The self-consistent perturbed projection method for high order response

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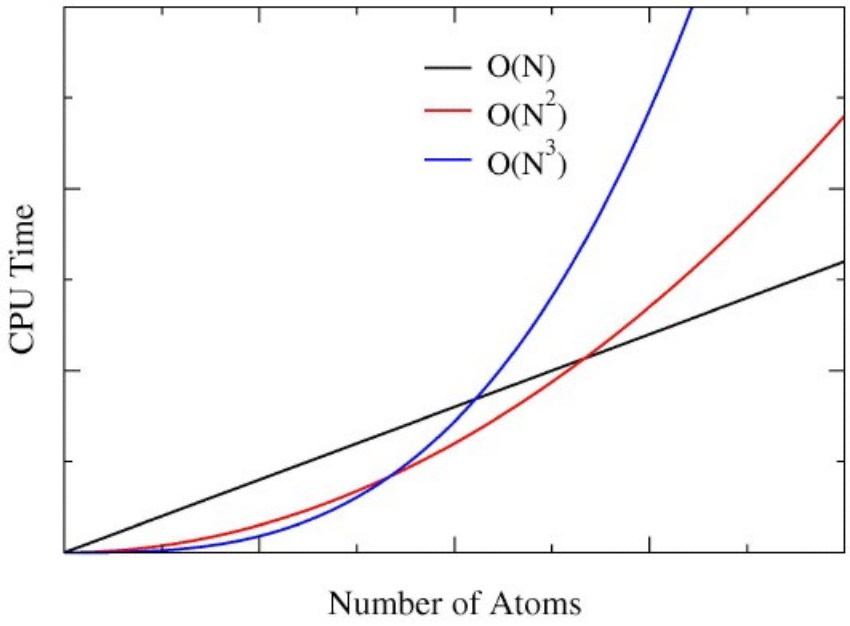
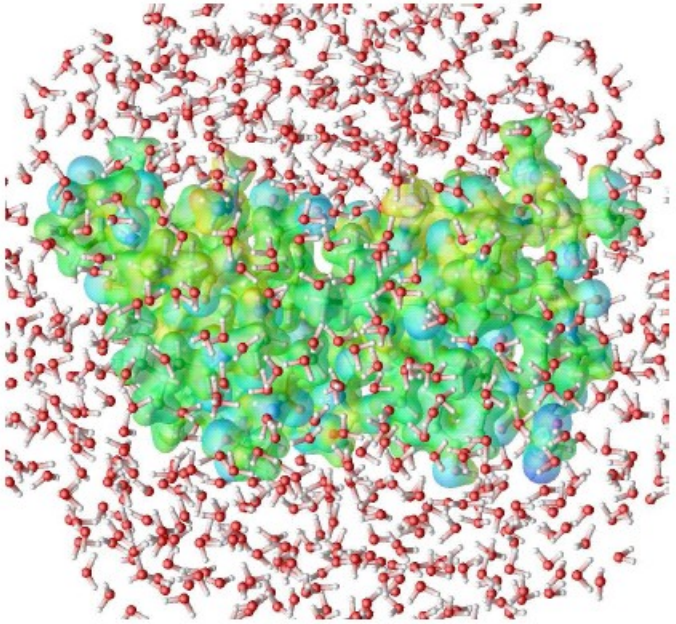
Why Are Linear Sclaling Methods So Important?

With conventional SCF methods, hardware improvements bring only small gains in capability due to the steep scaling of computational time with system size, N.





Achieving N-Scaling for Non-Metallic Systems: The Nearsighted Principle

- In a local basis, quantum effects are short ranged for non-metallic systems.
- Locality is manifested in approximate exponential decay of density matrix $|P_{ab}|$ with atom-atom separation $|\mathbf{A} - \mathbf{B}|$.
- Locality of P may be exploited to achieve $\mathcal{O}(N)$ algorithms for SCF theory and beyond.

Large Scale Electronic Structure Calculations

First principle prediction of:

- material properties: bulk modulus, elastic constants, equation of state.
- dynamical properties: thermal conductivity, viscosity, dislocation dynamics.
- chemical reactivity: reaction pathways at pressure and temperature, condensed phase chemistry, surface chemistry.

The Self-Consistent Perturbed Projection Method for Response Function

Orbital-Free Density Matrix Theories

$$P^{(0)},\ P^{(1)}, \ldots \quad \begin{cases} P(X) = e^{-X} P(0) e^{X} \\ \Omega = Tr[H(2P^3 - 3P^2)] - \mu(Tr[P] - N) \\ i\partial P/\partial t = [H, P] \\ P = \theta(\mu I - H) \\ \text{Other methods} \end{cases}$$

Conditions on the Density Matrix and Energy Minimization

- Idempotency $P = P^2$
- Symmetry $P = P^T$
- Trace $Tr[P] = N$
- Commutation $HP - PH = 0$
- Energy minimization $P = \arg\left(\min_{P'} Tr[HP']\right)$

Spectral Purification Projection

We can construct P by projecting occupied eigenvalues of H to 1 and unoccupied to 0.

$$\left.\begin{aligned} H\psi_i &= \varepsilon_i\psi_i \\ P\psi_i &= \theta(\mu-\varepsilon_i)\psi_i \end{aligned}\right\} P = \theta(\mu I - H)$$

This is equivalent to the expansion of $\theta(\mu I - H)$. High order expansion can be reached efficiently by recursion.

$$P = \theta(\mu I - H) \approx F_n(F_{n-1}(\ldots F_1(F_0(H))\ldots))$$

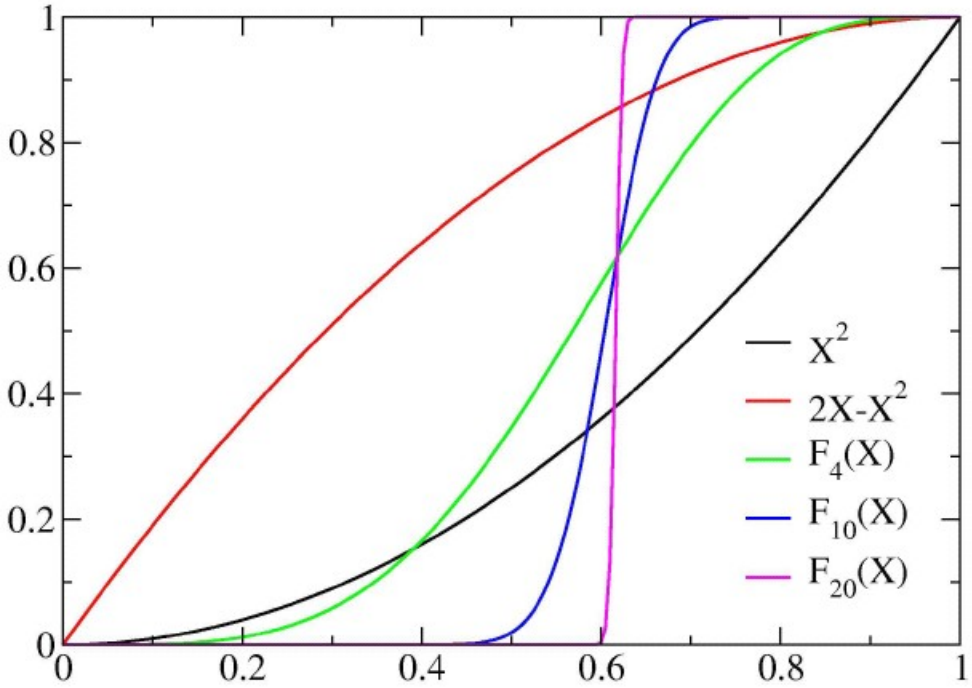
The Second Order Trace Correcting Spectral Projector Algorithm (TC2)

$$
\begin{aligned}
X_1 &= F_0(H) = (\varepsilon_{max} I - H)(\varepsilon_{max} - \varepsilon_{min})^{-1} \\
X_{i+1} &= F_i(X_i) = X_i^2 && \text{if } Tr[X_i] \geq N \\
X_{i+1} &= F_i(X_i) = 2X_i - X_i^2 && \text{if } Tr[X_i] < N \\
P &= \lim_{i \to \infty} X_i
\end{aligned}
$$

- ☞ Quadratically convergent
- ☞ Numerically stable
- ☞ Logarithmic compexity $\mathcal{O}(\log p)$ (standard expansion in $\mathcal{O}(\sqrt{p})$)
- ☞ Can solve degenerate stats and fractional occupancy

A.M.N. Niklasson, PRB, *66*, **2002**, 155115.

Spectral Purification Projection



Exact density matrix response by 2^{nd} order trace correcting perturbed projections

Let us suppose the Hamiltonian

$$H = H^{(0)} + U,$$

the perturbed density matrix is given by

$$\begin{aligned}
\Delta_1 &= F_0(U) \\
\Delta_{i+1} &= \{\Delta_i, X_i\} + \Delta_i^2 && \text{if } Tr[X_i] \geq N \\
\Delta_{i+1} &= 2\Delta_i - (\{\Delta_i, X_i\} + \Delta_i^2) && \text{if } Tr[X_i] < N \\
P &= P^{(0)} + \lim_{i \to \infty} \Delta_i
\end{aligned}$$

Density Matrix Perturbation Theory

We remember

$$E(\lambda) = E^{(0)} + E^{(1)}\lambda + E^{(2)}\lambda^2/2 + \dots$$
$$P(\lambda) = P^{(0)} + P^{(1)}\lambda + P^{(2)}\lambda^2/2 + \dots$$
$$H(\lambda) = H^{(0)} + H^{(1)}\lambda + H^{(2)}\lambda^2/2 + \dots$$

Perform perturbation expansion on each separate projection level F_n

$$P^{(m)} = \frac{\partial^m}{\partial\lambda^m}\theta(\mu I - H(\lambda))\Big|_{\lambda=0}$$ Discontinuity!

$$P^{(m)} \approx \frac{\partial^m}{\partial\lambda^m}F_n(F_{n-1}(\dots F_1(F_0(H(\lambda)))\dots))\Big|_{\lambda=0}$$

Finite density matrix response by 2^{nd} order trace correcting perturbed projections

Expanding the perturbation

$$\Delta_i = \Delta_i^{(1)}\lambda + \frac{1}{2}\Delta_i^{(2)}\lambda^2 + \dots$$

Collecting terms of same order, we find

$$\Delta_{i+1}^{(2)} = \{\Delta_i^{(2)}, X_i\} + 2(\Delta_i^{(1)})^2 \qquad \text{if } Tr[X_i] \geq N$$

$$\Delta_{i+1}^{(1)} = \{\Delta_i^{(1)}, X_i\}$$

$$\Delta_{i+1}^{(2)} = 2\Delta_i^{(2)} - (\{\Delta_i^{(2)}, X_i\} + 2(\Delta_i^{(1)})^2) \qquad \text{if } Tr[X_i] < N$$

$$\Delta_{i+1}^{(1)} = 2\Delta_i^{(1)} - \{\Delta_i^{(1)}, X_i\}$$

$$P^{(1)} = \lim_{i\to\infty} \Delta_i^{(1)}, \quad P^{(2)} = \lim_{i\to\infty} \Delta_i^{(2)}$$

The Coupled Perturbed Self Consistent Field Algorithm (Hartree-Fock)

$$P_0^{(m)} = 0$$ Starting density

$$F_n^{(m)} = h^{(m)} + J(P_n^{(m)}) + K(P_n^{(m)})$$ Fock build

$$F_n^{(m)} = \sum_{k=n-n_0}^{n} c_k F_k^{(m)}$$ DDIIS

$$P_{n+1}^{(m)} = \frac{\partial^m}{\partial \lambda^m} \theta(\mu I - F_n^{(m)})$$ Response

V. Weber, A.M.N. Niklasson, M. Challacombe, PRL, *92*, **2004**, 193002.

Avereged Effective Fockian Derivative

To improve upon the convergence of the CPSCF method, we may use the information from preceding iterations

$$F_n^{(m)} = \sum_{k=n-n_0}^{n} c_k F_k^{(m)} \quad \text{and} \quad \sum_{k=n-n_0}^{n} c_k = 1$$

A better strategy to obtain the coefficients c_k would be to minimize the norm of an averaged error matrix

$$e_n^{(m)} = \sum_{k=n-n_0}^{n} c_k e_k^{(m)}, \qquad \inf(|e_n^{(m)}|) \text{ with } \sum_{k=n-n_0}^{n} c_k = 1$$

Algorithm for Convergence Acceleration of the CPSCF Equation (DDIIS)

A working equation is obtained through the associated Euler-Lagrange equation

$$\begin{pmatrix} \mathbf{B} & \mathbf{1} \\ \mathbf{1}^T & 0 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{c} \\ \lambda \end{pmatrix} = \begin{pmatrix} \mathbf{0} \\ 1 \end{pmatrix},$$

where elements of the $\mathbf{B}$ matrix are given by $B_{ij} = Tr[e_i^{(m)}(e_j^{(m)})^T]$.

The first order error matrix is given by:

$$e_n^{(1)} = [F_n^{(1)}, D^{(0)}] + [F^{(0)}, D_n^{(1)}].$$

V. Weber, C. Daul, CPL, *370*, **2003**, 99.

An example: Electric Polarizabilites

The total HF electronic energy of a molecule in a static electric field $\mathcal{E}_z$:

$$E(\mathcal{E}_z) = Tr\left[P(h^{(0)} + \mu_z\mathcal{E}_z) + \frac{1}{2}P(J(P) + K(P))\right].$$

Expansion of E and P into the external field

$$E(\mathcal{E}_z) = E(0) - \left(\mu + \frac{1}{2}\alpha\mathcal{E}_z + \frac{1}{3!}\beta\mathcal{E}_z^2 + \frac{1}{4!}\gamma\mathcal{E}_z^3 + \ldots\right)\mathcal{E}_z,$$

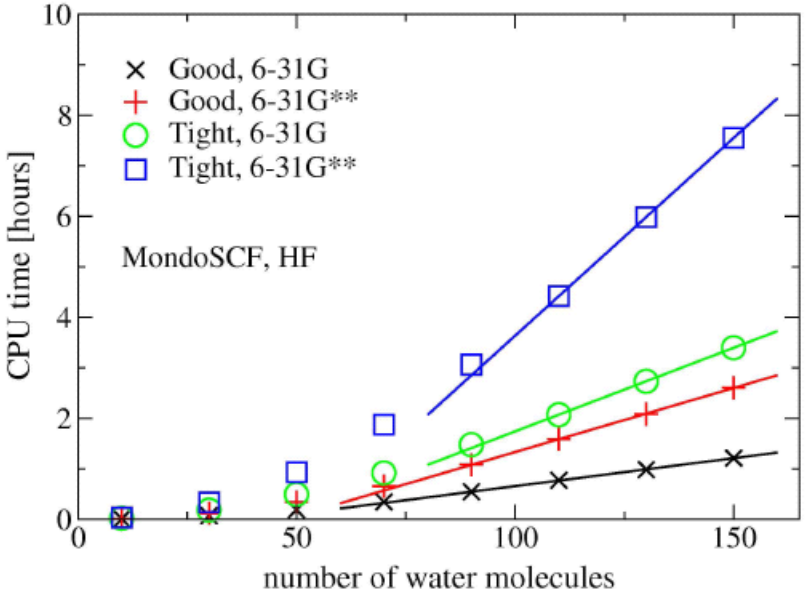
$$P(\mathcal{E}_z) = P^{(0)} + P^{(1)}\mathcal{E}_z + \frac{1}{2}P^{(2)}\mathcal{E}_z^2 + \frac{1}{3!}P^{(3)}\mathcal{E}_z^3 + \ldots$$

We can identify $\mu = -Tr[P^{(0)}\mu_z]$, $\alpha = -Tr[P^{(1)}\mu_z]$, $\beta = -Tr[P^{(2)}\mu_z]$ and $\gamma = -Tr[P^{(3)}\mu_z]$.

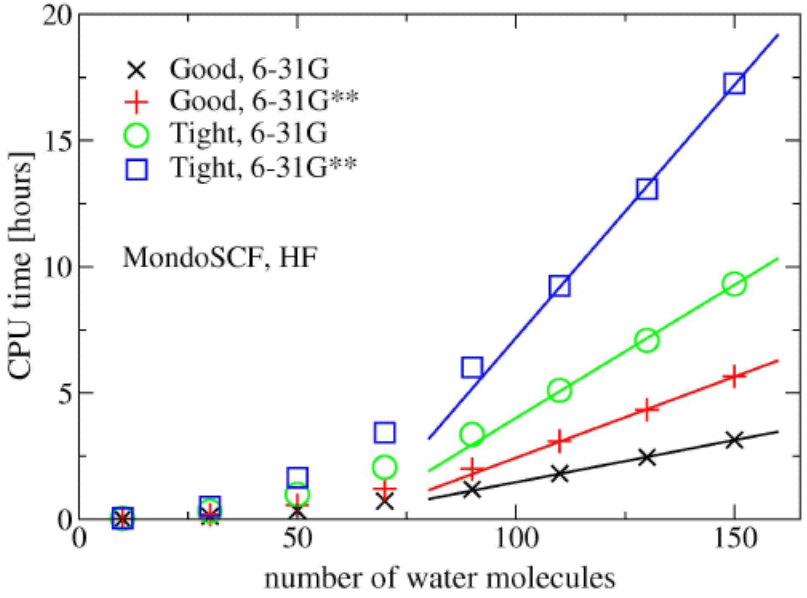
V. Weber, A.M.N. Niklasson, M. Challacombe, JCP, **2005**, accepted.

Polarizabilities in $\mathcal{O}(N)$

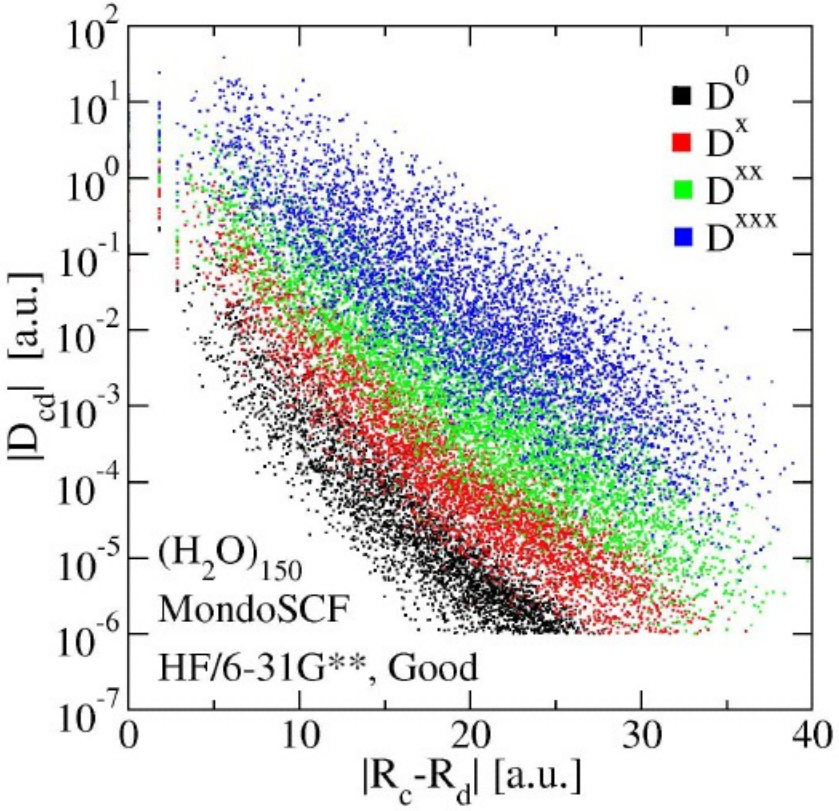
Scaling for α

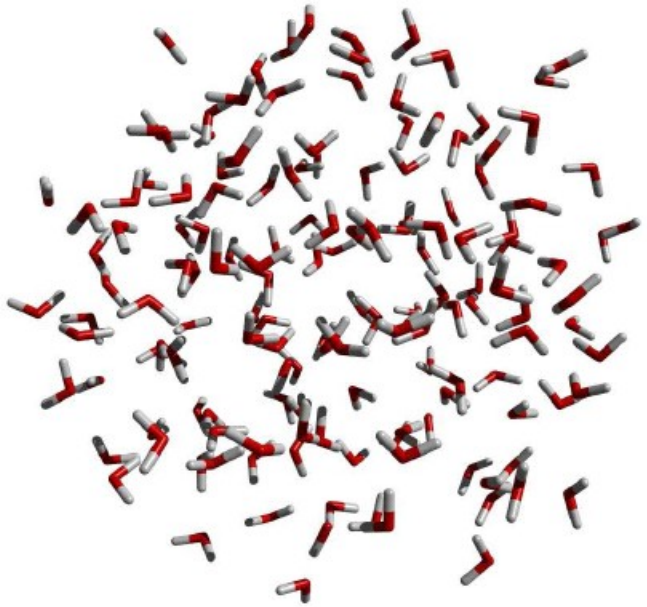


Scaling for γ



Exponential Decay of the Density Matrix Derivatives





Summary: Response Functions

- ☞ Linear scaling electronic structure calculations
- ☞ Simple, efficient and easy to implement
- ☞ Orbital-free $\mathcal{O}(N)$ quantum perturbation theory
- ☞ Response properties of nanomaterials

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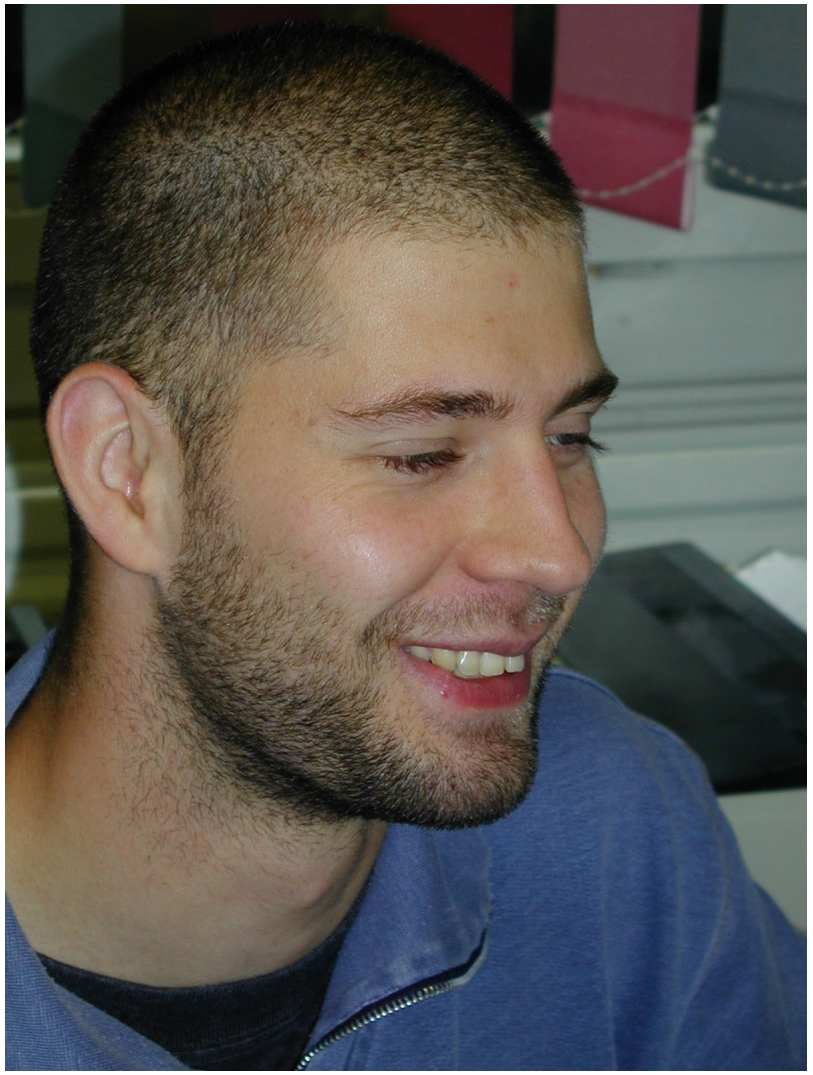

Valery

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