



So theory guys have got it made  
in rooms free of pollution.  
Instead of problems with the reflux,  
they have only solutions...  
In other words, experimentalists  
will likely die of cancer  
From working hard, yet fruitlessly...  
till theory gives the answer.

Thomas A. Holme, 1983

## Computing NMR parameters

*a brief outline of an introduction into the basics of  
how electronic structure theory packages work*

### Schrodinger's equation

Non-relativistic quantum mechanics stipulates the following equation of motion:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = -i\hat{H}\psi(\vec{r}, t) \quad \xrightarrow{\text{stationary solutions?}} \quad \hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

Hamiltonian
energies  
wavefunction
orbitals

The Hamiltonian is just energy – kinetic plus potential:

$$E_{\text{kin}} = \frac{mv^2}{2} = \frac{p^2}{2m} \quad E_{\text{pot}} = U(\vec{r}) \quad \hat{H}_{\text{kin}} = \frac{\hat{p}^2}{2m} \quad \hat{H}_{\text{pot}} = U(\vec{r})$$

classical mechanics
quantum mechanics

energy of the system:  $E = \int \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) dV$

Solving  $3n$ -dimensional PDEs analytically is a bit of a mess... need matrices!

► Computers are not good at manipulating analytical expressions.

## Basis sets

A "basis set" is a way of converting integrodifferential equations into matrix equations, which are easier to solve on digital computers.

$$\underbrace{\left(\frac{\hat{p}^2}{2m} + U(\vec{r})\right)}_{\text{Hamiltonian}} \psi(\vec{r}) = E \psi(\vec{r}) \quad \leftarrow \text{wavefunction}$$

$$\psi(\vec{r}) = \sum_k c_k \phi_k(\vec{r})$$

$\uparrow$  coefficients  
 $\uparrow$  basis functions (e.g. AOs)

The equation for the wavefunction is replaced by a system of linear equations for the expansion coefficients:

$$\sum_k c_k \underbrace{\left(\frac{\hat{p}^2}{2m} + U(\vec{r})\right) \phi_k(\vec{r})}_{\text{can be pre-computed}} = E \sum_k c_k \phi_k(\vec{r}) \quad \Rightarrow \quad \sum_k H_{nk} c_k = E c_n$$

$\underbrace{\hspace{10em}}_{\text{simple linear equations}}$

The best basis functions are easy to multiply, differentiate, and integrate.

► Atomic orbitals (1s, 2s, 2p, 3s, etc.) are an example of a basis set.

## Gaussian basis sets

Property	Benefits
A product of two Gaussian functions is another Gaussian at their centre of gravity.	All two-electron integrals are analytical. Massive time saving compared to numerical integration.

Gaussians fall off very steeply with distance.	Distance based cut-offs improve performance.
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Property	Drawbacks
Gaussians fall off very steeply with distance.	Incorrect asymptotic behaviour at large distances.
Gaussians have zero derivative at the origin.	Incorrect asymptotic behaviour at small distances.
Gaussians forming the basis are centred at the nuclei.	Basis set superposition error.

The angular part is borrowed from the hydrogen atom solution:

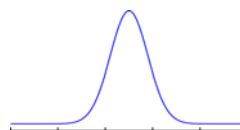
$$G_{n,l,m}(r, \theta, \varphi) = \underbrace{Y_{l,m}(\theta, \varphi)}_{\text{spherical harmonic}} e^{-r^2/b_n^2}$$

$\uparrow$  Gaussian

Contractions (linear combinations with fixed coefficients) are often used in the radial part:

$$G_{n,l,m}(r, \theta, \varphi) = Y_{l,m}(\theta, \varphi) \sum_i a_i e^{-r^2/b_{ni}^2}$$

$\uparrow$  contraction coefficients



► Gaussian basis sets are used by Gaussian03, GAMESS and similar packages.

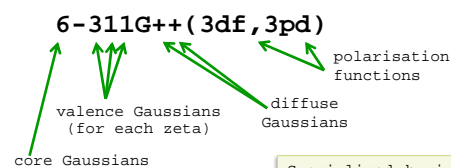
## Properties of atomic basis sets

Property	Explanation
Core functions	Basis functions intended to provide the description of the core electrons of an atom. Core electrons (e.g. 1s for carbon) do not participate in chemical bonding.
Valence functions	Basis functions intended to provide the description of the valence electrons of an atom that are involved in chemical bonding. Difference to core is often notional.
Zeta number	Number of independent sets of radial basis functions in the valence part of the basis (usually 2-4). They are introduced to improve basis flexibility.
Polarisation functions	Additional functions with a higher angular momentum number, introduced to allow atomic orbitals to be shifted ("polarised") relative to their nucleus.
Diffuse functions	Additional functions with very broad profile, introduced to improve description of the regions that are far away from the nuclei, usually used for anions.
Tight functions	Additional functions concentrated tightly around their nuclei to improve the description of the nuclear region for NMR and ESR interaction calculations.
Effective core potentials	Effective Coulomb interaction potentials designed to replace inner orbitals of heavy atoms that are not well described by non-relativistic methods.
Rydberg functions	Additional extremely diffuse basis functions required for accurate description of Rydberg states.

► A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry*, Section 3.6.

## Gaussian basis sets

### People's basis sets:



### Correlation-consistent basis sets:

#### aug-cc-pVTZ

"correlation consistent polarised valence triple-zeta basis set augmented with diffuse functions"

### What to look for:

Specialised basis sets exist for many calculation types. Check the literature for any such basis sets before using a general purpose one.

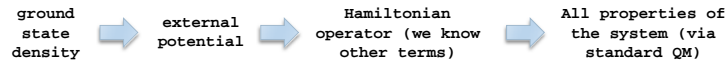
Zeta number	Polarisation functions	Diffuse functions	Tight functions	Effective core potentials	Rydberg functions
The more, the better/slower, usually 2-3.	The more, the better/slower, usually one or two $l+1$ sets.	The more, the better/slower, usually a single set for anions.	Only used for computing HFCs and $J$ -couplings.	Used to approximate inner shells of heavy elements	Only used to describe Rydberg states

Bigger and more flexible basis sets provide more accurate matrix representations for the original differential equations, and therefore yield more accurate energies.

► <https://bse.pnl.gov/bse/portal> (a collection of popular basis sets)

## Density functional theory

**The basic lemma of DFT:** the ground state density of a bound system of interacting electrons in some external potential determines this potential uniquely.



It should therefore be possible to reformulate quantum chemistry in terms of electron density alone (just three dimensions!) – a major simplification.

**Hohenberg-Kohn variational principle:** there exists a well-defined (though not explicitly known) functional of electron density, which attains a global minimum at the ground state density.

$$\min_{\rho} E[\rho] = \left\langle \Psi_0 \left| \hat{T} + \hat{V} + \hat{U} \right| \Psi_0 \right\rangle$$

nuclear attraction
electron repulsion
energy functional
inter-electron repulsion energy functional (not fully known)

$$E[\rho] = T[\rho] + U[\rho] + \int V(\vec{r})\rho(\vec{r})d^3\vec{r}$$

kinetic energy functional (known)
nuclear attraction energy functional (known)

ground state wavefunction
kinetic terms

► Energy functionals in DFT do unfortunately involve an element of witchcraft.

## Magnetic field in quantum mechanics

Maxwell's equations involve two potentials:

$$\vec{E}(\vec{r}, t) = -\nabla\phi(\vec{r}, t) - \frac{\partial\vec{A}(\vec{r}, t)}{\partial t} \quad \vec{B}(\vec{r}, t) = \nabla \times \vec{A}(\vec{r}, t)$$

electric field
scalar potential
magnetic field
vector potential

Vector potential term adds itself to momentum (aka Lorentz force):

$$\hat{H} = \frac{1}{2m} \left[ \hat{\vec{p}} + q\vec{A}(\vec{r}, t) \right]^2 + q\phi(\vec{r}, t)$$

The vector potential comes from the external field and from particles:

$$\vec{A}(\vec{r}) = \frac{\vec{B} \times \vec{r}}{2} + \sum_k \frac{\vec{\mu}_k \times (\vec{r} - \vec{r}_k)}{|\vec{r} - \vec{r}_k|^3}$$

external field
k<sup>th</sup> magnetic dipole

There are multiple thorny technicalities (gauges, divergences, etc.)

► Take-home message: software can compute *energies* of magnetic systems.

## Properties: susceptibility and shielding

Magnetic susceptibility tensor may be defined *via* energy derivatives:

$$\bar{\mu} = \frac{1}{\mu_0} \chi \cdot \bar{B} \quad \& \quad E = -\bar{\mu} \cdot \bar{B} \quad \Rightarrow \quad E = -\frac{1}{\mu_0} \bar{B}^T \cdot \chi \cdot \bar{B} \quad \Rightarrow \quad \chi = -\mu_0 \frac{\partial^2 E}{\partial \bar{B}^T \partial \bar{B}}$$

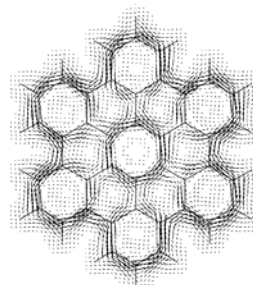
A similar argument defines chemical shift tensor:

$$E = -\bar{\mu}^T \cdot (\mathbf{1} + \delta) \cdot \bar{B}, \quad \mathbf{1} + \delta = -\frac{\partial^2 E}{\partial \bar{\mu}^T \partial \bar{B}}$$

From Hellmann-Feynman theorem:

$$\frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial \hat{H}}{\partial \lambda} | \Psi \rangle$$

$$\frac{\partial^2 E}{\partial \lambda^2} = \langle \Psi | \frac{\partial^2 \hat{H}}{\partial \lambda^2} | \Psi \rangle + \left\langle \frac{\partial \Psi}{\partial \lambda} \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \Psi \right\rangle + \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \frac{\partial \Psi}{\partial \lambda} \right\rangle$$



Ring current density in hexabenzocoronene.

► The technicalities can be brutal, but the principle is simple – just derivatives.

## Properties: NQI and $J$ -coupling

Electric quadrupole moments interact with electric field gradients:

$$\mathbf{V} = \left. \frac{\partial \vec{E}}{\partial \vec{r}} \right|_{\text{nucleus}} = \frac{\partial^2 \phi}{\partial \vec{r}^T \partial \vec{r}} \Big|_{\text{nucleus}}$$

Nuclear electric quadrupole is rigidly glued to nuclear spin, and therefore:

$$\hat{H} = \frac{1}{6} \sum_{nk} \hat{Q}_{nk} V_{nk} \quad \hat{Q}_{nk} = \frac{eQ}{S(2S+1)} \left[ \frac{3}{2} (\hat{S}_n \hat{S}_k + \hat{S}_k \hat{S}_n) - \delta_{nk} \hat{S}^2 \right]$$

Quadrupolar coupling is so large (MHz) because it is essentially electrostatic.

$J$ -coupling is also a derivative; people often forget that  $J$ -coupling is a *tensor*.

$$E = \bar{\mu}_A^T \cdot \mathbf{J} \cdot \bar{\mu}_B \quad \Rightarrow \quad \mathbf{J}_{AB} = \frac{\partial^2 E}{\partial \bar{\mu}_A^T \partial \bar{\mu}_B}$$

though the isotropic part dominates in CHNO molecules (up to 80% of the norm).

► Summary: all NMR tensors are simple derivatives of the energy.

## Recommended packages: *Gaussian*

### Notable Pro

Excellent internal coordinate module supporting very sophisticated scans, constraints and energy surface analysis.

Excellent solvation and reaction field support.

Very user-friendly, clear and forgiving input syntax.

### Notable Contra

Very expensive, carries severe licensing restrictions.

Does not scale to more than 4 (CISD) to 32 (DFT) cores, even on shared memory systems.

A real pain to install.



Gaussian is not the most CPU-efficient package in existence, but it takes much less time to set up a Gaussian job than a job for any other expert level package.

*N.B.:* CPU time is £0.02 per core-hour, brain time is £25+ an hour.

```
%Mem=16GB
%NProcShared=8
#p opt=tight rb3lyp/cc-pVDZ scf=(tight,dsymm)
integral=(grid=ultrafine)
```

Flavin anion geometry optimization

```
-1 1
C      0.00000000    0.00000000    0.00000000
C      0.00000000    0.00000000    1.41658511
C      1.23106864    0.00000000    2.09037416
C      2.43468421    0.00000000    1.39394037
```

► [http://www.gaussian.com/g\\_prod/g09\\_glance.htm](http://www.gaussian.com/g_prod/g09_glance.htm)

## Recommended packages: *ADF*

### Notable Pro

Slater type basis sets.

Excellent treatment of heavy and transition metals.

Excellent relativistic DFT implementation.

### Notable Contra

Fails to converge with many systems containing actinides and lanthanides.

Does not support non-DFT calculations.

Numerous, voluminous and poorly documented input / output files.

```
TITLE Geometry optimization of cyclohexane
XC
LDA Apply VWN
GGA Apply BLYP
END
MAXMEMORYUSAGE 30
SCF
ITERATIONS 250
CONVERGE 1E-7 1E-7
MIXING 0.2
DIIS N=10 OK=0.5 cyc=5 CX=5.0 BFAC=0
END
INTEGRATION 6.0 6.0
atoms
C -4.8948 1.9727 -0.2565
C -3.6335 1.2447 0.2567
```



► <http://www.scm.com/Products/Overview/ADFinfo.html>

## Recommended packages: ORCA

### Notable Pro

The best package in existence for spectroscopic properties.

Simple and forgiving input syntax.

Free (not open-source).

### Notable Contra

No symmetry factorization.

No analytical second derivatives.

Closed-source package.



```
! UHF HF
%basis basis SV
  newgto Cl "DUNNING-DZP" end
  end
* xyz -2 2
Cu 0 0 0 newgto "TZVPP" end
Cl  2.25  0  0
Cl -2.25  0  0
Cl  0    2.25  0
Cl  0    -2.25  0
*
```

```
! MP2 RHF TZVP TightSCF
%mp2    MaxCore 100
        end
%paras  rCO = 1.20
        ACOH = 120
        rCH = 1.08
        end
* int 0 1
C(1) 0 0 0 0.00 0.0 0.00
O(2) 1 0 0 {rCO} 0.0 0.00
H(3) 1 2 0 {rCH} {ACOH} 0.00
H(3) 1 2 3 {rCH} {ACOH} 180.00
*
```

ORCA is the package of choice for NMR and EPR properties, particularly the "difficult" ones, such as ZFS, exchange interaction, etc.

► <http://www.thch.uni-bonn.de/tc/orca/>

## Visualization software: GaussView

### Notable Pro

A truly outstanding GUI – very powerful and convenient.

Can set up Gaussian jobs and interpret Gaussian output.

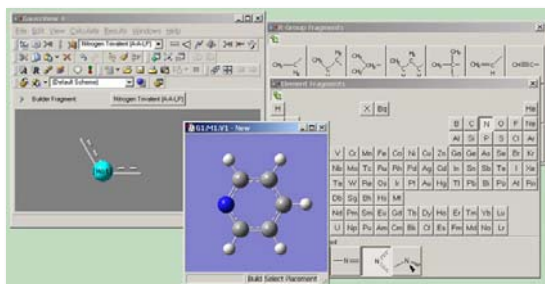
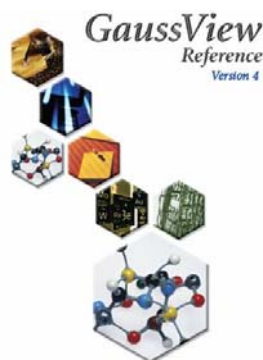
Supports all major molecule specification formats.

### Notable Contra

So good it's addictive.

Quite expensive.

Can only export 2D images.



GaussView is a must-have for most types of research involving QC calculations.

► [http://www.gaussian.com/g\\_prod/gv5b.htm](http://www.gaussian.com/g_prod/gv5b.htm)

## Visualization software: *VMD*

### *Notable Pro*

Very flexible large-scale structure visualizer.

Outputs 3D graphics.

Supports all major molecule specification formats.

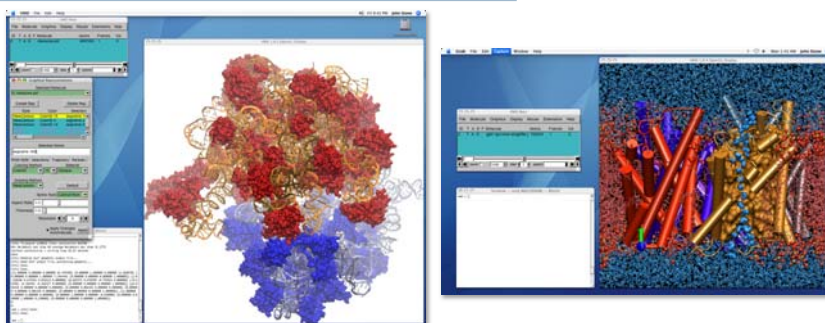
### *Notable Contra*

Specifically targets large biomolecules.

Lacks structure editing capabilities.

Very old school user interface.

**VMD**  
Visual Molecular Dynamics



► <http://www.ks.uiuc.edu/Research/vmd/>

## Visualization software: *Chemcraft*

### *Notable Pro*

Excellent structure editing capabilities.

Dedicated support for GAMESS, Gaussian and ADF.

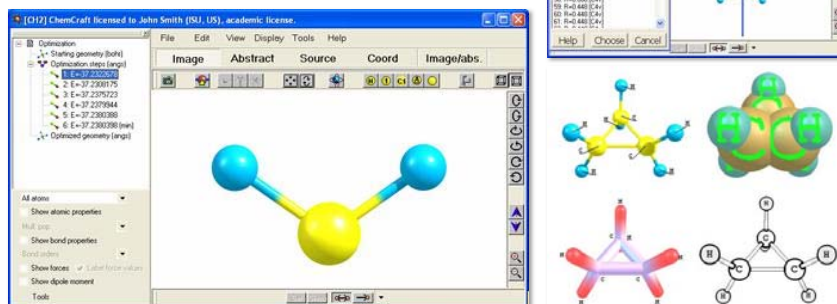
Outputs animations and calculation inputs.

### *Notable Contra*

Source code not available.

Commercial package (\$100-\$200 depending on the license)

Old school user interface.



► <http://www.chemcraftprog.com>