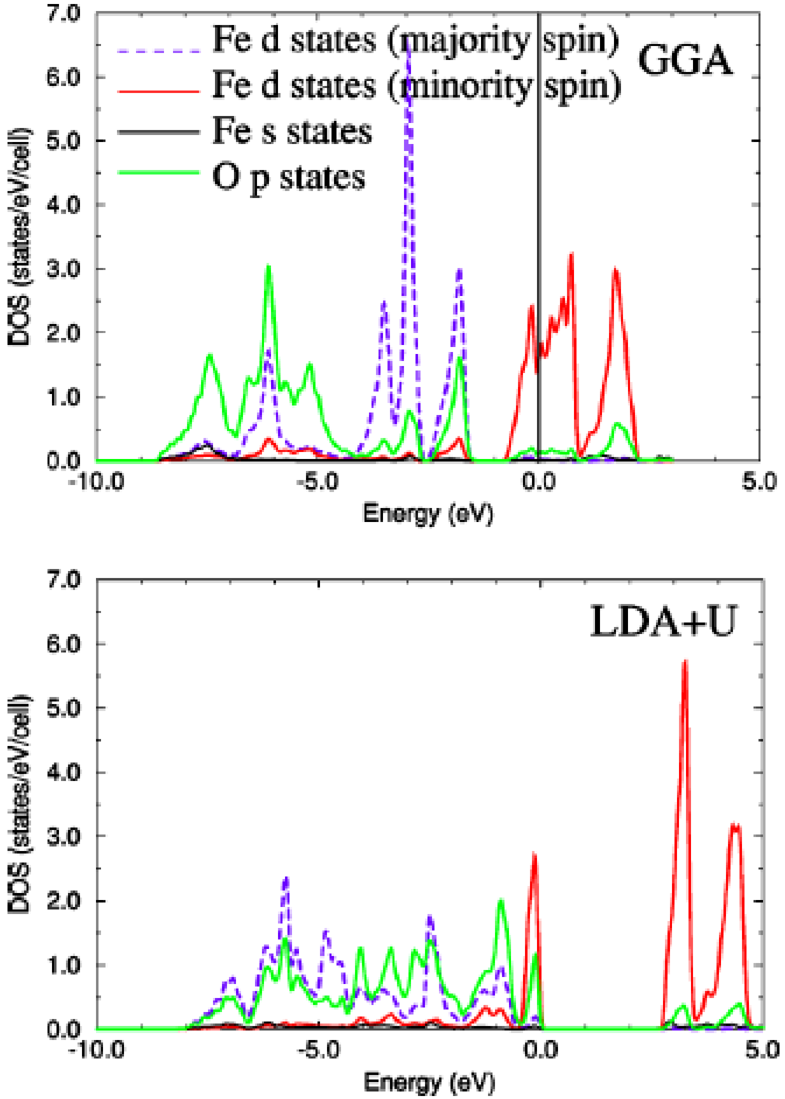
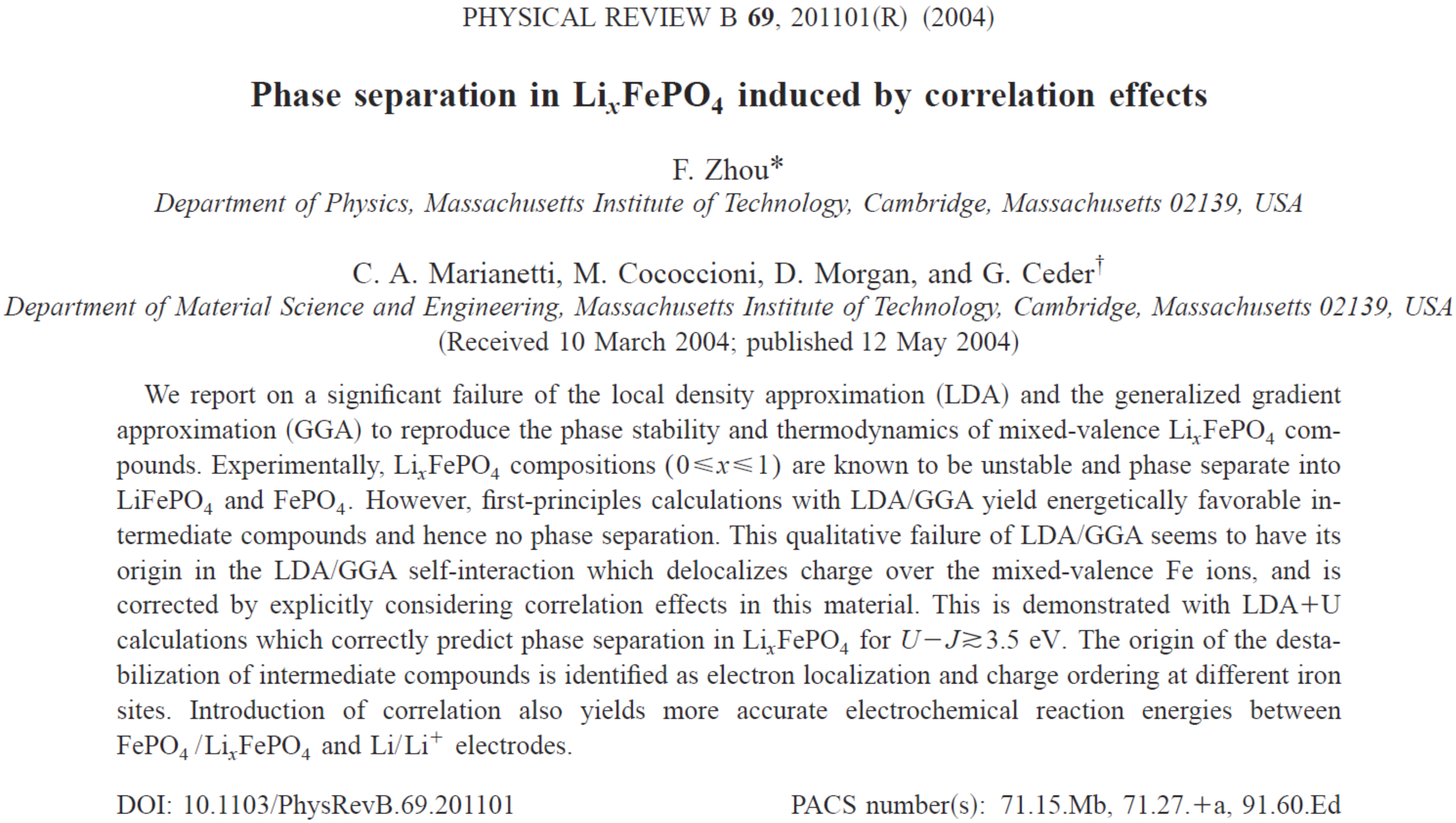


FIG. 9. (Color online) Projected density of states of FeO in the undistorted (cubic) AF configuration at the experimental lattice spacing obtained within GGA (top panel) and LDA+U using the computed Hubbard *U* of 4.3 eV (bottom panel).

Application of LDA+U to phase stability of Li$_x$FeO$_4$



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Phase separation in Li$_x$FePO$_4$ induced by correlation effects

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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$_x$FePO$_4$ compounds. Experimentally, Li$_x$FePO$_4$ 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$_x$FePO$_4$ for $U - J \gtrsim 3.5$ 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$_x$FePO$_4$ and Li/Li$^+$ electrodes.

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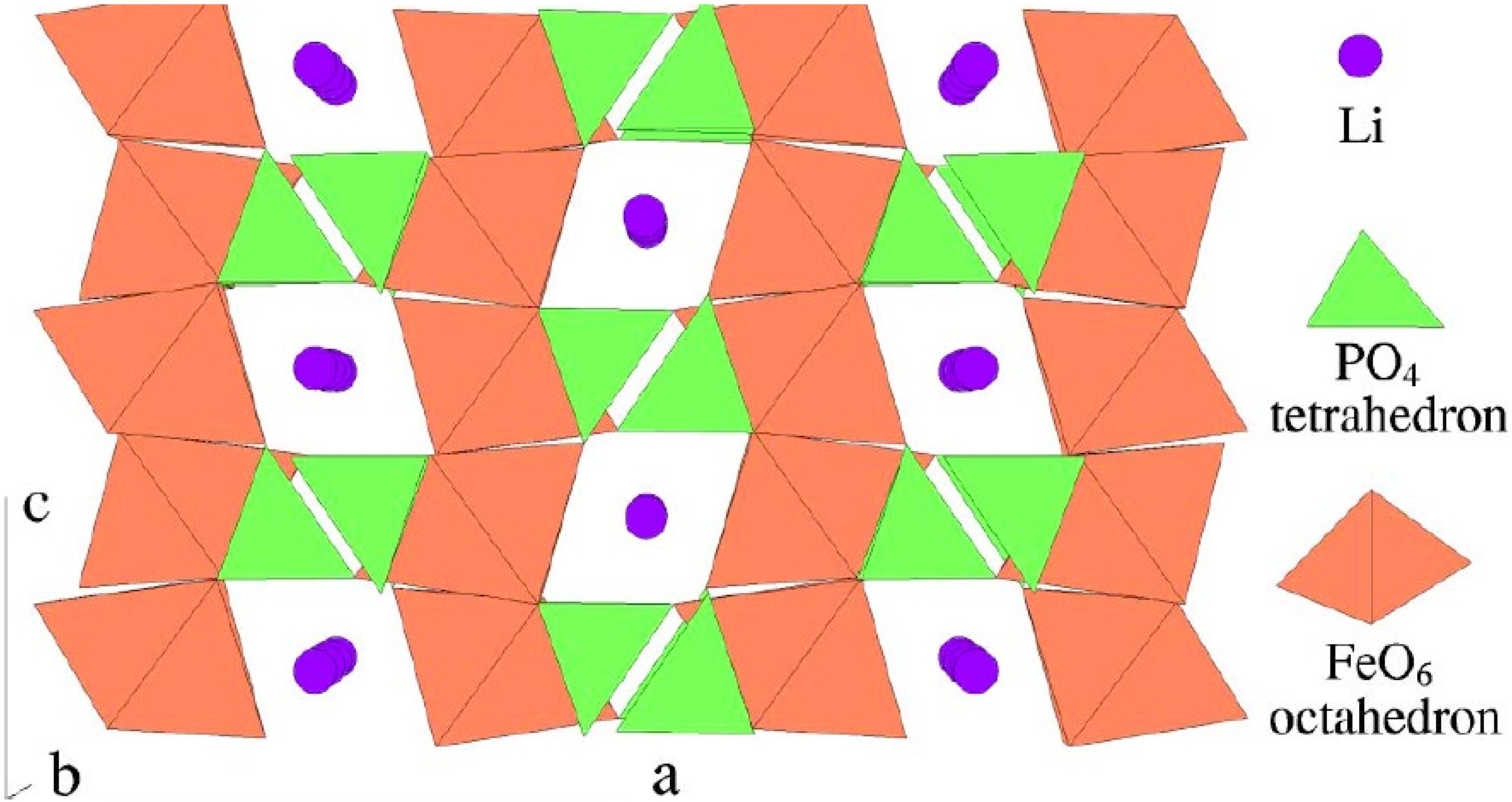

FIG. 1. Structure of $LiFePO_4$ with cation polyhedra.

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

Simplified LDA+U

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

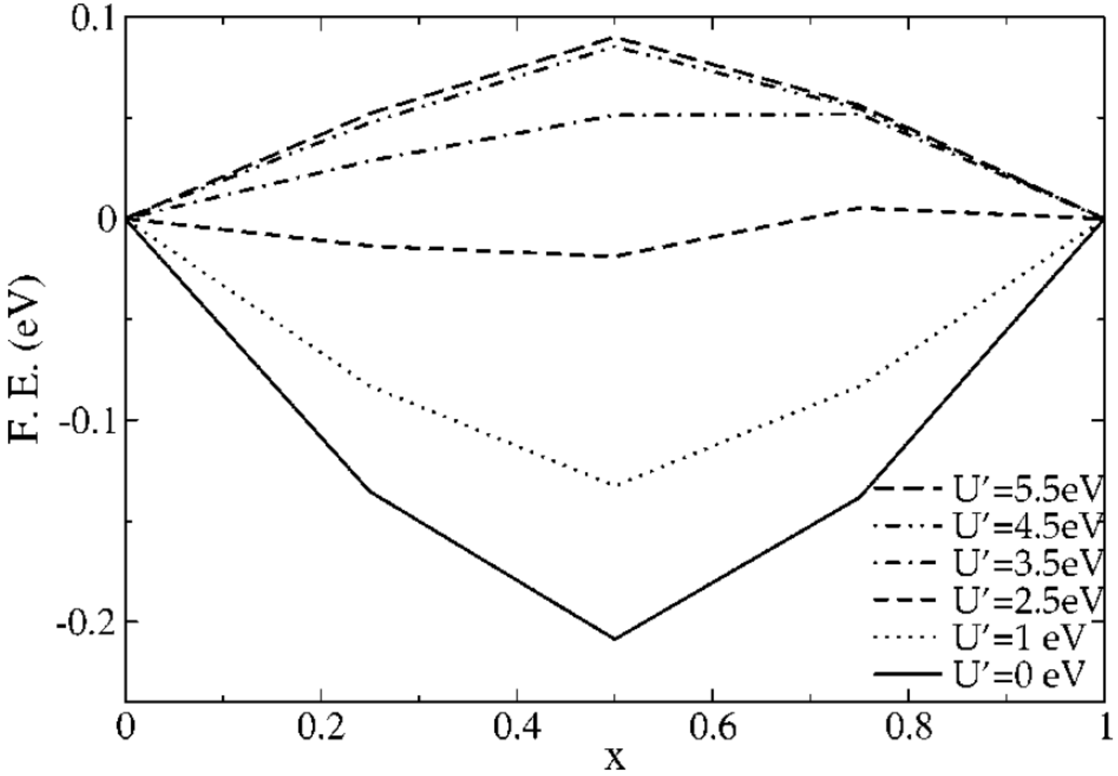

FIG. 2. Formation energy of Li_xFePO_4 at different x and U' values. Points at $x = 0.5$ correspond to structure 0.5a.