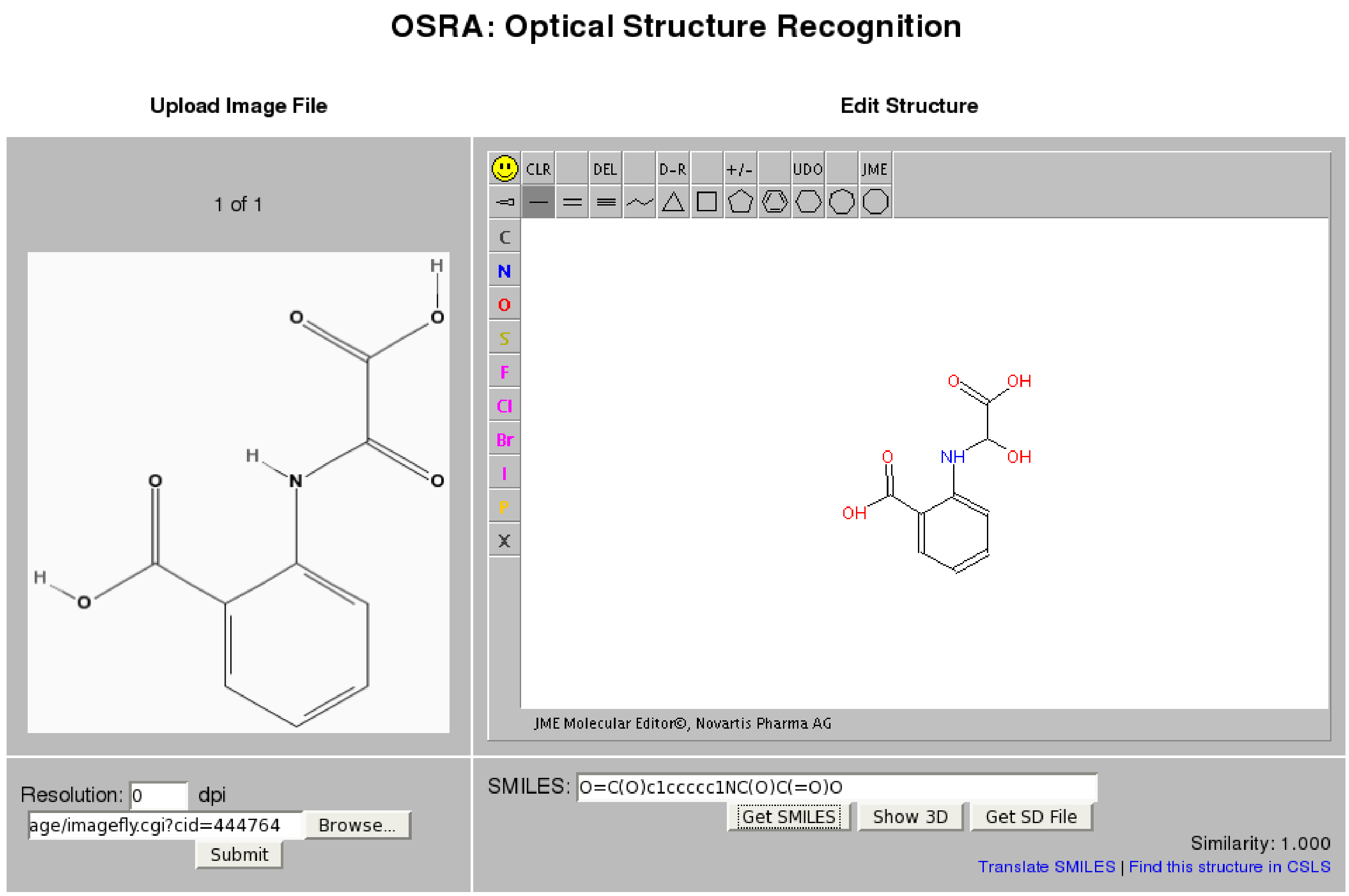
1. INFOMERCIAL 1



OSRA: Optical Structure Recognition

Upload Image File

Edit Structure

1 of 1

Resolution: 0 dpi

age/imagefly.cgi?cid=444764

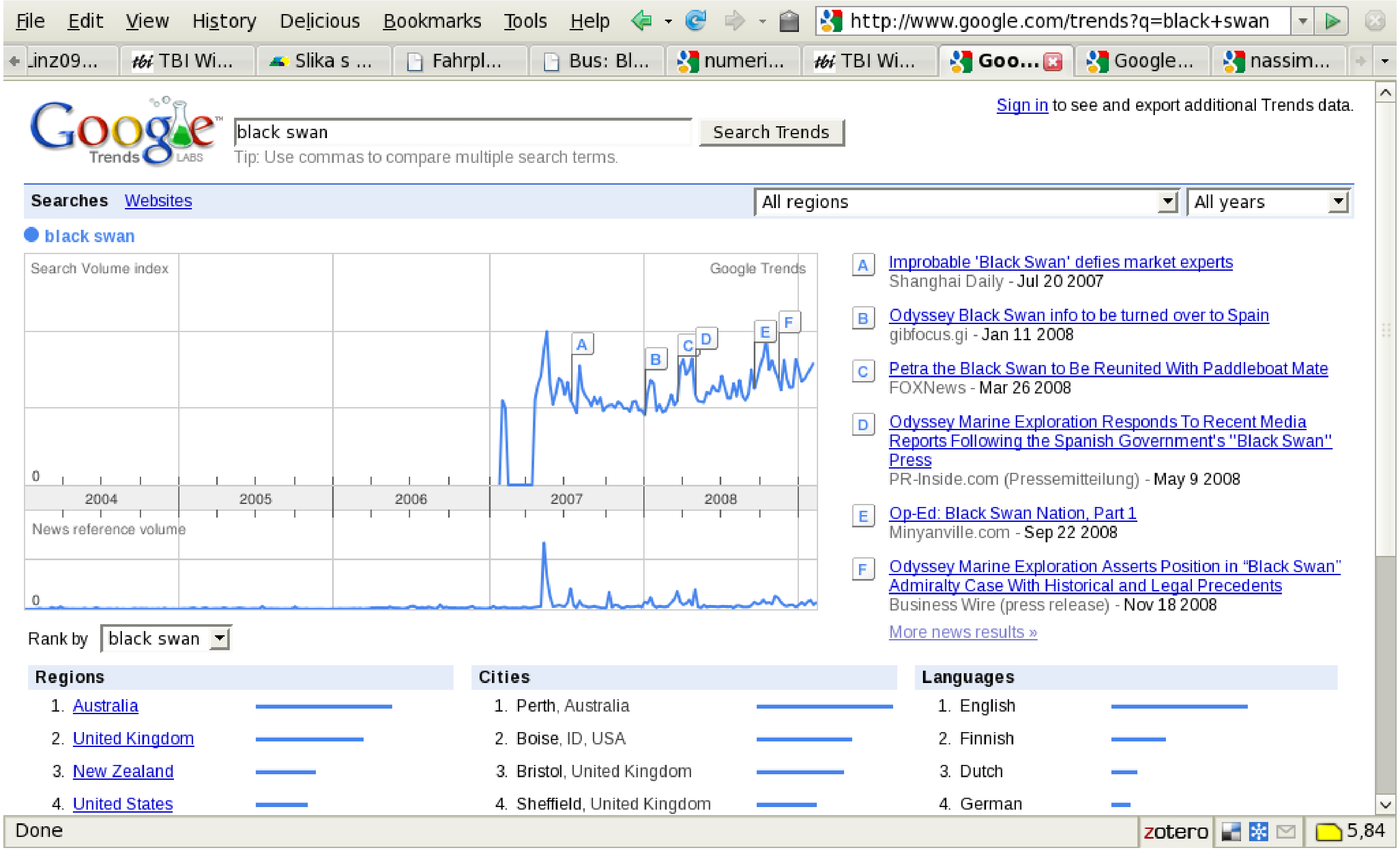
SMILES: O=C(O)c1ccccc1NC(O)C(=O)O

Similarity: 1.000

`http://cactus.nci.nih.gov/osra/`
`http://cactus.nci.nih.gov/cgi-bin/osra/index.cgi`

for chemical names http://oscar3-chem.sourceforge.net/

2. INFOMERCIAL 2



http://www.google.com/trends?q=black+swan

Sign in to see and export additional Trends data.

black swan

Tip: Use commas to compare multiple search terms.

All regions

All years

● black swan

A [Improbable 'Black Swan' defies market experts](#)
Shanghai Daily - Jul 20 2007

B [Odyssey Black Swan info to be turned over to Spain](#)
gibfocus.gi - Jan 11 2008

C [Petra the Black Swan to Be Reunited With Paddleboat Mate](#)
FOXNews - Mar 26 2008

D [Odyssey Marine Exploration Responds To Recent Media Reports Following the Spanish Government's "Black Swan" Press](#)
PR-Inside.com (Pressemitteilung) - May 9 2008

E [Op-Ed: Black Swan Nation, Part 1](#)
Minyanville.com - Sep 22 2008

F [Odyssey Marine Exploration Asserts Position in “Black Swan” Admiralty Case With Historical and Legal Precedents](#)
Business Wire (press release) - Nov 18 2008

More news results »

Rank by black swan

Regions	Cities	Languages
1. Australia	1. Perth, Australia	1. English
2. United Kingdom	2. Boise, ID, USA	2. Finnish
3. New Zealand	3. Bristol, United Kingdom	3. Dutch
4. United States	4. Sheffield, United Kingdom	4. German

”black swan” powered by Nassim Nicholas Taleb

”Cygnus atratus” XOR ”Cygnus atractus”

”kyknos” != ”kynos”

3. Lost in Translation

`http://de.wikipedia.org/wiki/John_von_Neumann#Zitat`

John Von Neumann in einer Diskussion mit einem englischen Physiker 1943 beim Studium von Bombenkratern auf Luftbildern [6]:

> Nein, nein, du siehst das nicht richtig. Dein visualisierender Verstand kann das nicht richtig sehen. Du musst abstrakt denken. Was passiert, ist, dass der erste Differentialquotient identisch verschwindet und daher das, was sichtbar wird, die Spur des zweiten Differentialquotienten ist.

4. JOHN VON NEUMANN

"The sciences do not try to explain, they hardly even try to interpret, they mainly make models. By a model is meant a mathematical construct which, with the addition of certain verbal interpretations describes observed phenomena. The justification of such a mathematical construct is solely and precisely that it is expected to work."

5. von Neumann Confession

”I would like to make a confession which may seem immoral: I do not believe absolutely in Hilbert space any more. After all Hilbert-space (as far as quantum-mechanical things are concerned) was obtained by generalizing Euclidean space, footing on the principle of conserving the validity of all formal rules”

6. Schrödinger Eqn.

6.1. **time dependent.**

$$\hat{H}\ |\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\ |\psi(t)\rangle \tag{6.1}$$

$$\left(\frac{\hat{p}^2}{2m} + V(\vec{x},t)\right)\ |\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\ |\psi(t)\rangle \tag{6.2}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x},t)\right)\ |\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\ |\psi(t)\rangle \tag{6.3}$$

6.2. **time independent.**

$$\hat{H}\ |\psi\rangle = E\ |\psi\rangle \tag{6.4}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})\right)\ |\psi\rangle = E\ |\psi\rangle \tag{6.5}$$

6.3. **discreete time independent.**

$$\hat{H}\ |\psi_n\rangle = E_n\ |\psi_n\rangle \tag{6.6}$$

$$\langle\psi_n|\ \hat{H}\ |\psi_n\rangle = E_n\langle\psi_n|\psi_n\rangle \tag{6.7}$$

$$\frac{\langle\psi_n|\ \hat{H}\ |\psi_n\rangle}{\langle\psi_n|\psi_n\rangle} = E_n \tag{6.8}$$

$$\langle\psi_n|\psi_n\rangle = 1 \tag{6.9}$$

$$\langle\psi_n|\ \hat{H}\ |\psi_n\rangle = E_n[\psi_n] \tag{6.10}$$

6.4. **Rayleigh-Ritz Ansatz.** The ultimate lowest possible energy eigenstate is the ground state energyE_0 :

$$E_0[\psi_0] \leq \langle\psi| \hat{H} |\psi\rangle \tag{6.11}$$

Of course we do not know E_0, as we can never know the *exact* ψ_0. But the can construct by linear combination an trial wave-function which tries to approximate the *exact* ψ_0:

$$\psi = \sum_n c_n \psi_n \tag{6.12}$$

where c_n are coefficients not yet defined / known.

Given our linear approximation of a wave-function we can write the expectation value of the Hamiltonian as:

$$\begin{aligned} \langle\phi| H |\phi\rangle &= \langle\sum_n c_n\psi_n| H |\sum_m c_m\psi_m\rangle & (6.13)\\ &= \sum_n\sum_m \langle c_n\psi_n| E_m |c_m\psi_m\rangle & (6.14)\\ &= \sum_n\sum_m c_n^* c_m E_m \langle\psi_n|\psi_m\rangle & (6.15)\\ &= \sum_n |c_n|^2 E_n & (6.16) \end{aligned}$$

6.5. **Other Variational Principles.** `http://en.wikipedia.org/wiki/Variational_method`

Robert K. Nesbet: Variational Principles and Methods in Theoretical Physics and Chemistry

7. WAVEFUNCTIONS / ORBITALS

7.1. **STO - Slater-Type Orbitals.**

$$S^{\zeta}_{nlm}(r,\vartheta,\varphi) = N r^{n-1} e^{-\zeta r} Y_l^m(\vartheta,\varphi) \tag{7.1}$$

where ζ controls the width of the orbital (large ζ gives tight function, small ζ gives diffuse function)

`http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/basis-sets.pdf`

7.2. **GTO - Gaussian-Type Orbitals.** The principal reason for the use of Gaussian basis functions in molecular quantum chemical calculations is the 'Gaussian Product Theorem', which guarantees that the product of two GTOs centered on two different atoms is a finite sum of Gaussians centered on a point along the axis connecting them. In this manner, four-center integrals can be reduced to finite sums of two-center integrals, and in a next step to finite sums of one-center integrals.

$$G^{\alpha,R}_{ijk}(r) = N^{\alpha}_{ijk}(x-R_1)^i(y-R_2)^j(z-R_3)^k e^{-\alpha(r-R)^2} \tag{7.2}$$

Correct form of atomic orbitals:
$R(r) = Ar^l e^{-\alpha r}$
GTO:
$R(r) = Ar^l e^{-\alpha r^2}$
Any STO can be composed by linear combination of GTOs:

$$STO(r) = \sum d e^{-\alpha f^2 r^2} \tag{7.3}$$

7.3. **Wavelets.**

- `http://arxiv.org/abs/0804.2583`
- `http://arxiv.org/abs/0805.1190`

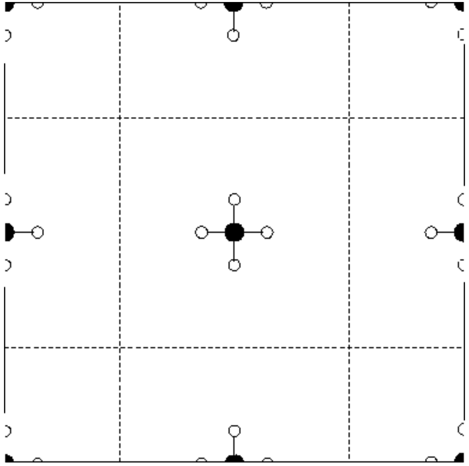
7.4. **Planewaves.** The choice of periodic boundary conditions (aka Born-von Karman boundary condition) is natural in the case of bulk solids which exhibit perfect translational symmetry. cf. Bloch's Theorem.

- Projector Augmented Wave (PAW) method developed by Blochl

- Linearized augmented plane-wave (LAPW)
- Full Potentional Linearized augmented plane-wave (FP-LAPW)

`http://en.wikipedia.org/wiki/Reciprocal_lattice`
`http://en.wikipedia.org/wiki/K-space_(MRI)`

7.5. **supercells.** `http://www.tcm.phy.cam.ac.uk/~mds21/thesis/node15.html`



7.6. **LCAO - Linear combination of atomic orbitals.** LCAO, LCAO-MO, LCMO, etc.)

Many names and even more abbreviations but actually a very simple concept:
a linear combination of n known basis functions $\chi_n = \{\, |\, s\rangle, |\, sp\rangle, |\, sp^2\rangle, |\, sp^3\rangle\}$, parametrized by not yet determined coefficients c_n .

7.7. **Hybrid Orbitals.**

The Hybrid Orbital was pioneered by Linus C. Pauling. John C. Slater was not impressed. It is a simple Linear Combination of Atomic Orbitals (LCAO) which tries to model covalent bonding. Atomic Orbitals are assumed to be STO's (Slater Type Orbitals) and the resulting hybrid orbitals are listed below:

- sp^3 **hybridization**

$$\psi_{sp^3 1} = \sqrt{\tfrac{1}{4}}\ (\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z}) = \frac{1}{2}(\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z}) \tag{7.4}$$

$$\psi_{sp^3 2} = \sqrt{\tfrac{1}{4}}\ (\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z}) = \frac{1}{2}(\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z}) \tag{7.5}$$

$$\psi_{sp^3 3} = \sqrt{\tfrac{1}{4}}\ (\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z}) = \frac{1}{2}(\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z}) \tag{7.6}$$

$$\psi_{sp^3 4} = \sqrt{\tfrac{1}{4}}\ (\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z}) = \frac{1}{2}(\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z}) \tag{7.7}$$

- sp^2 **hybridization** (the plain vanilla mix)

$$\psi_{sp^2 1} = \sqrt{\tfrac{1}{3}}\,(\psi_{2s} + \sqrt{2}\psi_{2p_x}) = \sqrt{\tfrac{1}{3}}\,\psi_{2s} + \sqrt{\tfrac{2}{3}}\,\psi_{2p_x} \tag{7.8}$$

$$\psi_{sp^2 2} = \sqrt{\tfrac{1}{3}}\,(\psi_{2s} - \sqrt{\tfrac{1}{2}}\,\psi_{2p_x} + \sqrt{\tfrac{3}{2}}\,\psi_{2p_y}) = \sqrt{\tfrac{1}{3}}\,\psi_{2s} - \sqrt{\tfrac{1}{6}}\,\psi_{2p_x} + \sqrt{\tfrac{1}{2}}\,\psi_{2p_y} \tag{7.9}$$

$$\psi_{sp^2 3} = \sqrt{\tfrac{1}{3}}\,(\psi_{2s} - \sqrt{\tfrac{1}{2}}\,\psi_{2p_x} - \sqrt{\tfrac{3}{2}}\,\psi_{2p_y}) = \sqrt{\tfrac{1}{3}}\,\psi_{2s} - \sqrt{\tfrac{1}{6}}\,\psi_{2p_x} - \sqrt{\tfrac{1}{2}}\,\psi_{2p_y} \tag{7.10}$$

$$\psi_{\pi 4} = \psi_{2p_z} \tag{7.11}$$

- sp^2 **hybridization** (alternative dub-club remix)

$$\psi_{sp^2 1} = \sqrt{\tfrac{1}{3}}\,\psi_{2s} - \sqrt{\tfrac{2}{3}}\,\psi_{2p_x} \tag{7.12}$$

$$\psi_{sp^2 2} = \sqrt{\tfrac{1}{3}}\,\psi_{2s} + \sqrt{\tfrac{1}{6}}\,\psi_{2p_x} + \sqrt{\tfrac{1}{2}}\,\psi_{2p_y} \tag{7.13}$$

$$\psi_{sp^2 3} = \sqrt{\tfrac{1}{3}}\,\psi_{2s} + \sqrt{\tfrac{1}{6}}\,\psi_{2p_x} - \sqrt{\tfrac{1}{2}}\,\psi_{2p_y} \tag{7.14}$$

$$\psi_{\pi 4} = \psi_{2p_z} \tag{7.15}$$

- sp **Hybrid-MO**

$$\psi_{sp1} = \sqrt{\tfrac{1}{2}}\,(\psi_{2s} + \psi_{2p_x}) \tag{7.16}$$

$$\psi_{sp2} = \sqrt{\tfrac{1}{2}}\,(\psi_{2s} - \psi_{2p_x}) \tag{7.17}$$

$$\psi_{\pi 3} = \psi_{2p_y} \tag{7.18}$$

$$\psi_{\pi 4} = \psi_{2p_z} \tag{7.19}$$

- Online Refs

`http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/hybrid.html`

`http://winter.group.shef.ac.uk/orbitron/AO-hybrids/sp2/equations.html`

7.8. Slater-Koster scheme.

orbitals were considered. Actually, here as in other cases, there are nondiagonal matrix components of energy between all these types of Bloch functions, at an arbitrary **k** value, and the *d* band does not split into two subbands. This unwarranted simplification is also found in the first work of Fletcher and Wohlfarth[7] on nickel, though it is removed in their second paper,[8] which seems to be the first proper treatment of the structure of the *d* band by the LCAO method.

In addition to the misunderstanding which we have just been describing, there is another widespread misconception about the method. This is the supposition that it is desirable for some reason to start by hybridizing the atomic orbitals, for instance, to introduce directed orbitals of some sort suggested by the symmetry of the crystal. This misconception occurs particularly in the writings of those who, like for instance Pauling[9] and Ganzhorn,[10] do not make it clear whether they are using an energy band calculation, or a modified Heitler-London method. In the case of Lennard-Jones and his associates,[11] using their equivalent orbitals, one gathers that they feel that there is some virtue in using hybridized orbitals of one type or another (that is, linear combinations of several atomic orbitals, on the same or adjacent atoms) for a straightforward calculation of energy bands, or of molecular orbitals in a molecular problem. This procedure is in fact of no value in most cases.

One can start with atomic orbitals of the ordinary sort, space quantized with respect to a particular direction in space, or can use orbitals set up with reference to cubic axes, such as the p_x, p_y, p_z combinations of the p orbitals and the d orbitals varying as xy, yz, zx, x^2-y^2, and $3z^2-r^2$, or finally one can use more complicated hybridized orbitals, such as the four tetrahedral directed orbitals formed from the s and the three p functions. With any one of these starting points, one can set up the Bloch sums of the atomic orbitals, and then can solve the secular problem between these Bloch sums. The final result will obviously be the same no matter which set of atomic orbitals we start with. In fact, if we were going to use n atomic orbitals per unit cell, we could make any n linear combinations of the original orbitals, form Bloch sums of these modified orbitals, and solve a secular problem using the modified Bloch sums, and in every case come out with the same answer in the end. The only advantage in one choice of atomic orbitals over another is convenience in calculating the matrix components or solving the secular equation. We shall be dealing in the present paper with cubic crystals, and shall use orbitals of the p_x, p_y, p_z, xy, yz, etc., type, since they give about as much simplification as we can get. But in addition, these are just as useful in discussing the diamond structure as tetrahedral orbitals would be. At an arbitrary point of **k** space, in any case the matrix components will not simplify, no matter what form of atomic orbitals we use. Along special symmetry lines and planes, we can sometimes choose atomic orbitals leading to a factoring of the secular equation, and this is obviously useful; but the choice is different for different symmetry lines and planes.

For solving the one-electron problem, in other words, there is no advantage in using hydridized or directed orbitals when dealing with crystals, or similarly in using directed or equivalent orbitals in solving the molecular orbital problem in a molecule. The advantages of such orbitals, if there are any, seem to lie in treating the many-electron problem, either by methods of configuration interaction or by other methods. It seems likely that by using directed or hybridized or equivalent orbitals, one can set up approximate treatments of electron correlation which express the preference of two electrons of opposite spin to be found in an orbital representing a covalent bond. But this use of such orbitals lies entirely outside the scope of the present paper, which deals with energy band theory, or one-electron solutions of Schrödinger's equation for a periodic potential.

II. SIMPLIFICATION OF THE LCAO METHOD

We have seen in the preceding section the general outlines of the LCAO method for solids. We shall now examine it in more detail, show how complicated it is when applied rigorously, but indicate the simplifications which can be made if we treat it as an interpolation method. There is one complication which we can remove at the outset. If we start with the atomic orbitals ϕ_n, located on the various atoms of a unit cell, and make Bloch sums from them, then we shall find that these Bloch sums are not orthogonal to each other. The reason is that the ϕ_n's connected with orbitals on different atoms are not orthogonal to each other. We can remove this difficulty by immediately setting up new atomic orbitals, linear combinations of the original ones, which are orthogonal to each other. This can be done most symmetrically by the method of Löwdin.[12] We shall assume that this is done, and shall call the resulting orbitals ψ_n. By this procedure we still have not solved the periodic potential problem. We shall still find nondiagonal matrix components of energy between the Bloch sums formed from different Löwdin

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[7] G. C. Fletcher and E. P. Wohlfarth, Phil. Mag. **42**, 106 (1951).

[8] G. C. Fletcher, Proc. Phys. Soc. (London) **A65**, 192 (1952).

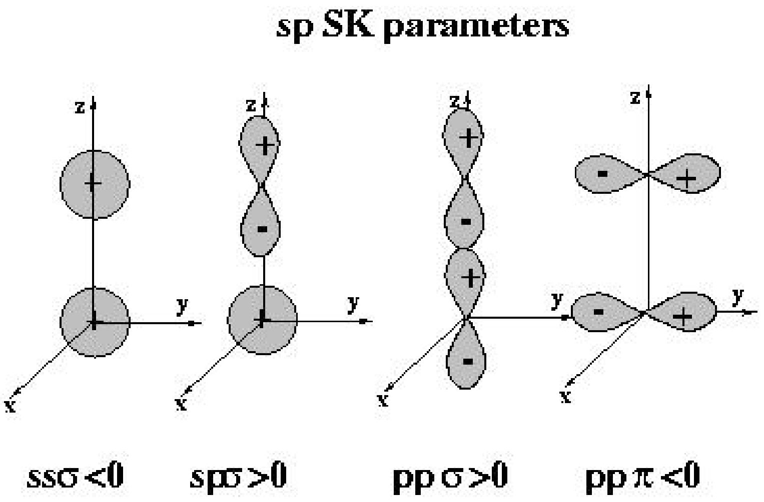
[9] L. Pauling, Phys. Rev. **54**, 899 (1938).

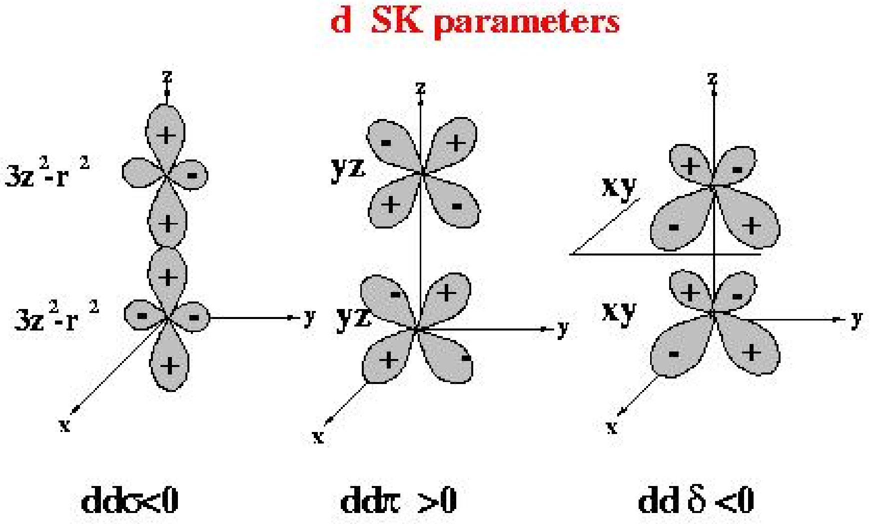
[10] K. Ganzhorn, "Gruppentheorie und Quantenmechanik der Übergangs metall-Strukturen," thesis, Technischen Hochschule, Stuttgart, 1952 (unpublished); Z. Naturforsch. **7a**, 291 (1952); Z. Naturforsch. **8a**, 330 (1953).

[11] J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); J. Lennard-Jones and G. G. Hall, Proc. Roy. Soc. (London) **A202**, 155 (1950); J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A202**, 166 (1950); G. G. Hall, Proc. Roy. Soc. (London) **A202**, 336 (1950); Proc. Phys. Soc. (London) **A66**, 1162 (1953). (This last reference, which was not available when the present paper was written, has some resemblance to it in its general point of view.)

[12] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

Simplified LACO Method "with modern digital computers". Bloch-wave in k-space and Molecular Orbitals shown below:


sp SK parameters


d SK parameters

8. EXTENDED HÜCKEL THEORY / TIGHT BINDING

8.1. **Generalized Eigenvalue Problem.**

$$\mathbb{H}\mathbf{c} = \mathbf{e}\mathbb{S}\mathbf{c} \tag{8.1}$$

where c is the eigenvector for eigenvalue e. if $\mathbb{S}$ is a identity matrix the generalized Eigenvalue Problem reduces to the Special Eigenvalue Problem

8.2. **analogy to FEM (finite element method).**

In the language of the finite element method, structural analysis, structural engineering, etc. the discrete Hamiltonian H_{kj} is the Stiffness Matrix A_{kj} and the overlap matrix S_{kj} is the mass matrix M_{kj} (aka inertia matrix).

8.3. **Overlap Matrix S.**

$$S_{ij} = \langle \chi_i | \chi_j \rangle \tag{8.2}$$

where the value S_{ij} is within the range $[0, 1]$

$$[0, 1] = \{x \in \mathbb{R} \mid 0 \leq x \leq 1\} \tag{8.3}$$

physics: $\langle \chi_i | \chi_j \rangle$ is the probability amplitude for the state χ_j to collapse into state χ_j
math: Gram Matrix, positive-(semi)definite

8.4. **Hamiltonian Matrix H.**

The inverse of the VISP (Valence State Ionization Potential) value P_i is used for the diagonal matrix elements:

$$H_{ii} = -P_i \tag{8.4}$$

Whereas non-diagonal matrix elements are *guesstimated* through some crude Wolfsberg-Helmholz formula. The literature offers some variety here:

- **arithmetic-mean Wolfsberg-Helmholz / Mulliken-Wolfsberg-Helmholz**
  M. Wolfsberg and L. Helmholz, J. Chem. Phys., 20, 837 (1952)

$$H_{ij} = \kappa \, \frac{H_{ii} + H_{jj}}{2} \, S_{ij} \tag{8.5}$$

  where $\kappa = 1.75$ (An Extended Hückel Theory, R. Hoffmann, J. Chem. Phys., 39,1397 (1963)) or $\kappa = 1.3681$ (Empirically adjusted and consistent set of EHT valence orbital parameters for all elements of the periodic table, A. Herman, Modelling Simul. Mater. Sci. Eng. 12, 21-32 (2004)) Most well-known, since it was the initial favorite pet of Hoffmann. Like generations before them Gil et al also used it and the well-trained eye of a sound and sober chemist can easily spot some similarity to the ΔEN rule from the chemistry lab:

$$\Delta EN = H_{ii} - H_{jj}$$

- **Ballhausen-Gray expression / geometric mean Wolfsberg-Helmholz** C.J. Ballhausen and H. B. Gray, Inorg. Chem., 1, 111 (1962)

$$H_{ij} = \kappa \, \sqrt{H_{ii} H_{jj}} \, S_{ij} \tag{8.6}$$

- **Cusachs expression**
  L. C. Cusachs and B. B. Cusachs, J. Phys. Chem., 71, 1060 (1967)

$$H_{ij} = (2 - |S_{ij}|) \frac{H_{ii} + H_{jj}}{2} \, S_{ij} \tag{8.7}$$

However either way there are obviously very serious issues due to oversimpification. And in 1978 finnally even Hoffmann himself wrote about the so called *"counterintuitive orbital mixing" (COM)* [**?**], (a similar if not the same issue was also known as *"lower molecular orbital catastrophe" (LMOC)* .

To combat this problem Hoffmann proposed some vodoo-corrections:

- **weighted H_{ij} formula / weighted Wolfsberg-Helmholz**
  J. H. Ammeter, H. B. Bürgi, J. C. Thibeault and R. Hoffmann, J. Amer. Chem. Soc., 100, 3686-3692 (1978)

$$H_{ij} = \kappa \, \frac{H_{ii} + H_{jj}}{2} \, S_{ij} \tag{8.8}$$

$$\kappa = k + \Delta^2 + \Delta^4(1 - k) \tag{8.9}$$

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} \tag{8.10}$$

where Δ is the so-called *"orbital asymmetry parameter"* .
(e.g. implemented in the YAeHMOP code)

- **Anderson expression, distance-dependent**
  A. B. Anderson, J. Chem. Phys. 62, 1187 (1975)

$$H_{ij} = \kappa \, \frac{H_{ii} + H_{jj}}{2} \, S_{ij} \tag{8.11}$$

$$\kappa = k \; exp(-\delta R) \tag{8.12}$$

where $k = 2.25$ and $\delta = 0.13$ Å^{-1} and R some distance dependency.

- **distance-dependent weighted Wolfsberg-Helmholz**
  G. Calzaferri, L. Forss and I. Kamber, J. Phys. Chem., 93, 5366-5371 (1989)

$$H_{ij} = \kappa \, \frac{H_{ii} + H_{jj}}{2} \, S_{ij} \tag{8.13}$$

$$\kappa = 1 + \frac{exp(-\Delta(R - d_0))}{1 + ((R - d_0) - |R - d_0|\Delta)^2} \tag{8.14}$$

$$\tag{8.15}$$

where $\Delta = 0.35$ and d_0 the average bond distance .
(implemented e.g. in the BICON-CEDiT and ICON-EDiT codes)

Distance dependency is a good thing but given the brokeness of the underlying assumptions it neither solves the problem.

8.5. **Parametrization of Slater-Koster Tables.**

- LUTs (Look-Up Tables)
- In the TB-community these pre-calulated tables are known as Slater-Koster Tables.
- different naming convention btwn. the EHT (mainly chemists) and the TB community (mainly material physicists). (Linus Pauling Hybrid-Orbitals notation vs. Slater TB notation)

- Gil according to the hints given in his PHD Thesis used the formulae and data-tables from the infamous Mulliken paper [**?**]. Unfortunately it is well known amongst the experts of the field that this paper is old and contains subtle errors. (cf. also `http://www.ccl.net/chemistry/resources/messages/1997/11/05.007-dir/index.html`)

- scb: tried to abuse popular off-theshelf Electronic-Structure Prediction Packages (e.g. Gaussian 03, Jaguar, etc.) to generate the LUT.

  The plan turned out to be possible but useless.

8.6. **Parametrization of Slater-Koster Tables, cont.**

- Roger Sayle: PDB – Cruft to Content (Perception of Molecular Connectivity from 3D Coordinates) `http://www.daylight.com/meetings/mug01/Sayle/m4xbondage.html`

- General AMBER Force Field (GAFF) `http://ambermd.org/antechamber/gaff.html`

- Thomas Kleinoeder: Prediction of Properties of Organic Compounds – Empirical Methods and Management of Property Data `http://deposit.ddb.de/cgi-bin/dokserv?idn=978268148&dok_var=d1&dok_ext=pdf&filename=978268148.pdf` (J. Gasteiger, T. Clark)

4. ATOM TYPE DEFINATION

Compared to traditional AMBER force field, atom types in GAFF are more general and cover most of the organic chemical space.Table I lists the basic (a) and special (b) atom types in GAFF.

Table I (a). Basic Atom Types in GAFF

Atom type	Description	Atom type	Description
c	sp2 C in C=O, C=S	o	sp2 O in C=O, COO-
c1	sp1 C	oh	sp3 O in hydroxyl group
c2	sp2 C, aliphatic	os	sp3 O in ether and ester
c3	sp3 C		
ca	sp2 C, aromatic		
n	sp2 N in amide	s2	sp2 S (p=S, C=S etc)
n1	sp1 N	sh	sp3 S in thiol group
n2	sp2 N with 2 subst. readl double bond	ss	sp3 S in -SR and SS
n3	sp3 N with 3 subst.	s4	hypervalent S, 3 subst.
n4	sp3 N with 4 subst.	s6	hypervalent S, 4 subst.
na	sp2 N with 3 subst	hc	H on aliphatic C
nh	amine N connected to the aromatic rings	ha	H on aromatic C
no	N in nitro group	hn	H on N
		ho	H on O
		hs	H on S
		hp	H on P
f	any F	p2	sp2 P (C=P etc)
cl	any Cl	p3	sp3 P, 3 subst.
br	any Br	p4	hypervalent P, 3 subst.
i	any I	p5	hypervalent P, 4 subst.

Table I (b). Special Atom Types in GAFF

Atom type	Description	Atom type	Description
h1	H on aliphatic C with 1 EW group;	cc(cd)	inner sp2 C in conj. ring systems
h2	H on aliphatic C with 2 EW group;	ce(cf)	inner sp2 C in conj. chain systems
h3	H on aliphatic C with 3 EW group;	cp(cq)	bridge aromatic C
h4	H on aromatic C with 4 EW group;	cu	sp2 C in three-memberred rings
h5	H on aromatic C with 5 EW group;	cv	sp2 C in four-memberred rings
		cx	sp3 C in three-memberred rings
		cy	sp3 C in four-memberred rings
n	aromatic nitrogen	pb	aromatic phosphorus
nb	inner sp2 N in conj. ring systems	pc(pd)	inner sp2 P in conj. ring systems
nc(nd)	inner sp2 N in conj. chain systems	pe(pf)	inner sp2 P in conj. chain systems
sx	conj. S, 3 subst.	px	conj. P, 3 subst.
sy	conj. S, 4 subst.	py	conj. P, 4 subst.

9. Semi-Empirical Methods

use only valence electrons, ignore core electrons, neglect some integrals Parametrize the other integrals from experimental values

Neglect of differential overlap approaches:

- CNDO complete neglect
- INDO intermediate neglect
- MINDO modified intermediate neglect
- MNDO - modified neglect
- AM1 - Austin model 1
- PM3 - Parametrization 3
- RM1 - Recife Model 1 (a reparameterization of AM1) G. B. Rocha, R. Oliveira Freire, A. Mayall Simas and J. J. P. Stewart. J. of Comp. Chem. 27(10), 1101-1111, 2006

10. DENSITY FUNCTIONAL THEORY

Density functional theory is based on the notion that for a many electron system there is a one-to-one mapping between the electron density and the external potential:

$$\rho(r) \leftrightarrow V_{ext}(r) \tag{10.1}$$

In other words: The (ground-state) density $\rho_0(r)$ of a many electron system is uniquely determined given an external potential $V_{ext}(r)$ and vice versa. (Most often the external potential is given by the Coulomb potential of a set of nuclei in a molecule or a crystal.)

A functional is a function which takes a function as its input (aka argument) and returns a scalar as output (aka return value).

It is thus possible for any operator F (e.g. the Hamilton operator $\hat{H}$) to construct a density-functional:

$$\mathcal{F} : \rho(r) \longmapsto \mathcal{F}[\rho(r)] := f \tag{10.2}$$

which takes the density-function $\rho(r)$ as input and returns the quantum-mechanical expecation value f of the requested operator F.

Thus the get the energy in the following way:

Let $\rho(r)$ be an arbitrary electron density from we construct $\rho(r)$ the external potential $V_{ext}(r)$ according to the Hohenberg-Kohn theorem. The external potential now determines the ground state electron density $\rho(r)$ of a any quantum-mechanical operator F.

From the one-electron Schrödinger equation we obtain the one-electron wavefunction $\Psi[\rho]$ and the expectation value f of the operator F:

$$\langle \Psi[\rho] | \; F \; | \Psi[\rho] \rangle = f \tag{10.3}$$

Thus in our case the expectation value f is the energy $E[\rho]$ since our operator F was the Hamilton operator $\hat{H}$:

$$\langle \Psi[\rho] | \; \hat{H} \; | \Psi[\rho] \rangle = E[\rho] \geq E_0[\rho] \tag{10.4}$$

The density determines the potential, which determines the Hamilton operator $\hat{H}$, which determines the energy $E[\rho]$.

10.1. **Kohn-Sham ansatz.**

Given a electron density ρ we write the total energy $E[\rho]$ as a linear combination of functionals:

$$E_{tot}[\rho] = E_{kin}[\rho] + \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + V_H[\rho] + E_{xc}[\rho] \tag{10.5}$$

$$V_H = \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \tag{10.6}$$

$$\tag{10.7}$$

where $E_{kin}[\rho]$ is the kinetic energy (of a non-interacting electron gas with density ρ), V_H the classical electrostatic (Hartree / Coulomb) energy of the electrons. These are all terms which can be given exact in practial implementation. The only term which needs to be approximated is $E_{xc}[\rho]$ the exchange-correlation functional which accounts for everything not contained in the other terms.

10.2. **Why are we doing this?**

The DFT formulation therefore allows to decompose any full self-interacting quantum system with one system-wide many-electron Schrödinger wave equation into a equivalent system which features only single-electron Schroedinger wave equations. All one-electron Schrödinger wave equations are linked to each other via the exchange-correlation functional, which needs to be approximated.

10.3. **Exchange-Correlation functionals.**

Exchange interaction is the increase or decrease of the energy or distance expectation value of between two or more electrons with overlapping wave functions.

And electronic correlation refers to the interaction between an electron and its neighbor electrons.

The Exchange-correlation functional therefore accounts for effects like due to Pauli exclusion principle and kinetic energy contributions that are not taken into account in the idealized kinetic energy $T[\rho]$

Further since we do not know the exact Exchange-correlation functional, we have to approximate it - obviously at an affordable price in FLOPS and memory cost.

10.4. **local-density approximation (LDA).**

"We do not expect an accurate description of chemical bonding with the Local Density Approximation (LDA)" – Kohn and Sham, 1965

In solid-state physics the most widely used approximation is the local-density approximation (LDA), where the functional depends only on the electron density at the coordinate where the functional is evaluated which keeps computational cost low):

$$E_{xc}^{\mathrm{LDA}}[\rho] = \int \epsilon_{xc}(\rho(r))\rho(r)\mathrm{d}\vec{r} \tag{10.8}$$

where $\epsilon_{xc}(\rho(r))$ is the exchange correlation energy density function:

$$\epsilon_{xc}(\rho(r)) = \frac{1}{2}\int \frac{\rho_x(r,r')}{|r-r'|}d\vec{r'} \tag{10.9}$$

Vosko-Wilk-Nusair (VWN) is a popular LDA correlation functional. It was fitted to accurate numerical results by Ceperley and Alder, (quantum Monte-Carlo calculations on a uniform electron gas at low- and high-spin limits for several electron densities.)

In covalent systems the LD-approximation can (sometimes) quite accurately predict structures, vibrations, and relative energies of covalent systems. However, bond energies are seriously overestimated. The LDA should not be used for systems with weak bonds, such as hydrogen bonds. These problems with the LSD method can be corrected to a large extent by using the so-called gradient-corrected (or non-local) functionals.

10.5. **generalized gradient approximation (GGA).**

The generalized gradient approximation (GGA) is still local but includes the gradient of the density (very useful for chemistry!) at the price of increased computational cost:

$$E_{xc}^{\mathrm{GGA}}[\rho, \nabla\rho(r)] = \int \epsilon_{xc}(\rho(r), \vec{\nabla}\rho(r))\rho(r)\mathrm{d}\vec{r} \tag{10.10}$$

$$E_{xc} = E_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]. \tag{10.11}$$

very popular choice is the Becke [**?**] exchange functional which defines the exchange and correlation energy per particle as:

$$\epsilon_{\mathrm{xc}}^{\mathrm{B88}} = -\beta\rho^{1/3}\frac{x^2}{(1+6\beta x\sinh^{-1}x)} \tag{10.12}$$

$$x = \frac{|\nabla\rho|}{\rho^{4/3}} \tag{10.13}$$

where $\beta = 0.0042$ is an empirical parameter fitted to reproduce the exact exchange energies of the first six noble gas elements.

One note-worthy deficiency of Becke's functional is that the potential decays asymptotically:

$$\lim_{r\to\infty} v_x^{B88}(\mathbf{r}) = \frac{1}{r^2}. \tag{10.14}$$

" instead of the correct

$$\lim_{r\to\infty} v_x(\mathbf{r}) = \frac{1}{r} \tag{10.15}$$

Often the Becke exchange functional (B88) is used in conjunction with the Perdew-Wang correlation functional (BP) or the Lee-Yang-Parr correlation functional (BLYP). The latest, so-called generalized gradient corrected (GGA) functional, by Perdew and Wang (P91) was derived by considering low- and high-density regimes and by enforcing various summation rules.

10.6. **meta-GGA functional (mGGA).**

Like a GGA electron density and its gradient but additionally the laplacian (aka ”non-interacting kinetic energy density”) $\tau_S(r)$ enters the equation:

$$E_{xc}^{\text{mGGA}}[\rho] = \int \epsilon_{xc}(\rho(r), \nabla\rho(r), \nabla^2\rho_{ik}(r))\rho(r)\mathrm{d}\vec{r} \tag{10.16}$$

$$\tag{10.17}$$

A Meta-GGA is quite expensive

10.7. **hybrid functional.**

A hybrid functional is an exchange-correlation functional that incorporates portions of "exact" exchange E_x^{HF} derived from rigorous Hartree-Fock calculation with exchange and correlation from other sources (ab inito, LDA, GGA, empirical, etc.) by linear combination. The parameters relating the amount of each functional can be arbitrarily assigned and is usually fitted to reproduce well some set of observables (bond lengths, band gaps, etc.). For example, the very popular B3LYP (Becke Exchange Functional, 3 empirical fitting parameters, and Lee-Yang-Parr) functional combines the Hartree-Fock exchange term with the Becke [**?**] exchange and Lee-Yang-Parr [**?**] correlation functionals according to the formula proposed by Becke [**?**]:

$$E_{xc}^{\mathrm{B3LYP}} = E_{xc}^{\mathrm{LDA}} + a_0(E_x^{\mathrm{HF}} - E_x^{LDA}) + a_x(E_x^{\mathrm{GGA}} - E_x^{LDA}) + a_c(E_c^{\mathrm{GGA}} - E_c^{LDA}) \tag{10.18}$$

where $a_0 = 0.20$, $a_x = 0.72$ and $a_c = 0.81$ are three empirical parameters.

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10.8. **Harris / Harris-Foulkes functional approximation.**

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11. REACTION RATE

Arrhenius equation, Eyring equation
Activation energy, saddle-point energy

11.1. Koopmans' theorem.

11.2. Klopman-Salem equation.

Fuki Frontier Orbital Theory

11.3. Janak's theorem.

J. F. Janak, Proof that $\partial E/\partial n_i = \epsilon$ in density-functional theory, Phys. Rev. B, 18, 7165 - 7168 (1978)

12. APPENDIX

- `http://cccbdb.nist.gov/`
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- `http://en.wikipedia.org/wiki/Covalent_radius_of_fluorine`
- `http://en.wikipedia.org/wiki/Hydrogen_bond`
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