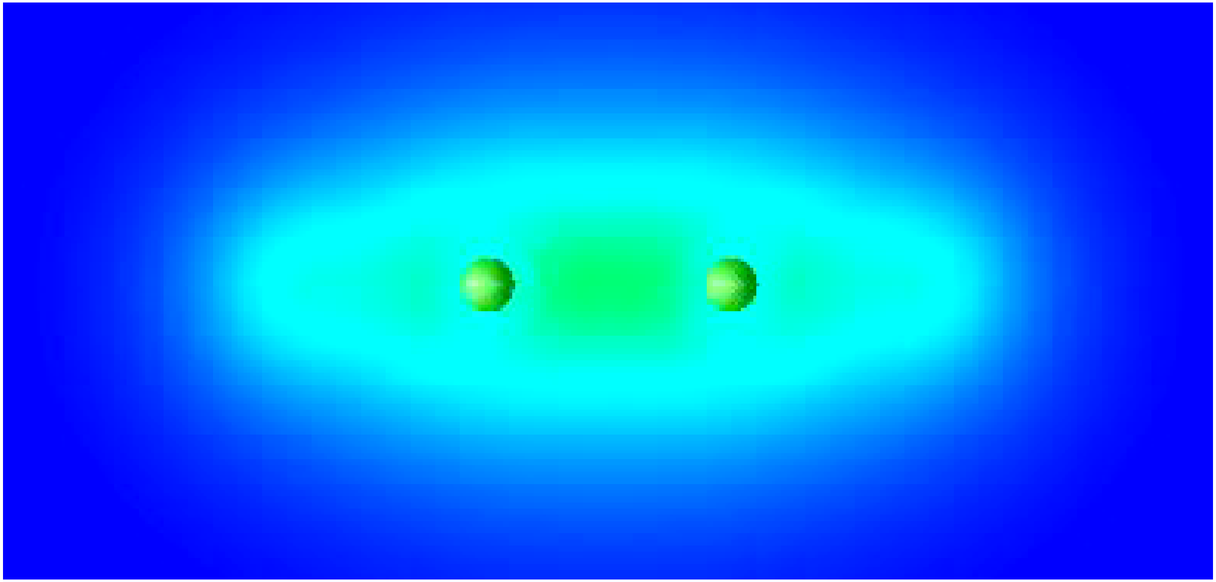
LDA – and beyond

A primer into density-functional theory and related techniques

Tobias Burnus



SFB 608

Diploma and PhD colloquium
22 November 2006

Pre-remarks I

Functionals

A function f maps a number to another number:

$$x \mapsto y = f(x) \qquad \text{example: } f(x) = x^2$$

A functional F maps a function to another function:

$$f \mapsto g = F[f] \qquad \text{example: } F[f](x) = \int_0^x f(x')\,\mathrm{d}x'$$

Notation

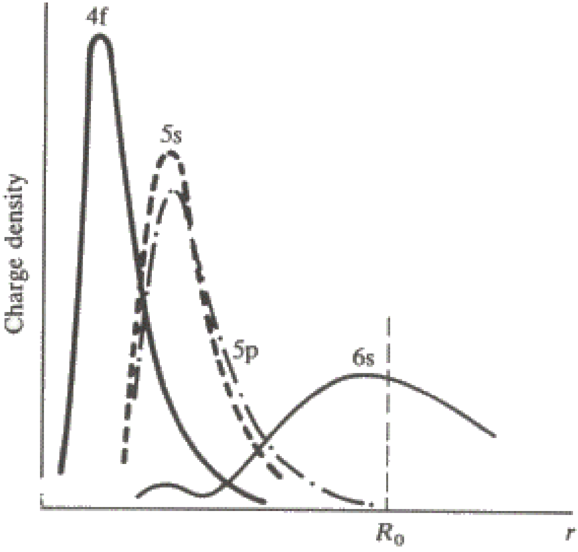
Capital Greek letters denote a many-body wavefunction

$$\Psi(r_1, r_2, \ldots, r_N); \Phi(r_1, r_2, \ldots, r_N).$$

Small Greek letters denote a single-particle wavefunction

$$\psi(r); \phi(r).$$

Pre-remarks II



Featurelessness of the density

In many books one can find charge-density curves with many features.
They show, however, not $\rho(r)$ but $r\rho(r)$!

(Figure: Sawatzky, `http://www.cpht.polytechnique.fr/houches/Interplay.ppt`)

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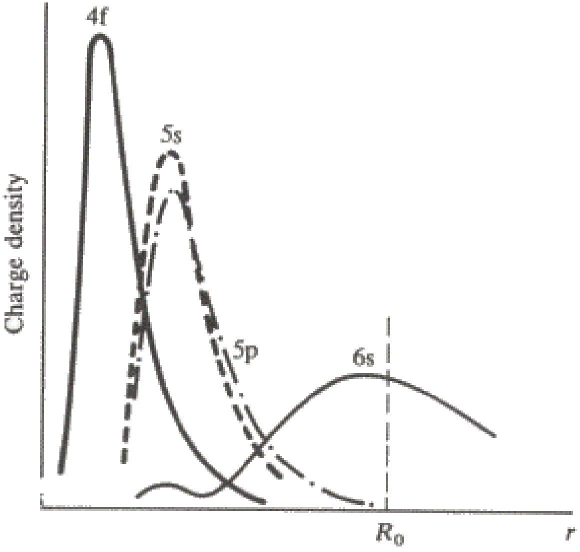

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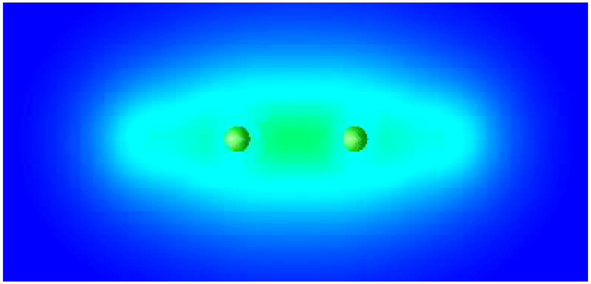


Even at logscale the density is rather featureless with (mostly only) maxima the the nuclei and otherwise (almost) monotonically decreasing.

(Figure: Acetylene, C_2H_2, molecule; T.B. et al. Phys. Rev. A **71**, 010501(R) (2005).

Content

Motivation I: Solving the Schrödinger equation

We want to solve the Schrödinger equation of an atom, a molecule, a solid

- Solve directly (works nicely and analytically for hydrogen and helium atoms; going beyond is difficult)

"The physical laws necessary [. . .] are [. . .] completely known, [. . .] only that the exact application [. . .] leads to equations much too complicated to be soluble." (Paul Dirac, Proc. Royal Soc. (London) **123**, 714; 1929).

- Use some atomic calculation like configuration interaction (only for small systems feasible; for solids only as clusters in insulators and using parameters)
- Get rid of anything negligible and create a model Hamiltonian (helps to understand the physics, but is not ab inito)
- Do it in the Hartree–Fock or density-functional way (ab inito, more on the next pages)

Motivation II: Storing Many-Body Wavefunctions

Using the fully interacting wavefunction is usually not feasible:

Assume a carbon atom (6 electrons) with the wavefunction

$$\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_6) \tag{5.1}$$

saving on a grid of 10 points for each direction $\boldsymbol{r} = (x, y, z)$ gives

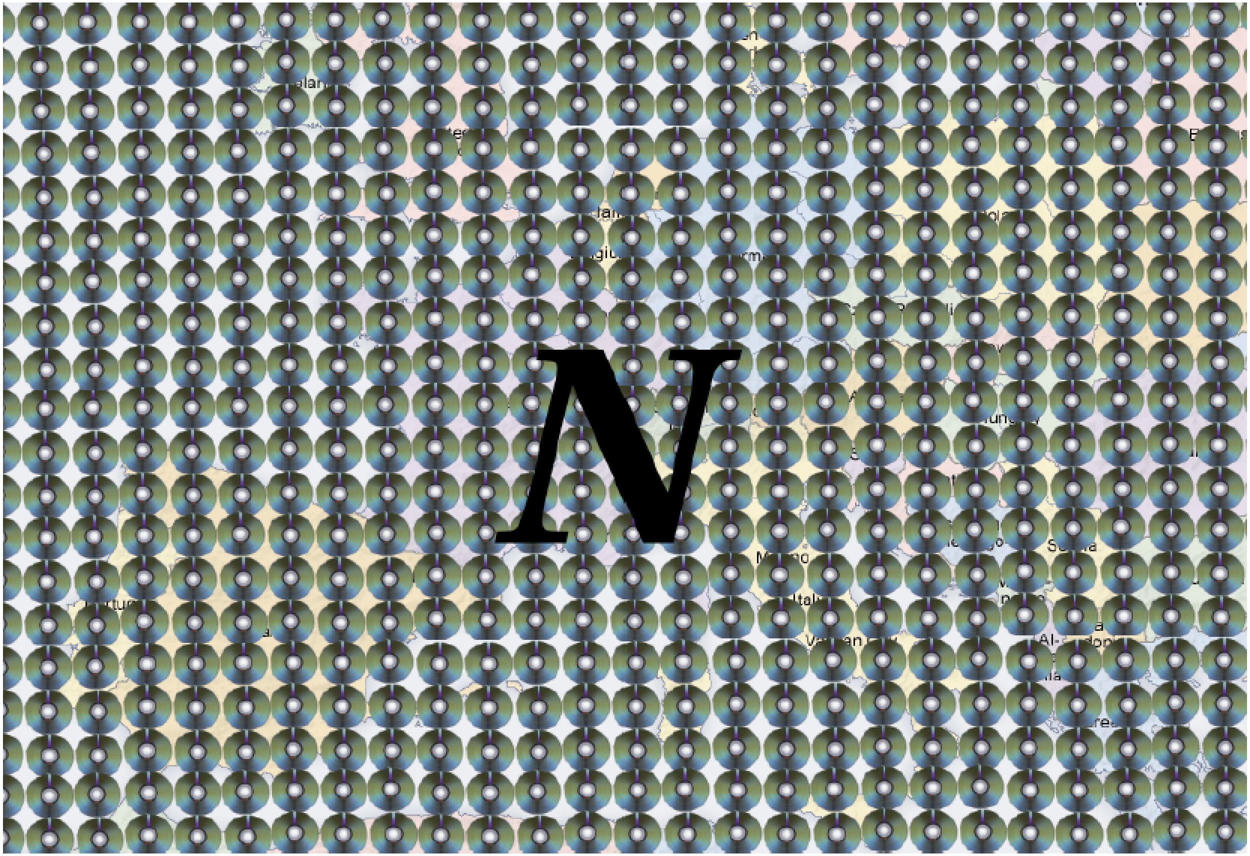
- $10^{3 \cdot 6} = 10^{18}$ entries
- As 8-byte variables: 8×10^{18} bytes
- 5×10^{9} bytes per DVD gives 10^{13} DVDs!

Carbon: Spreading out these DVDs creates a shiny landscape

Taken from Francesco Sottile (Ecole Polytechnique),

`http://cpht.polytechnique.fr/houches/tddft_francescosottile.pdf`

And for nitrogen (9 electrons, one more) . . .



Hohenberg–Kohn Theorem I

External potential V determines the (ground-state) wavefunction Ψ_0 uniquely (up to a phase), determines the density:

$$n(\boldsymbol{r}) = N \sum_{\sigma_1,\dots,\sigma_N} \int \mathrm{d}^3 r_2 \cdots \int \mathrm{d}^3 r_N \, |\Psi_0(\boldsymbol{r}, \sigma_1, \boldsymbol{r}_2, \sigma_2, \dots, \boldsymbol{r}_N, \sigma_N)|^2, \tag{6.1}$$

Is this invertible? That is: Density determines the potential uniquely (up to a purely additive constant)?
(Assuming non-degenerate ground-state for simplicity.)

We use in the following:

T	Kinetic energy operator, $\sum_i^N \frac{1}{2}\nabla_i^2$
$V(\boldsymbol{r})$	External potential (mainly due to nuclei), depends on $\boldsymbol{r}$, e.g. $\sum_i^{\tilde{N}} Z/\lvert\boldsymbol{R}_i - \boldsymbol{r}\rvert$
W	Electron-electron interaction – the hard part, $\sum_{i<j}^N 1/\lvert\boldsymbol{r}_i - \boldsymbol{r}_j\rvert$

P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964). 5014 times cited!

Hohenberg–Kohn Theorem II

Proof by reductio ad absurdum: Assume $V \neq V' + \text{const}$ and

$$H|\Psi_0\rangle = (T + W + V)|\Psi_0\rangle = E_0|\Psi_0\rangle \tag{7.1}$$

$$H'|\Psi_0'\rangle = (T + W + V')|\Psi_0'\rangle = E_0'|\Psi_0'\rangle, \tag{7.2}$$

If $\Psi_0 \equiv \Psi_0'$ then $(V - V')|\Psi_0\rangle = (E - E')|\Psi_0\rangle$, which is a contradiction. (Proves $V \Leftarrow \Psi$.)
Assume now: $n \equiv n'$ ground-state densities of $V \neq V' + \text{const}$
Rayleigh-Ritz minimal principle (using $n \equiv n'$):

$$\begin{aligned} E < \langle\Psi'|H|\Psi'\rangle &= \langle\Psi'|(T + W)|\Psi'\rangle + \int V(\boldsymbol{r})n(\boldsymbol{r})\,\mathrm{d}^3r \\ &= E' + \int \big(V(\boldsymbol{r}) - V'(\boldsymbol{r})\big)n(\boldsymbol{r})\,\mathrm{d}^3r, \end{aligned} \tag{7.3}$$

Analogously for E'. Adding gives:

$$E + E' < E + E' + \int \big(V(\boldsymbol{r}) - V'(\boldsymbol{r}) + V'(\boldsymbol{r}) - V(\boldsymbol{r})\big)n(\boldsymbol{r})\,\mathrm{d}^3r = E + E'. \tag{7.4}$$

Hohenberg–Kohn Theorem III

Ground-state energy via Rayleigh-Ritz:

$$E = \min_{\tilde{\Psi}\in\{\tilde{\Psi}\}} \langle\tilde{\Psi}|H|\tilde{\Psi}\rangle, \tag{8.1}$$

and thus:

$$E[n] = \langle\Psi_0[n]|(T+W+V)|\Psi_0[n]\rangle = F_{\mathrm{HK}}[n] + \int V(\boldsymbol{r})n(\boldsymbol{r})\,\mathrm{d}^3r, \tag{8.2}$$

with the functional

$$F_{\mathrm{HK}}[n] = \langle\Psi_0[n]|(T[n]+W[n])|\Psi_0[n]\rangle. \tag{8.3}$$

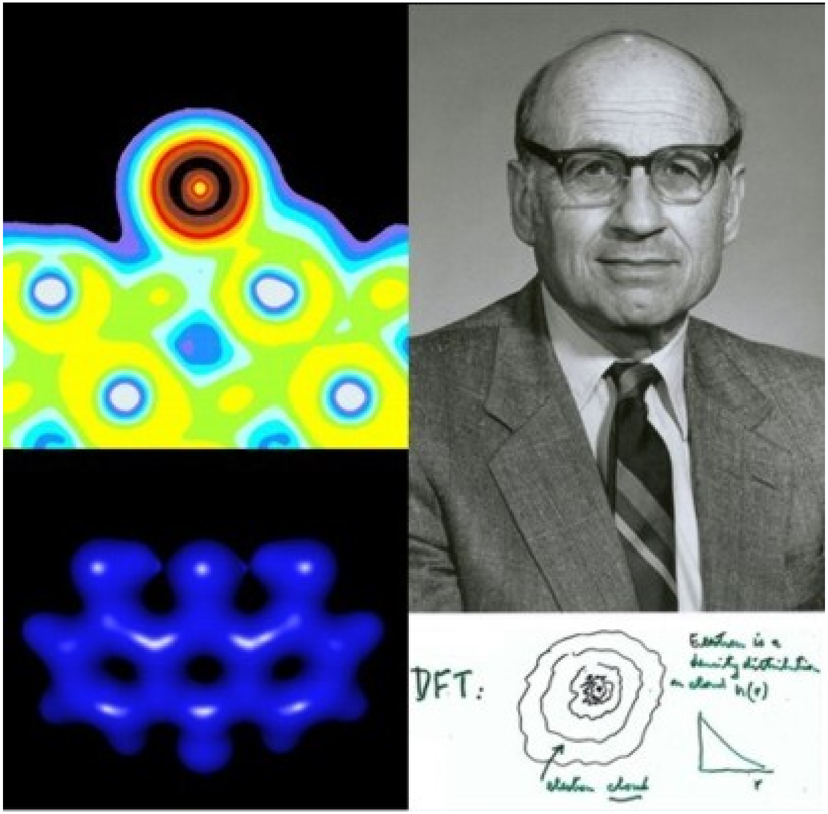
Ground-state energy:

$$E = \min_{\tilde{n}\in\tilde{N}} \left(F_{\mathrm{HK}}[\tilde{n}] + \int \tilde{n}(\boldsymbol{r})V(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} \right), \tag{8.4}$$

($\tilde{N}$: set of all V-representable trial densities)
NOTE: F_{HK} is universal functional (for given N and interaction [e.g. Coulomb])

Walter Kohn

Born in 1923 in Vienna; Nobel Price in Chemistry 1998 (for developing DFT; price shared with John A. Pope [MO, Gaussian orbitals, "GAUSSIAN"]). Kohn lives in Santa Barbara, CA. (Hirsch index 59.)



Walter Kohn in front of the Konzerthaus on Gendarmenmarkt (Whitsunday 2003). He was in Berlin to receive this sixteenth honary doctor degree, this time granted by the Freie Universität.

(Kohn pictures taken from `http://www.fhi-berlin.mpg.de/th/Photoalbum/slideshow/kohn-hc2003/kohn-hc2003.html`)

Kohn–Sham Formalism I

How to make use of Hohenberg–Kohn computationally?
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with Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{KS}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i \phi_i(\boldsymbol{r}), \tag{10.1}$$

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Via Hohenberg-Kohn:

$$\begin{aligned} E[n] &= T[n] + W[n] + \int n(\boldsymbol{r}) V(\boldsymbol{r})\, \mathrm{d}^3 r \qquad (10.3)\\ &= T_{\mathrm{KS}}[n] + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2}\int\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|r-r'|}\,\mathrm{d}^3 r\,\mathrm{d}^3 r' + \int n(\boldsymbol{r})V(\boldsymbol{r})\,\mathrm{d}^3 r + E_{\mathrm{xc}}[n]. \end{aligned}$$

(Second term: Hartree/direct, last: exchange-correlation energy functional)

Kohn–Sham Formalism II

Exchange-correlation energy functional

$$E_{\mathrm{xc}}[n] = F_{\mathrm{HK}}[n] - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{2}\int\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|r - r'|}\,\mathrm{d}^3r\,\mathrm{d}^3r' - T_{\mathrm{KS}}[n]. \tag{11.1}$$

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Exchange-correlation potential (via calculation of $\delta E[n]/\delta n(\boldsymbol{r})$)

$$v_{\mathrm{xc}}[n](\boldsymbol{r}) := \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\boldsymbol{r})}. \tag{11.2}$$

Kohn sham potential:

$$V_{\mathrm{KS}}(\boldsymbol{r}) = V(\boldsymbol{r}) + \frac{1}{4\pi\varepsilon_0}e^2\int\frac{n(\boldsymbol{r}')}{|r-r'|}\,\mathrm{d}^3r' + v_{\mathrm{xc}}(\boldsymbol{r}). \tag{11.3}$$

We now need only to approximate E_{xc} . . .

W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965). 11790 times cited!

Local density approximation (LDA)

Simple approximation of the exchange-correlation energy:

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] := \int n(\boldsymbol{r})\varepsilon_{\mathrm{uni}}(n(\boldsymbol{r}))\,\mathrm{d}^3r, \tag{12.1}$$

$\varepsilon_{\mathrm{uni}}(n)$ is the energy of an uniform electron gas as function (!) of the density.

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Approximated via $\varepsilon_x(n) \equiv -0.458/r_s$ with the one-electron sphere $(4\pi)/3r_s^3 = n^{-1}$ and $\varepsilon_c(n) = -0.44/(r_s + 7.8)$ (Wigner). Or as parameterization from Monte Carlo.

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Solving KS equations in LDA slightly more effort than Hartree equation, much easier than the Hartree-Fock equation.

Fails for systems (like e.g. heavy fermion systems), dominated by electron-electron interactions non-existing in the noninteracting electron gas

Small example I

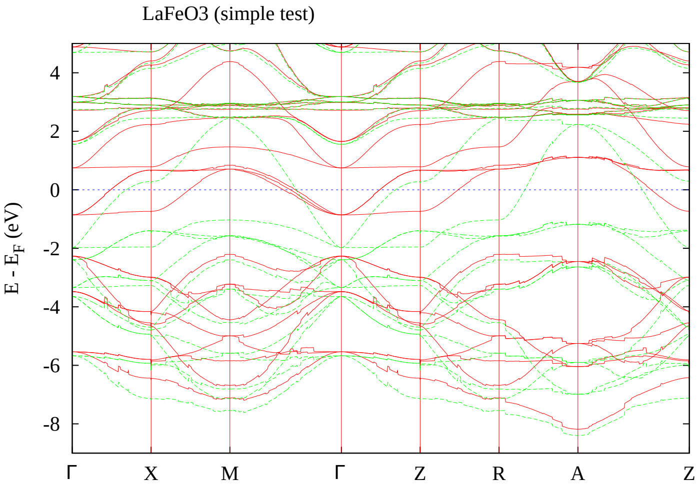
“Parameter-free” calculation (with Fleur, `www.flapw.de`):

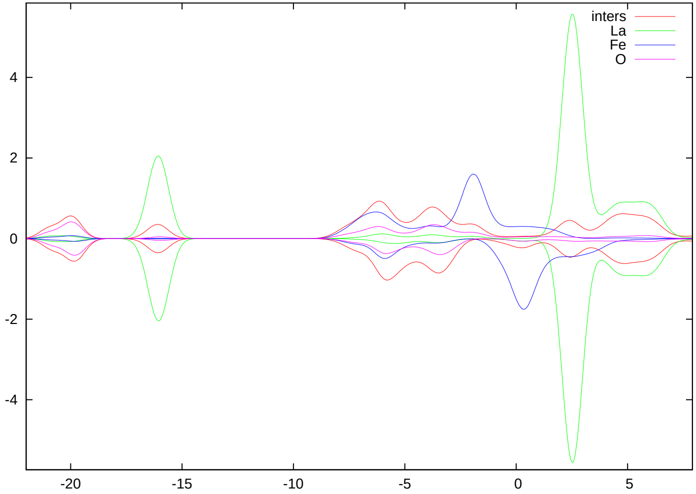
```
LaFeO3 (simple test), square lattice

&input oldfleur=f cartesian=f film=f /  ! Some Fleur specifics
&lattice latsys=’cP’               ! primitive cubic lattice
         a0=1.88972687777435527243 ! Å to atomic units (Bohr radii)
         a=3.82 /                  ! Lattice constant in ångström

5                 ! number of atoms
57   0.5 0.5 0.5  ! La at [0.5, 0.5, 0.5]
26   0.0 0.0 0.0  ! Fe
8    0.5 0.0 0.0  ! O1
8    0.0 0.5 0.0  ! O2
8    0.0 0.0 0.5  ! O3
```

That’s it!

(Or not quite – it does not converge; one needs to twist muffin-tin radii, l cutoffs, add local orbitals.)

. . . and the resulting band structure and density of states





What is the meaning of the Bandstructure and DOS?

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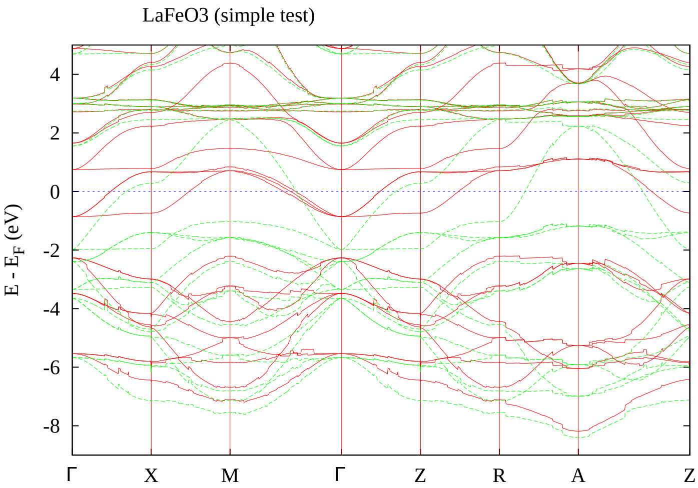
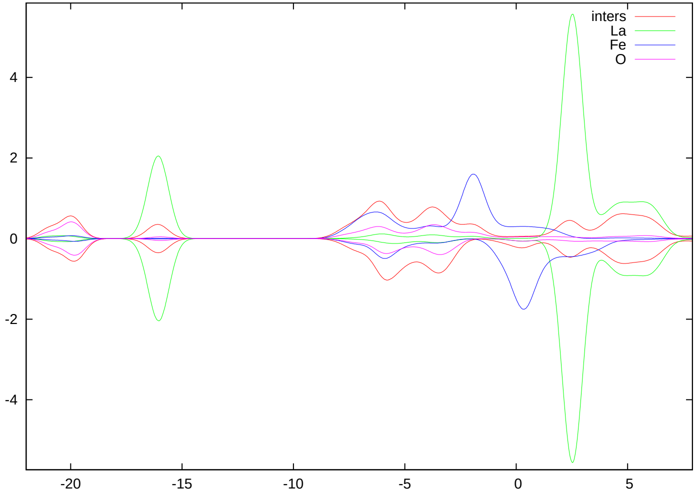

LaFeO3 (simple test)



What is the meaning of the Bandstructure and DOS?

Very simplified picture:

- DOS = how many electrons are how strongly bound
  can be measured with (Inverse) Photoemission Spectroscopy (IPES/PES)
- Bands: The same, but k resolved (compare with ARPES)

What is the meaning of the Bandstructure and DOS? (Cont.)

Problem:

- In PES/IPES, an electron is removed or added to the system, in DFT the charge is always conserved
- Electrons are treated as noninteracting (sudden approximation)

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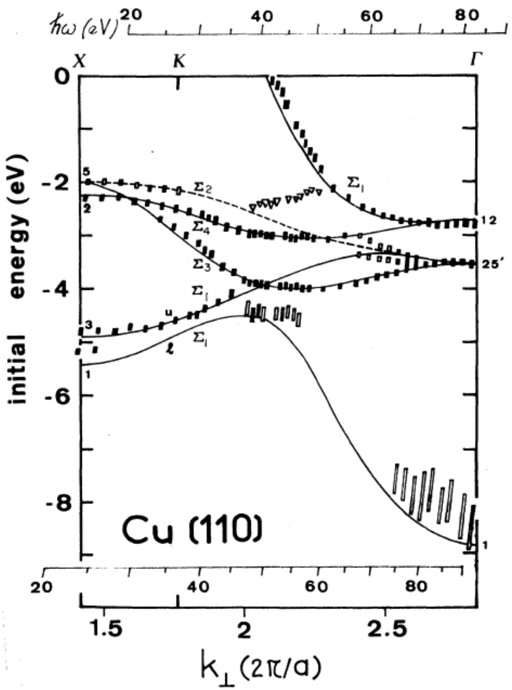
Fundamental problem

- Band structure and DOS are based on the eigenenergies $\varepsilon_{i,\boldsymbol{k}}^{\mathrm{KS}}$ of the Kohn–Sham system!
  There is no theorem which guarantees any direct relation to the eigenenergies of the fully interacting system. (Functional needed for total energy.)
- Only the density of the Kohn–Sham system has a direct meaning*
- (Photoemission) band gap is an excited state property and standard DFT is a ground-state technique

(* and few other properties, e.g. the energy of the highest occupied orbital (HOMO) is the first ionization energy.)

Small example II

LDA calculation (lines) and Cu(110) ARPES data (dots):



Matches rather well!

Why does the local density work that well – and not only for slowly varying densities?

- Contains all correlations of the homogeneous electron gas
- Fulfils several sum rules
- Exchange correlation hole

(Thiry et al, Phys. Rev. Lett. **43**, 82 (1979). Copyright American Physical Society 1979.; actually not LDA functional but Slater's $X\alpha$.)

Theories come and go, but the heat capacity of copper stays the same – Doug Bonn (UBS, Cargèse 2005 Summer School)

Triva

- Calculating the forces and moving the atoms, a structure can be “relaxed” (structure optimization)
- Local spin-density approximation (LSDA): Replace $n(\boldsymbol{r})$ by $n_\sigma(\boldsymbol{r})$ $\Rightarrow$ collinear and non-collinear magnetism
- Support for relativistic effects or spin-orbit coupling possible
- Simulating pressure: Simply change volume of the unit cell. Caveat: need to test total energy of all structures to find right structure. (Used to simulate core of the earth.)

Going beyond LDA

Using Gradients of the Density

The LDA works fairly well, but how can one do better?
Idea: Use the gradient of the density.

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The LDA works fairly well, but how can one do better?
Idea: Use the gradient of the density.

- Result: Much worse than LDA – several sum rules where violated.
- Solution: Carefully crafted functions using the so-called Generalized Gradient Approximation (GGA)
- No unique GGA. Two ways of constructing: Dream up a form and fit to collection of data (protagonist A. Becke) – or fulfil as many sum rules as possible (J. Perdew).

For molecules the GGA functionals give (often) “chemical accuracy” and LDA was much worse.
For solids: Often better, but not unanimously. Better forces for structure optimization. Does not help with the band gap (should it?)

Going beyond GGA

- Meta-GGA (Perdew/Kurth) – uses also Laplacian of the density or kinetic energy density

- "OEP:" Optimized Effective Potential. Functionals of the KS wavefunctions $E_{\text{xc}}[\psi[n]]$ rather than explicit functionals of the density $E_{\text{xc}}[n]$; Exact exchange (EXX).

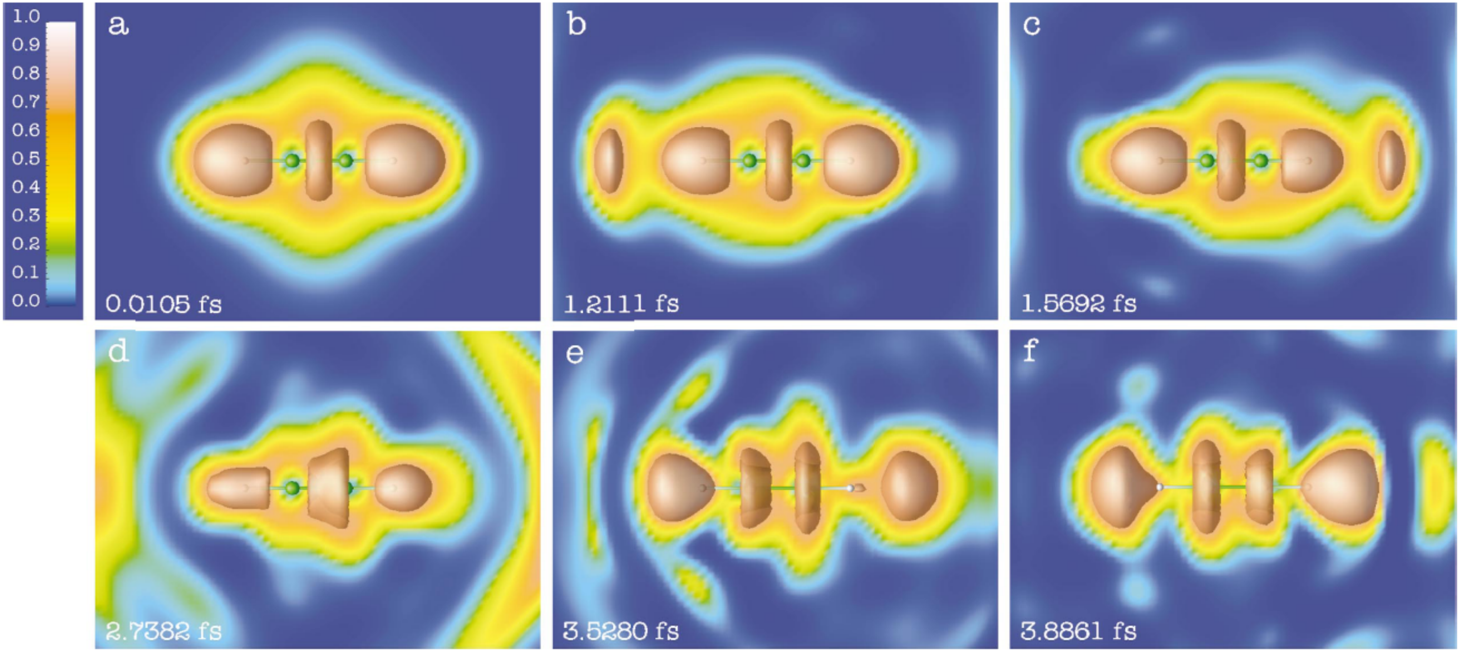
Calculation becomes heavy, but no break through in terms of results; usually better; does still not help for the band gap.

Further functions: Current-density functionals, DFT for superconductors (ab initio T_c); multi-component DFT to go beyond Born–Oppenheimer approximation, density-matrix functional theory, …

Problems that remain

- Wrong asymptotic of the potential (not $1/r$ for $r \to \infty$)
- Multiplets: Triplet states etc. In principle, with the exact functional correctly treated. The Kohn–Sham wavefunctions are by construction single-slater determinants $\Rightarrow$ problem when assigning a physical meaning. Some ideas how to work around exist, but only used for simple cases (e.g. He).
- Self interaction: An electron can interact with itself in LDA (and GGA) which is unphysical. (Term cancels in Hartree–Fock.) Self-interaction correction (SIC) functional exists, but scales with system size (vanishes for infinite systems) and is not basis independent. (Solid: Wannier basis.)

Time-dependent Density-Functional Theory



Acetylene (Ethyne) in a laserfield – breaking of bonds. (Not density, but "electron-localization function". (T.B. et al. Phys. Rev. A **71**, 010501(R) (2005).)

It is more important to have beauty in one's equations than to have them fit experiment . . . It seems that if one is working from the point of view of getting beauty in one's equations, and if one has a really sound insight, one is on a sure line of progress. If there is not complete agreement between the results of one's work and experiment, one should not allow oneself to be too discouraged, because the discrepancy may well be due to minor features that are not properly taken into account and that will get cleared up with further developments of the theory. — *Paul Dirac (Scientific American, May 1963)*

Time-dependent Density-Functional Theory

Static DFT	**Time-dependent DFT**
Any physical observable is a unique functional of the density $n(\mathbf{r})$	Any physical time-dependent observable is a unique functional of the TD density $n(\boldsymbol{r},t)$ and the initial state $\phi_0 = \phi(t=0)$
Second-order differentical equation (boundary-value problem): $H\Phi(\{\boldsymbol{r}\}) = E\Phi(\{\boldsymbol{r}\})$	First-order differential equation (initial-value problem): $H\Phi(\{\boldsymbol{r}\},t) = \mathrm{i}\partial_t\Phi(\{\boldsymbol{r}\},t)$
Total energy functional has a minimum E_0, the ground state	TD Schödinger equation corresponds to a stationary point in the Hamiltonian action $A = \int_{t_0}^{t_1} \langle\Phi(t)\|[\mathrm{i}\partial - H(t)]\|\Phi(t)\rangle \,\mathrm{d}t$
$V_{\mathrm{xc}}[n](\boldsymbol{r}) = \dfrac{\delta E_{\mathrm{xc}}}{\delta n(\boldsymbol{r})}$	$V_{\mathrm{xc}}[n](\boldsymbol{r},t) = \dfrac{\delta A_{\mathrm{xc}}}{\delta n(\boldsymbol{r},t)}$
(unknown) V_{xc} depends on the density	(unknown) V_{xc} depends on the initial state and the density at all times

Due to the time-dependence the V_{xc} is inherently non local. Most functionals ignore the history of the system but there are also functionals with memory.

E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984). 812 citations.

Linear responds

For weak pertubations, $n(\boldsymbol{r},t) = n_{\mathrm{GS}}(\boldsymbol{r},t) + \delta n(\boldsymbol{r},t)$ and thus:

$$v_{\mathrm{xc}}[n_{\mathrm{GS}} + \delta n] = v_{\mathrm{xc}}[n_{\mathrm{GS}}] + \int \mathrm{d}t' \int \mathrm{d}^3 r' f_{\mathrm{xc}}[n_{\mathrm{GS}}](\boldsymbol{r},\boldsymbol{r}',t-t')\delta n(\boldsymbol{r}',t')$$

with the exchange-correlation kernel (a functional of the ground-state density alone)

$$f_{\mathrm{xc}}[n_{\mathrm{GS}}](\boldsymbol{r},\boldsymbol{r}',t-t') = \frac{\delta v_{\mathrm{xc}}(\boldsymbol{r},t)}{\delta n(\boldsymbol{r}',t}).$$

Linear response equation:

$$\begin{aligned}\chi(\boldsymbol{r},\boldsymbol{r}',\omega) =&\chi_{\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}',\omega)\\ &+\int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \chi_{\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}_1,\omega)\left(\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} + f_{\mathrm{xc}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega)\right)\chi_{\mathrm{KS}}(\boldsymbol{r}_2,\boldsymbol{r}',\omega)\end{aligned}$$

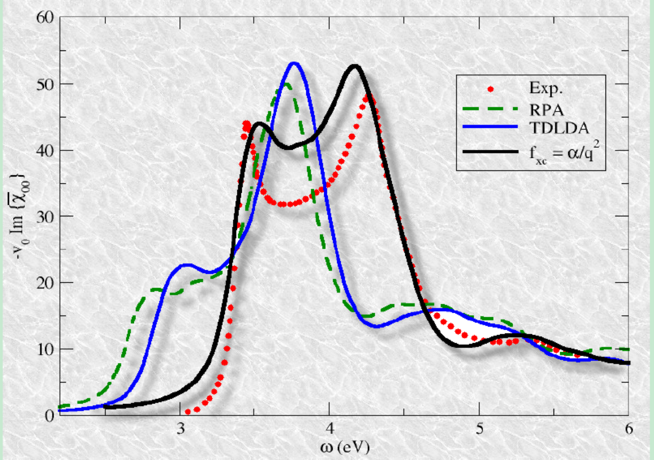
Main use: Excitation spectra (implemented in standard chemistry codes). Also for absorption spectra of solids and simple molecules, electron energy loss spectra (EELS), refraction indices, inelastic x-ray scattering spectroscopy.
Commond approximations:

- $f_{\mathrm{xc}} = 0$ (Random-phase approximations)
- $f_{\mathrm{xc}} = \delta V_{\mathrm{cx}}(\boldsymbol{r})/\delta n(\boldsymbol{r}')\delta(\boldsymbol{r}-\boldsymbol{r}')$ (Adiabatic LDA)

Good results for photo-absorptions of small molecules and for Electron Energy Loss Spectra (EELS), but bad for absorptions in solids.

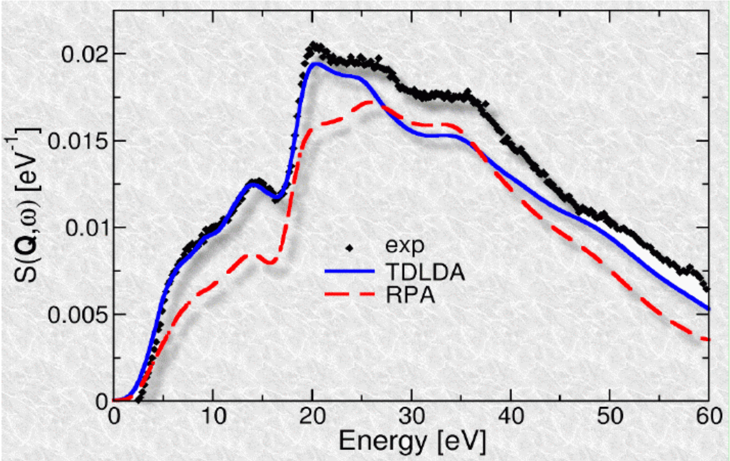
Linear response II

Reason: f_{xc}^{ALDA} is short ranged (falls off to quickly). Ansatz: $f_{\text{xc}} = \alpha/q^2$.



Absorption of silicon

L. Reining et al., Phys. Rev. Lett. **88**, 66404 (2002)



Inelastic x-ray scattering of silicon

H.-C. Wissker *et al.*, submitted

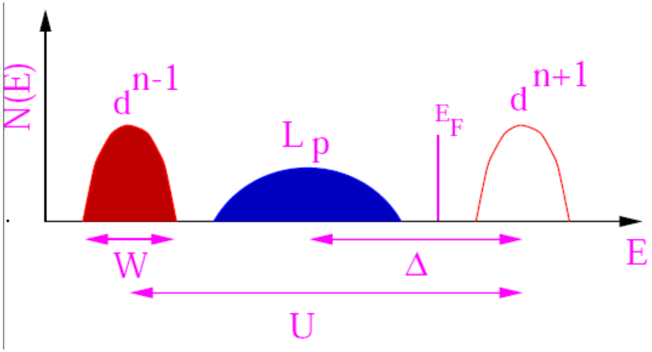
Taken from Francesco Sottile (Ecole Polytechnique),

`http://cpht.polytechnique.fr/houches/tddft_francescosot`

`pdf`

LDA+U

Zaanen-Sawatzkey-Allen phase diagram



- Model Hamiltonian: Hubbard and Anderson models, unknown parameters, many body, explicit Coulomb correlations

- Density-Functional Theory: LDA, GGA, *ab initio*, one electron, averaged Coulomb interation

- Combination: LDA+U and LDA+DMFT (alternative: GW, TDDFT)

Taken from Alexander Lichtenstein (Univ. Hamburg),

`http://cpht.polytechnique.fr/houches/Les_Houches_LDA+U.pdf`

LDA+U

LDA+U functional

$$E = E_{\mathrm{LDA}} + \frac{U}{2}\sum_{i,j} n_i n_j - \frac{U}{2} n_d(n_d - 1) \tag{17.1}$$

One-electron energies

$$\varepsilon_i = \frac{\partial E}{\partial n_i} = \varepsilon_{\mathrm{LDA}} + U(\frac{1}{2} - n_i) \tag{17.2}$$

Occupied states:

$$n_i = 1 \Rightarrow \varepsilon_i = \varepsilon_{\mathrm{LDA}} - \frac{\mathbf{U}}{\mathbf{2}} \tag*{\textbf{(17.3)}}$$

Unoccupied states:

$$n_i = 0 \Rightarrow \varepsilon_i = \varepsilon_{\mathrm{LDA}} + \frac{\mathbf{U}}{\mathbf{2}} \tag*{\textbf{(17.4)}}$$

⇒ Mott-Hubbard gap.

See also: V. Anisimov, Phys. Rev. B, **44**, 943 (1991).

Conclusions

- Density-functional theory is a relatively computational inexpensive ab inito technique, which is in principle exact. Ground-state technique!

- Good results for non-correlated matterials, singlet states

- Bandstructure/PDOS/Band gap fits often well with with experiment, even though nothing guarantees for a meaning of $\varepsilon_{i,\boldsymbol{k}}$

- TDDFT: Charge-neutral excitations, good for EELS and optical excitations (e.g. via linear response); can treat van-der-Waals forces

- GW (or better G_0W_0): Excitations, especially non-particle-number-conserving; excitation energies of (inverse) photoemission. Perturbative, no multiplet effect (with G_0W_0)

- LDA+U: Ad hoc fix to better include Coulomb interaction (Hubbard U), fixes self-interaction problem; works well for $U/t \gg 1$

- LDA+DMFT: Computationally costlier method to include U. Works also in the intermediately correlated area and reproduces quasi-particle/Kondo peak.

References

- Short introduction in (TD)DFT:
  R. M. Martin, *Electronic Structure* (Cambridge, 2004) [and Vol. 2 (in preparation)], `http://electronicstructure.org/`.

- DFT primers: W. Kohn, Review of Modern Physics 71, 1253 (1999). J. P. Perdew *et al.*, in *Density functionals: theory and applications*, Vol. 500 of Lecture notes in physics, edited by D. P. Joubert (Springer, 1998); `http://www.physik.fu-berlin.de/%7Ekurth/publ.html`. K. Burke and friends, *The ABC of DFT.* (2003); `http://dft.rutgers.edu/kieron/beta`. F. Carlos *et al.* (Ed.), *A Primer in Density Functional Theory* (Springer, 2003).

- TDDFT: Marques *et al.* (Ed.), *Time-dependent Density Functional Theory* (Springer, 2006).

- GW (and TDDFT): G. Onida *et al.*, Rev. Mod. Phys. **74**, 601 (2002).

- LDA+U: V. I. Anisimov *et al.*, J. Phys.: Condens. Matter **9**, 767 (1997).

- LDA+DMFT: A. Georges, `arXiv:cond-mat/0403123`. G. Kotliar, J. Phys. Soc. Jpn. **74**, 147 (2005).

Impact of DFT

Physical review impact analysis by S. Redner, arXiv.org:physics/0407137

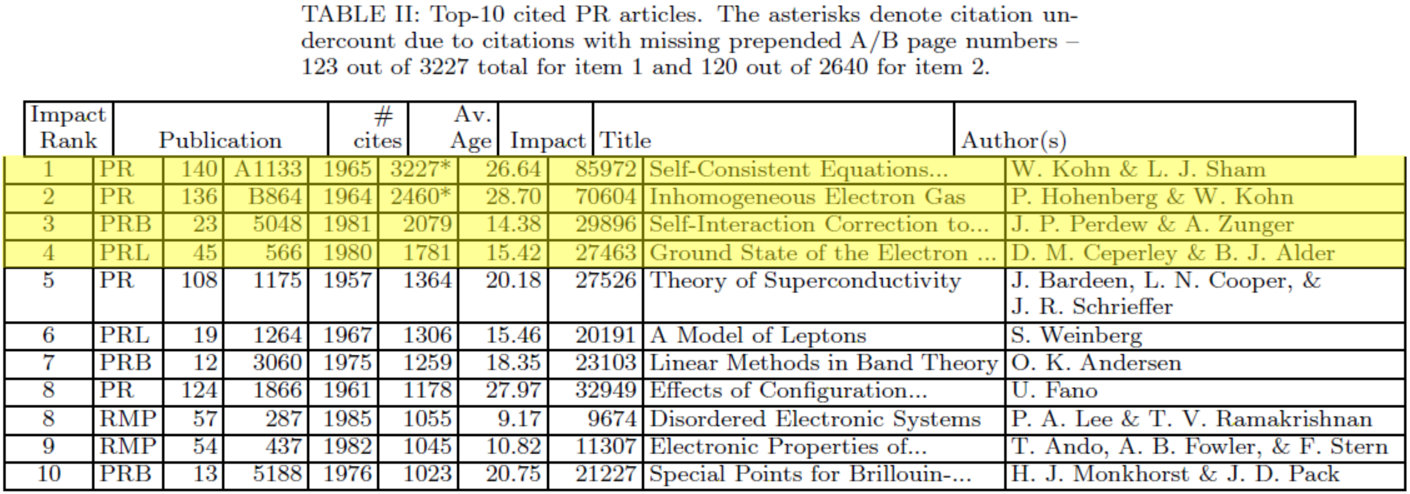


TABLE II: Top-10 cited PR articles. The asterisks denote citation undercount due to citations with missing prepended A/B page numbers – 123 out of 3227 total for item 1 and 120 out of 2640 for item 2.

Impact Rank	Publication				# cites	Av. Age	Impact	Title	Author(s)
1	PR	140	A1133	1965	3227*	26.64	85972	Self-Consistent Equations...	W. Kohn & L. J. Sham
2	PR	136	B864	1964	2460*	28.70	70604	Inhomogeneous Electron Gas	P. Hohenberg & W. Kohn
3	PRB	23	5048	1981	2079	14.38	29896	Self-Interaction Correction to...	J. P. Perdew & A. Zunger
4	PRL	45	566	1980	1781	15.42	27463	Ground State of the Electron ...	D. M. Ceperley & B. J. Alder
5	PR	108	1175	1957	1364	20.18	27526	Theory of Superconductivity	J. Bardeen, L. N. Cooper, & J. R. Schrieffer
6	PRL	19	1264	1967	1306	15.46	20191	A Model of Leptons	S. Weinberg
7	PRB	12	3060	1975	1259	18.35	23103	Linear Methods in Band Theory	O. K. Andersen
8	PR	124	1866	1961	1178	27.97	32949	Effects of Configuration...	U. Fano
8	RMP	57	287	1985	1055	9.17	9674	Disordered Electronic Systems	P. A. Lee & T. V. Ramakrishnan
9	RMP	54	437	1982	1045	10.82	11307	Electronic Properties of...	T. Ando, A. B. Fowler, & F. Stern
10	PRB	13	5188	1976	1023	20.75	21227	Special Points for Brillouin-...	H. J. Monkhorst & J. D. Pack

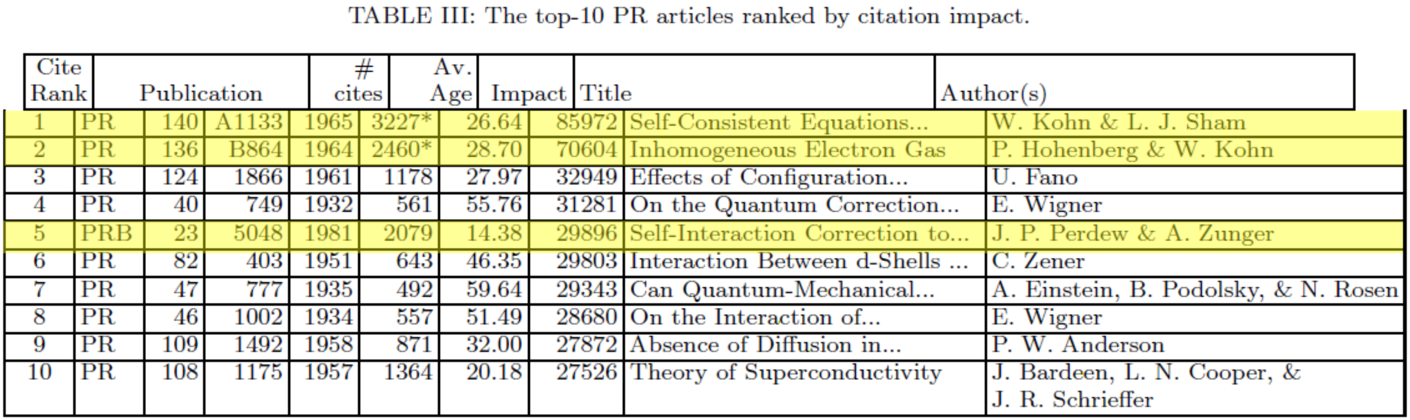


TABLE III: The top-10 PR articles ranked by citation impact.

Cite Rank	Publication				# cites	Av. Age	Impact	Title	Author(s)
1	PR	140	A1133	1965	3227*	26.64	85972	Self-Consistent Equations...	W. Kohn & L. J. Sham
2	PR	136	B864	1964	2460*	28.70	70604	Inhomogeneous Electron Gas	P. Hohenberg & W. Kohn
3	PR	124	1866	1961	1178	27.97	32949	Effects of Configuration...	U. Fano
4	PR	40	749	1932	561	55.76	31281	On the Quantum Correction...	E. Wigner
5	PRB	23	5048	1981	2079	14.38	29896	Self-Interaction Correction to...	J. P. Perdew & A. Zunger
6	PR	82	403	1951	643	46.35	29803	Interaction Between d-Shells ...	C. Zener
7	PR	47	777	1935	492	59.64	29343	Can Quantum-Mechanical...	A. Einstein, B. Podolsky, & N. Rosen
8	PR	46	1002	1934	557	51.49	28680	On the Interaction of...	E. Wigner
9	PR	109	1492	1958	871	32.00	27872	Absence of Diffusion in...	P. W. Anderson
10	PR	108	1175	1957	1364	20.18	27526	Theory of Superconductivity	J. Bardeen, L. N. Cooper, & J. R. Schrieffer

Hartree–Fock

Assumption: Can write solution as a single Slater-determinant wavefunctions

$$\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \begin{vmatrix} \phi_1(\boldsymbol{r}_1) & \cdots & \phi_1(\boldsymbol{r}_N) \\ \vdots & \ddots & \vdots \\ \phi_N(\boldsymbol{r}_1) & \cdots & \phi_N(\boldsymbol{r}_N) \end{vmatrix}. \tag{21.1}$$

With the Hamiltonian

$$\begin{aligned} \hat{H}_{\mathrm{HF}}\phi_\alpha(\boldsymbol{r}) = \left(-\frac{1}{2}\nabla^2 + V(\boldsymbol{r}) + \int \mathrm{d}^3r' n(\boldsymbol{r}')v(\boldsymbol{r}, \boldsymbol{r}')\right)\phi_\alpha(\boldsymbol{r}) \\ - \int n(\boldsymbol{r}, \boldsymbol{r}')v(\boldsymbol{r}, \boldsymbol{r}')\phi_\alpha(\boldsymbol{r}')\,\mathrm{d}^3r' = \varepsilon_\alpha\phi_\alpha(\boldsymbol{r}). \end{aligned} \tag{21.2}$$

Density: $n(\boldsymbol{r}) = \sum_{i=1}^N \phi_i^*(\boldsymbol{r})\phi_i(\boldsymbol{r})$; density matrix: $n(\boldsymbol{r}, \boldsymbol{r}') = \sum_{i=1}^N \phi_i^*(\boldsymbol{r})\phi_i(\boldsymbol{r}')$

- System is determined by number of electrons N and form of the “external” potential $V(\boldsymbol{r})$.
- Self-interaction cancels exactly
- Koopmans’ theorem: HOMO = ionization energy; LUMO = electron affinity