

Supercomputers applications in quantum chemistry

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$$H\Psi = E\Psi$$

$$H = T_e + T_n + V_{en} + V_{ee} + V_{nn}$$

$$T_e = -\frac{h^2}{8\pi^2 m} \sum_{i=1}^n \left[\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right]$$

$$V_{en} = -\sum_{i=1}^n \sum_{\nu=1}^N \frac{Z_\nu e^2}{r_{i\nu}}$$

$$T_n = -\frac{h^2}{8\pi^2} \sum_{\nu=1}^N \frac{1}{M_\nu} \nabla_\nu^2$$

$$V_{ee} = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \frac{e^2}{r_{ij}}$$

$$V_{nn} = \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1, \nu \neq \mu}^N \frac{Z_\mu Z_\nu e^2}{R_{\mu\nu}}$$

Born – Oppenheimer approximation

$$\Psi(r, R) = \Psi_R^e(r) \Psi^n(r)$$

Slater determinant – one-electron approximation

$$\Psi(1,2,3,\dots,n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \Psi_1(1) & \Psi_1(2) & \dots & \Psi_1(n) \\ \Psi_2(1) & \Psi_2(2) & \dots & \Psi_2(n) \\ \vdots & \vdots & & \vdots \\ \Psi_n(1) & \Psi_n(2) & & \Psi_n(n) \end{vmatrix}$$

LCAO approximation

$$\varphi_i = \sum_{\nu}^m c_{i\nu} \chi_{\nu}$$

Primitive functions: $\sim \exp(-a.r)$ or $\sim \exp(-a.r^2)$

Hartree-Fock method: Roothaan equations

$$FC = SCE$$

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \qquad S_{\mu\nu} = \int \chi_{\mu}(1)\chi_{\nu}(1)d\nu_1$$

$$H_{\mu\nu} = \int \chi_{\mu}(1)h(1)\chi_{\nu}d\nu_1$$

$$G_{\mu\nu} = \sum_{\lambda\rho} P_{\lambda\rho} \left[\langle \mu\nu | \lambda\rho \rangle - \frac{1}{2} \langle \mu\lambda | \nu\rho \rangle \right]$$

$$P_{\lambda\rho} = 2 \sum_{i=1}^n c_{\lambda i} c_{\rho i}$$

$$\langle \mu\nu | \lambda\rho \rangle = \iint \chi_{\mu}(1)\chi_{\nu}(1) \frac{e^2}{r_{12}} \chi_{\lambda}(2)\chi_{\rho}(2) d\nu_1 d\nu_2$$

Configuration interaction (CI) – correlation energy

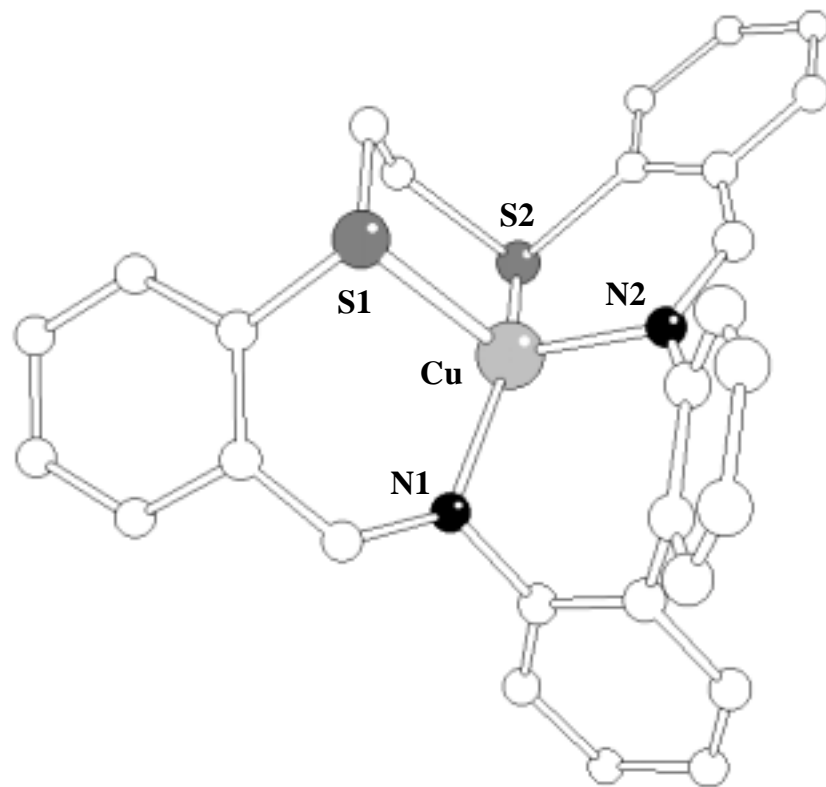
$$\Psi = b_0 \Psi_0 + \sum_{s>0} b_s \Psi_s$$

- Energy hypersurface
 - geometry optimization (gradient methods)
 - Hessian matrix
- Molecular dynamics
- Physico-chemical properties (← electron structure)
 - vibration, electron, NMR, ESR spectra
 - reactivity, catalysis

Program packages

- operation memory and integrals storage management
- details of SCF procedure
- details of geometry optimization
- physico-chemical properties evaluated etc.

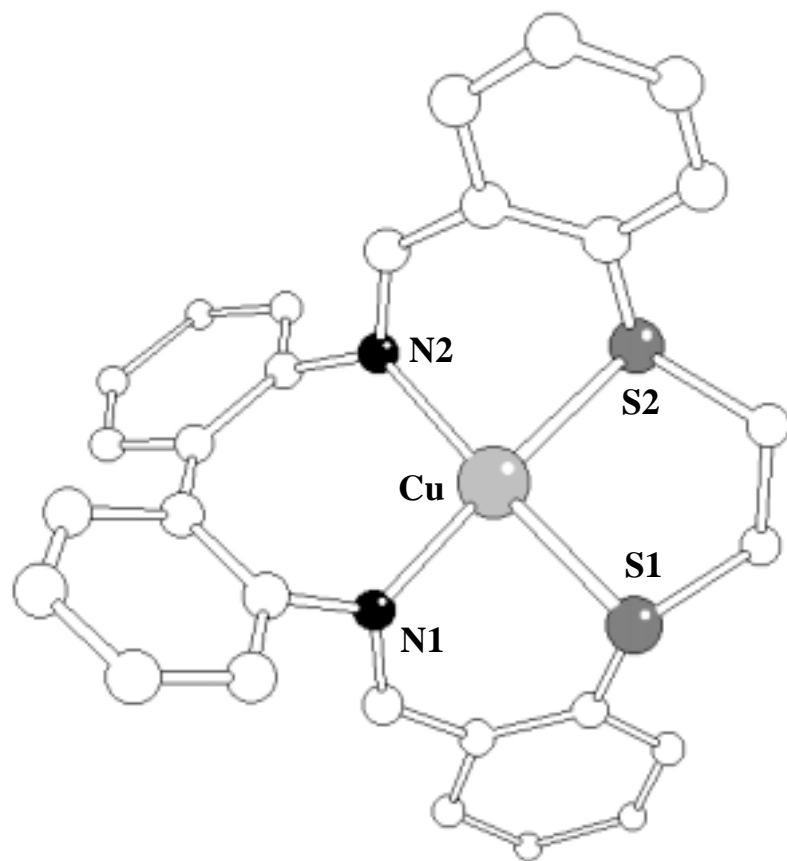
Computer	Location	Software package
SGI Origin 2000	CCR of SUNY at Buffalo, USA	ADF2002
NEC SX-6	HLRS Stuttgart, Germany	Gaussian98
IBM p690-Cluster Jump	NIC Juelich, Germany	Gaussian03



$1[\text{C}_{28}\text{H}_{22}\text{CuN}_2\text{S}_2]^+$

DFT

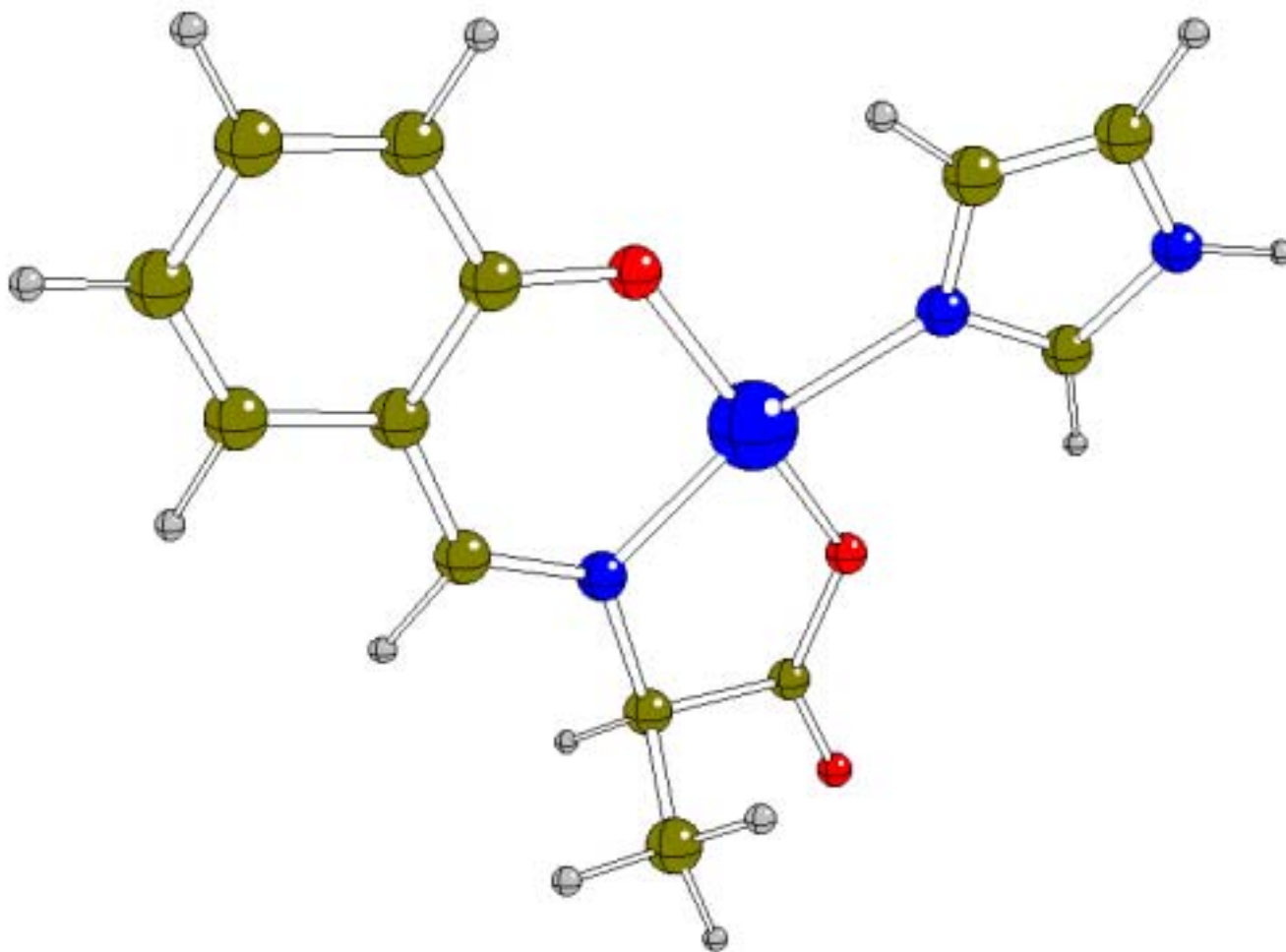
651 basis functions



${}^2[\text{C}_{28}\text{H}_{22}\text{N}_2\text{S}_2]^{2+}$

DFT

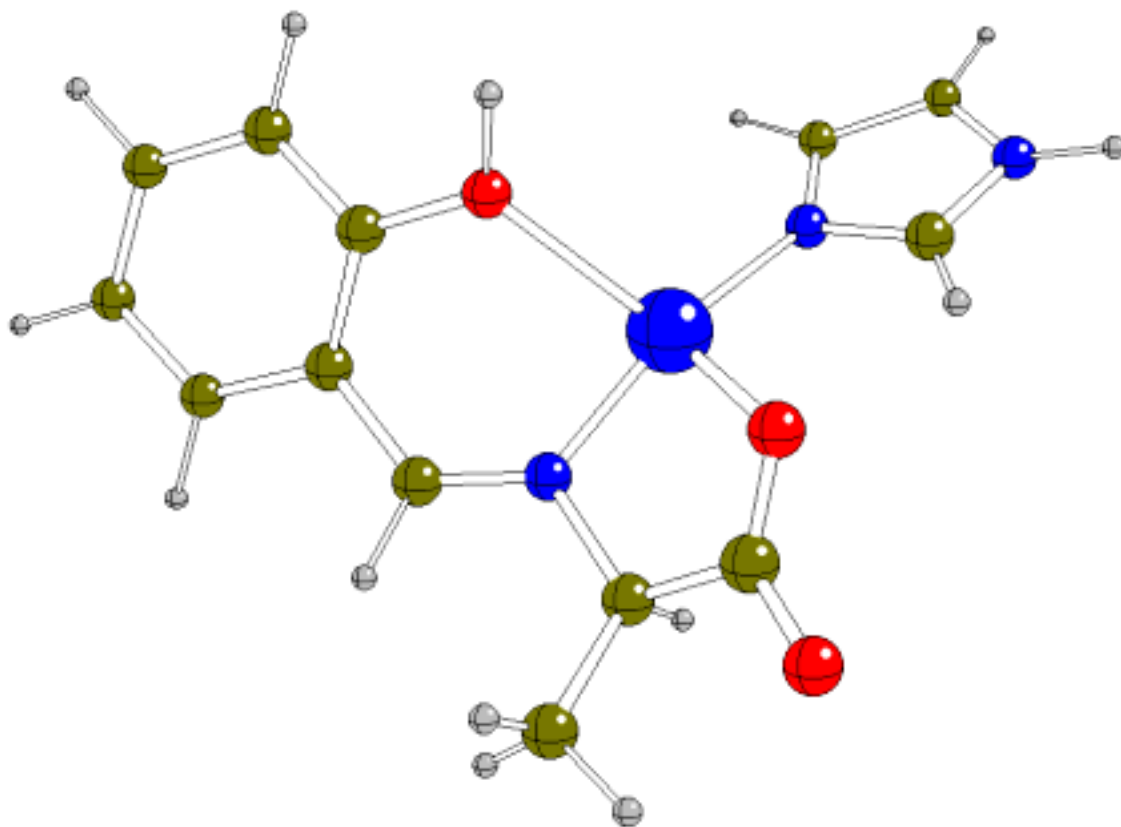
651 basis functions



$^2[\text{C}_{13}\text{H}_{13}\text{CuN}_3\text{O}_2]^0$

DFT

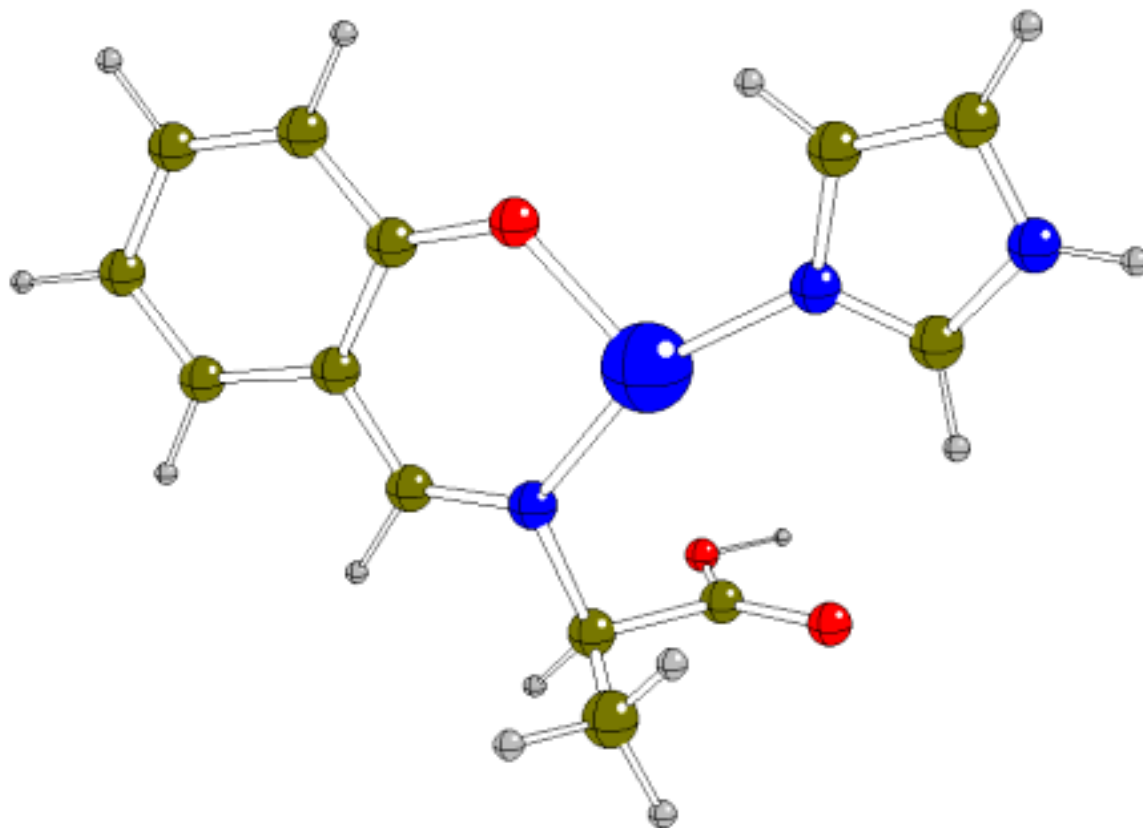
347 basis functions/688 gaussians



$^1[\text{C}_{13}\text{H}_{14}\text{CuN}_3\text{O}_2]^+$

DFT

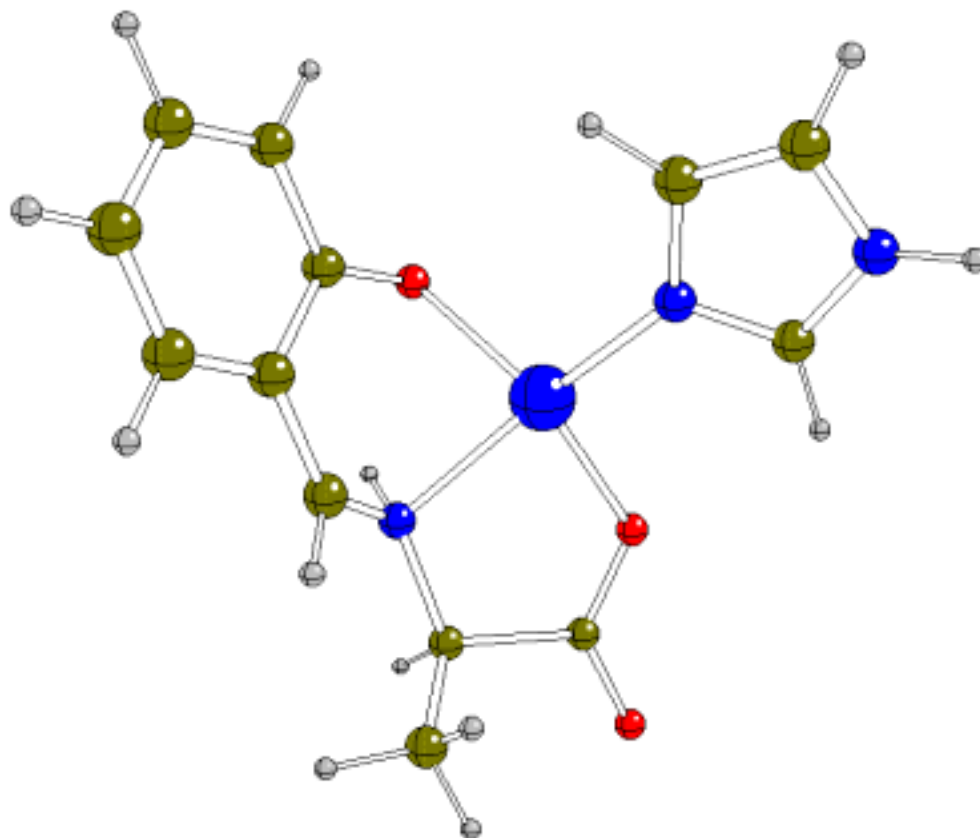
349 basis functions/692 gaussians



$^1[\text{C}_{13}\text{H}_{14}\text{CuN}_3\text{O}_2]^0$

DFT

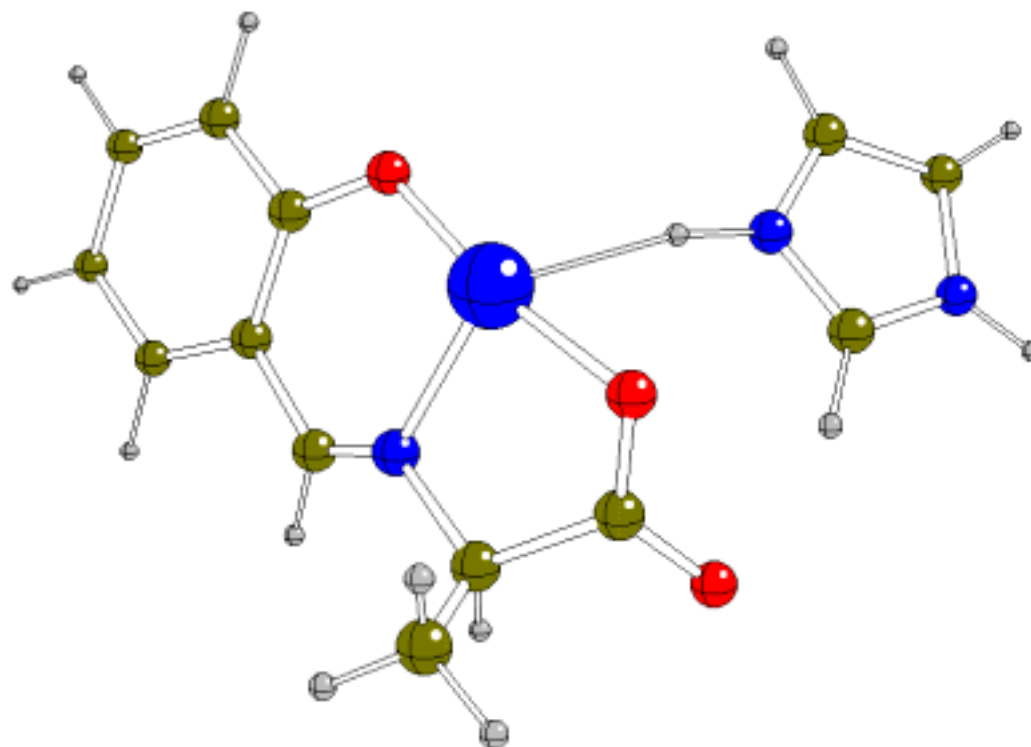
349 basis functions/692 gaussians



$^1[\text{C}_{13}\text{H}_{14}\text{CuN}_3\text{O}_2]^0$

DFT

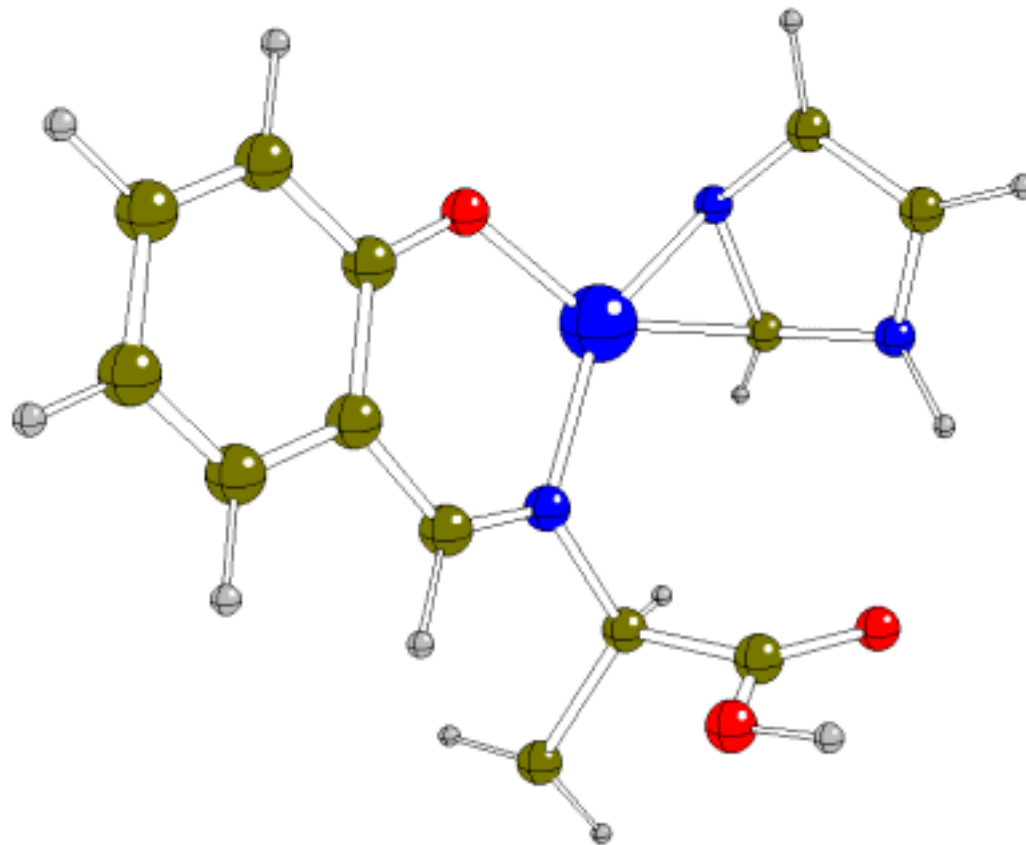
349 basis functions/692 gaussians



$^1[\text{C}_{13}\text{H}_{14}\text{CuN}_3\text{O}_2]^+$

DFT

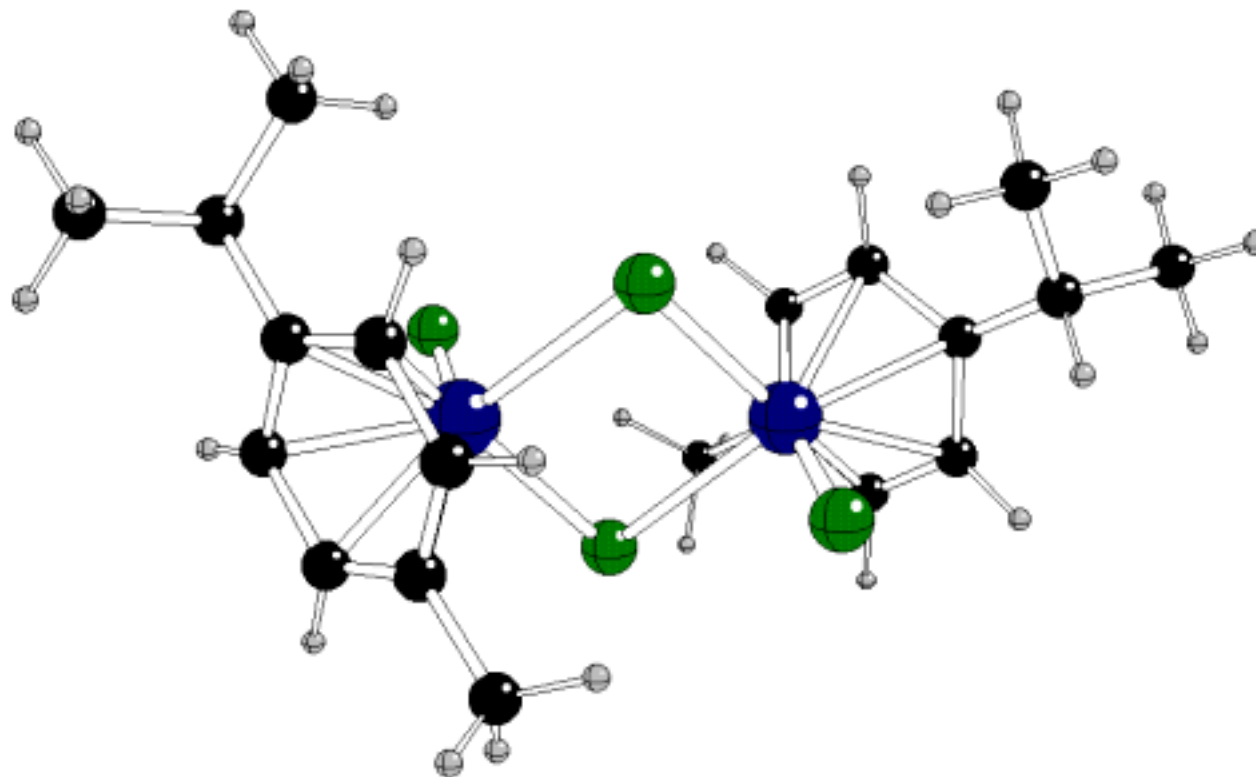
349 basis functions/692 gaussians



$^1[\text{C}_{13}\text{H}_{14}\text{CuN}_3\text{O}_2]^0$

DFT

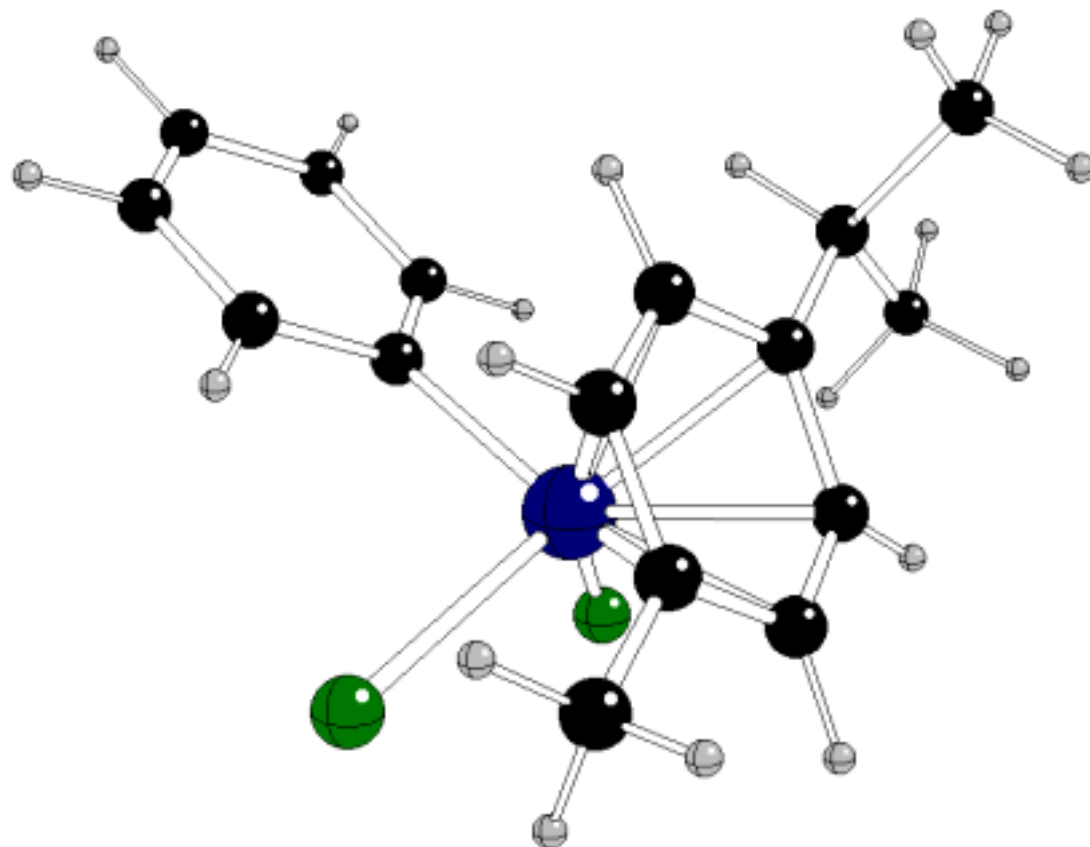
349 basis functions/692 gaussians



$^1[\text{C}_{20}\text{H}_{28}\text{Cl}_4\text{Ru}_2]^0$

DFT

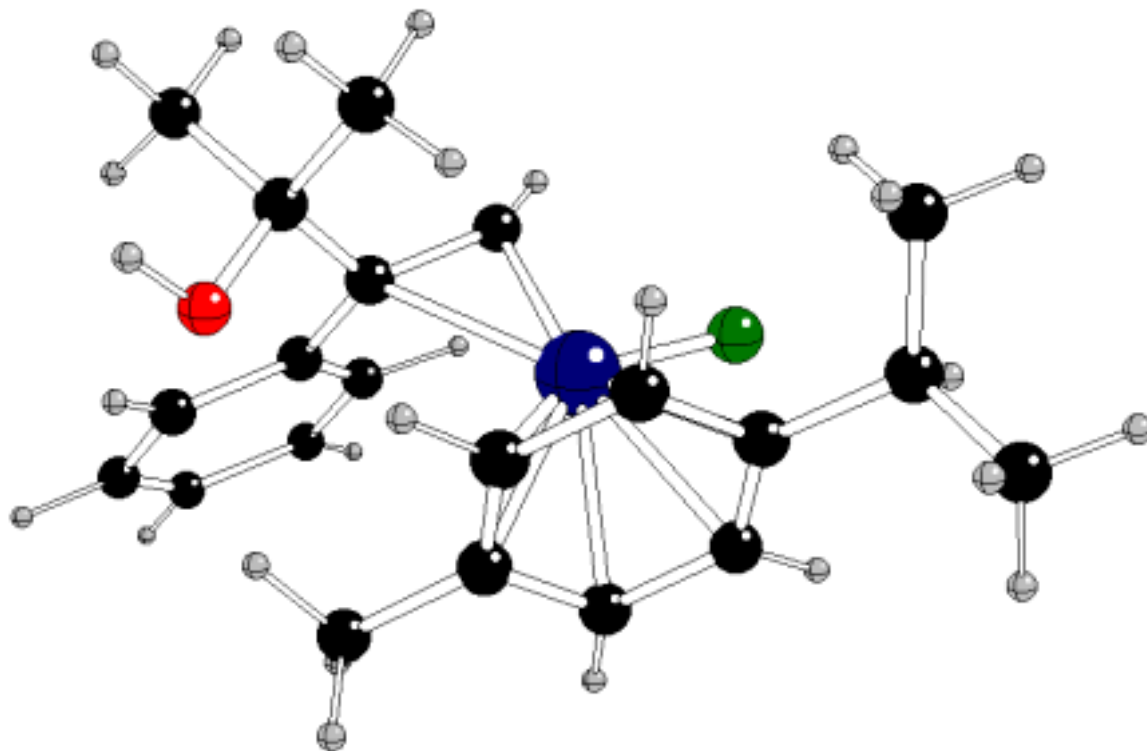
610 basis functions/1064 gaussians



$^1[\text{C}_{16}\text{H}_{19}\text{Cl}_2\text{Ru}]^-$

DFT

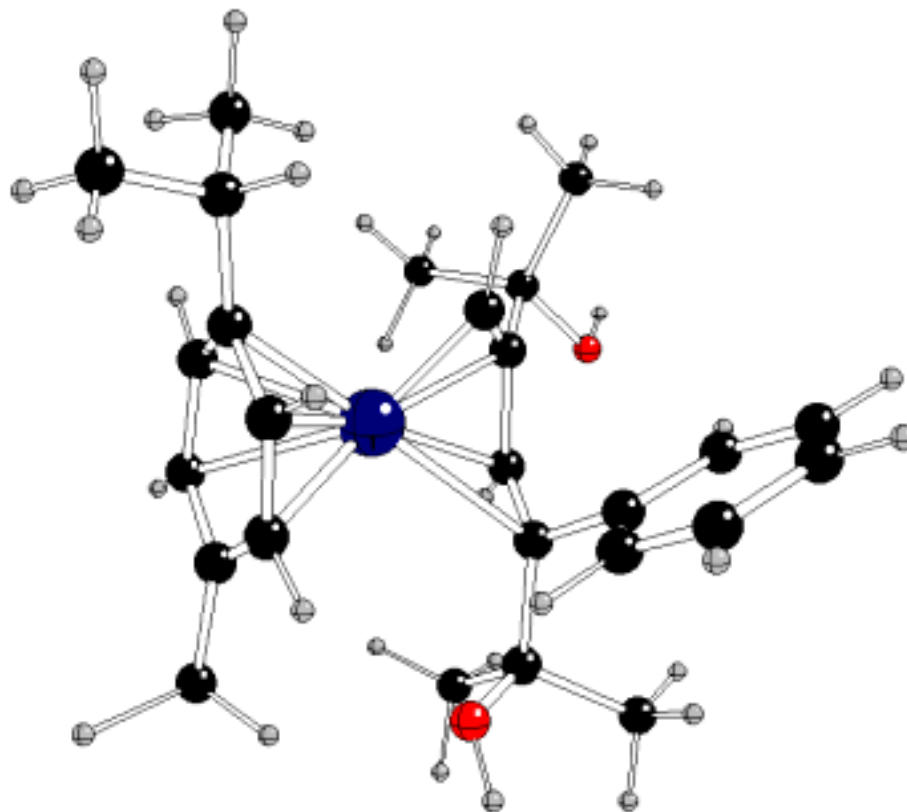
414 basis functions/785 gaussians



$^1[\text{C}_{21}\text{H}_{27}\text{ClORu}]^0$

DFT

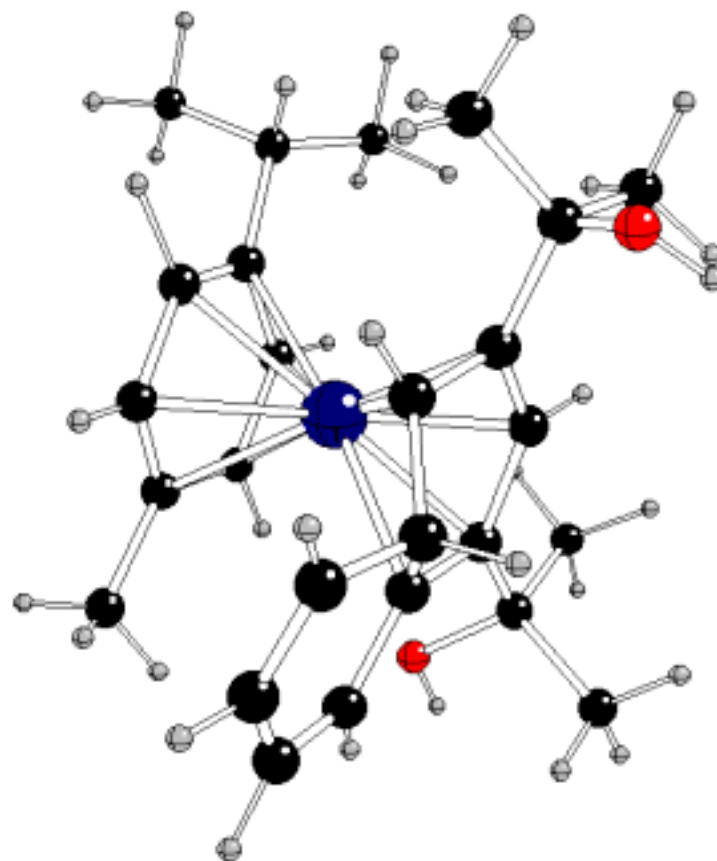
520 basis functions/957 gaussians



$^1[\text{C}_{28}\text{H}_{39}\text{O}_2\text{Ru}]^+$

DFT

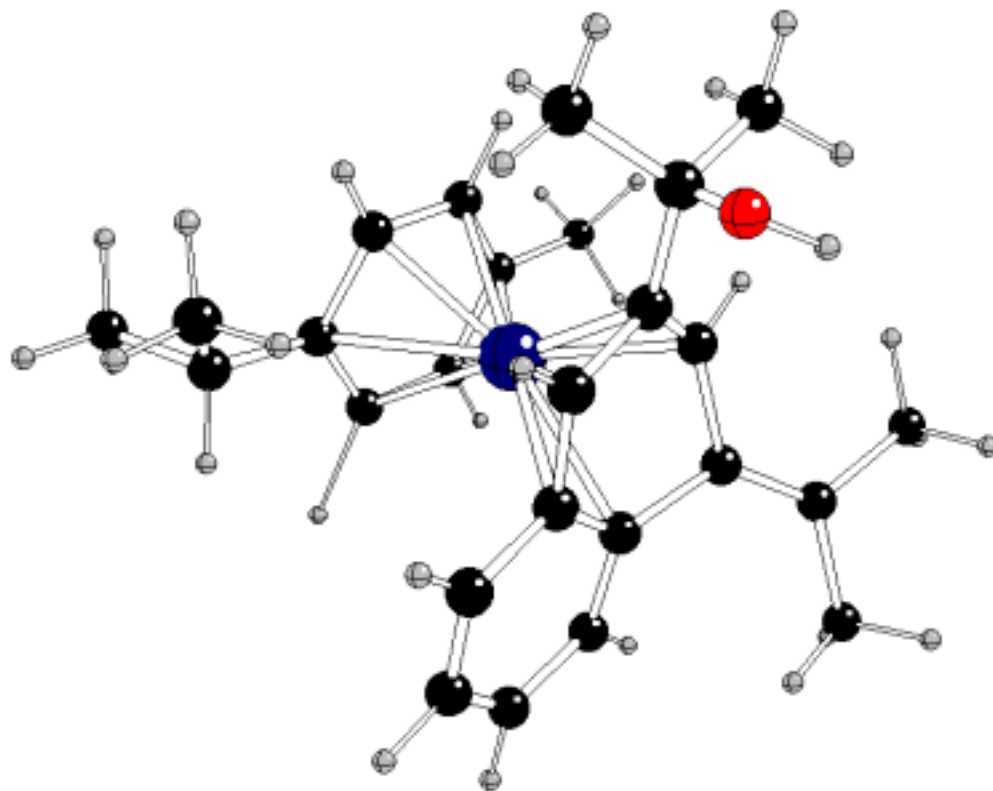
674 basis functions/1213 gaussians



$^1[\text{C}_{27}\text{H}_{37}\text{O}_2\text{Ru}]^+$

DFT

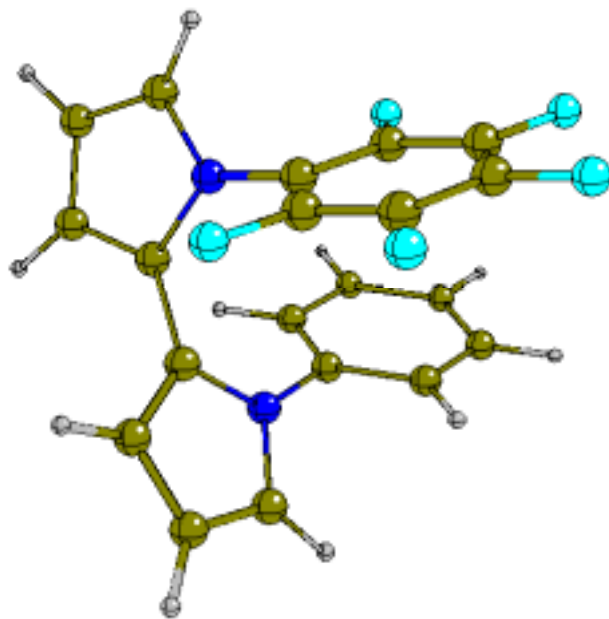
650 basis functions/1171 gaussians



$1[\text{C}_{27}\text{H}_{35}\text{ORu}]^+$

DFT

626 basis functions/1129 gaussians



${}^1[\text{C}_{20}\text{H}_{11}\text{F}_5\text{N}_2]^0$

MP2

579 basis functions/952 gaussians

Conclusions

- Large matrices, integrals storage
- Operation memory vs. external space
- SCF convergence
- Parallelization
- Administrative rules, restarts