Solving Schrödinger equations in strong magnetic fields

High order operator splitting methods

S. Janecek, E. Krotscheck, S.A. Chin

Johannes Kepler University, Linz, Austria

Outline:

Outline:

1. **Fast solvers** for Schrödinger equations
   - Density Functional Theory
   - Some results for Multi-product splitting

Outline:

1. **Fast solvers** for Schrödinger equations
   - Density Functional Theory
   - Some results for Multi-product splitting

2. Schrödinger equations in strong **magnetic fields**
   - Nuclear magnetic resonance (NMR) properties
   - Quantum dots in strong magnetic fields
   - Quantum Hall effects
   - Aharanov Bohm effects
   - Graphene

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

fixed external potential

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

fixed external potential

Kohn-Sham orbitals $\phi_i(\mathbf{r})$

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

(2) Calculate density

$$\rho(r) = \sum_{i=1}^{N} \left| \phi_i(r) \right|^2$$

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

(2) Calculate density

$$\rho(r) = \sum_{i=1}^{N} \left|\, \phi_i(r) \,\right|^2$$

(3) Calculate effective potential

$$V_{eff}[\rho](r) = v(r) + v_H[\rho](r) + v_{xc}[\rho](r)$$

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

(2) Calculate density

$$\rho(r) = \sum_{i=1}^{N} \left|\, \phi_i(r) \,\right|^2$$

(3) Calculate effective potential

$$V_{eff}[\rho](r) = v(r) + v_H[\rho](r) + v_{xc}[\rho](r)$$

Solve self-consistently!

Practical DFT calculations: the "Kohn-Sham recipe":

(1) Solve Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}[\rho](\mathbf{r})\right]\phi_i(\mathbf{r}) = E_i\phi_i(\mathbf{r})$$

Solve self-consistently!

(2) Calculate density

$$\rho(r) = \sum_{i=1}^{N} \left|\, \phi_i(r) \,\right|^2$$

(3) Calculate effective potential

$$V_{eff}[\rho](r) = v(r) + v_H[\rho](r) + v_{xc}[\rho](r)$$

Find lowest *n* eigenvalues of $(T+V)\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r})$

Assume we're lucky: Use $\psi_i(\mathbf{r})$'s as a basis:

$$\psi(\mathbf{r}) = c_1\psi_1(\mathbf{r}) + c_2\psi_2(\mathbf{r}) + \cdots + c_n\psi_n(\mathbf{r})$$

Action of evolution operator $\mathcal{T}(\varepsilon) = e^{-\varepsilon(T+V)}$

$$\begin{bmatrix} e^{-\varepsilon E_1} & & & & \\ & e^{-\varepsilon E_2} & & & \\ & & e^{-\varepsilon E_3} & & \\ & & & e^{-\varepsilon E_4} & \\ & & & & \ddots \end{bmatrix} \cdot \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \end{bmatrix}$$

initial states

$$\{\psi_1^{(0)}, \ldots, \psi_n^{(0)}\}$$

The Diffusion algorithm:

$$\mathcal{T}(\varepsilon) = e^{-\varepsilon(T+V)}$$

"imaginary time propagation"

initial states

$$\{\psi_1^{(0)}, \ldots, \psi_n^{(0)}\}$$

Apply evolution operator

$$\phi_i^{(k+1)}(\mathbf{r}) = \mathcal{T}(\varepsilon)\,\psi_i^{(k)}$$

The Diffusion algorithm:

$$\mathcal{T}(\varepsilon) = e^{-\varepsilon(T+V)}$$

"imaginary time propagation"

initial states

$$\{\psi_1^{(0)}, \ldots, \psi_n^{(0)}\}$$

Apply evolution operator

$$\phi_i^{(k+1)}(\mathbf{r}) = \mathcal{T}(\varepsilon)\,\psi_i^{(k)}$$

Orthogonalize states

$$\psi_i^{(k+1)} = \sum_j c_{ij}\,\phi_j^{(k+1)}$$

The Diffusion algorithm:

$$\mathcal{T}(\varepsilon) = e^{-\varepsilon(T+V)}$$

"imaginary time propagation"

initial states

$$\{\psi_1^{(0)}, \ldots, \psi_n^{(0)}\}$$

Apply evolution operator

$$\phi_i^{(k+1)}(\mathbf{r}) = \mathcal{T}(\varepsilon)\,\psi_i^{(k)}$$

Orthogonalize states

$$\psi_i^{(k+1)} = \sum_j c_{ij}\,\phi_j^{(k+1)}$$

Good enough?

The Diffusion algorithm:

$$\mathcal{T}(\varepsilon) = e^{-\varepsilon(T+V)}$$

"imaginary time propagation"

Trial states converge ...

$$\{\psi_1^{(k)}, \ldots, \psi_n^{(k)}\}$$

$$k \to \infty$$

$$\{\psi_1, \ldots, \psi_n\}$$

... towards lowest n states

initial states

$$\{\psi_1^{(0)}, \ldots, \psi_n^{(0)}\}$$

Apply evolution operator

$$\phi_i^{(k+1)}(\mathbf{r}) = \mathcal{T}(\varepsilon)\,\psi_i^{(k)}$$

Orthogonalize states

$$\psi_i^{(k+1)} = \sum_j c_{ij}\,\phi_j^{(k+1)}$$

Good enough?

The Diffusion algorithm:

$$\mathcal{T}(\varepsilon) = e^{-\varepsilon(T+V)}$$

"imaginary time propagation"

Trial states converge ...

$$\{\psi_1^{(k)}, \ldots, \psi_n^{(k)}\}$$

$$k \to \infty$$

$$\{\psi_1, \ldots, \psi_n\}$$

... towards lowest n states

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\,\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

➡Factorization ("operator splitting")

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

➡Factorization ("operator splitting")

"**Trotter formula**": Second order in timestep

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\,\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

➡ Factorization ("operator splitting")

"**Trotter formula**": Second order in timestep

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

- diagonal in real space
- diagonal in Fourier space

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\,\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

➡ Factorization ("operator splitting")

"**Trotter formula**": Second order in timestep

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

- diagonal in real space
- diagonal in Fourier space

Knowledge about eigenspace of T, V alone

➡ Calculate eigenstates of (T+V)

Calculate Action of evolution operator

$$\phi_i^{(k+1)} = e^{-\varepsilon(T+V)}\,\psi_i^{(k)}$$

(**without** knowing the eigenspace of *(T+V)* in advance)

➡ Factorization ("operator splitting")

"**Trotter formula**": Second order in timestep

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

- diagonal in real space
- diagonal in Fourier space

Knowledge about eigenspace of T, V alone

➡ Calculate eigenstates of (T+V)

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} \psi(\mathbf{r})$$

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} \boxed{e^{-\frac{1}{2}\epsilon V}} \psi(\mathbf{r})$$

(1) Multiply with potential

$$\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$$

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} \psi(\mathbf{r})$$

(1) Multiply with potential

$$\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})} \psi(\mathbf{r})$$

(2) Fourier transform

$$\psi(\mathbf{k}) \leftarrow \mathcal{F}\left[\psi(\mathbf{r})\right]$$

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = e^{-\frac{1}{2}\epsilon V}\boxed{e^{-\epsilon T}}e^{-\frac{1}{2}\epsilon V}\ \psi(\mathbf{r})$$

(1) Multiply with potential $\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$

(2) Fourier transform $\psi(\mathbf{k}) \leftarrow \mathcal{F}\left[\psi(\mathbf{r})\right]$

(3) Multiply with kinetic energy $\psi(\mathbf{k}) \leftarrow e^{-\epsilon T(\mathbf{k})}\ \psi(\mathbf{k})$

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} \psi(\mathbf{r})$$

(1) Multiply with potential $\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$

(2) Fourier transform $\psi(\mathbf{k}) \leftarrow \mathcal{F}\left[\psi(\mathbf{r})\right]$

(3) Multiply with kinetic energy $\psi(\mathbf{k}) \leftarrow e^{-\epsilon T(\mathbf{k})}\ \psi(\mathbf{k})$

(4) Fourier transform back $\psi(\mathbf{r}) \leftarrow \mathcal{F}^{-1}\left[\psi(\mathbf{k})\right]$

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = \boxed{e^{-\frac{1}{2}\epsilon V}} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V}\ \psi(\mathbf{r})$$

(1) Multiply with potential $\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$

(2) Fourier transform $\psi(\mathbf{k}) \leftarrow \mathcal{F}\left[\psi(\mathbf{r})\right]$

(3) Multiply with kinetic energy $\psi(\mathbf{k}) \leftarrow e^{-\epsilon T(\mathbf{k})}\ \psi(\mathbf{k})$

(4) Fourier transform back $\psi(\mathbf{r}) \leftarrow \mathcal{F}^{-1}\left[\psi(\mathbf{k})\right]$

(5) Multiply with potential $\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$

Calculate Action of evolution operator

$$e^{-\epsilon(T+V)}\psi(\mathbf{r}) = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} \psi(\mathbf{r})$$

(1) Multiply with potential $\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$

(2) Fourier transform $\psi(\mathbf{k}) \leftarrow \mathcal{F}\left[\psi(\mathbf{r})\right]$

(3) Multiply with kinetic energy $\psi(\mathbf{k}) \leftarrow e^{-\epsilon T(\mathbf{k})}\ \psi(\mathbf{k})$

(4) Fourier transform back $\psi(\mathbf{r}) \leftarrow \mathcal{F}^{-1}\left[\psi(\mathbf{k})\right]$

(5) Multiply with potential $\psi(\mathbf{r}) \leftarrow e^{-\frac{1}{2}\epsilon V(\mathbf{r})}\ \psi(\mathbf{r})$

Effort: Assume $\psi_i(\mathbf{r})$ is stored on N^3 grid points:

3 vector-vector multiplications $3N^3$

2 3D Fast Fourier Transforms $2N^3 \ln N^3$

Accuracy of states: proportional to total evolution time

$$\tau = k\ \epsilon$$

Accuracy of states: proportional to total evolution time

$$\tau = k\ \epsilon$$

number of iterations

Accuracy of states: proportional to total evolution time

$$\tau = k\ \epsilon$$

number of iterations

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

Accuracy of states: proportional to total evolution time

$$\tau = k\ \epsilon$$

number of iterations

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

Large ϵ: Fast Convergence ⟷ Large error

Small ϵ: Slow Convergence ⟷ Small error

Accuracy of states: proportional to total evolution time

$$\tau = k\ \epsilon$$

number of iterations

$$e^{-\epsilon(T+V)} = e^{-\frac{1}{2}\epsilon V} e^{-\epsilon T} e^{-\frac{1}{2}\epsilon V} + \mathcal{O}(\epsilon^3)$$

Large ϵ: Fast Convergence ⟷ Large error

Small ϵ: Slow Convergence ⟷ Small error

➡ Higher order factorizations?

Bad news first:

"No-go" theorem (Suzuki, Chin):

There is **no** factorization of the product form

$$\mathcal{T}(\epsilon) = e^{-\epsilon(T+V)} = \prod_{i=1}^{M} e^{-a_i\,\epsilon T} e^{-b_i\,\epsilon V} + \mathcal{O}(\epsilon^N)$$

with entirely positive coefficients a_i, b_i

Positive coefficients required:

- Negative coefficients = backwards diffusion in time

➡ Result: numerically unstable algorithms

(M. Suzuki, J. Math. Phys. 32 (1991) 319)

Way out #1: Additional double commutator

Factorization **4A** (Suzuki, Chin, Forbert):

$$\mathcal{T}_{4A}(\epsilon) = e^{-\frac{1}{6}\epsilon V} e^{-\frac{1}{2}\epsilon T} e^{-\frac{2}{3}\epsilon \widetilde{V}} e^{-\frac{1}{2}\epsilon T} e^{-\frac{1}{6}\epsilon V} + \mathcal{O}(\epsilon^5)$$

$$\widetilde{V} = V + \frac{\epsilon^2}{48}[\hat{V},[\hat{T},\hat{V}]] = V(\mathbf{r}) + \frac{\hbar^2\epsilon^2}{48m}|\nabla V(\mathbf{r})|^2$$

- Additional correction term is local in real space!
- Effort: ~ 2 x second order
- Improves convergence by a **factor ~10** (compared to second order splitting)

(M. Suzuki, Phys. Lett. A201 (1995) 425)

Way out **#2**: Multi-product splitting

Factorize into **sum** of products:

$$\mathrm{e}^{-\epsilon(T+V)} = \sum_k c_k \prod_i \mathrm{e}^{-a_{k,i}\epsilon T}\mathrm{e}^{-b_{k,i}\epsilon V}$$

- No-go theorem: Single products can be at most $\mathcal{O}(\epsilon^2)$

Multi-product splitting (Chin '09):

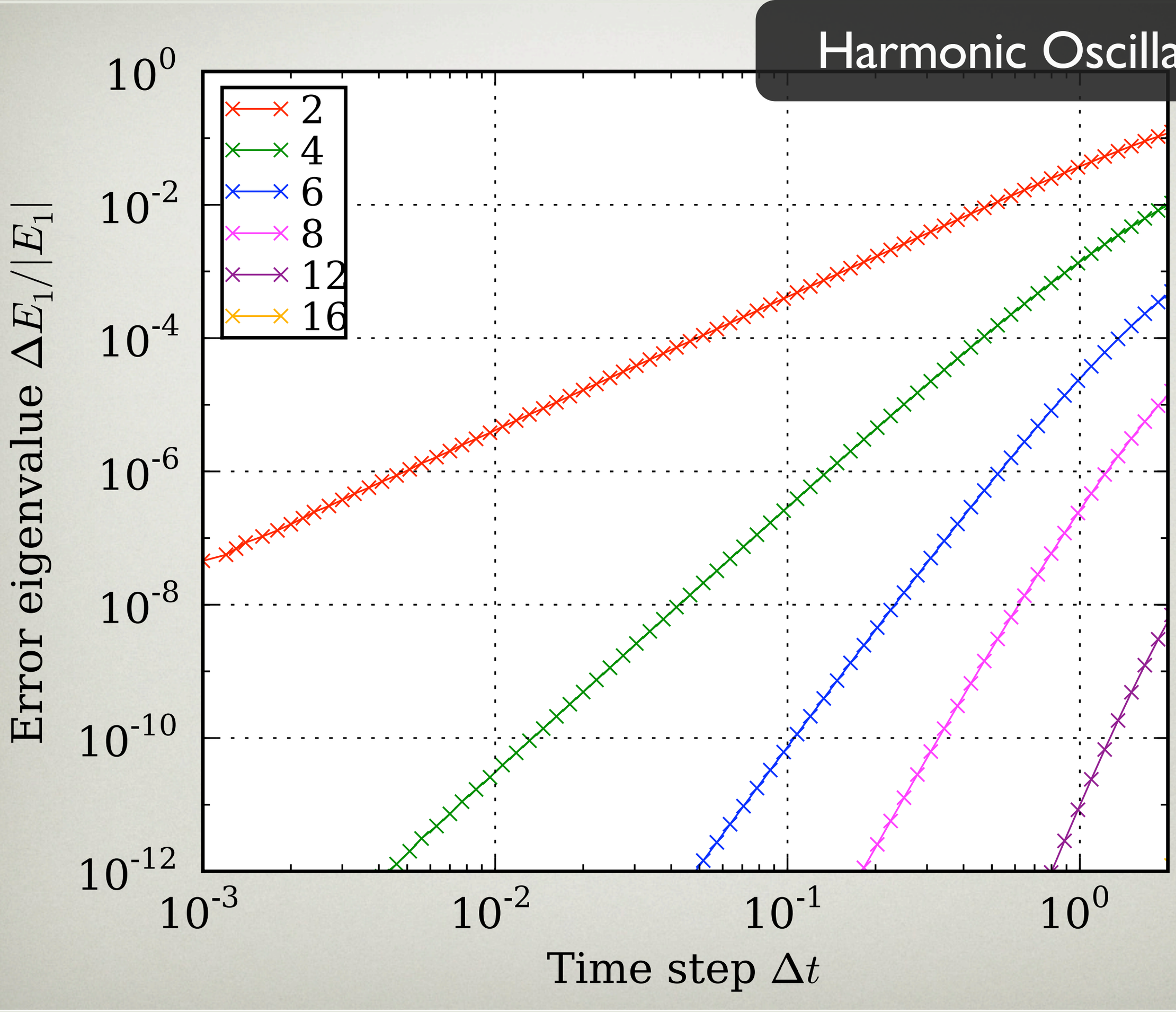
$$\mathrm{e}^{-\epsilon(T+V)} = \sum_{k=1}^{n} c_k \mathcal{T}_2^k\left(\frac{\epsilon}{k}\right) + \mathcal{O}(\epsilon^{2n+1})$$

with coefficients $c_i = \prod_{j=1(\neq i)}^{n} \frac{k_i^2}{k_i^2 - k_j^2}$

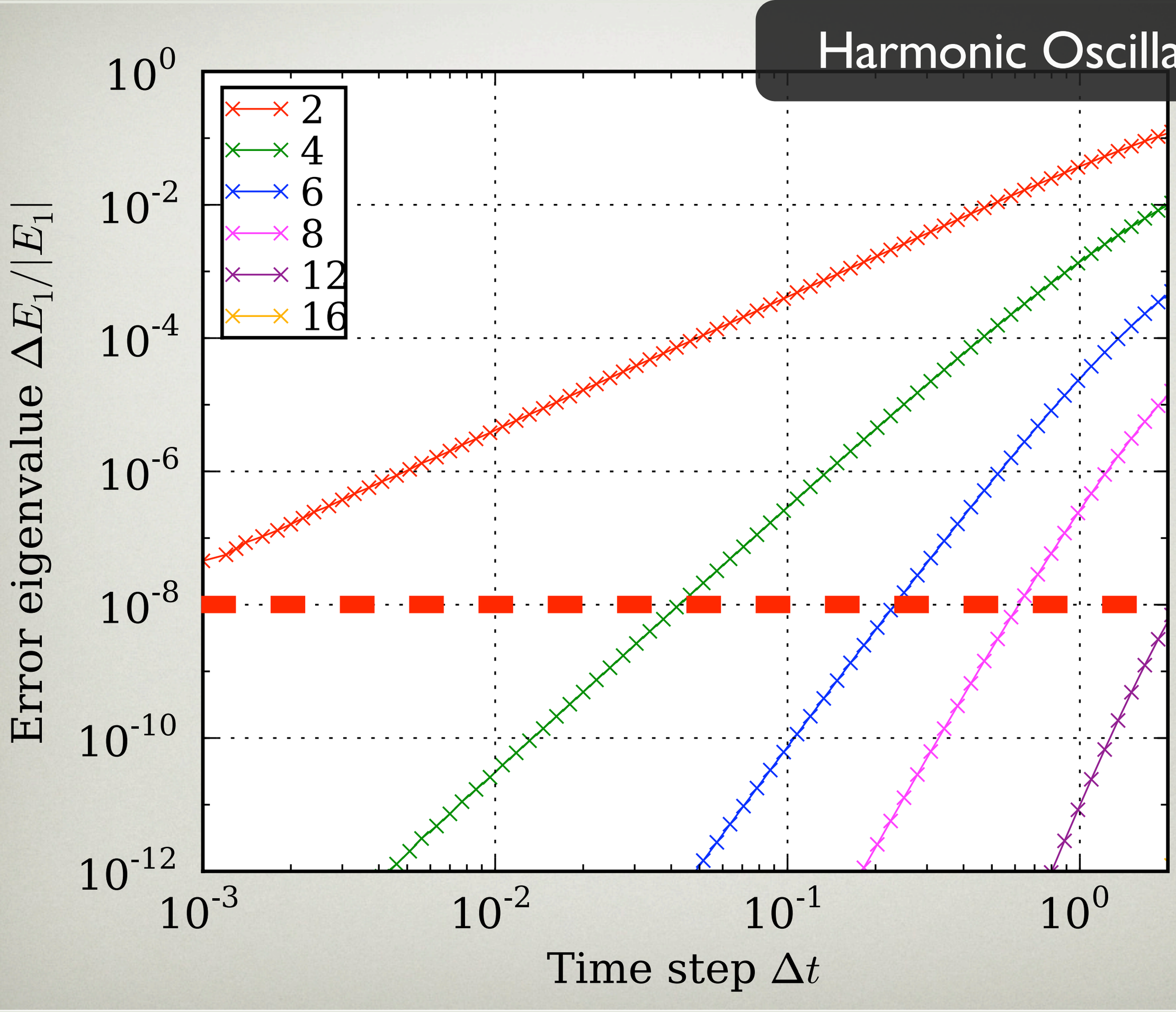
Effort: $\frac{1}{2}n(n-1)$ for $\mathcal{O}(\epsilon^{2n})$

(S.A. Chin, arXiv math.NA.0809.0914v1)

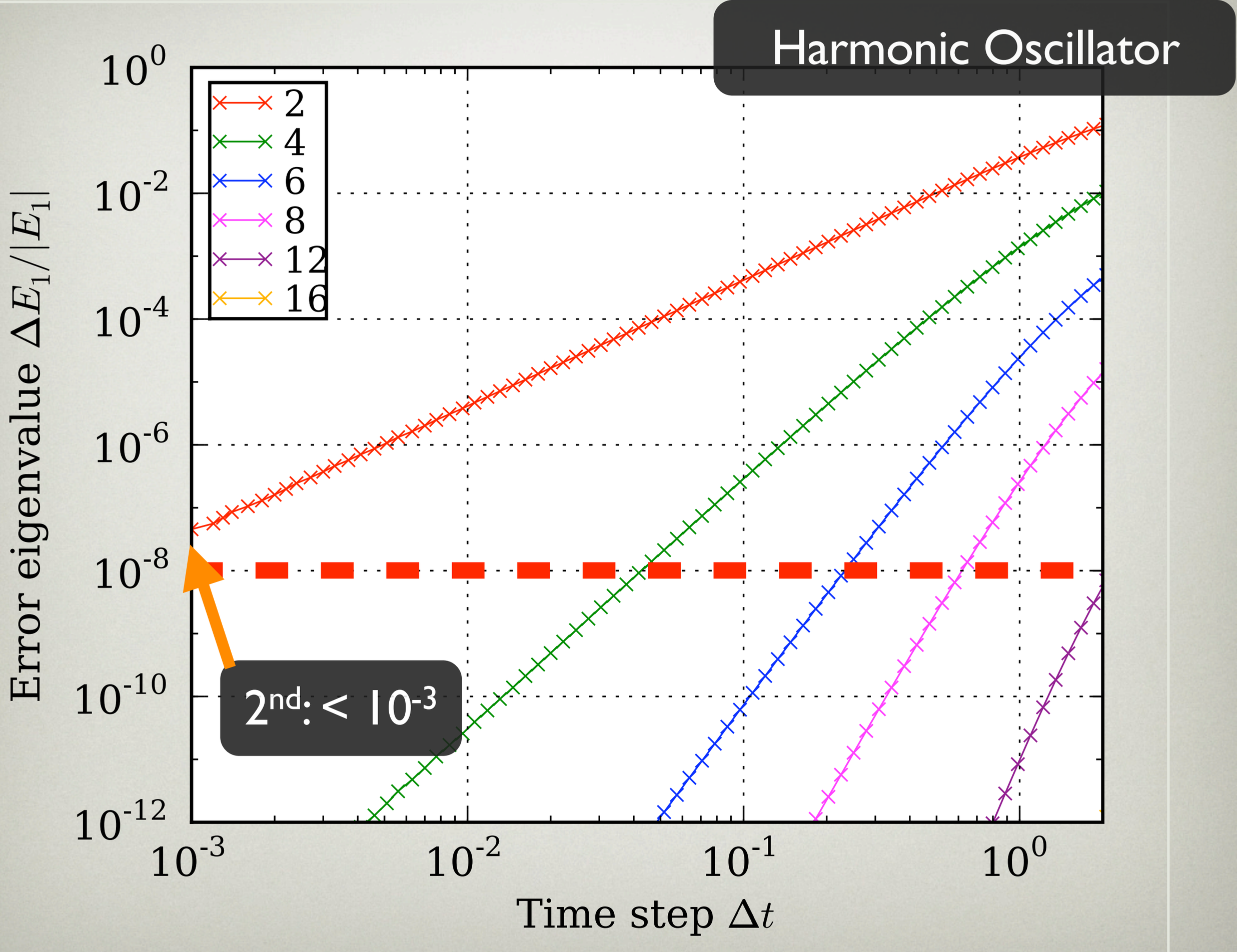
Harmonic Oscillator



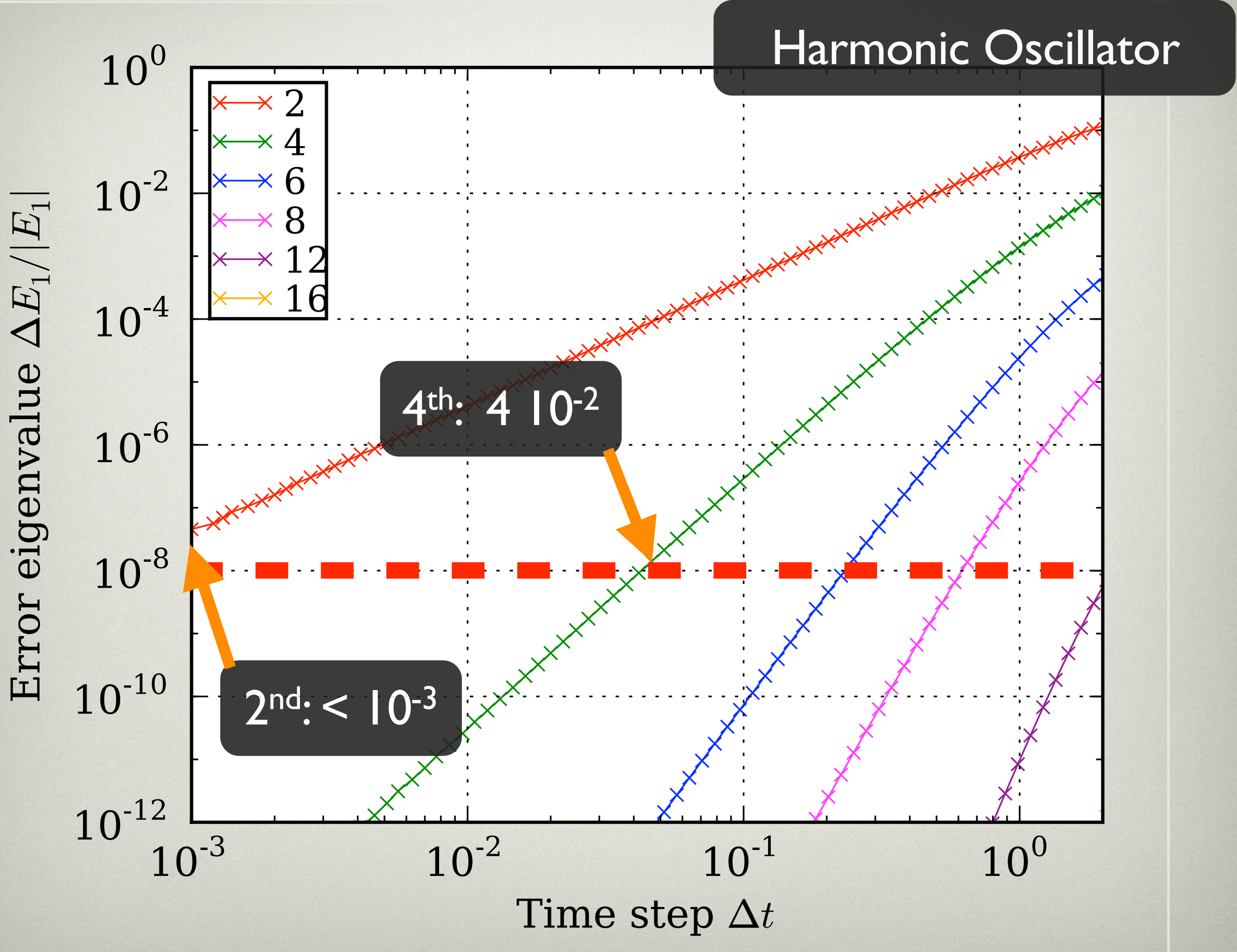
Harmonic Oscillator



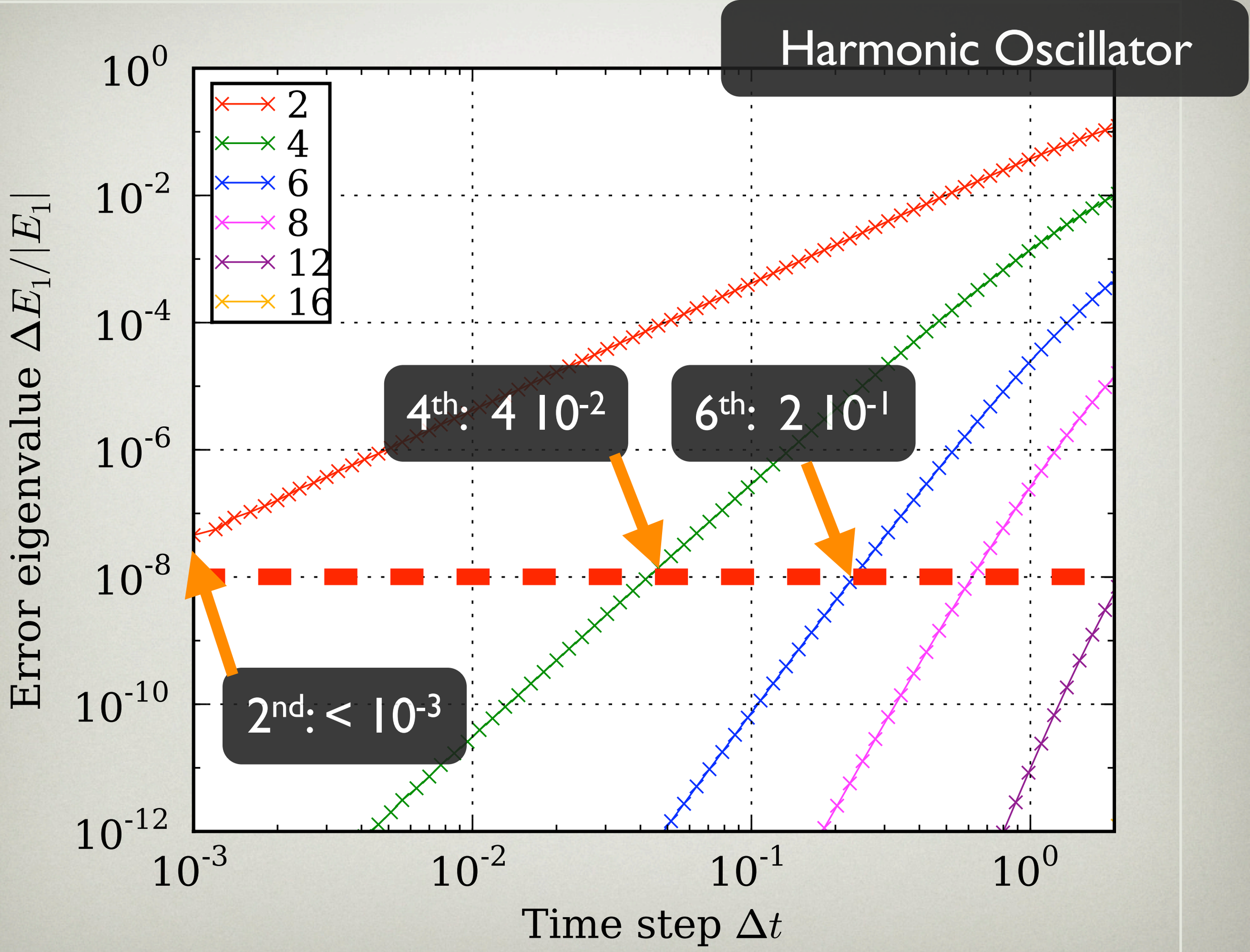
Harmonic Oscillator



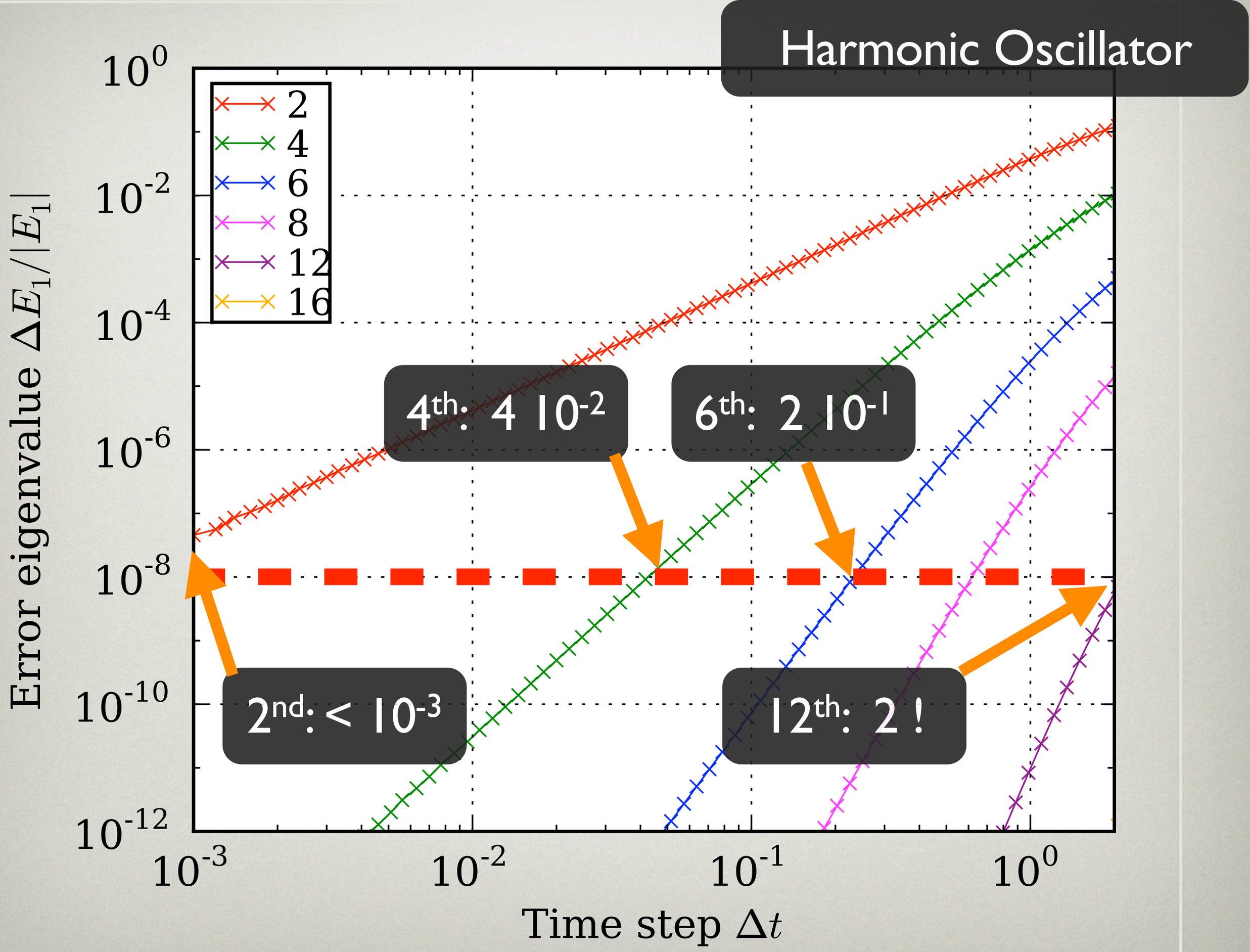
Harmonic Oscillator



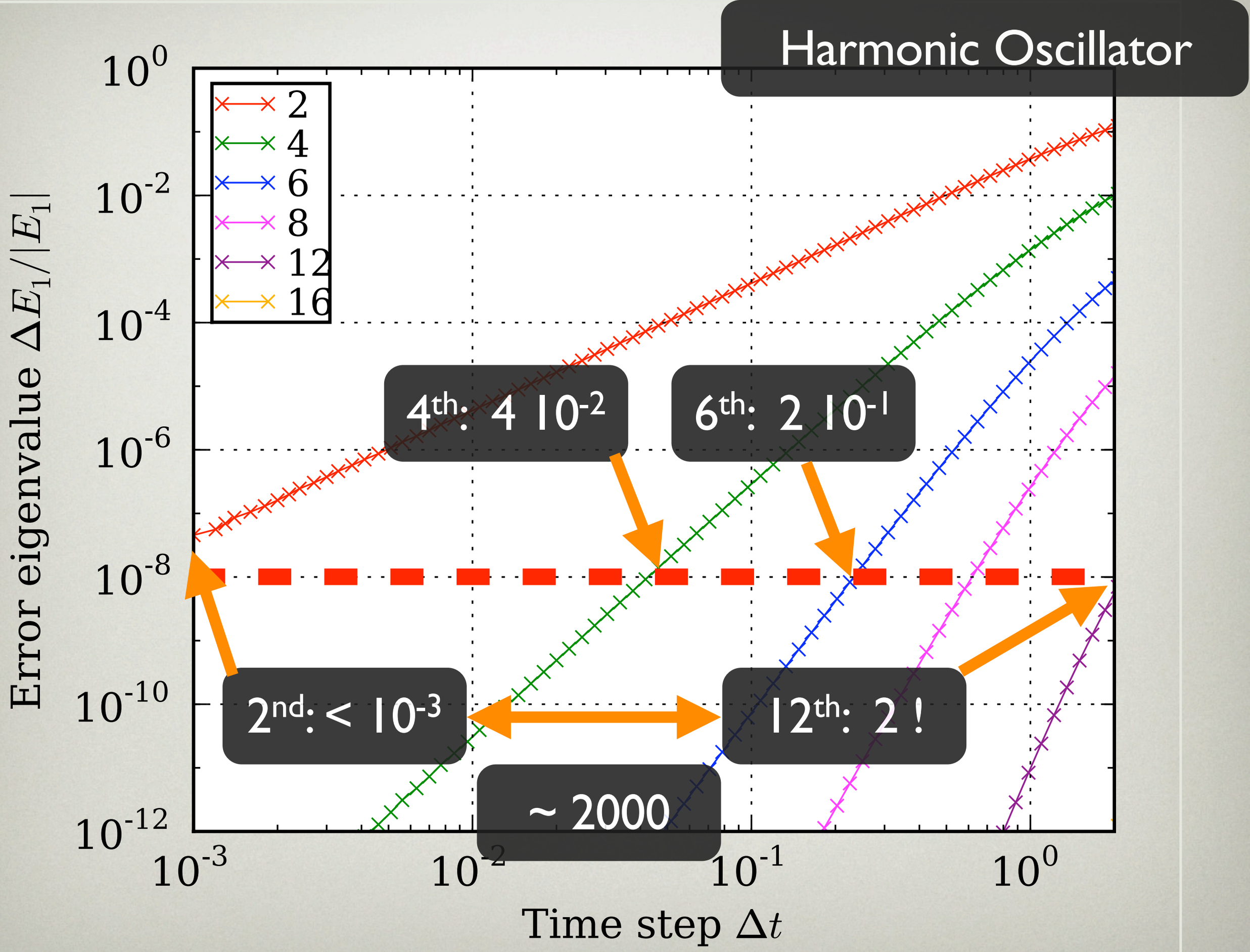
Harmonic Oscillator



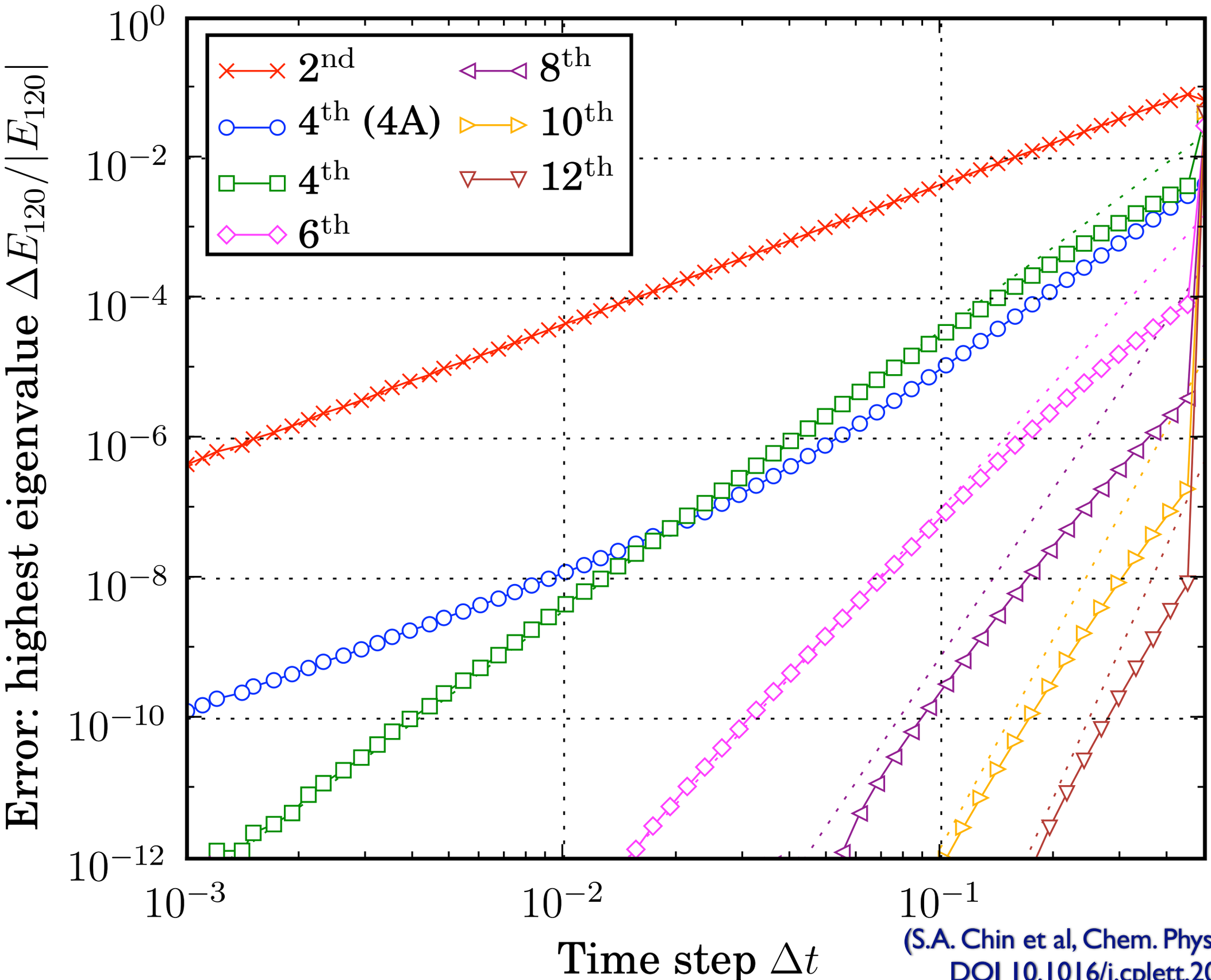
Harmonic Oscillator



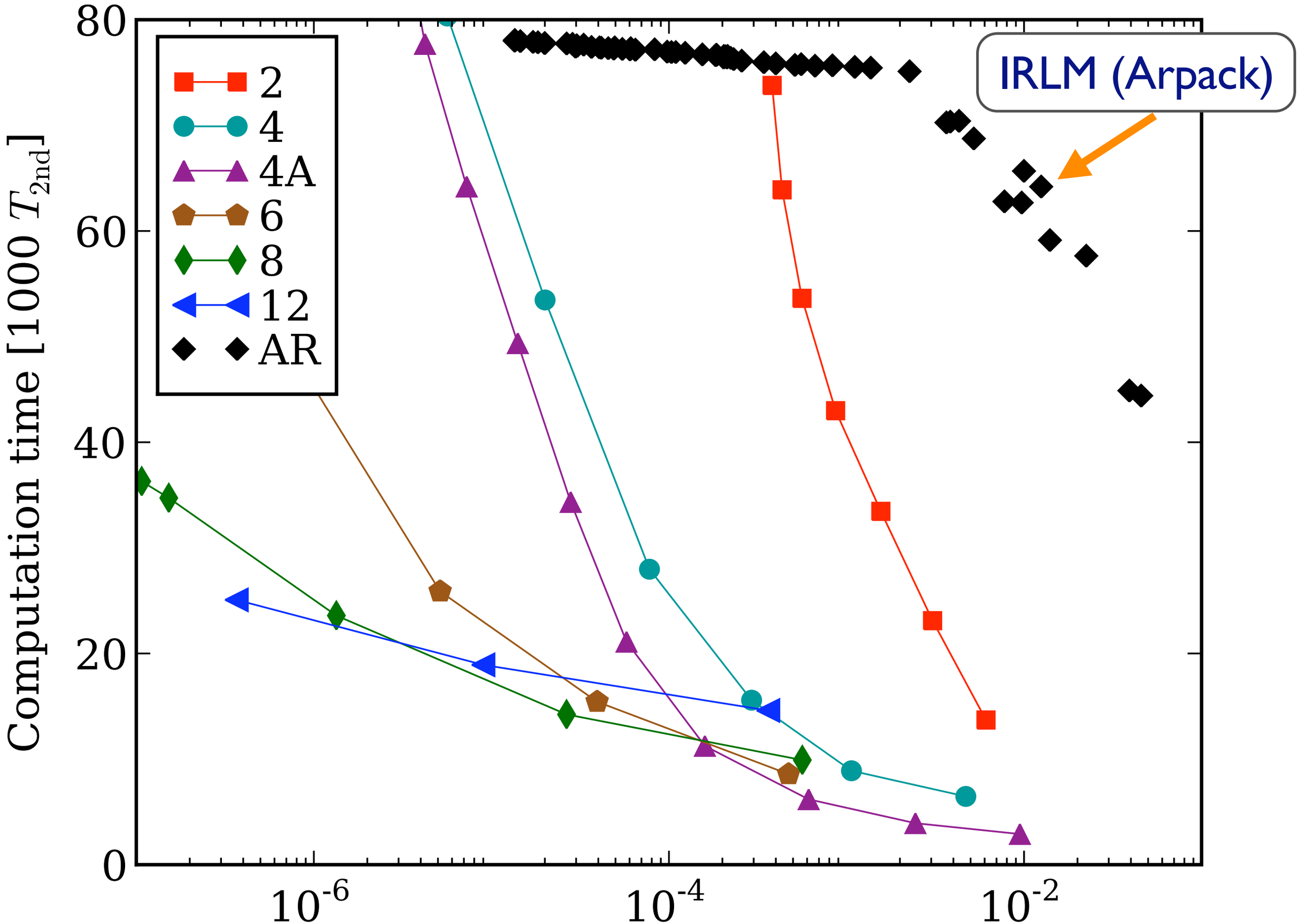
Harmonic Oscillator



C^{60} model, 120th state



(S.A. Chin et al, Chem. Phys. Lett. , in press, DOI 10.1016/j.cplett.2009.01.068)



(S.A. Chin et al, Chem. Phys. Lett. , in press, DOI 10.1016/j.cplett.2009.01.068)

2 Schrödinger equations in strong **magnetic fields**

- Nuclear magnetic resonance (NMR) properties
- Quantum dots in strong magnetic fields

Magnetic field is described by **vector potential**

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$$

➡Enters Schrödinger equation through **minimal substitution:**

$$\mathbf{p} \rightarrow \mathbf{\Pi} = \mathbf{p} + \mathbf{eA}$$

Magnetic field is described by **vector potential**

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$$

➡Enters Schrödinger equation through **minimal substitution:**

$$\mathbf{p} \rightarrow \mathbf{\Pi} = \mathbf{p} + \mathrm{e}\mathbf{A}$$

➡Kinetic energy operator becomes:

$$T = \frac{1}{2m}\left[-\mathrm{i}\hbar\nabla + e\mathbf{A}(\mathbf{r})\right]^2 = \frac{1}{2m}\left[\Pi_x^2 + \Pi_y^2 + \Pi_z^2\right]$$

Magnetic field is described by **vector potential**

$$\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$$

➡Enters Schrödinger equation through **minimal substitution:**

$$\mathbf{p} \rightarrow \mathbf{\Pi} = \mathbf{p} + \mathrm{e}\mathbf{A}$$

➡Kinetic energy operator becomes:

$$T = \frac{1}{2m}\left[-\mathrm{i}\hbar\nabla + e\mathbf{A}(\mathbf{r})\right]^2 = \frac{1}{2m}\left[\Pi_x^2 + \Pi_y^2 + \Pi_z^2\right]$$

Common gauge choices for homogeneous fields

Symmetric gauge: $\mathbf{A}(\mathbf{r}) = \frac{B}{2}\left(-(y-y_0)\mathbf{e}_x + (x-x_0)\mathbf{e}_y\right)$

Landau gauge: $\mathbf{A}(\mathbf{r}) = B(x-x_0)\mathbf{e}_y$

Diffusion method for magnetic fields ?

Diffusion method for magnetic fields ?

Kinetic energy changed: $$T = \frac{1}{2m}\mathbf{p}^2 \longrightarrow T = \frac{1}{2m}\left(\mathbf{p} + e\mathbf{A}\right)^2$$

Diffusion method for magnetic fields ?

Kinetic energy changed: $$T = \frac{1}{2m}\mathbf{p}^2 \longrightarrow T = \frac{1}{2m}\left(\mathbf{p} + e\mathbf{A}\right)^2$$

Reconsider:

Diffusion method for magnetic fields ?

Kinetic energy changed: $T = \frac{1}{2m}\mathbf{p}^2 \longrightarrow T = \frac{1}{2m}\left(\mathbf{p} + e\mathbf{A}\right)^2$

Reconsider:

(1) Kinetic energy propagator: $e^{-\epsilon T}$

Diffusion method for magnetic fields ?

Kinetic energy changed: $T = \frac{1}{2m}\mathbf{p}^2 \longrightarrow T = \frac{1}{2m}\left(\mathbf{p} + e\mathbf{A}\right)^2$

Reconsider:

(1) Kinetic energy propagator: $e^{-\epsilon T}$

(2) Double commutator: $[V,[T,V]]$

(Fourth order algorithm **4A** only)

Diffusion method for magnetic fields ?

Kinetic energy changed: $T = \frac{1}{2m}\mathbf{p}^2 \longrightarrow T = \frac{1}{2m}\left(\mathbf{p} + e\mathbf{A}\right)^2$

Reconsider:

(1) Kinetic energy propagator: $e^{-\epsilon T}$

(2) Double commutator: $[V,[T,V]] = \frac{\hbar^2}{m}|\nabla V(\mathbf{r})|^2$

(Fourth order algorithm **4A** only)

A cancels

Diffusion method for magnetic fields ?

Kinetic energy changed: $T = \frac{1}{2m}\mathbf{p}^2 \longrightarrow T = \frac{1}{2m}\left(\mathbf{p} + e\mathbf{A}\right)^2$

Reconsider:

(1) Kinetic energy propagator: $e^{-\epsilon T}$

(2) Double commutator: $[V,[T,V]] = \frac{\hbar^2}{m}|\nabla V(\mathbf{r})|^2$

(Fourth order algorithm **4A** only)

A cancels

Task: Factorize $e^{-\epsilon T} = e^{-\frac{\epsilon}{2m}(\Pi_x^2+\Pi_y^2+\Pi_z^2)}$

Task: Factorize $e^{-\epsilon T} = e^{-\frac{\epsilon}{2m}(\Pi_x^2+\Pi_y^2+\Pi_z^2)}$

Task: Factorize $e^{-\epsilon T} = e^{-\frac{\epsilon}{2m}(\Pi_x^2+\Pi_y^2+\Pi_z^2)}$

- T is no longer diagonal in Fourier space
- Free electrons in uniform field ⟷ Harmonic oscillator

Task: Factorize $e^{-\epsilon T} = e^{-\frac{\epsilon}{2m}(\Pi_x^2+\Pi_y^2+\Pi_z^2)}$

- T is no longer diagonal in Fourier space
- Free electrons in uniform field ⟷ Harmonic oscillator

- Feynman: density matrix of the HO can be factorized exactly.
- Chin: kinetic energy propagator can be factorized exactly:

$$e^{-\frac{\epsilon}{2m}\Pi^2} = e^{-\frac{\epsilon}{2m}C_y(\xi)\Pi_y^2} e^{-\frac{\epsilon}{2m}C_x(\xi)\Pi_x^2} e^{-\frac{\epsilon}{2m}C_y(\xi)\Pi_y^2} e^{-\frac{\epsilon}{2m}\Pi_z^2}$$

$$C_y(\xi) = \frac{\cosh(\xi)-1}{\xi\sinh(\xi)} \qquad C_x(\xi) = \frac{\sinh(\xi)}{\xi} \qquad \xi = \epsilon\hbar eB/m$$

(M. Aichinger, S.A. Chin, E. Krotscheck, Comp. Phys. Comm. 171 (2005) 197)

Task: Factorize $e^{-\epsilon T} = e^{-\frac{\epsilon}{2m}(\Pi_x^2+\Pi_y^2+\Pi_z^2)}$

- T is no longer diagonal in Fourier space
- Free electrons in uniform field ⟷ Harmonic oscillator

- Feynman: density matrix of the HO can be factorized exactly.
- Chin: kinetic energy propagator can be factorized exactly:

$$e^{-\frac{\epsilon}{2m}\Pi^2} = e^{-\frac{\epsilon}{2m}C_y(\xi)\Pi_y^2} e^{-\frac{\epsilon}{2m}C_x(\xi)\Pi_x^2} e^{-\frac{\epsilon}{2m}C_y(\xi)\Pi_y^2} e^{-\frac{\epsilon}{2m}\Pi_z^2}$$

$$C_y(\xi) = \frac{\cosh(\xi)-1}{\xi\sinh(\xi)} \qquad C_x(\xi) = \frac{\sinh(\xi)}{\xi} \qquad \xi = \epsilon\hbar eB/m$$

(M. Aichinger, S.A. Chin, E. Krotscheck, Comp. Phys. Comm. 171 (2005) 197)

Exact for **arbitrarily large** fields!

Action of $e^{-\epsilon T}$ in Landau gauge: $\mathbf{A}(\mathbf{r}) = Bx\mathbf{e}_y$

$$e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_x p_x^2} \; e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_z p_z^2} \; \psi(x, y, z)$$

Action of $e^{-\epsilon T}$ in Landau gauge: $\mathbf{A}(\mathbf{r}) = Bx\mathbf{e}_y$

$$e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_x p_x^2} \; \boxed{e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_z p_z^2}} \; \psi(x, y, z)$$

(I) 2D FFT for each *x*

$$\boxed{\rightarrow \psi(x, k_y, k_z)} \qquad N \; N^2 \ln N^2$$

Action of $e^{-\epsilon T}$ in Landau gauge: $\mathbf{A}(\mathbf{r}) = Bx\mathbf{e}_y$

$$e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_x p_x^2} \; e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_z p_z^2} \; \psi(x, y, z)$$

(1) 2D FFT for each *x* $\quad \rightarrow \psi(x, k_y, k_z) \qquad N \; N^2 \ln N^2$

(2) 1D FFT for each k_y,k_z $\quad \rightarrow \psi(k_x, k_y, k_z) \qquad N^2 \; N \ln N$

Action of $e^{-\epsilon T}$ in Landau gauge: $\mathbf{A}(\mathbf{r}) = Bx\mathbf{e}_y$

$$e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_x p_x^2} \; e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_z p_z^2} \; \psi(x, y, z)$$

(1) 2D FFT for each *x* $\quad \rightarrow \psi(x, k_y, k_z) \qquad N \; N^2 \ln N^2$

(2) 1D FFT for each k_y,k_z $\quad \rightarrow \psi(k_x, k_y, k_z) \qquad N^2 \; N \ln N$

(3) 1D FFT^{-1} for each k_y,k_z $\quad \rightarrow \psi(x, k_y, k_z) \qquad N^2 \; N \ln N$

Action of $e^{-\epsilon T}$ in Landau gauge: $\mathbf{A}(\mathbf{r}) = Bx\mathbf{e}_y$

$$e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_x p_x^2} \; e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_z p_z^2} \; \psi(x, y, z)$$

(1) 2D FFT for each *x* $\rightarrow \psi(x, k_y, k_z)$ $N \; N^2 \ln N^2$

(2) 1D FFT for each k_y,k_z $\rightarrow \psi(k_x, k_y, k_z)$ $N^2 \; N \ln N$

(3) 1D FFT^{-1} for each k_y,k_z $\rightarrow \psi(x, k_y, k_z)$ $N^2 \; N \ln N$

(4) 2D FFT^{-1} for each *x* $\rightarrow \psi(x, y, z)$ $N \; N^2 \ln N^2$

Action of $e^{-\epsilon T}$ in Landau gauge: $\mathbf{A}(\mathbf{r}) = Bx\mathbf{e}_y$

$$e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_x p_x^2} \; e^{-\epsilon c_y (p_y + Bx)^2} \; e^{-\epsilon c_z p_z^2} \; \psi(x, y, z)$$

(1) 2D FFT for each *x* $\rightarrow \psi(x, k_y, k_z)$ $N \; N^2 \ln N^2$

(2) 1D FFT for each k_y,k_z $\rightarrow \psi(k_x, k_y, k_z)$ $N^2 \; N \ln N$

(3) 1D FFT^{-1} for each k_y,k_z $\rightarrow \psi(x, k_y, k_z)$ $N^2 \; N \ln N$

(4) 2D FFT^{-1} for each *x* $\rightarrow \psi(x, y, z)$ $N \; N^2 \ln N^2$

Overall effort: $2 \; N^3 \; \ln N^3$

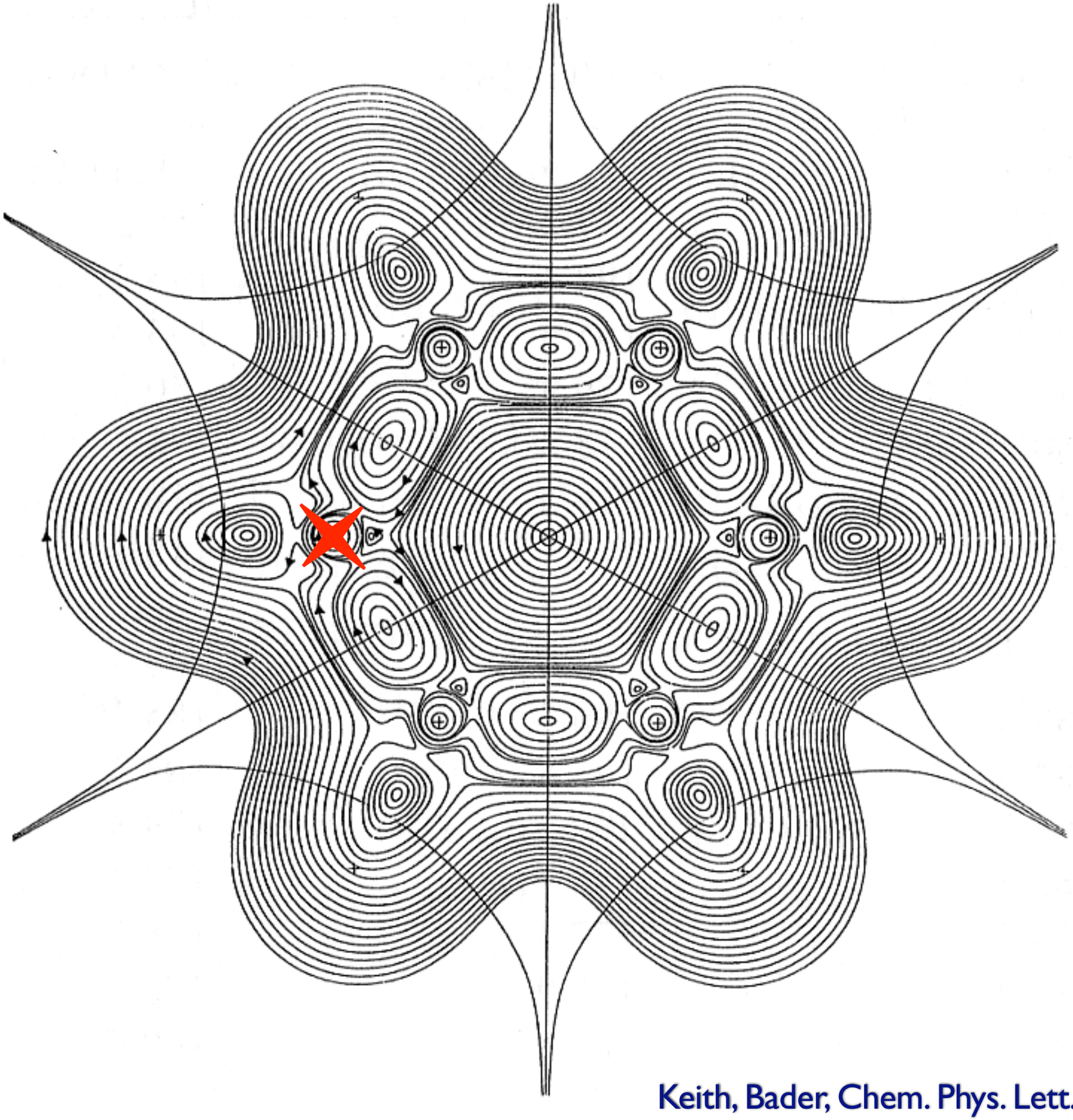
= Time needed for 2 3D FFT's

Effort identical to field free case!

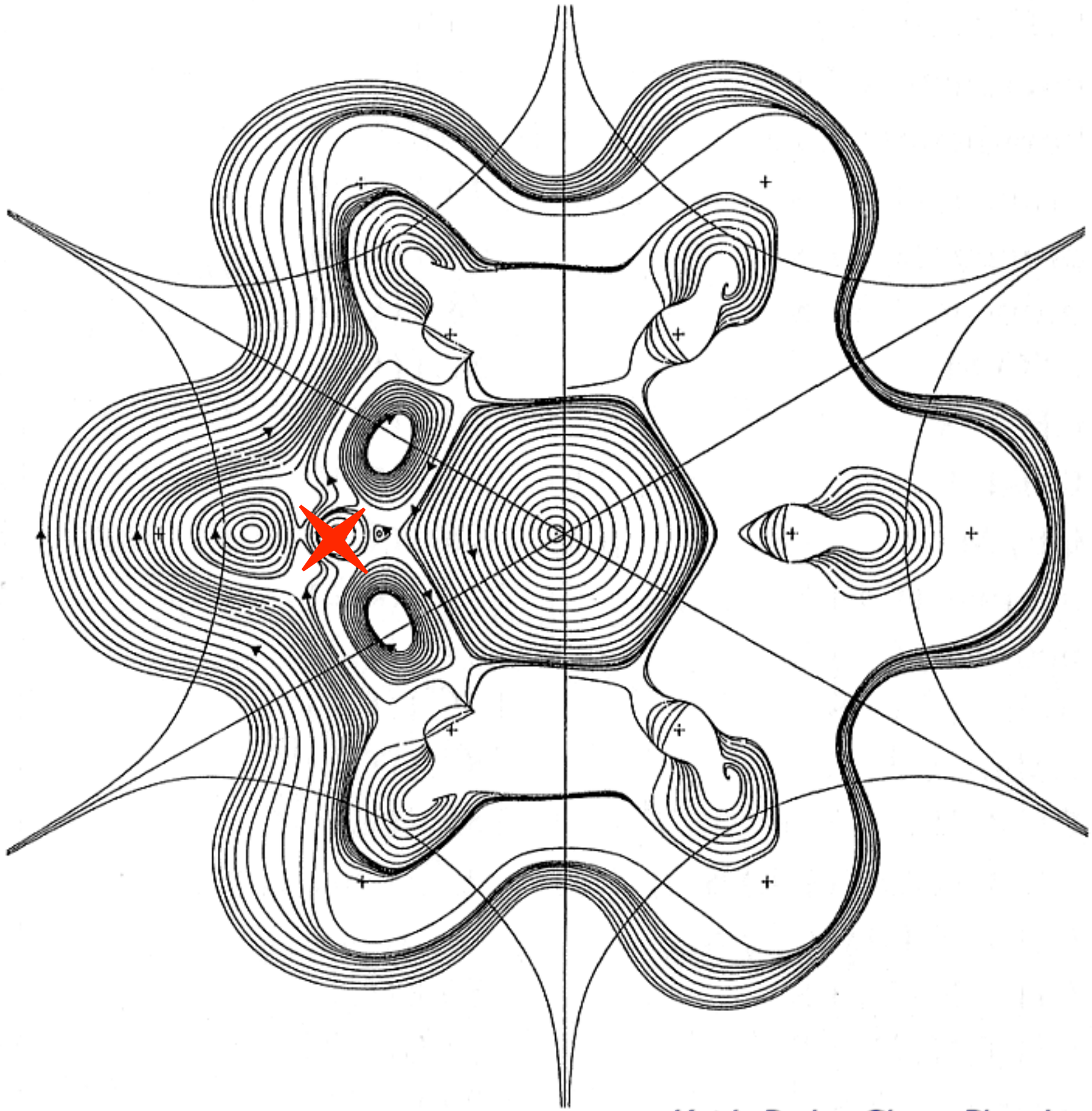
Let's do something useful...

- Calculate current density of Benzene

$$\mathbf{j}(\mathbf{r}) = \frac{e}{2m} \sum_j \left[\psi_j^* \mathbf{\Pi} \psi_j + \psi_j \left(\mathbf{\Pi} \psi_j \right)^* \right]$$



Keith, Bader, Chem. Phys. Lett. 210, 223 (1993)



Keith, Bader, Chem. Phys. Lett. 210, 223 (1993)

Problem well known in quantum chemistry
(since early 1970's)

"Gauge origin problem"

Problem well known in quantum chemistry
(since early 1970's)

"Gauge origin problem"

Physics of course is gauge invariant, but correct symmetry gets destroyed by truncating the basis

Problem well known in quantum chemistry
(since early 1970's)

"Gauge origin problem"

Physics of course is gauge invariant, but correct symmetry gets destroyed by truncating the basis

See, e.g. , Helgaker, Jazunsky, Ruud, Chem. Rev. 99 (1999)

"Within a finite linear variational subspace, gauge origin invariance can never be obtained exactly, only approximately for small displacements of the gauge origin."

Problem well known in quantum chemistry
(since early 1970's)

"Gauge origin problem"

Physics of course is gauge invariant, but correct symmetry gets destroyed by truncating the basis

See, e.g. , Helgaker, Jazunsky, Ruud, Chem. Rev. 99 (1999)

"Within a finite linear variational subspace, gauge origin invariance can never be obtained exactly, only approximately for small displacements of the gauge origin."

See Siu Chin's talk: Understand the physics to make good algorithms

Observables **should** be independent of gauge ...

Observables **should** be independent of gauge ...

Gauge transformation: $\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$

Should not change the physics: $\psi(\mathbf{r}) \rightarrow \psi'(\mathbf{r}) = e^{\mathrm{i}e\chi(\mathbf{r})/\hbar}\psi(\mathbf{r})$

Observables **should** be independent of gauge ...

Gauge transformation: $\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$

Should not change the physics: $\psi(\mathbf{r}) \rightarrow \psi'(\mathbf{r}) = e^{ie\chi(\mathbf{r})/\hbar}\psi(\mathbf{r})$

Observables **should** be independent of gauge ...

Gauge transformation: $\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$

Should not change the physics: $\psi(\mathbf{r}) \rightarrow \psi'(\mathbf{r}) = e^{ie\chi(\mathbf{r})/\hbar}\psi(\mathbf{r})$

Introduce "Gauge transport function" (J. Schwinger)

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i$$

Observables **should** be independent of gauge ...

Gauge transformation: $\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$

Should not change the physics: $\psi(\mathbf{r}) \rightarrow \psi'(\mathbf{r}) = e^{\mathrm{i}e\chi(\mathbf{r})/\hbar}\psi(\mathbf{r})$

Introduce "Gauge transport function" (J. Schwinger)

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r})dx_i$$

Then: Covariant derivative

$$\pi_i^2 = \left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 = e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\frac{\partial^2}{\partial x_i^2}e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

Chain rule, product rule

Gauge transformation:

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$$

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i \qquad f_j(\mathbf{r}) \rightarrow f'_j(\mathbf{r}) = f_j(\mathbf{r}) + \chi(\mathbf{r})$$

Gauge transformation:

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$$

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i \qquad f_j(\mathbf{r}) \rightarrow f'_j(\mathbf{r}) = f_j(\mathbf{r}) + \chi(\mathbf{r})$$

Operators transform in a gauge covariant way:

$$T = \frac{1}{2m} \sum_i \left[-\mathrm{i}\hbar \frac{\partial}{\partial x_i} + eA_i(\mathbf{r}) \right]^2 = -\frac{\hbar^2}{2m} \sum_j e^{-\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})} \frac{\partial^2}{\partial x_j^2} e^{\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})}$$

Gauge transformation:

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$$

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i \qquad f_j(\mathbf{r}) \rightarrow f'_j(\mathbf{r}) = f_j(\mathbf{r}) + \chi(\mathbf{r})$$

Operators transform in a gauge covariant way:

$$T = \frac{1}{2m} \sum_i \left[-\mathrm{i}\hbar \frac{\partial}{\partial x_i} + eA_i(\mathbf{r}) \right]^2 = -\frac{\hbar^2}{2m} \sum_j e^{-\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})} \frac{\partial^2}{\partial x_j^2} e^{\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})}$$

$$\rightarrow T' = \frac{1}{2m} e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \Pi^2 e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}$$

and the same for $V(\mathbf{r})$

Gauge transformation:

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$$

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i \qquad f_j(\mathbf{r}) \rightarrow f'_j(\mathbf{r}) = f_j(\mathbf{r}) + \chi(\mathbf{r})$$

Operators transform in a gauge covariant way:

$$T = \frac{1}{2m} \sum_i \left[-\mathrm{i}\hbar \frac{\partial}{\partial x_i} + eA_i(\mathbf{r}) \right]^2 = -\frac{\hbar^2}{2m} \sum_j e^{-\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})} \frac{\partial^2}{\partial x_j^2} e^{\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})}$$

$$\rightarrow T' = \frac{1}{2m} e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \Pi^2 e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}$$

and the same for *V(**r**)*

Transformed Schrödinger equation:

$$e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \hat{H} e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \psi'_j(\mathbf{r}) = e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} E'_j e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \psi'_j(\mathbf{r})$$

Gauge transformation:

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r})$$

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i \qquad f_j(\mathbf{r}) \rightarrow f'_j(\mathbf{r}) = f_j(\mathbf{r}) + \chi(\mathbf{r})$$

Operators transform in a gauge covariant way:

$$T = \frac{1}{2m} \sum_i \left[-\mathrm{i}\hbar \frac{\partial}{\partial x_i} + eA_i(\mathbf{r}) \right]^2 = -\frac{\hbar^2}{2m} \sum_j e^{-\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})} \frac{\partial^2}{\partial x_j^2} e^{\mathrm{i}\frac{e}{\hbar} f_j(\mathbf{r})}$$

$$\rightarrow T' = \frac{1}{2m} e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \Pi^2 e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}$$

and the same for *V(**r**)*

Transformed Schrödinger equation:

$$e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \hat{H} e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \psi'_j(\mathbf{r}) = e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} E'_j e^{+\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \psi'_j(\mathbf{r})$$

$$\psi'(\mathbf{r}) = e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})} \psi(\mathbf{r})$$

Key relation:

$$\left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 = e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\frac{\partial^2}{\partial x_i^2}e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

Numerical calculations: approximate LHS on finite basis

Key relation:

$$\left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 \not\equiv e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\frac{\partial^2}{\partial x_i^2}e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

Numerical calculations: approximate LHS on finite basis

Equality is **never** fulfilled exactly on a finite-size basis set

- Finite differences: Chain- and product-rules not exact
- Equality only fulfilled in the limit $h \to 0$

Key relation:

$$\left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 \not\equiv e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\frac{\partial^2}{\partial x_i^2}e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

Numerical calculations: approximate LHS on finite basis

Equality is **never** fulfilled exactly on a finite-size basis set

- Finite differences: Chain- and product-rules not exact
- Equality only fulfilled in the limit $h \to 0$

Result: phase factor not reproduced exactly

$$\psi'(\mathbf{r}) = e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}\psi(\mathbf{r}) \qquad \psi'(\mathbf{r}) = \Gamma(\mathbf{r})e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}\ \psi(\mathbf{r})$$

Key relation:

$$\left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 \not\equiv e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\frac{\partial^2}{\partial x_i^2}e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

Numerical calculations: approximate LHS on finite basis

Equality is **never** fulfilled exactly on a finite-size basis set

- Finite differences: Chain- and product-rules not exact
- Equality only fulfilled in the limit $h \to 0$

Result: phase factor not reproduced exactly

$$\psi'(\mathbf{r}) = e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}\psi(\mathbf{r}) \qquad \psi'(\mathbf{r}) = \Gamma(\mathbf{r})e^{-\mathrm{i}\frac{e}{\hbar}\chi(\mathbf{r})}\psi(\mathbf{r})$$

➡Position-dependent error in the wave function!

- All discretizations are gauge covariance in the limit $h \to 0$
- Need coarse discretization/small basis
  - 3D: effort goes ~N^3

(S. Janecek, E. Krotscheck, Phys. Rev. B 77 (2008) 245115)

- All discretizations are gauge covariance in the limit $h \to 0$
- Need coarse discretization/small basis
  - 3D: effort goes ~N^3

Cure:

$$\left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 = e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\,\frac{\partial^2}{\partial x_i^2}\,e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

(S. Janecek, E. Krotscheck, Phys. Rev. B 77 (2008) 245115)

- All discretizations are gauge covariance in the limit $h \to 0$
- Need coarse discretization/small basis
  - 3D: effort goes ~N^3

Cure:

$$\left[-\mathrm{i}\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 = e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}\,\frac{\partial^2}{\partial x_i^2}\,e^{-\mathrm{i}ef_i(\mathbf{r})/\hbar}$$

- RHS yields gauge covariant operator for any discrete approximation of the Laplacian!

(S. Janecek, E. Krotscheck, Phys. Rev. B 77 (2008) 245115)

Laplacian is diagonal in Fourier space (in any discretization)

$$\hbar^2 \frac{d^2}{dx^2}\psi(x,y,z) = \sum_{k_x} \tilde{\psi}(k_x,y,z) t_n(k_x) e^{ik_x x_j}$$

Expand wave function

$$e^{\mathrm{i}\frac{e}{\hbar}f_y(\mathbf{r})}\psi(x,y,z) = \sum_{k_y} \tilde{\psi}(x,k_y,z) e^{\mathrm{i}y(k_y+\frac{e}{\hbar}A_y(x,z))}$$

$$\Pi_y^2\psi(x,y_j,z) = e^{-\mathrm{i}\frac{e}{\hbar}f_y(x,y_j,z)}\left[-\hbar^2\frac{d^2}{dy^2}e^{+\mathrm{i}\frac{e}{\hbar}f_y}\psi\right]_n (x,y_j,z) =$$

$$= \sum_{k_y} \tilde{\psi}(x,k_y,z) t_n\left(k_y+\frac{e}{\hbar}A_y(x,z)\right) e^{\mathrm{i}k_y y_j}$$

Applications

- Current densities of Molecules

Applications

- Current densities of Molecules

- Induced current in turn induces magnetic field (Biot-Savart)

$$\mathbf{B}^{\mathrm{ind}}(\mathbf{r}) = \frac{\mu_0}{4\pi}\int d^3r' \, \frac{\mathbf{r}' - \mathbf{r}}{|\mathbf{r}' - \mathbf{r}|^3} \times \mathbf{j}(\mathbf{r}'), \qquad \mathbf{m} = \frac{1}{2}\int \mathbf{r} \times \mathbf{j}(\mathbf{r})\, d^3\mathbf{r}$$

Susceptibility $\chi_{ij} = \mu_0 \dfrac{\partial M_i}{\partial B_j^{\mathrm{ext}}}$

Applications

- Current densities of Molecules

- Induced current in turn induces magnetic field (Biot-Savart)

$$\mathbf{B}^{\mathrm{ind}}(\mathbf{r}) = \frac{\mu_0}{4\pi}\int d^3r'\,\frac{\mathbf{r}'-\mathbf{r}}{|\mathbf{r}'-\mathbf{r}|^3}\times\mathbf{j}(\mathbf{r}'), \qquad \mathbf{m} = \frac{1}{2}\int \mathbf{r}\times\mathbf{j}(\mathbf{r})\,d^3\mathbf{r}$$

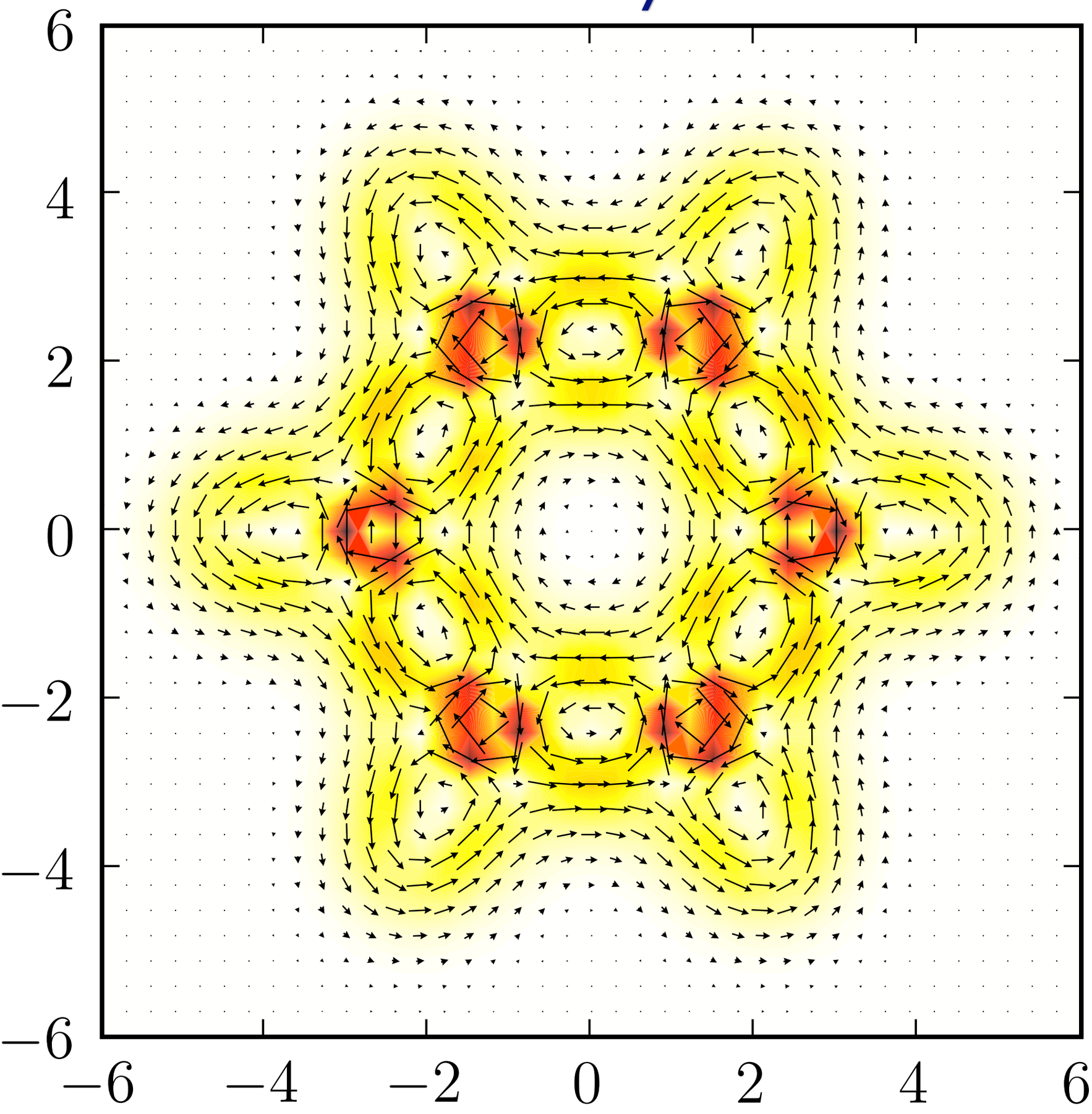
Susceptibility $\chi_{ij} = \mu_0 \dfrac{\partial M_i}{\partial B_j^{\mathrm{ext}}}$

- Local field modifications due to induced field can be measured very accurately in NMR experiments.

$$\sigma_{ij}(\mathbf{R}) = \frac{\partial B_i^{\mathrm{ind}}(\mathbf{R})}{\partial B_j^{\mathrm{ext}}}.$$

... NMR shift

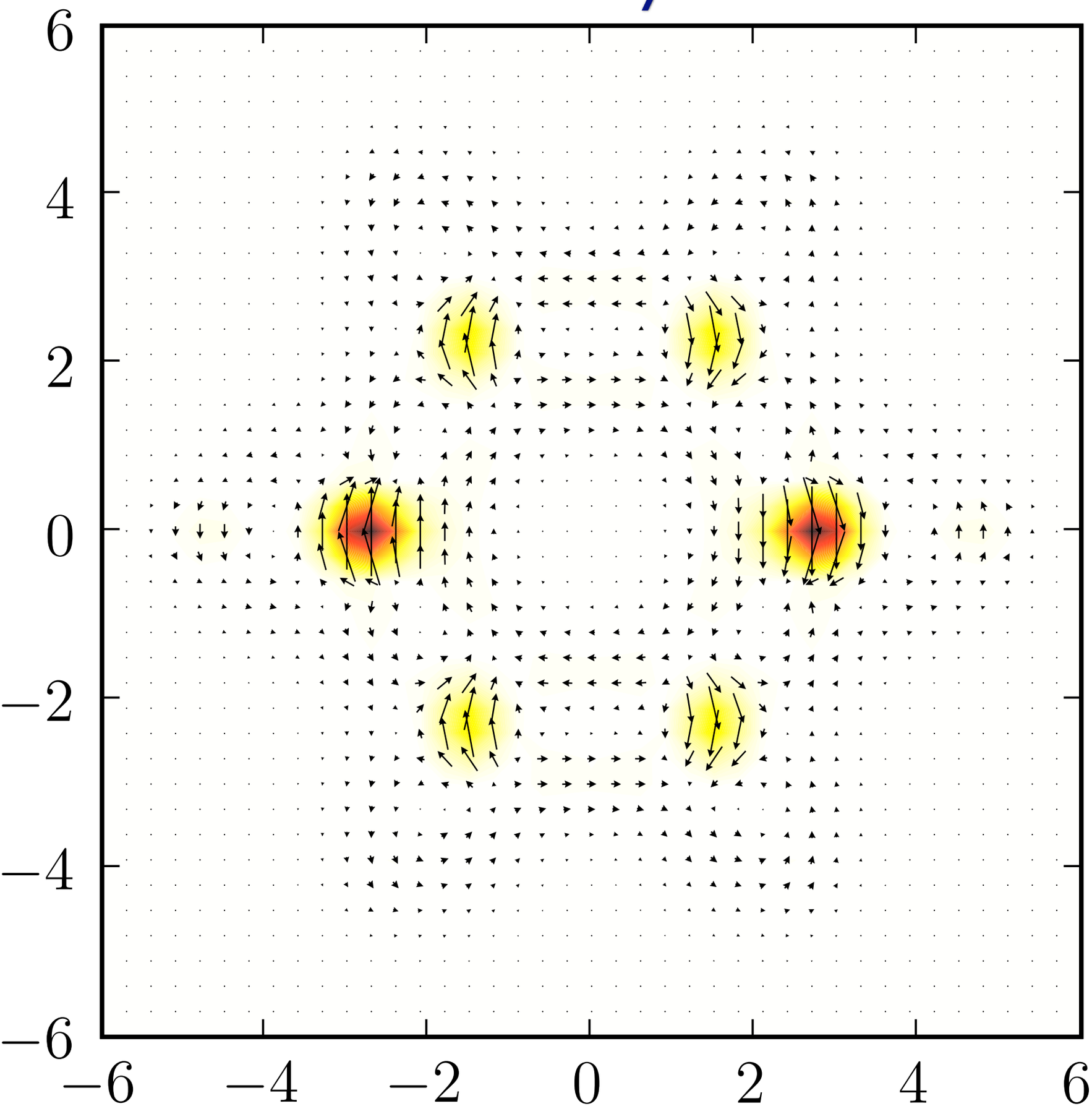
Current density of Benzene



Field: 1 Tesla

Gauge covariant calculation

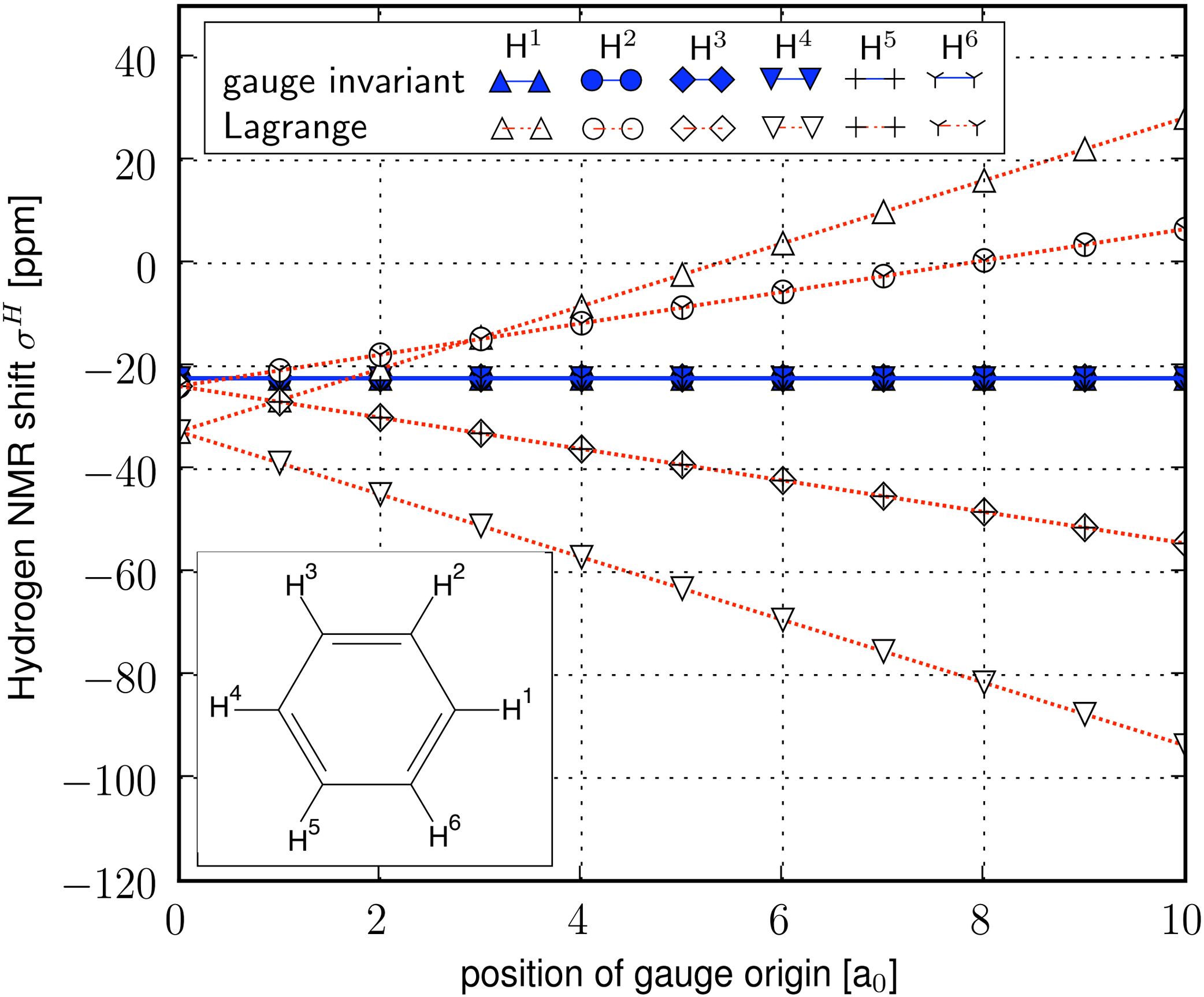
Current density of Benzene



Field: 1 Tesla

Gauge covariant calculation

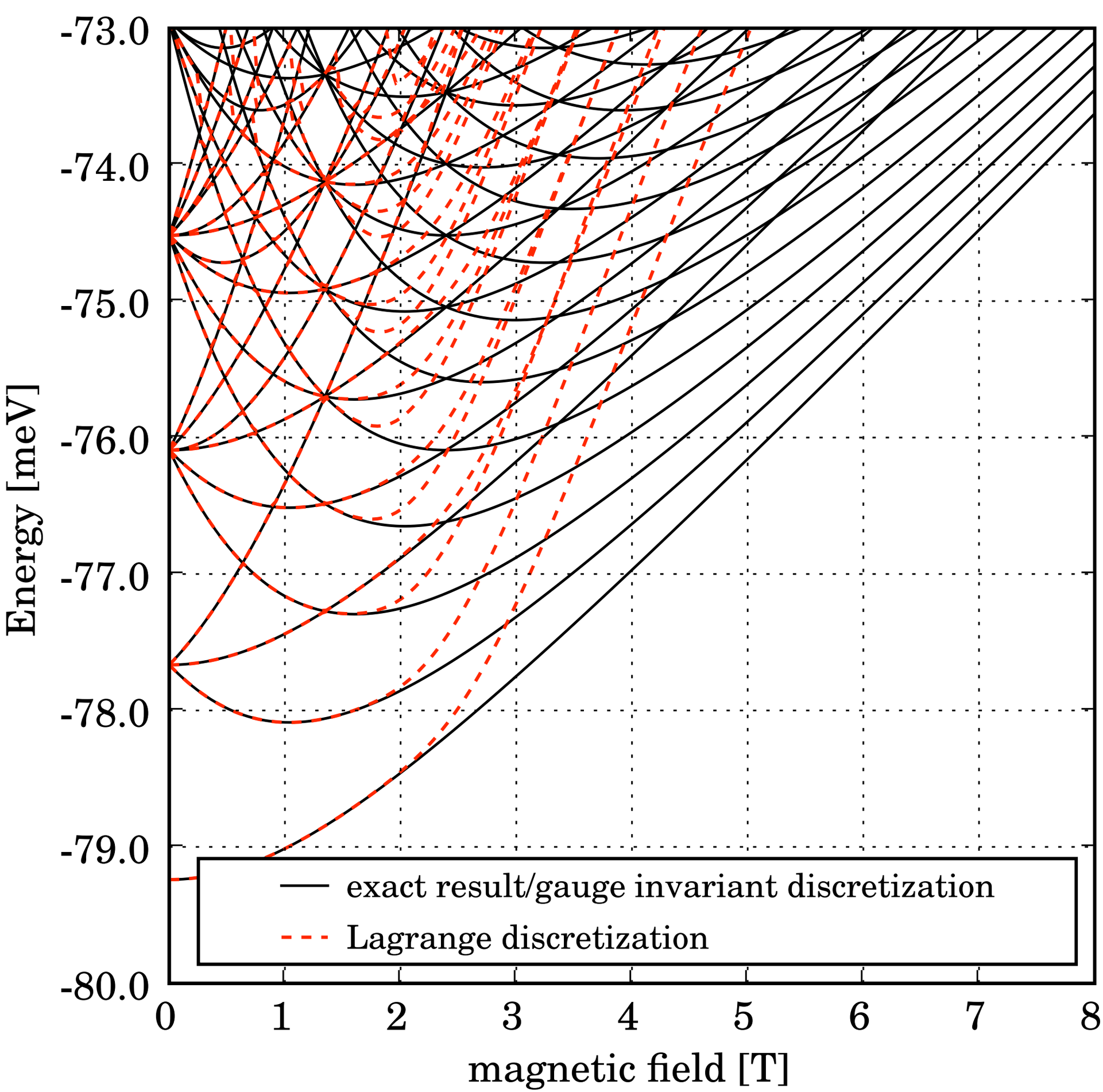
Hydrogen NMR shift of Benzene



(S. Janecek, E. Krotscheck, Phys. Rev. B 77 (2008) 245115)

Strong magnetic fields

- 3D Fock Darwin Model: Harmonic oscillator in strong, homogeneous magnetic field
- Analytically solvable
- Model for Quantum dots in strong fields



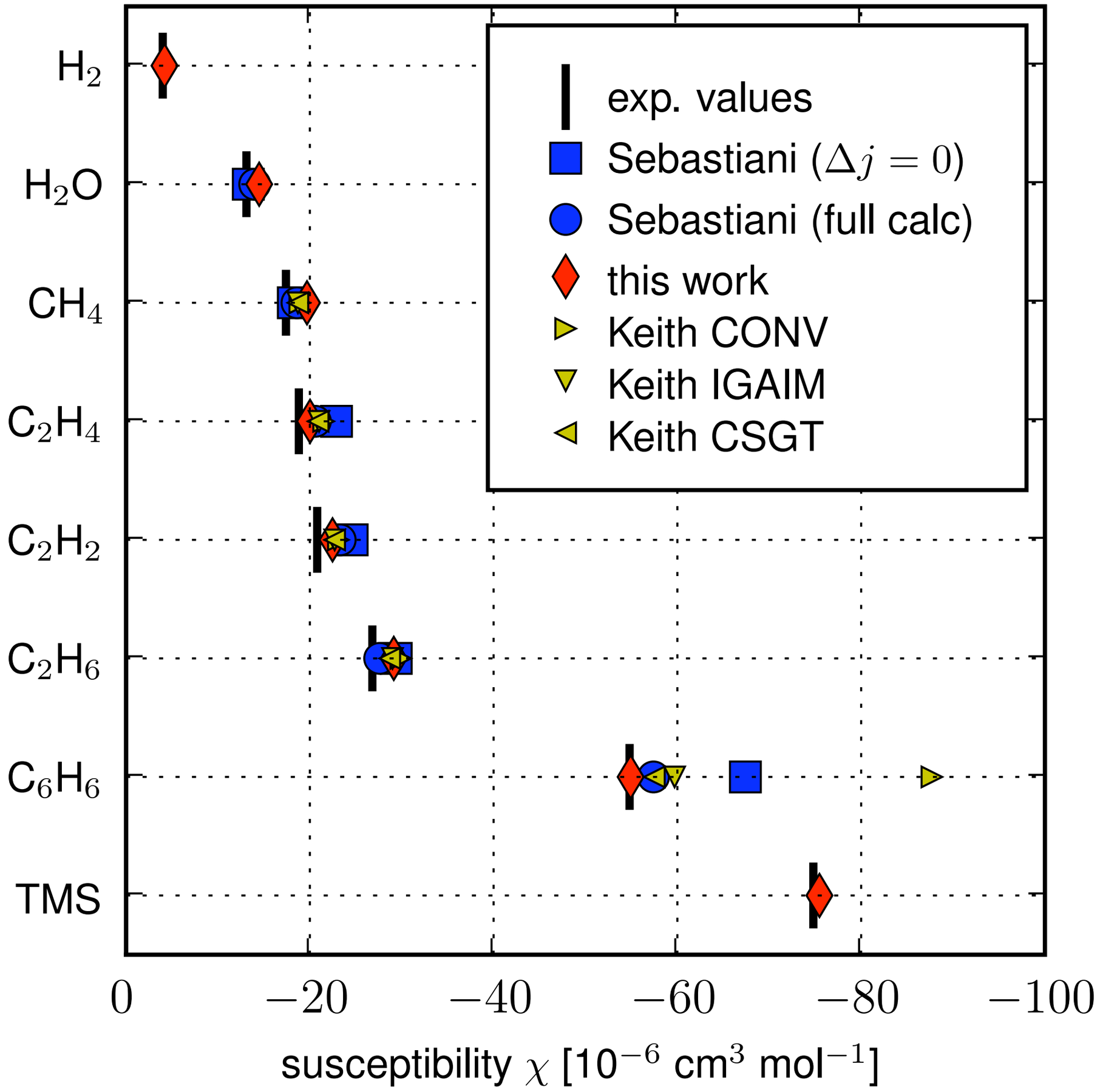
96^3 grid points

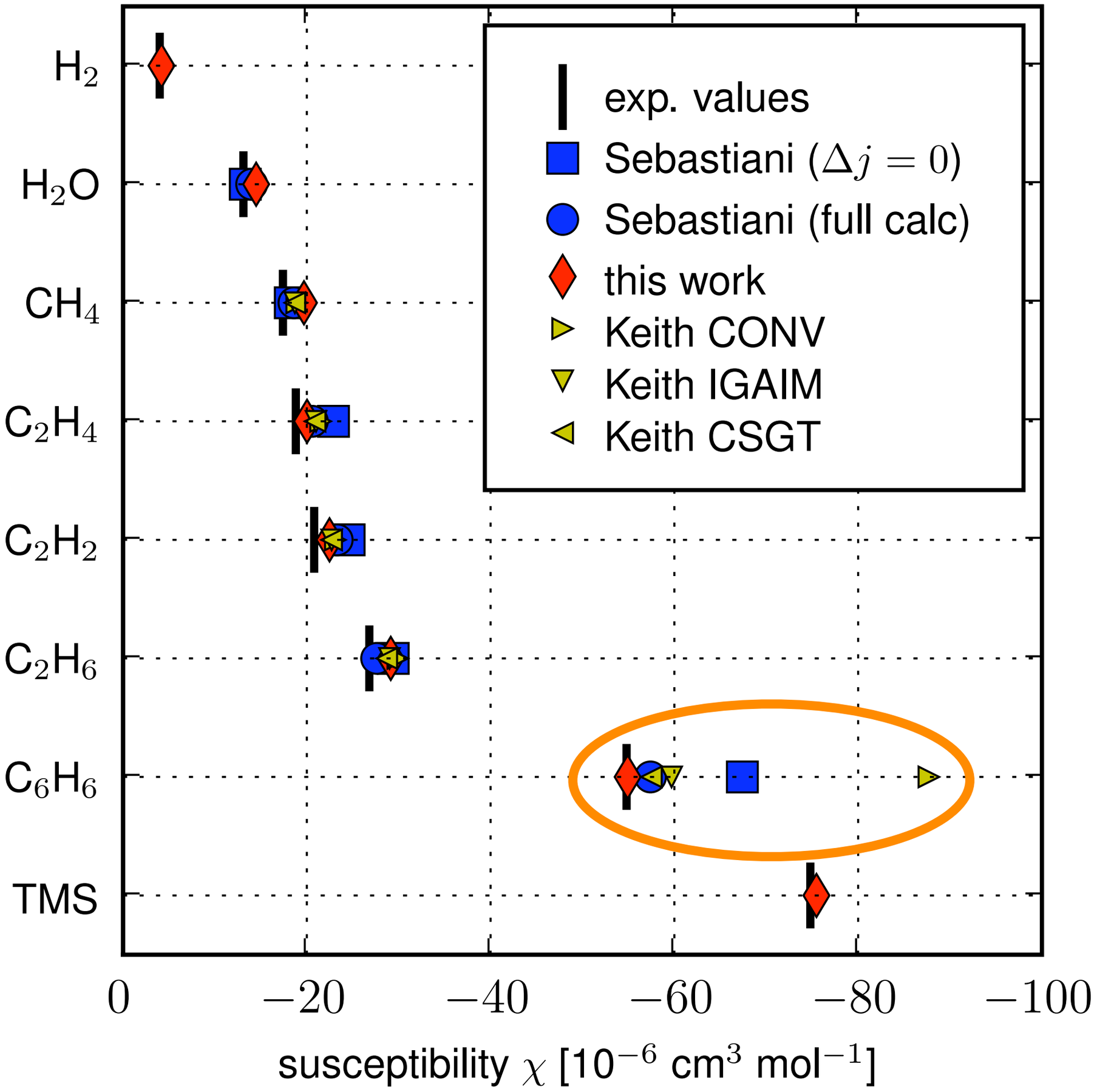
~60 states

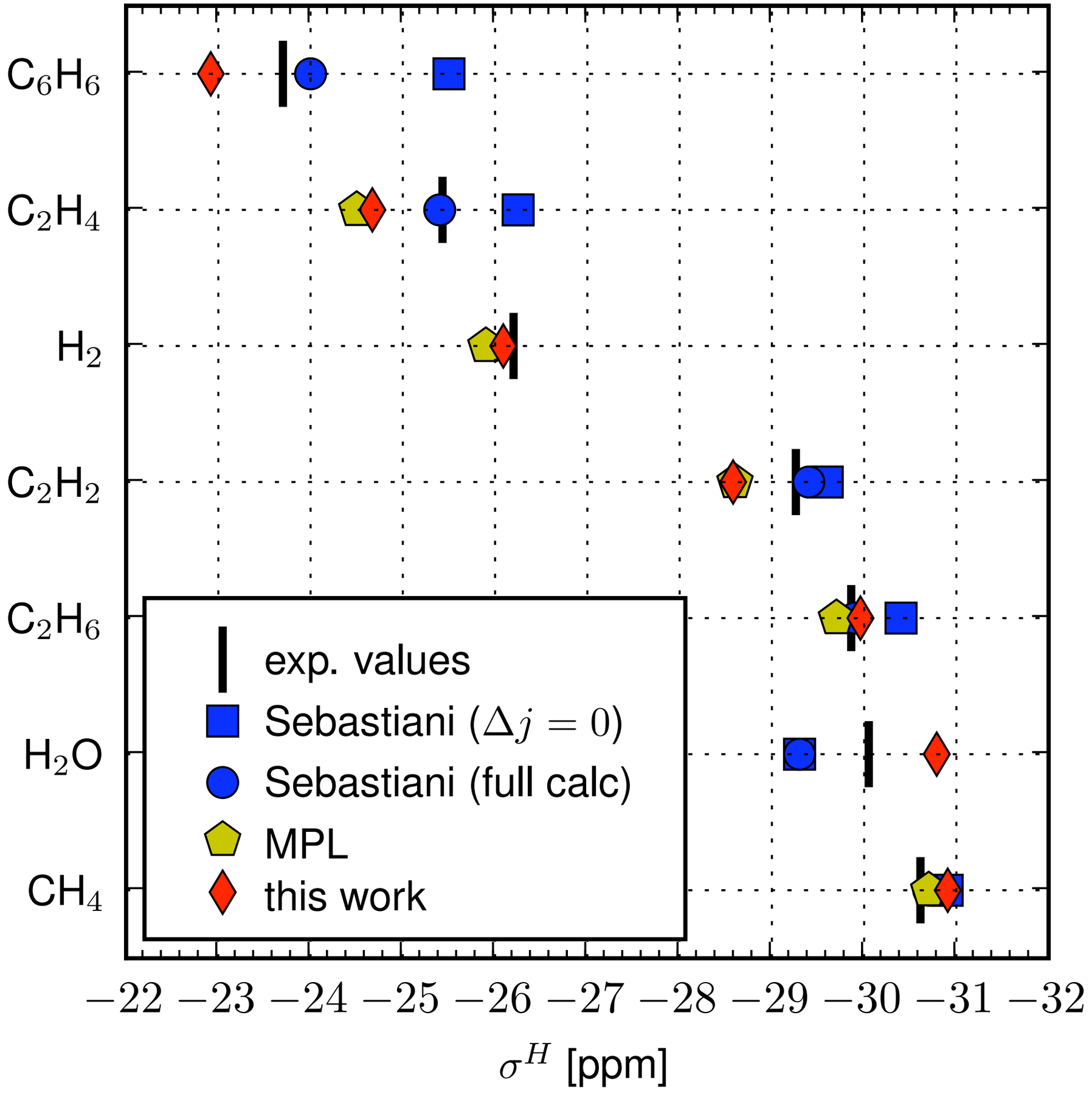
Susceptibilities & NMR shifts of some molecules

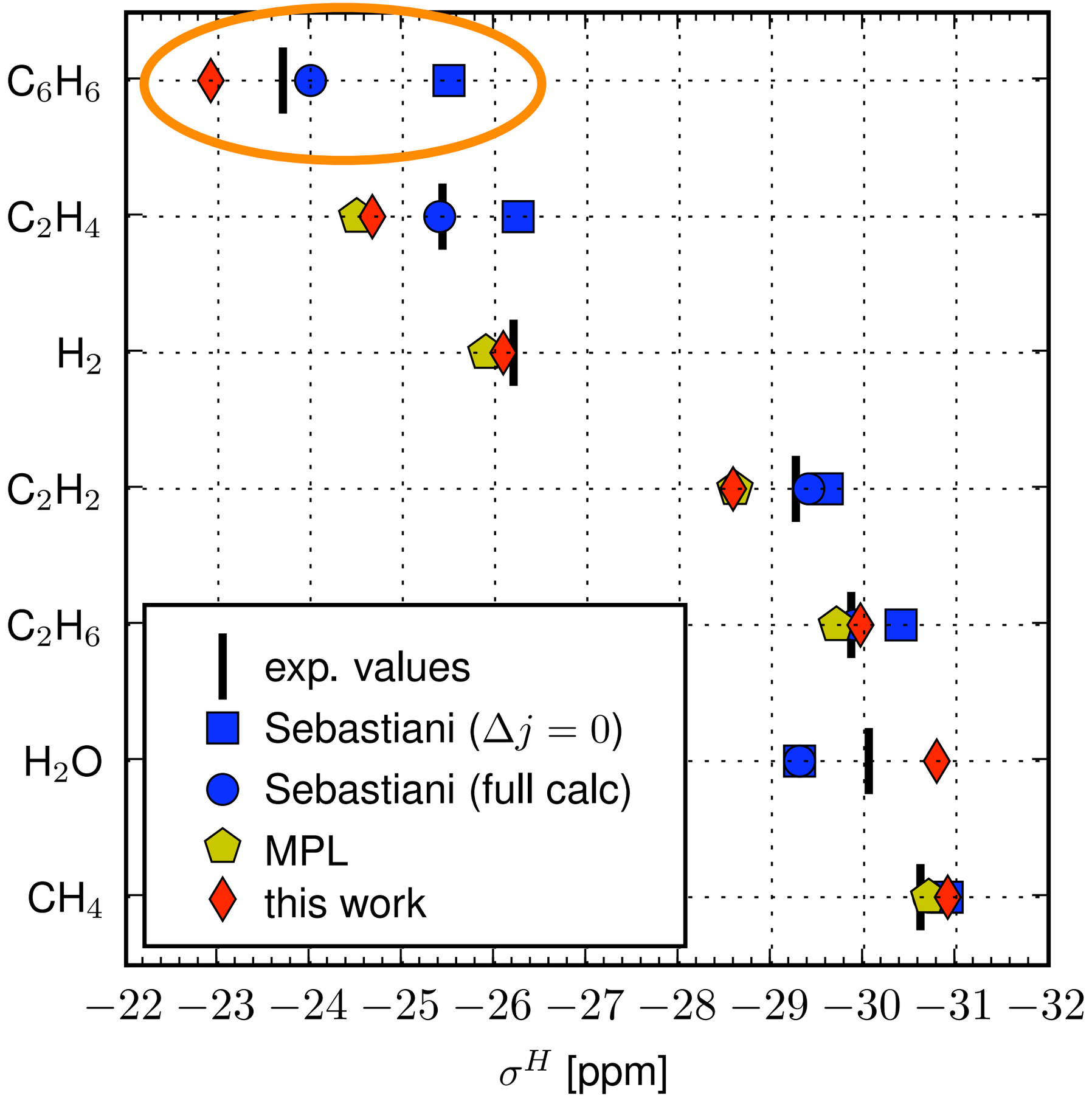
Addidional approximations:

- LDA (local density approximation)
- Pseudopotentials (not very good for NMR properties)


H2
H2O
CH4
C2H4
C2H2
C2H6
C6H6
TMS
exp. values
Sebastiani (Δj = 0)
Sebastiani (full calc)
this work
Keith CONV
Keith IGAIM
Keith CSGT
0
−20
−40
−60
−80
−100
susceptibility χ [10−6 cm3 mol−1]


H2
H2O
CH4
C2H4
C2H2
C2H6
C6H6
TMS
exp. values
Sebastiani (Δj = 0)
Sebastiani (full calc)
this work
Keith CONV
Keith IGAIM
Keith CSGT
0
−20
−40
−60
−80
−100
susceptibility χ [10−6 cm3 mol−1]


C_6H_6
C_2H_4
H_2
C_2H_2
C_2H_6
H_2O
CH_4
exp. values
Sebastiani ($\Delta j = 0$)
Sebastiani (full calc)
MPL
this work
-22 -23 -24 -25 -26 -27 -28 -29 -30 -31 -32
σ^H [ppm]


C_6H_6
C_2H_4
H_2
C_2H_2
C_2H_6
H_2O
CH_4
exp. values
Sebastiani ($\Delta j = 0$)
Sebastiani (full calc)
MPL
this work
-22 -23 -24 -25 -26 -27 -28 -29 -30 -31 -32
σ^H [ppm]

Conclusions

1. Multi-product expansions: fast solvers for Schrödinger equations

   Factor ~10 with respect to Implicitly Restarted Lanczos Method (IRLM)

2. Diffusion method allows for elegant inclusion of arbitrarily strong magnetic fields

   Some care needed for correct gauge covariant implementation

Conclusions

1. Multi-product expansions: fast solvers for Schrödinger equations
   - Factor ~10 with respect to Implicitly Restarted Lanczos Method (IRLM)
2. Diffusion method allows for elegant inclusion of arbitrarily strong magnetic fields
   - Some care needed for correct gauge covariant implementation

Thank you for your attention!

Happy Birthday, Siu !