

Dalton Quantum Chemistry Program

- Quotation from home page:

Dalton QCP represents a powerful quantum chemistry program for the calculation of molecular properties with SCF, MP2, MCSCF or CC wave functions. The strengths of the program are mainly in the areas of magnetic and (frequency-dependent) electric properties, and for studies of molecular potential energy surfaces, both for static and dynamical investigations.

- Since late 1999, there has been an active development in Dalton towards density-functional theory (DFT).
- The DFT functionality will become available with Dalton 2.0, to be released later this year.

Dalton distribution

- License agreement
 - copyright rests with authors
 - further distribution not allowed
 - use of program must be cited
 - no fee may be charged for its use
 - personal license: code may be modified for own use
 - site license: only executables and scripts should be available to users
- code downloaded as tar file
 - Fortran 77 source code (some code in C and Fortran 90)
 - scripts for compilation and linking
 - run scripts
 - test inputs and outputs
- support
 - extensive online documentation
 - no user support as such but active mailing list

Some Dalton distribution statistics

- 917 licenses as of 22.05.03
 - 98% personal
 - 12% site
- About 150 licenses issued every year:
 - 1997 – 146, 1998 – 98, 1999 – 135, 2000 – 158, 2001 – 165, 2002 – 174
- Geographical distribution:
 - Europe 517, America 211, Asia 175, Australia 13, Africa 1
 - US 149, Germany 79, Japan 49, Italy 44, Brazil 37, UK 37, Russia 34, China 33, France 31, Poland 27, Denmark 24, Spain 24, Sweden 24

Dalton functionality

- electronic-structure models
 - RHF, MCSCF (CAS, RAS), FCI, MP2, CCSD, CCSD(T)
 - R12 and DFT under development
- potential-energy surfaces
 - gradients and Hessians
 - minima and transition states; paths and trajectories
 - frequencies, IR and Raman intensities
- linear, quadratic and cubic response theory
 - multipole moments and EFGs
 - singlet and triplet excitation energies; transition moments
 - static and frequency-dependent polarizabilities and hyperpolarizabilities
 - nuclear shielding and spin-rotation constants
 - magnetizabilities and rotational g tensors
 - hyperfine and spin-spin coupling constants
 - circular dichroism (VCD, ECD, and VROA)

Some Dalton history

- Dalton was developed as an MCSCF package in the mid and late 1980s
 - HERMIT, SIRIUS, ABACUS, and RESPONSE
 - very robust and flexible CASSCF and RASSCF code
 - a strong property functionality, up to cubic response theory
 - released as Dalton 1.0 in 1997; Dalton 1.1 in 2000
- In the early and mid 1990s, coupled-cluster theory was included
 - direct coupled-cluster theory enabled large-scale CCSD and CCSD(T) calculations
 - coupled-cluster response theory developed based on the (static and dynamic) Lagrangian formulation
 - released as Dalton 1.2 in 2001
- Since 1999, DFT has been implemented in Dalton
 - LDA, GGA, and hybrid theories
 - again, focus is on the calculation of molecular properties
 - to be released as Dalton 2.0 later this year
 - original implementation based in part on that in Cadpac

Basic DFT functionality in Dalton

- Functionals implemented
 - LDA, GGA (BLYP), and hybrid (B3LYP) functionals
 - original LDA, BLYP, and B3LYP routines from Cadpac have been rewritten
 - PW86, LB94, and PW92 implemented but not yet extensively used
- Grid generation
 - the Becke and the Stratmann–Scuseria–Frisch partitioning schemes
 - the Lebedev–Laikov angular scheme
 - the Gauss–Chebychev (second kind) and Lindh–Malmqvist–Gagliardi radial schemes
 - adaptive grid generation
- Gaussian basis sets
 - segmented and generally contracted basis sets
 - Cartesian and spherical harmonic angular forms
 - McMurchie–Davidson scheme
 - no hard-coded limits on angular momentum
- D_{2h} point-group symmetry and its subgroups

DFT calculations of properties in Dalton

- A large number of molecular properties can now be calculated at the DFT level of theory in Dalton
- Molecular gradients for first-order geometry optimization
 - Molecular Hessians are currently being implemented
- Linear and quadratic response functions
 - static and dynamic polarizabilities and hyperpolarizabilities
 - singlet and triplet excitation energies and transition moments
 - optical rotation
 - vibrational Raman optical activity
 - Sternheimer shieldings and EFG polarizabilities
 - two-photon absorption cross sections
 - NMR parameters (shieldings and spin–spin coupling constants)
 - parity violation

Some comments on the DFT property calculations

- The properties are all calculated by analytical response theory
- The scheme is essentially that of MCSCF theory, suitably extended to include the contributions from the exchange–correlation functionals
 - second-quantization parametrization of the Kohn–Sham noninteracting reference state:

$$|t\rangle = \exp[-\hat{\kappa}(t)]|0\rangle; \quad \hat{\kappa}(t) = \sum_{pq} \kappa_{pq}(t) E_{pq} \quad (\text{anti-Hermitian})$$

- noninteracting reference Schrödinger equation:

$$i \frac{d}{dt} |t\rangle = \sum_{pq} (h_{pq} + j_{pq}[\rho] + v_{xc,pq}[\rho] + V_{pq}(t)) E_{pq}$$

- electron density

$$\hat{\rho}(\mathbf{r}_1) = \sum_{pq} \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) E_{pq}; \quad \rho(\mathbf{r}, t) = \langle t | \hat{\rho} | t \rangle$$

- from this, everything follows...
- linear equations solved in the usual manner, invoking direct techniques

Benchmarking of hyperpolarizabilities

- Comparison of DFT with different wave-function methods:

	nm	HF	CCSD	CC3	LDA	BLYP	B3LYP	exp.
HF	∞	-5.7	-7.9	-7.5	-9.1	-8.9	-7.6	
	632.8	-6.1	-8.8	-8.3	-10.6	-10.4	-8.6	-9.9 ± 1.0
CO	∞	25.0	25.4	27.2	30.8	30.2	28.0	
	632.8	28.2	29.6	31.9	37.0	36.6	33.2	30.2 ± 3.2
H ₂ O	∞	-10.7	-17.7	-17.0	-23.8	-23.7	-18.5	
	632.8	-12.5	-21.7	-21.0	-32.1	-32.8	-24.1	-20.9 ± 1.0

- LDA and GGA are very similar and overshoot
- B3LYP performs as well as CC3
- same performance observed for large molecules such as PNA
- the importance of benchmarking

NMR parameters by DFT

- we have implemented the central parameters of high-resolution NMR spectroscopy
- nuclear shielding constants
 - London atomic orbitals used for gauge invariance

$$\omega_{lm}(\mathbf{A}_O) = \exp\left[\frac{1}{2}i\mathbf{B} \times (\mathbf{N} - \mathbf{O}) \cdot \mathbf{r}\right] \chi_{lm}(\mathbf{r})$$

- indirect nuclear spin–spin coupling constants
 - all contributions in Ramsey’s nonrelativistic theory calculated by response theory

$$\mathbf{K}_{KL} = \left\langle 0 \left| \mathbf{h}_{KL}^{\text{DSO}} \right| 0 \right\rangle + 2 \sum_{n_S \neq 0} \frac{\langle 0 | \mathbf{h}_K^{\text{PSO}} | n_S \rangle \langle n_S | (\mathbf{h}_L^{\text{PSO}})^T | 0 \rangle}{E_{n_S} - E_0} + 2 \sum_{n_T} \frac{\langle 0 | \mathbf{h}_K^{\text{FC}} + \mathbf{h}_K^{\text{SD}} | n_T \rangle \langle n_T | (\mathbf{h}_L^{\text{FC}})^T + (\mathbf{h}_L^{\text{SD}})^T | 0 \rangle}{E_{n_T} - E_0}.$$

- DSO = diamagnetic spin–orbit; PSO = paramagnetic spin–orbit; SD = spin–dipole, FC = Fermi contact

NMR spin–spin coupling constants: vibrational contributions

		$J_{\text{eq}}^{\text{RAS}}$	$J_{\text{eq}}^{\text{B3LYP}}$	$J_{\text{eq}}^{\text{emp}}$	$J_{\text{vib}}^{\text{B3LYP}}$	$J_{\text{tot}}^{\text{exp}}$
HF	$^1J_{\text{HF}}$	544.2	416.6	538	-38	500
CO	$^1J_{\text{CO}}$	16.1	18.4	15.7	0.7	16.4
N ₂	$^1J_{\text{NN}}$	0.8	1.4	1.7	0.1	1.8
H ₂ O	$^1J_{\text{OH}}$	-76.7	-76.6	-86.0	5.4	-80.6
	$^1J_{\text{HH}}$	-7.8	-7.1	-8.2	0.9	-7.3
HCN	$^1J_{\text{CN}}$	-19.7	-19.2	-20.5	2.0	-18.5
	$^1J_{\text{CH}}$	269.9	283.5	262.2	5.1	267.3
	$^2J_{\text{NH}}$	-6.9	-7.8	-8.2	0.8	-7.4
NH ₃	$^1J_{\text{NH}}$	43.6	45.7	44.1	-0.3	43.8
	$^2J_{\text{HH}}$	-11.3	-10.1	-10.4	0.7	-9.7
CH ₄	$^1J_{\text{CH}}$	120.6	132.6	120.0	5.3	125.3
	$^2J_{\text{HH}}$	-13.2	-13.3	-12.1	-0.7	-12.8
C ₂ H ₂	$^1J_{\text{CC}}$	184.7	205.1	184.8	-10.0	174.8
	$^1J_{\text{CH}}$	244.3	271.9	242.9	4.7	247.6
	$^2J_{\text{CH}}$	53.1	56.0	53.0	-2.9	50.1
	$^3J_{\text{HH}}$	10.9	10.6	9.7	-0.1	9.6
C ₂ H ₄	$^1J_{\text{CC}}$	68.8	74.7	66.7	0.9	67.6
	$^1J_{\text{CH}}$	151.6	165.3	151.2	5.1	156.3
	$^2J_{\text{CH}}$	-1.6	-1.3	-1.2	-1.2	-2.4
	$^2J_{\text{HH}}$	1.1	2.9	2.0	0.3	2.3
	$^3J_{\text{cis}}$	11.5	13.5	10.5	1.2	11.7
	$^3J_{\text{trans}}$	17.8	20.7	16.7	2.3	19.0

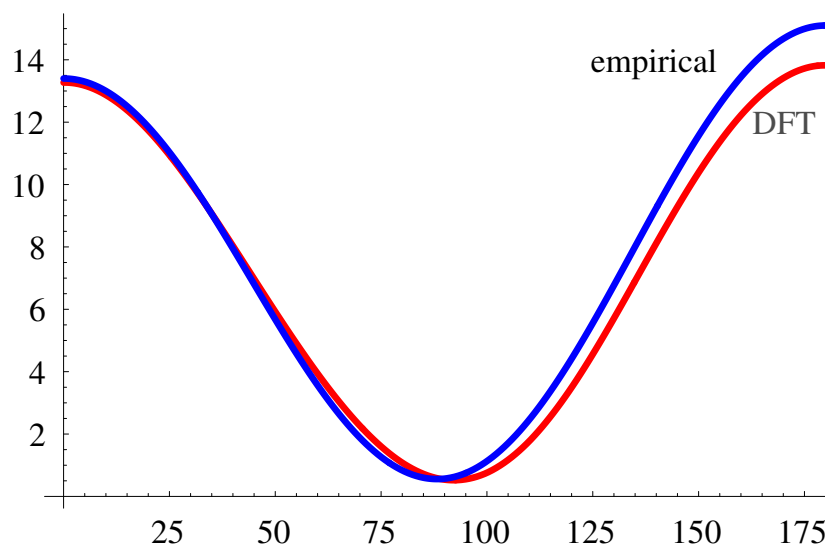
NMR spin–spin coupling constants in C₆₀

- For the spin–spin coupling constants in C₆₀, we find (at the B3LYP level):
 - ¹J couplings within one pentagon and between two pentagons are 62 and 77 Hz.
 - ²J couplings within one pentagon and between two pentagons are 7 and 1 Hz.
 - ³J couplings are 4 Hz.
 - ⁴J couplings and all other couplings are smaller than 1 Hz.

The Karplus curve

- Vicinal couplings depend critically on the dihedral angle:

- ³J_{HH} in ethane as a function of the dihedral angle:
- The agreement with the empirical Karplus curve is good.



The Hartree energy

$$E_H = - \sum_K \int \frac{\rho(\mathbf{r}_1) Z_K}{r_{1K}} d\mathbf{r}_1 + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

- For large systems, straightforward calculation of all nonnegligible Coulomb integrals yields a scheme that scales quadratically with system size.
- For systems containing several hundred atoms, it becomes necessary to use more efficient schemes, whose cost scales linearly with systems size.
- We recently implemented the fast multipole method (FMM) for the evaluation of the classical (i.e., nonoverlapping) contributions to the Hartree energy.
- In addition, a new code has been written for the efficient evaluation of the nonclassical (i.e., overlapping) contributions to the Hartree energy.
- Combined with a linearly-scaling functional evaluation, this has allowed to us carry out LDA and GGA calculations on systems containing more than 1000 atoms in Dalton.

DFT energy optimization

- the energy optimization in Dalton is based on the DIIS method
 - optimization more difficult than in Hartree–Fock theory (small HOMO–LUMO gap)
 - second-order optimization not yet implemented but can easily be added
 - start guesses: Huckel guess, diagonalization of one-electron Hamiltonian matrix
 - for large systems, convergence must be improved further (semi-empirical guess?)
- diagonalization bottleneck for large systems
 - diagonalization becomes expensive and must be avoided beyond 1000 atoms
 - the new scheme will be based on a direct minimization of the density matrix

$$\mathbf{D}(\mathbf{X}) = \exp(-\mathbf{X}\mathbf{S})\mathbf{D}\exp(\mathbf{S}\mathbf{X})$$

where \mathbf{D} is a reference density matrix, \mathbf{S} is the overlap matrix, and \mathbf{X} is an antisymmetric matrix

- at each DIIS iteration, we minimize the function

$$E(\mathbf{X}) = 2 \operatorname{tr} \mathbf{F} \exp(-\mathbf{X}\mathbf{S})\mathbf{D}\exp(\mathbf{S}\mathbf{X})$$

where \mathbf{F} is the Kohn–Sham matrix by some technique (e.g., conjugate gradient)

Further Dalton DFT developments

- a greater variety of functionals, with emphasis on GGAs
- more accurate integration—in particular, for molecular properties
- better start guesses
- more reliable and more rapid convergence
- current density functionals
- asymptotic corrections
- open shell systems—in particular, unrestricted open-shell theory
- full implementation of linear-scaling technology
- full implementation of response theory to third order