Density functional theory & practice

1. **Introduction & Perspective:**
   electronic structure methods
   Born-Oppenheimer approximation
   units

2. **Theorems:**
   HK: Density as the basic variable
   KS: mapping to single-electron problem

3. **Practice:**
   practical density functionals
   self-consistency
   basis sets
   large systems: $\mathcal{O}(N)$

4. **Applications:**
   ground state: energy, structure
   forces: molecular dynamics
   excited states?
   parameters for correlated systems

References

W. Kohn:
Electronic structure of matter —
wave functions and density functionals
Rev. Mod. Phys. **71**, 1253-1266 (1998)

K. Capelle:
A bird's eye view of density-functional theory
`cond-mat/0211443`

U. von Barth:
Basic Density-Functional Theory – An Overview
`www.fysik4.fysik.uu.se/~thor/vonBarth_lecture.pdf`
K. Burke: The ABC of DFT
`dft.rutgers.edu/kieron/beta`

R.M. Martin: Electronic Structure
Basic Theory and Practical Methods
Cambridge University Press, 2003

R.M. Dreizler and E.K.U. Gross:
Density Functional Theory
Springer, 1990

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Teubner, 1999

`www.mpi-stuttgart.mpg.de/andersen/users/koch/DFT.html`

$$\begin{aligned}\hat{H} = & - \frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} \\ & + \sum_{i,I}\frac{Z_I e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{R}_I|} \\ & - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{4\pi\epsilon_0|\mathbf{R}_I - \mathbf{R}_J|}\end{aligned}$$

The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble.

P.M.A. Dirac, Proc. Roy. Soc. **A 123**, 714 (1929)

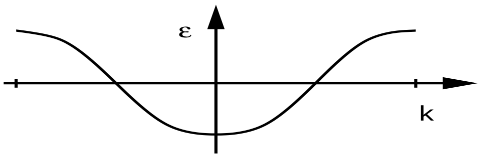
More is different

[. . .] the reductionist hypothesis does not by any means imply a "constructionist" one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. Sometimes, as in the case of superconductivity, the new symmetry — now called broken symmetry because the original symmetry is no longer evident — may be of an entirely unexpected kind and extremely difficult to visualize. In the case of superconductivity, 30 years elapsed between the time when physicists were in possession of every fundamental law necessary for explaining it and the time when it was actually done.
P.W. Anderson, Science **177**, 393 (1972)

Mott transition

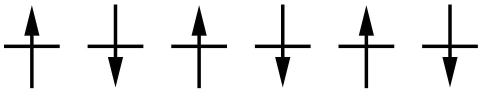
$$\begin{aligned} H &= -t \sum_{\langle ij\rangle\sigma} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \\ &= \sum_{k\sigma} \varepsilon_k \, c^\dagger_{k\sigma} c_{k\sigma} + \frac{U}{M} \sum_{k,k',q} c^\dagger_{k\uparrow} c_{k-q\uparrow} c^\dagger_{k'\downarrow} c_{k'+q\downarrow} \end{aligned}$$

$t \gg U$: band-limit



filling of a band
$\rightsquigarrow$ metal

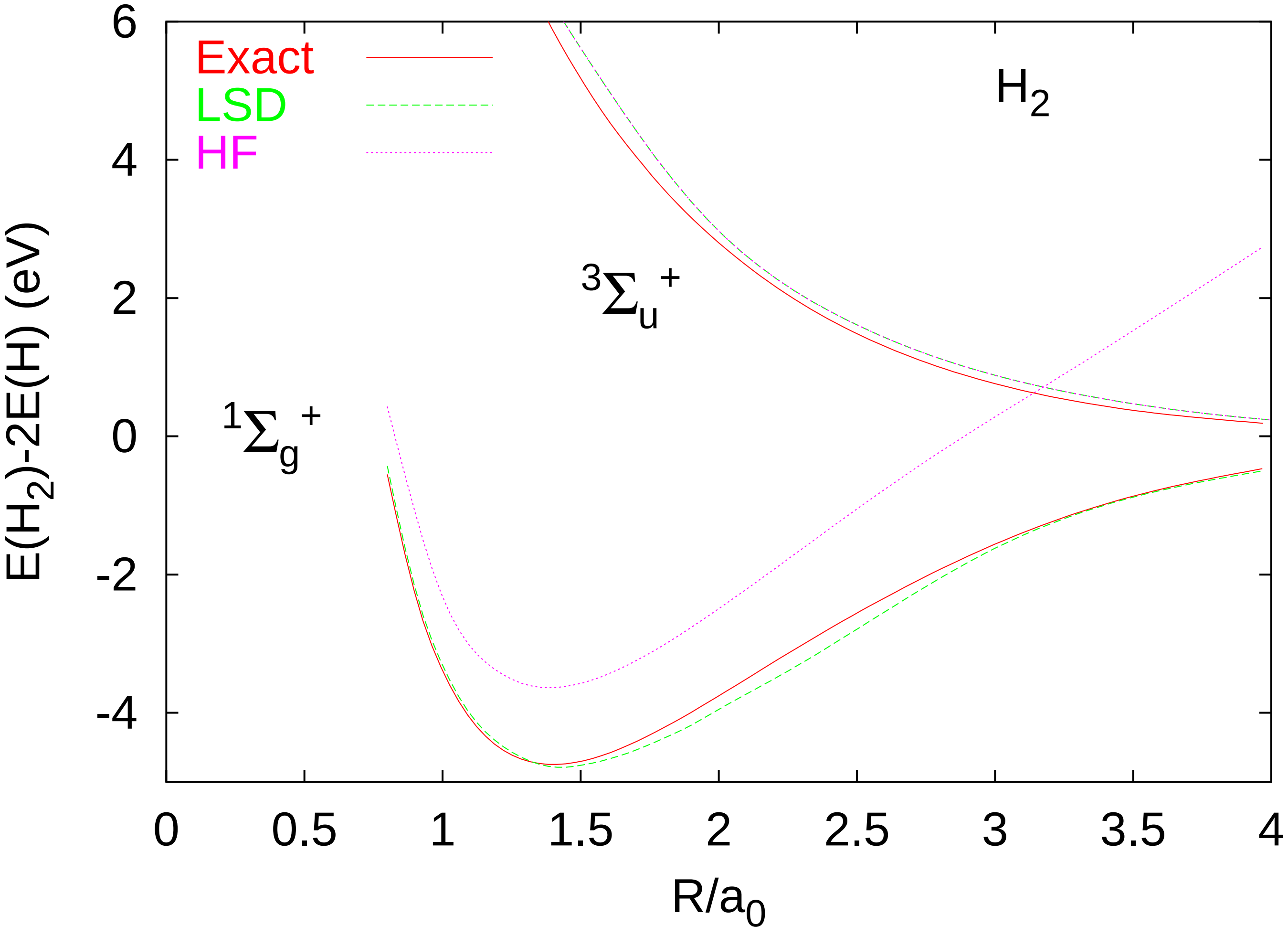
$t \ll U$: atomic limit



no hopping for
integer filling
$\rightsquigarrow$ insulator

metal-insulator transition for integer fillings

Born-Oppenheimer surfaces for H_2



atomic units

$$\begin{array}{rlll}
\hbar & = 1.0546 \cdot 10^{-34} & \text{Js} & [ML^2T^{-1}] \\
m_e & = 9.1094 \cdot 10^{-31} & \text{kg} & [M] \\
e & = 1.6022 \cdot 10^{-19} & \text{C} & [Q] \\
4\pi\epsilon_0 & = 1.1127 \cdot 10^{-10} & \text{F/m} & [M^{-1}L^{-3}T^2Q^2]
\end{array}$$

`http://physics.nist.gov/cuu/`

solve

$$\begin{aligned}
\hbar &= 1\, a_0^2\, m_e \,/\, t_0 \\
m_e &= 1\, m_e \\
e &= 1\, e \\
4\pi\epsilon_0 &= 1\, t_0^2\, e^2 \,/\, a_0^3\, m_e
\end{aligned}$$

to obtain

$$\begin{array}{llll}
1 \text{ a.u. length} = a_0 = & \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} & \approx 5.2918 \cdot 10^{-11} & \text{m} \\
1 \text{ a.u. mass} = m_e = & & \approx 9.1095 \cdot 10^{-31} & \text{kg} \\
1 \text{ a.u. time} = t_0 = & \frac{(4\pi\epsilon_0)^2\hbar^3}{m_e e^4} & \approx 2.4189 \cdot 10^{-17} & \text{s} \\
1 \text{ a.u. charge} = e = & & \approx 1.6022 \cdot 10^{-19} & \text{C}
\end{array}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

The tabulation of one variable requires a page, of two variables a volume, and of three variables a library; but the full specification of a single wavefunction of neutral Fe is a function of seventy eight variables. It would be rather crude to restrict to ten the number of values at which to tabulate this function, but even so, full tabulation of it would require 10^{78} entries, and even if this number could be reduced somewhat from considerations of symmetry, there would still not be enough atoms in the whole solar system to provide the material for printing such a table.
D.R. Hartree