What can applied mathematicians do for you?

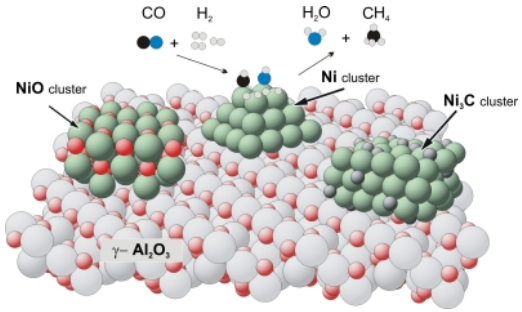
Eric CANCES

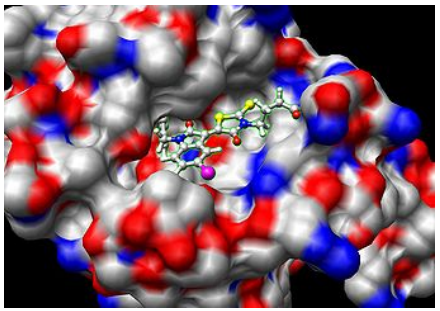
Ecole des Ponts - ParisTech and Inria Paris

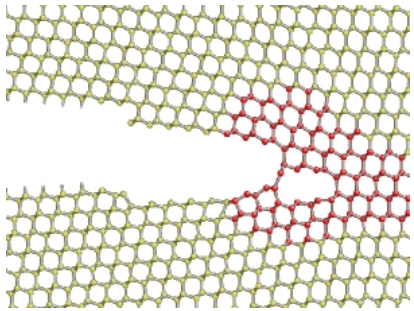
IPAM, August 27-29, 2018

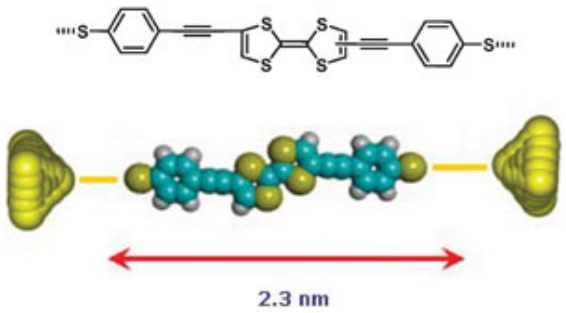
Molecular simulation at a glance

- ∼30,000 research articles in 2017
- ∼25% of CPU time in scientific computing centers in 2017
- very broad scope of applications in









chemistry drug design materials science nanotechnologies

- 1998 and 2013 Nobel Prizes in Chemistry
  (Kohn & Pople; Karplus, Levitt & Warshel)
- inexhaustible source of exciting problems for mathematicians and computer scientists

Molecular simulation is commonly used

- to explain experimental data
- to predict the properties of new molecules, materials and nanodevices

Possible contributions of applied mathematicians

1. design faster algorithms

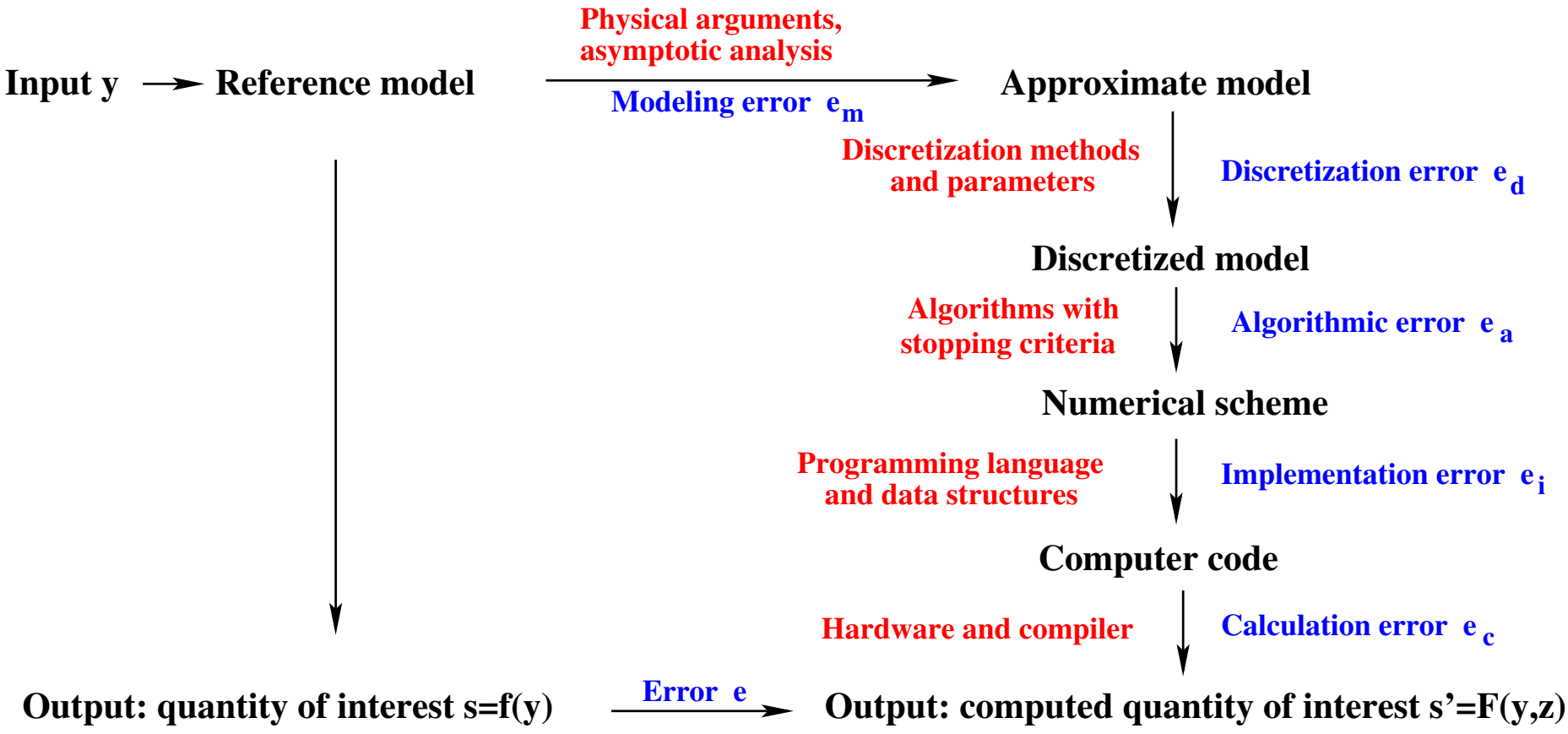
2. assess the accuracy of simulation results (error analysis)

   $\longrightarrow$ part I of the talk

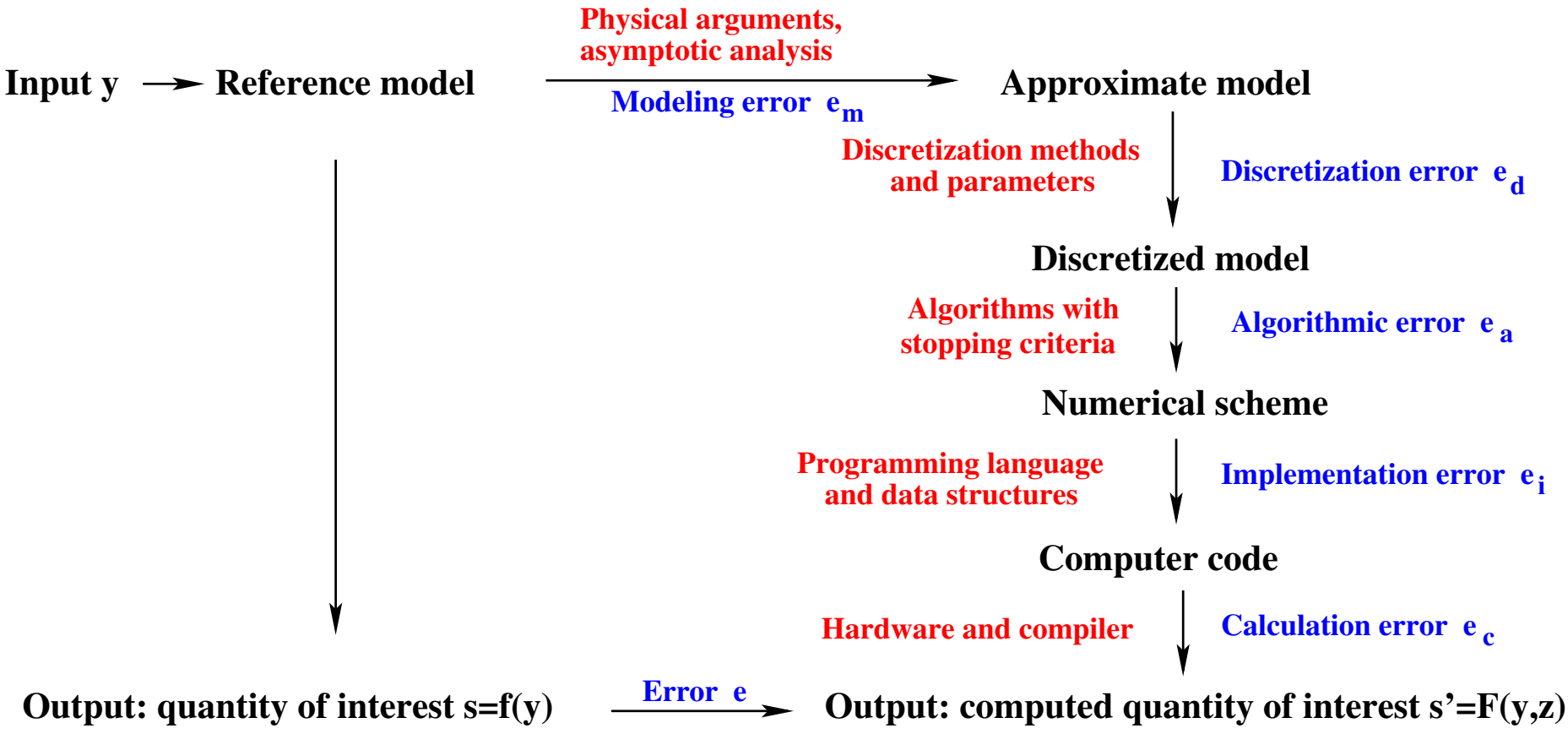
3. design mathematically justified reduced models more amenable to numerical simulation

   $\longrightarrow$ part II of the talk (quantum dots in crystalline matrices)

1 - Toward certified and optimized first-principle simulations

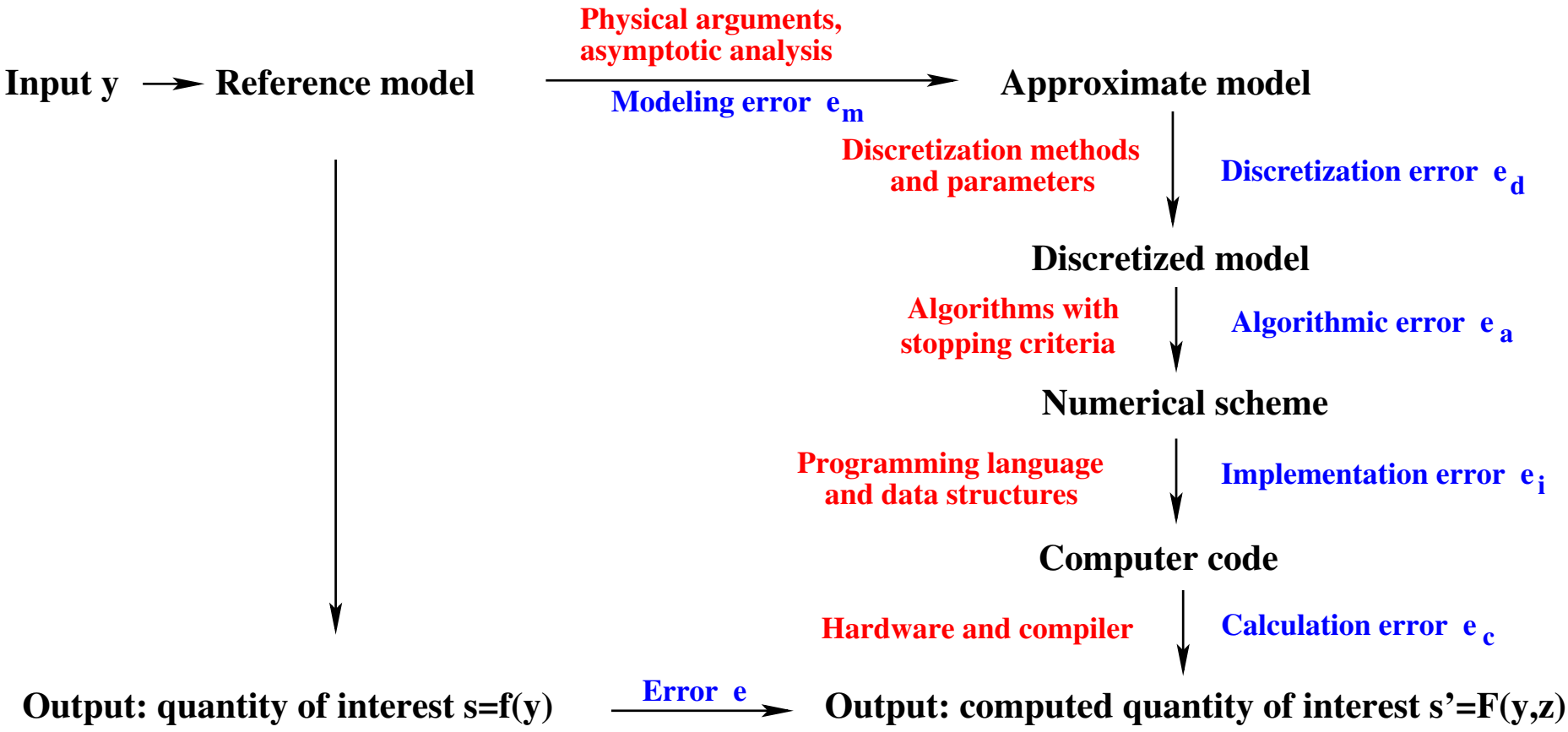


Total error: $\mathbf{e} = \mathbf{e}_{\mathrm{m}} + \mathbf{e}_{\mathrm{d}} + \mathbf{e}_{\mathrm{a}} + \mathbf{e}_{\mathrm{i}} + \mathbf{e}_{\mathrm{c}}$



Total error: $e = e_m + e_d + e_a + e_i + e_c$

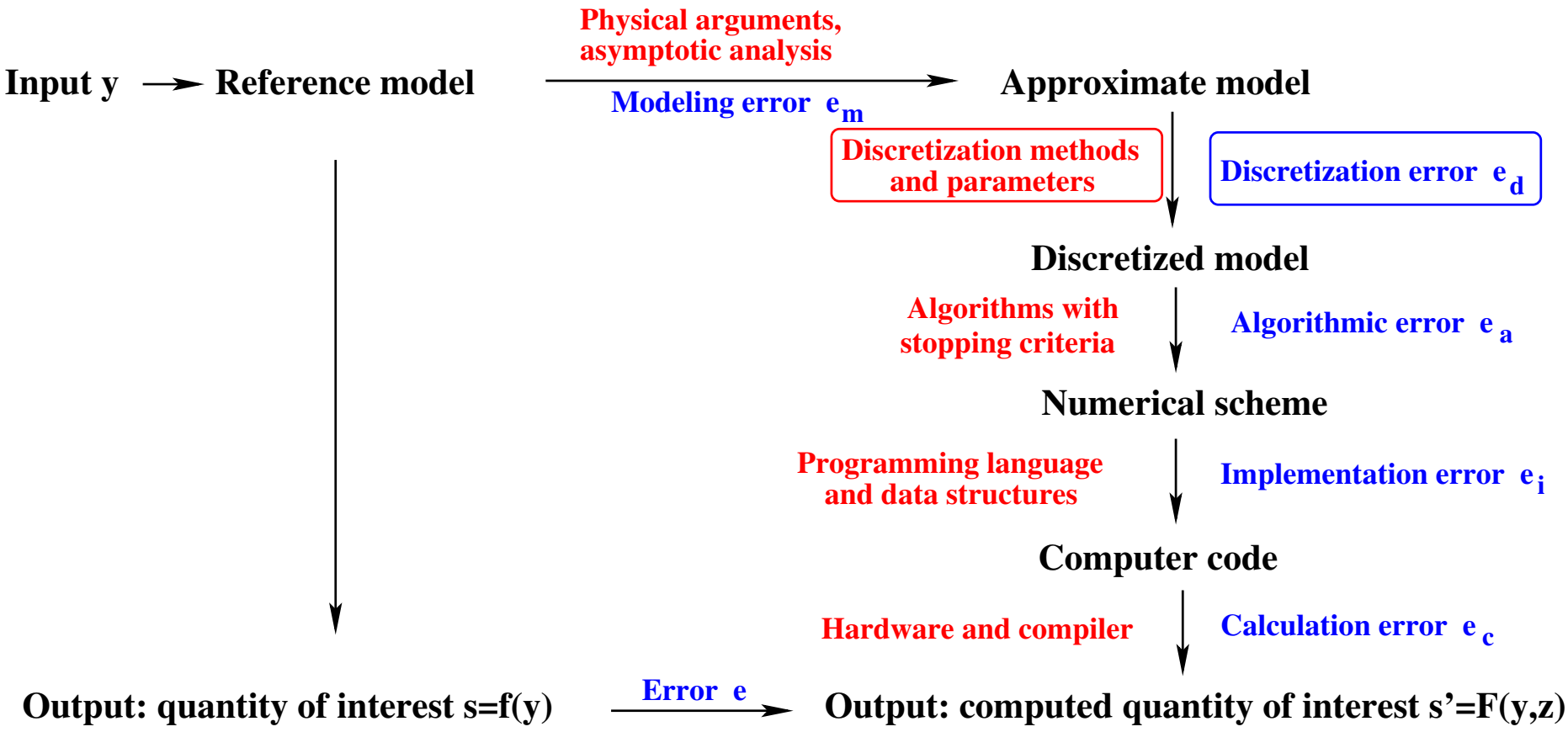
Goal 1: provide error estimates (certification)



Total error: $e = e_m + e_d + e_a + e_i + e_c$

Goal 1: provide error estimates (certification)

Goal 2: optimize dynamically the computational resources (error balancing)



Total error: $e = e_m + e_d + e_a + e_i + e_c$

Goal 1: provide error estimates (certification)

Goal 2: optimize dynamically the computational resources (error balancing)

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**
- **they are obtained from the solution u of an auxiliary infinite-dimensional problem (e.g. a PDE such as the Schrödinger equation).**

Exact value of the QOI: $q(u)$

Computed value of the QOI: $q(u_{\mathcal{N}})$ **($\mathcal{N}$: discretization parameters)**

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**
- **they are obtained from the solution u of an auxiliary infinite-dimensional problem (e.g. a PDE such as the Schrödinger equation).**

Exact value of the QOI: $q(u)$

Computed value of the QOI: $q(u_{\mathcal{N}})$ **($\mathcal{N}$: discretization parameters)**

Assessing the quality of a scalar QOI is usually easy

$$|q(u_{\mathcal{N}}) - q(u)| \leq \textbf{tolerance} \quad \Rightarrow \quad \textbf{OK}$$
$$|q(u_{\mathcal{N}}) - q(u)| > \textbf{tolerance} \quad \Rightarrow \quad \textbf{not OK}$$

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**
- **they are obtained from the solution u of an auxiliary infinite-dimensional problem (e.g. a PDE such as the Schrödinger equation).**

Exact value of the QOI: $q(u)$

Computed value of the QOI: $q(u_{\mathcal{N}})$ **($\mathcal{N}$: discretization parameters)**

Assessing the quality of a scalar QOI is usually easy

$$|q(u_{\mathcal{N}}) - q(u)| \leq \textbf{tolerance} \quad \Rightarrow \quad \textbf{OK}$$
$$|q(u_{\mathcal{N}}) - q(u)| > \textbf{tolerance} \quad \Rightarrow \quad \textbf{not OK}$$

There are however some caveats

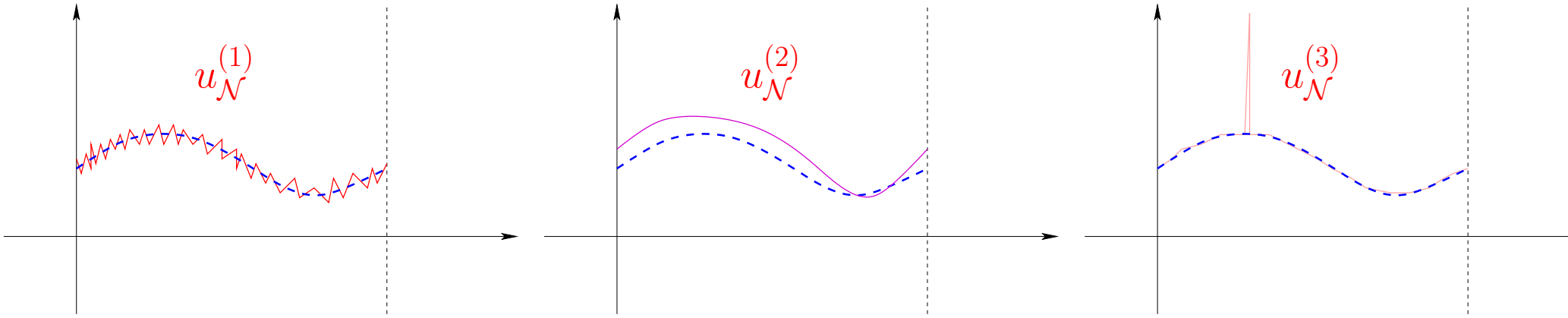
For example, energy errors *per atom* are irrelevant QOI for

- **large, inhomogeneous systems (e.g. local defects in crystals);**
- **when seeking rare events in the framework of large deviation theory.**

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**
- **they are obtained from the solution u of an auxiliary infinite-dimensional problem (e.g. a PDE such as the Schrödinger equation).**

The quality of the numerical solution $u_{\mathcal{N}}$ depends on the QOI

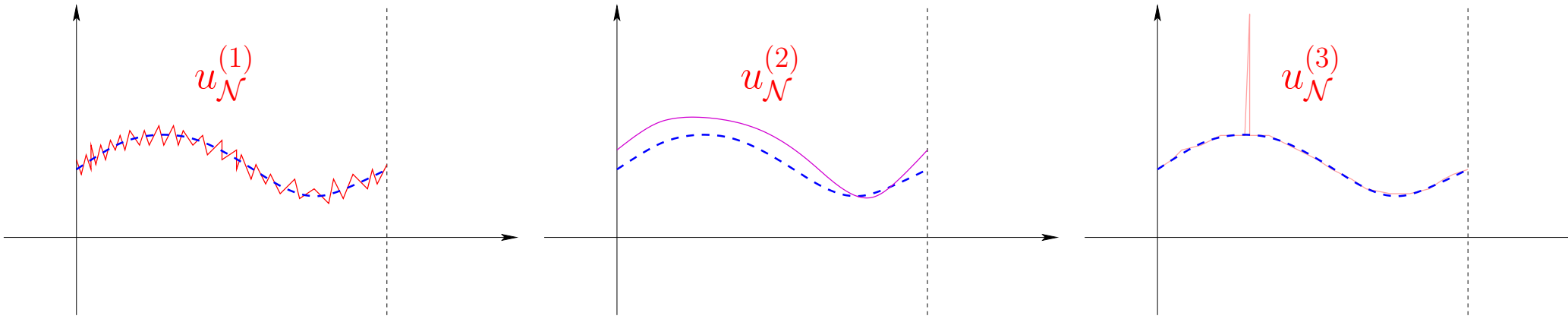


Which of these three approximations is the best?

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**
- **they are obtained from the solution u of an auxiliary infinite-dimensional problem (e.g. a PDE such as the Schrödinger equation).**

The quality of the numerical solution $u_{\mathcal{N}}$ depends on the QOI

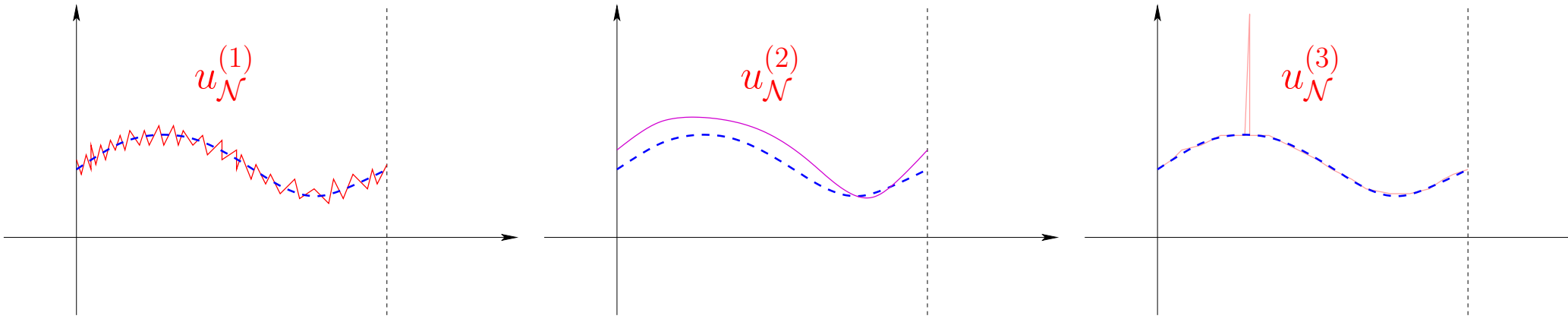


Quantity of interest	$q_1(u) = \int_0^1 u(x)^2\,dx$	$q_2(u) = \int_0^1 u'(x)^2\,dx$	$q_3(u) = \int_{1/2}^1 u(x)^2\,dx$
Best approximation	$u_{\mathcal{N}}^{(1)}$	$u_{\mathcal{N}}^{(2)}$	$u_{\mathcal{N}}^{(3)}$
Worse approximation	$u_{\mathcal{N}}^{(3)}$	$u_{\mathcal{N}}^{(1)}$	$u_{\mathcal{N}}^{(2)}$

Usual setting in science and engineering

- **the quantities of interest (QOI) can be scalar quantities (energies), finite-dimensional vectors (interatomic forces), or functions (spectra);**
- **they are obtained from the solution u of an auxiliary infinite-dimensional problem (e.g. a PDE such as the Schrödinger equation).**

The quality of the numerical solution $u_{\mathcal{N}}$ depends on the QOI



As a consequence, we need to have at our disposal several norms to measure distances between u and its approximation $u_{\mathcal{N}}$

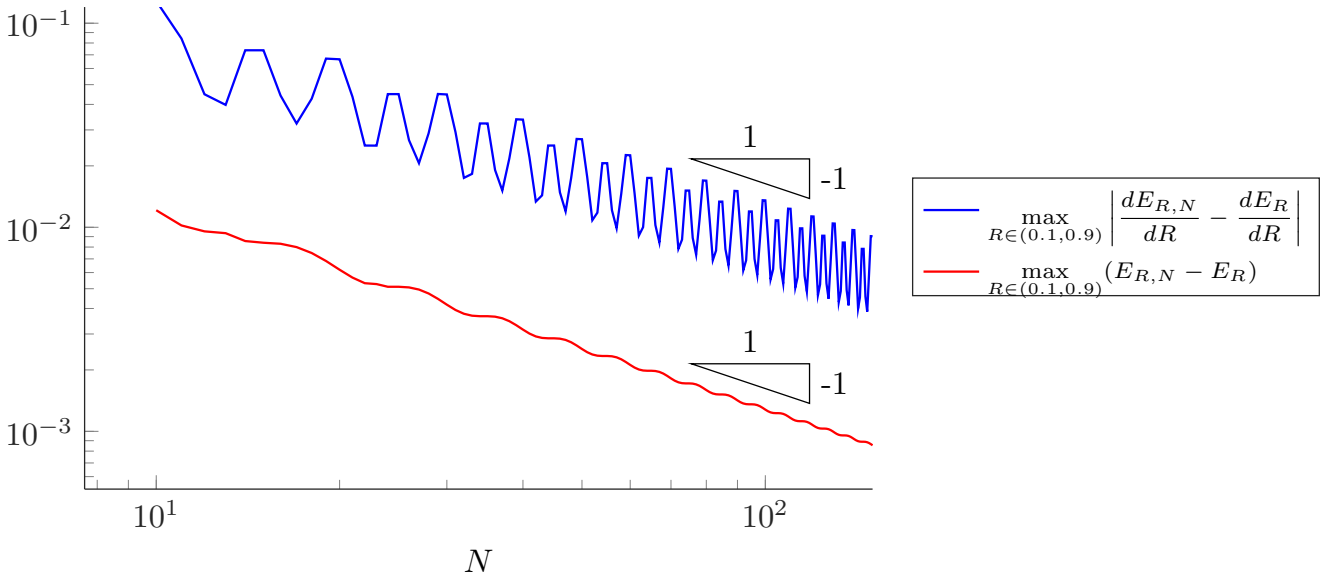
$\longrightarrow$ **deriving useful error estimators requires advanced functional analysis**

Three kinds of error analysis results

1. *A priori* error estimators

$$|q(u_{\mathcal{N}}) - q(u)| \leq C_1 \|u_{\mathcal{N}} - u\|_\star^\sigma, \quad \|u_{\mathcal{N}} - u\|_\star \leq \frac{C_2}{\mathcal{N}^s} \quad (\textbf{or } C_2\, e^{-\alpha N})$$

- **the norm $\|\cdot\|_\star$ depends on the QOI**
- **the rate of decay $s > 0$ depends on the norm $\|\cdot\|_\star$ and on the PDE**
- **the constants C_1 and C_2 are (usually) not known explicitly**



Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \precsim q(u_{\mathcal{N}}) - q(u) \precsim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

↑	↑	↑	↑
lower bound of the error	**computed value**	**exact value**	**upper bound of the error**

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \;\precsim\; q(u_{\mathcal{N}}) - q(u) \;\precsim\; \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

- **guaranteed ($\precsim$ can be replaced by $\leq$)**

  or at least:

  – asymptotically guaranteed (for $\mathcal{N}$ large enough)

  – or guaranteed provided some checkable condition is satisfied

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \lesssim q(u_{\mathcal{N}}) - q(u) \lesssim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

- **guaranteed**
- **fully computable (from $u_{\mathcal{N}}$ and the data)**
  or at least, the leading terms (for $\mathcal{N}$ large) should be fully computable

$$\eta_{j,\text{l.b.}}(u_{\mathcal{N}}, u) = \underbrace{\eta^{(1)}_{j,\text{l.b.}}(u_{\mathcal{N}})}_{\sim C\mathcal{N}^{-s}} + \underbrace{\eta^{(2)}_{j,\text{l.b.}}(u_{\mathcal{N}}, u)}_{o(\mathcal{N}^{-s})}$$

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \lesssim q(u_{\mathcal{N}}) - q(u) \lesssim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

- **guaranteed**
- **fully computable**
- **accurate**

  Efficiency factor: $C_{\text{eff}} \geq 1$ such that for all (possibly large enough) $\mathcal{N}$,

  $$|q_j(u_{\mathcal{N}}) - q_j(u))| \leq \max(|\eta_{j,\text{l.b.}}(u_{\mathcal{N}})|, |\eta_{j,\text{u.b.}}(u_{\mathcal{N}})|) \leq C_{\text{eff}} |q_j(u_{\mathcal{N}}) - q_j(u))|.$$

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \lesssim q(u_{\mathcal{N}}) - q(u) \lesssim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

- **guaranteed**
- **fully computable**
- **accurate**

  Some *a posteriori* **estimators are asymptotically exact:**

$$\eta_{j,\text{l.b.}}(u_{\mathcal{N}}) \underset{\mathcal{N}\to\infty}{\sim} q_j(u_{\mathcal{N}}) - q_j(u) \underset{\mathcal{N}\to\infty}{\sim} \eta_{j,\text{u.b.}}(u_{\mathcal{N}})$$

  The *a posteriori* **error estimator can then be used for post-treatment: for large $\mathcal{N}$, $q_j(u_{\mathcal{N}}) - \eta_{j,\star\text{.b.}}(u_{\mathcal{N}})$ provide better approximations of $q_j(u)$**

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \lesssim q(u_{\mathcal{N}}) - q(u) \lesssim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

- **guaranteed**
- **fully computable**
- **accurate**
- **cheap to compute**

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \lesssim q(u_{\mathcal{N}}) - q(u) \lesssim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

- **guaranteed**
- **fully computable**
- **accurate**
- **cheap to compute**
- **robust, e.g. valid for any molecular configuration, or at least valid in some interesting set of molecular configurations**

Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

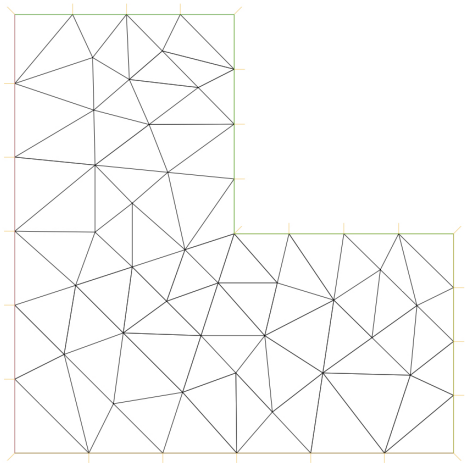
$$\eta_{\text{l.b.}}(u_{\mathcal{N}}) \lesssim q(u_{\mathcal{N}}) - q(u) \lesssim \eta_{\text{u.b.}}(u_{\mathcal{N}})$$

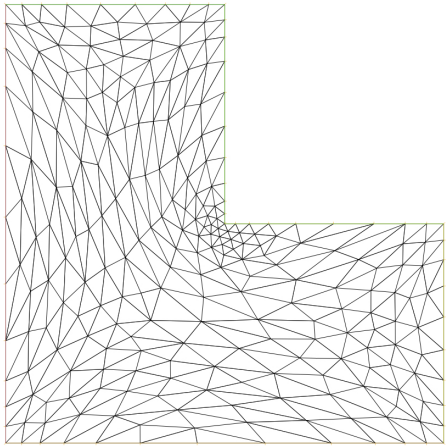
Ideally, the lower and upper bounds $\eta_{\text{l.b.}}(u_{\mathcal{N}})$ and $\eta_{\text{u.b.}}(u_{\mathcal{N}})$ should be

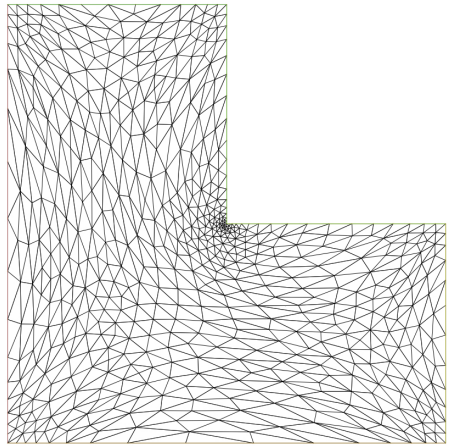
- **guaranteed**
- **fully computable**
- **accurate**
- **cheap to compute**
- **robust**
- **able to guide black-box improvement methods**

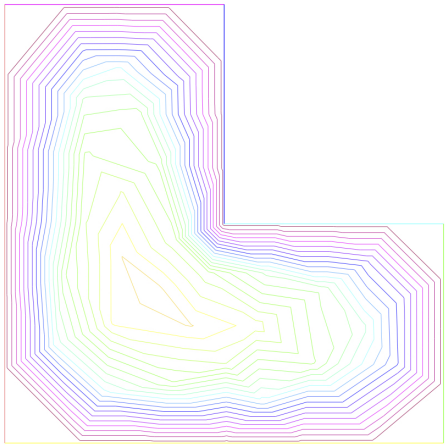
Automatic mesh refinement for a finite element computation

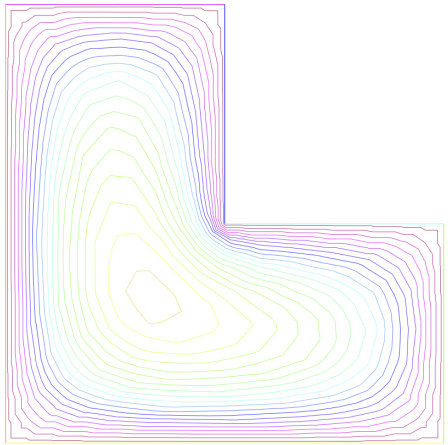
find $u : \Omega \to \mathbb{R}$ **such that** $-\Delta u(x) = 1$ **in** Ω, $u(x) = 0$ **on** $\partial\Omega$

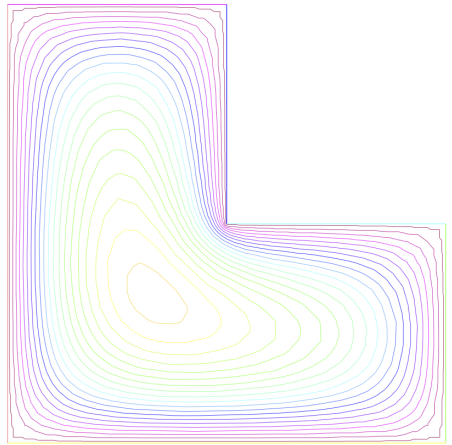












86 triangles **448 triangles** **1119 triangles**

A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

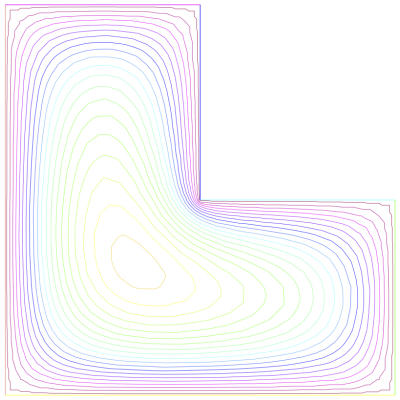
	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace							
Schrödinger							
Gross-Pitaevskii							
Kohn-Sham							

A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace	**FE**	✓	✓	✓	✓	**fairly**	✓
Schrödinger							
Gross-Pitaevskii							
Kohn-Sham							

Laplace operator on a bounded polyhedral domain

$$-\Delta u = \lambda u \quad \textbf{in } \Omega, \qquad u = 0 \quad \textbf{on } \partial\Omega, \qquad \int_\Omega u^2 = 1$$



QOI: the j^{th} eigenvalue (robustness $\downarrow$ when $j \uparrow$)

EC, Dusson, Maday, Stamm, Vohralík, SINUM '17 + submitted

following many previous works by many authors listed in the bibliography

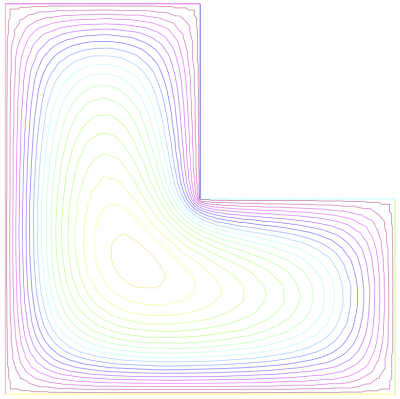
A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace	**FE**	✓	✓	✓	✓	**fairly**	✓
Schrödinger							
Gross-Pitaevskii							
Kohn-Sham							

Laplace operator on a bounded polyhedral domain

$$-\Delta u = \lambda u \quad \textbf{in } \Omega, \qquad u = 0 \quad \textbf{on } \partial\Omega, \qquad \int_\Omega u^2 = 1$$

QOI: the j^{th} eigenvalue (robustness $\downarrow$ when $j \uparrow$)



EC, Dusson, Maday, Stamm, Vohralík, SINUM '17 + submitted

Main ideas: residual norm estimates, local conforming residual liftings (lower bound) and equilibrated flux reconstruction (upper bound).

A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace	**FE**	✓	✓	✓	✓	**fairly**	✓
Schrödinger	**FE**	✓	✓	✓	✓	**not much**	✓
Gross-Pitaevskii							
Kohn-Sham							

Schrödinger equation on a bounded polyhedral domain

$$-\Delta u + Vu = Eu \quad \textbf{in } \Omega, \qquad u = 0 \quad \textbf{on } \partial\Omega, \qquad \int_\Omega u^2 = 1$$

QOI: the j^{th} eigenvalue (robustness $\downarrow$ when $j \uparrow$ or $\|V\|_{L^\infty} \uparrow$)

EC, Dusson, Maday, Stamm, Vohralík, submitted

Main ideas: residual norm estimates, local conforming residual liftings (lower bound) and equilibrated flux reconstruction (upper bound).

A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace	**FE**	✓	✓	✓	✓	**fairly**	✓
Schrödinger	**PW**	**asymp.**	✓	**a. exact**	✓	✓	**NA**
Gross-Pitaevskii							
Kohn-Sham							

Schrödinger equation with periodic boundary conditions

$$-\Delta u + Vu = Eu, \quad u \in H^1_{\mathrm{per}}(\Omega), \quad \Omega = (0, 2\pi)^d, \quad \int_\Omega u^2 = 1$$

QOI: clusters of eigenvalues (gap assumption)

EC, Dusson, Maday, Stamm, Vohralík, in preparation

Main idea: consider the exact solution as a perturbation of the approximate solution and use Rayleigh-Schrödinger perturbation theory.

A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace	**FE**	✓	✓	✓	✓	**fairly**	✓
Schrödinger	**PW**	**asymp.**	✓	**a. exact**	✓	✓	**NA**
Gross-Pitaevskii	**PW**	**asymp.**	**lead. terms**	**a. exact**	✓	✓	**NA**
Kohn-Sham							

Gross-Pitaevskii equation with periodic boundary conditions

$$-\Delta u + Vu + \mu u^3 = \lambda u, \quad u \in H^1_{\mathrm{per}}(\Omega), \quad \Omega = (0, 2\pi)^d, \quad \int_\Omega u^2 = 1$$

QOIs: ground state energy and density

EC, Dusson, Maday, Stamm, Vohralík, CRM '14

Main idea: consider the exact solution as a perturbation of the approximate solution and use nonlinear Rayleigh-Schrödinger perturbation theory.

A posteriori error estimators for linear and nonlinear elliptic eigenvalue problems

	disc.	guaranteed	fully comput.	accurate	cheap	robust	aut. improv.
Laplace	**FE**	✓	✓	✓	✓	**fairly**	✓
Schrödinger	**PW**	**asymp.**	✓	**a. exact**	✓	✓	**NA**
Gross-Pitaevskii	**PW**	**asymp.**	**lead. terms**	**a. exact**	✓	✓	**NA**
Kohn-Sham	**PW**	**asymp.**	**lead. terms**	**a. exact**	✓	✓	**NA**

Kohn-Sham LDA equations on a periodic supercell Ω

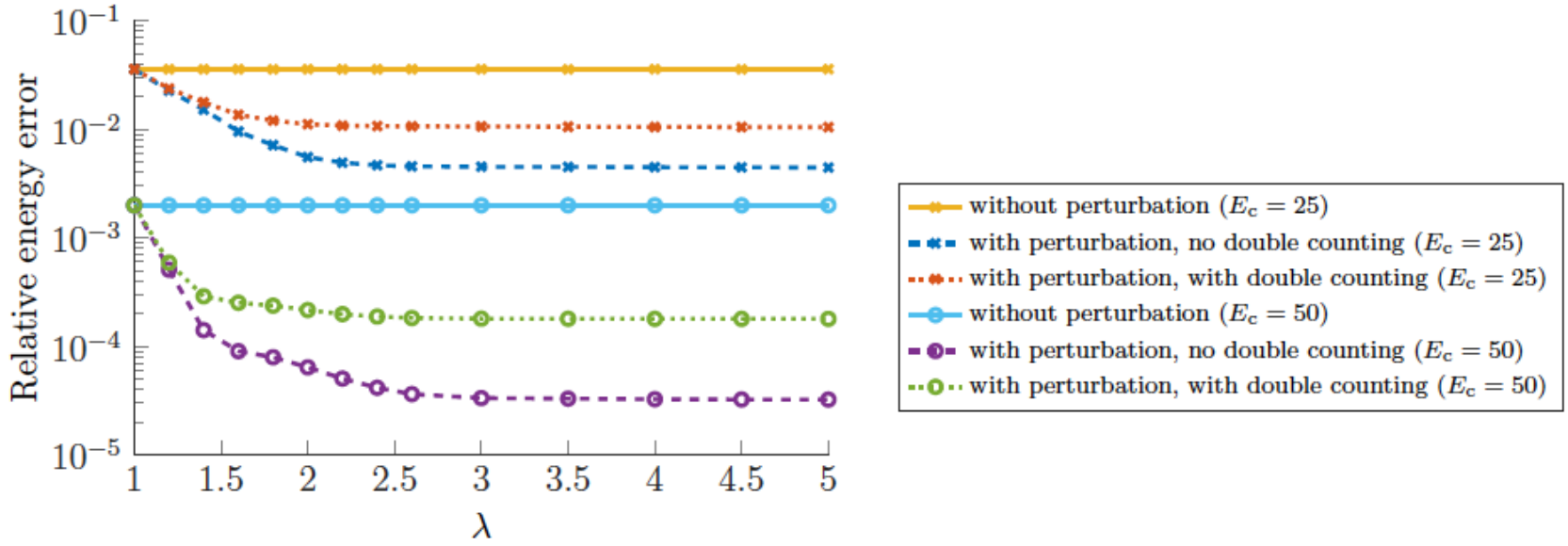
$$-\frac{1}{2}\Delta\phi_i + V_{\rho_\Phi}^{\mathrm{KS}}\phi_i = \varepsilon_i\phi_i, \quad \Phi = (\phi_1, \cdots, \phi_N) \in (H^1_{\mathrm{per}}(\Omega))^N, \quad \int_\Omega \phi_i\phi_j = \delta_{ij}, \quad \rho_\Phi = \sum_{i=1}^N |\phi_i|^2$$

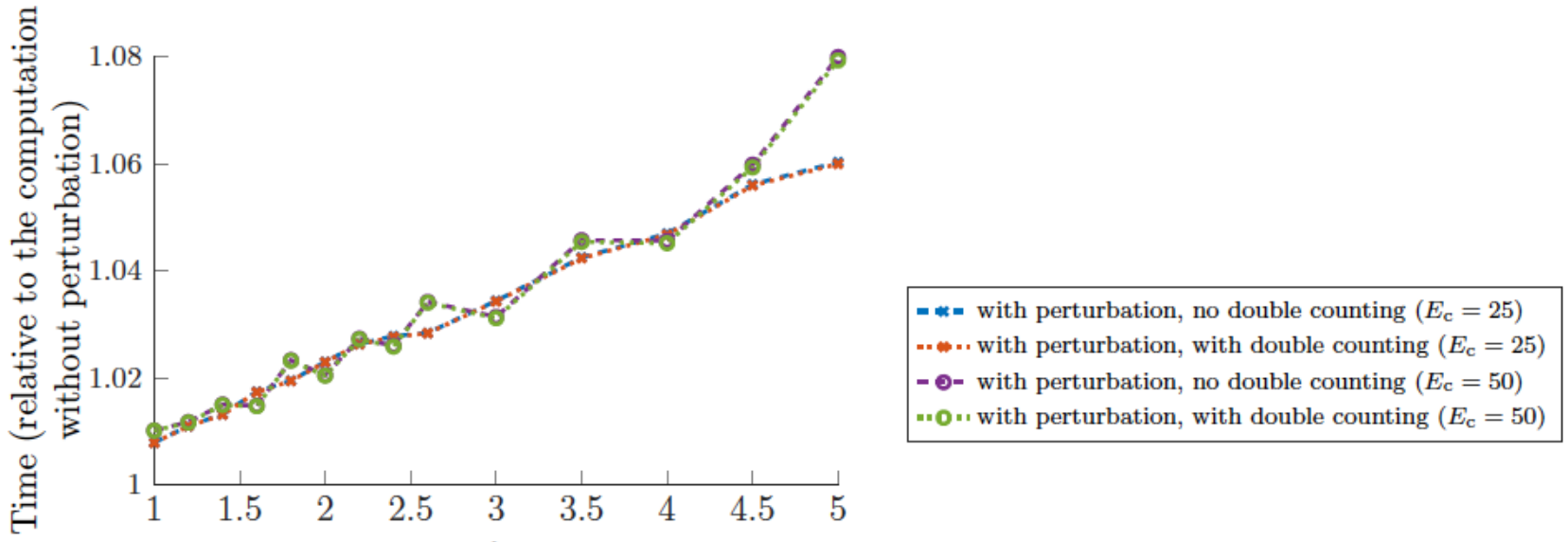
QOIs: ground state energy and density

EC, Dusson, Maday, Stamm, Vohralík, J. Comp. Phys. '16

Main idea: consider the exact solution as a perturbation of the approximate solution and use nonlinear Rayleigh-Schrödinger perturbation theory.

CO_2 molecule, KS-LDA, Troullier-Martins pseudopotentiels, KSSOLV





Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

3. Asymptotic expansions

$$q(u_{\mathcal{N}}) - q(u) = \frac{\alpha}{\mathcal{N}^{5/3}} + \frac{\beta}{\mathcal{N}^{2}} + \frac{\gamma}{\mathcal{N}^{7/3}} + o\left(\frac{1}{\mathcal{N}^{7/3}}\right)$$

- **allow extrapolation**

  Makov-Payne correction, Gontier & Lahbabi '15

  smearing methods for k-point sampling in metals, EC et al. submitted

- **not so common in practice**
- **only useful in the asymptotic regime**
- **completely useless in the pre-asymptotic regime**

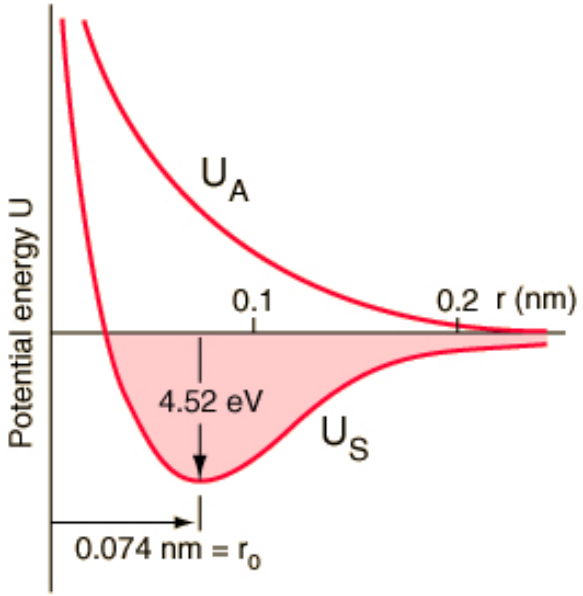
Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

3. Asymptotic expansions

$$q(u_{\mathcal{N}}) - q(u) = \frac{\alpha}{\mathcal{N}^{5/3}} + \frac{\beta}{\mathcal{N}^{2}} + \frac{\gamma}{\mathcal{N}^{7/3}} + o\left(\frac{1}{\mathcal{N}^{7/3}}\right)$$



Three kinds of error analysis results

1. *A priori* **error estimators**

2. *A posteriori* **error estimators**

3. Asymptotic expansions

$$q(u_{\mathcal{N}}) - q(u) = \frac{\alpha}{\mathcal{N}^{5/3}} + \frac{\beta}{\mathcal{N}^{2}} + \frac{\gamma}{\mathcal{N}^{7/3}} + o\left(\frac{1}{\mathcal{N}^{7/3}}\right)$$

- **allow extrapolation**
- **not so common in practice**
- **only useful in the asymptotic regime**
- **completely useless in the pre-asymptotic regime**

Warning: in general, it is not possible to derive asymptotic expansions w.r.t. external parameters

e.g.: error estimators for energy differences and forces (EC, Dusson '17)

2 - Quantum dots embedded in crystalline matrices

Reference model for the mathematical analysis: reduced Hartree-Fock (Kohn-Sham with $E^{\rm xc} = 0$)

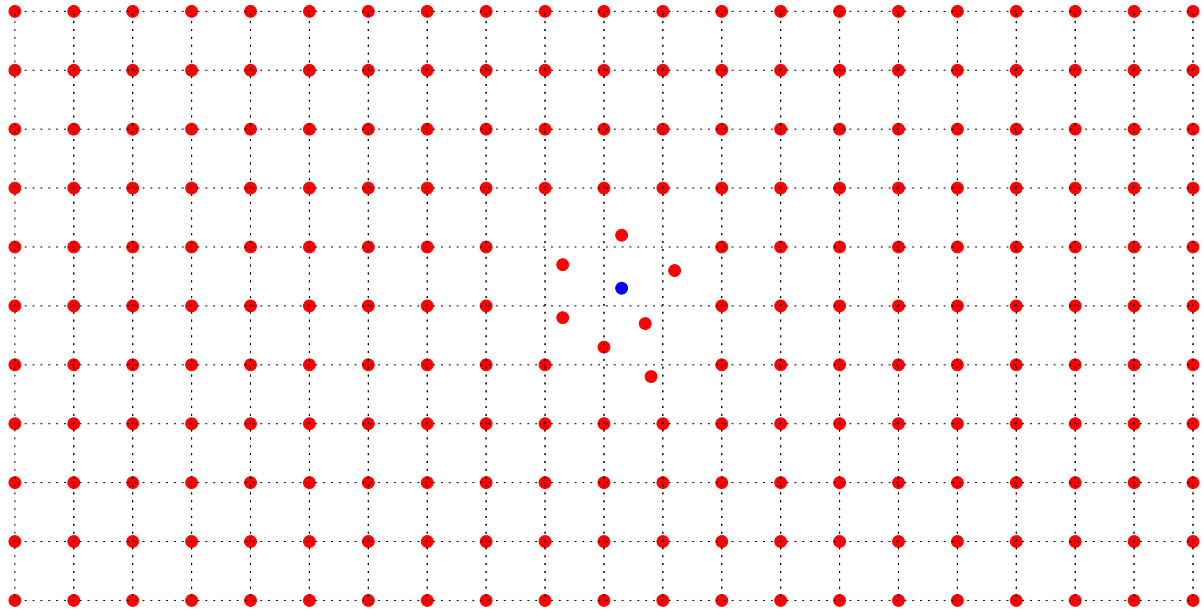
Existence of a ground state density matrix for neutral systems
Uniqueness of the ground state density (Solovej, Invent. Math. '91)

EC, A. Deleurence and M. Lewin, Comm. Math. Phys. '08
EC and M. Lewin, Arch. Ration. Mech. Anal. '10
EC and G. Stoltz, Ann. IHP '12
EC, S. Lahbabi and M. Lewin, J. Pure Appl. Math. '13

The resulting embedding model can be used for Kohn-Sham calculations

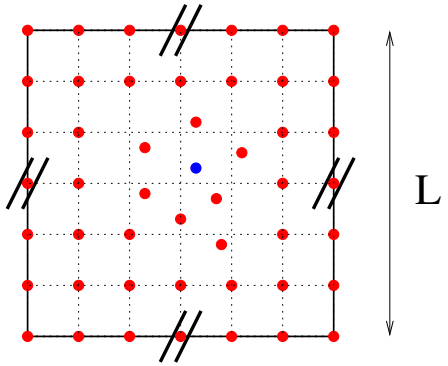
EC, A. Deleurence and M. Lewin, J. Phys.: Cond. Mat. '08

A quantum dot can be seen as a defect on the surface or in the bulk of an insulator or a semiconductor

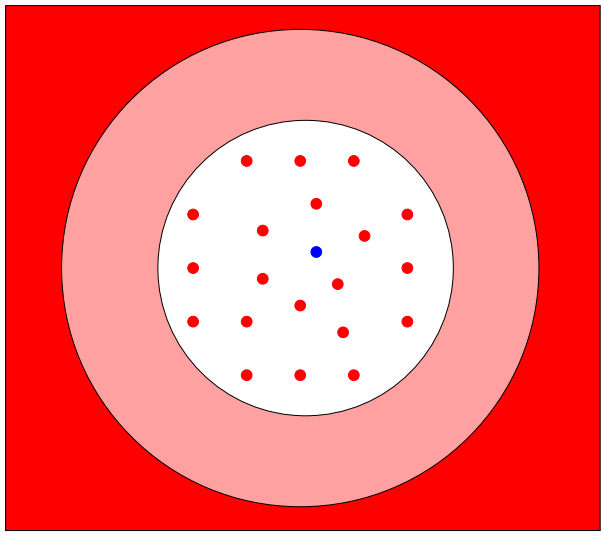


Usual approaches:

- supercell model
- perturbative methods, Green functions
- phenomenological embedding methods

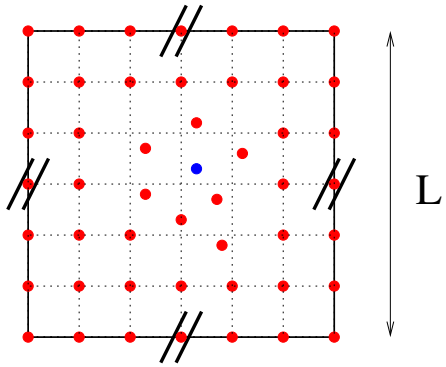


Supercell



Phenomenological embedding

The supercell method and its shortcomings

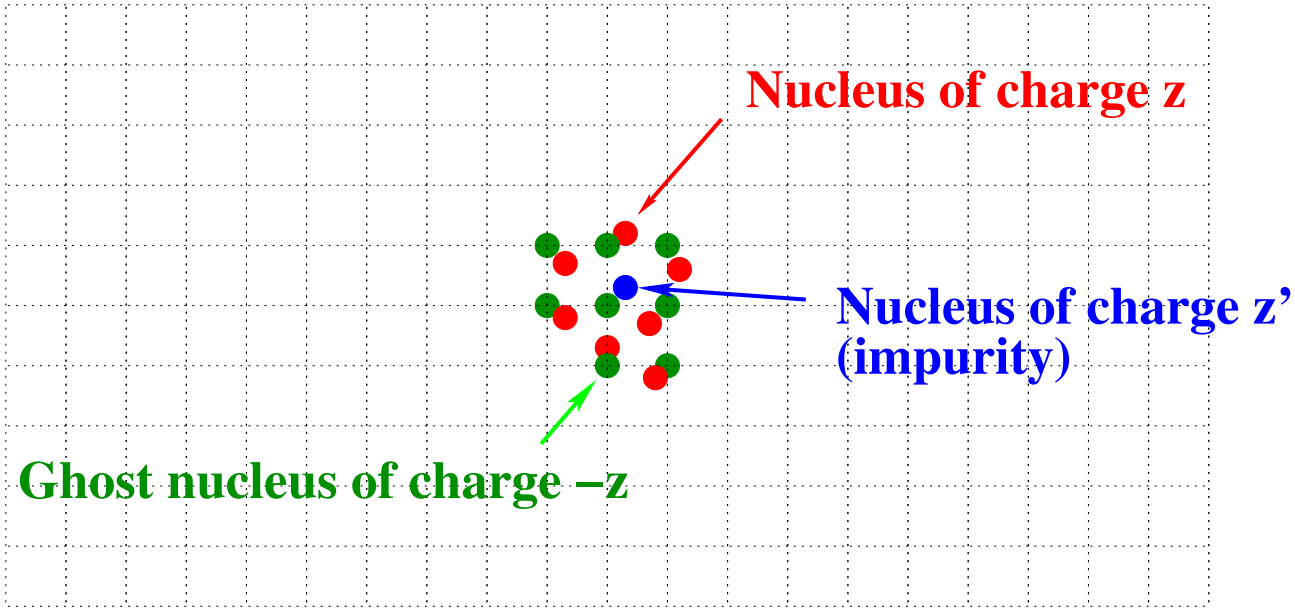


- **spurious interactions between the defects and its periodic images**
- **the total charge distribution ρ in the supercell must be neutral; otherwise the Poisson equation $-\Delta V = 4\pi\rho$ has no periodic solution**

Defect = quasi-molecule embedded in the host crystal

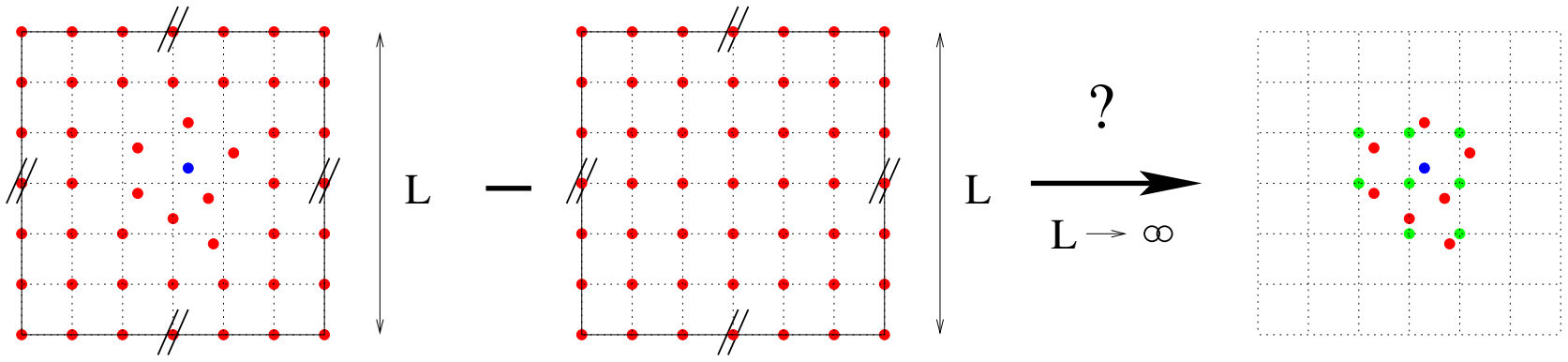
$$\rho^{\mathrm{nuc}} = \rho^{\mathrm{nuc}}_{\mathrm{per}} + m \qquad \gamma^{0} = \gamma^{0}_{\mathrm{per}} + Q^{m,\varepsilon_{\mathrm{F}}} \qquad \rho^{0} = \rho^{0}_{\mathrm{per}} + \rho^{m,\varepsilon_{\mathrm{F}}}$$

Nuclear charge m of the quasi-molecule



Goal: **find a way to directly compute $Q^{m,\varepsilon_{\mathrm{F}}}$ and $\rho^{m,\varepsilon_{\mathrm{F}}}$**

Bulk limit of the supercell model, with and without defect



$E^{m,\varepsilon_{\rm F}}_{{\rm sc},L}, \rho^{m,\varepsilon_{\rm F}}_{{\rm sc},L}, \gamma^{m,\varepsilon_{\rm F}}_{{\rm sc},L}$ $\qquad$ $E^{0}_{{\rm sc},L}, \rho^{0}_{{\rm sc},L}, \gamma^{0}_{{\rm sc},L}$ $\qquad$ $\varepsilon^{m,\varepsilon_{\rm F}}, \rho^{m,\varepsilon_{\rm F}}, Q^{m,\varepsilon_{\rm F}}$

Theorem (EC, Deleurence, Lewin, Comm. Math. Phys. '08). Assume that the host crystal is an insulator or a semiconductor. Then

1. $(\rho^{0}_{{\rm sc},L}, \gamma^{0}_{{\rm sc},L})$ **converges to** $(\rho^{0}_{\rm per}, \gamma^{0}_{\rm per})$ **when** L **goes to infinity**

2. $E^{m,\varepsilon_{\rm F}}_{{\rm sc},L} - E^{0}_{{\rm sc},L}$ **has a finite limit** $\varepsilon^{m,\varepsilon_{\rm F}}$

• **A self-adjoint operator Q on $L^2(\mathbb{R}^3)$ is called trace-class if**

$$Q = \sum_{i=1}^{+\infty} \lambda_i |\phi_i\rangle\langle\phi_i| \qquad \textbf{with} \qquad \langle\phi_i|\phi_j\rangle = \delta_{ij}, \qquad \sum_{i=1}^{+\infty} |\lambda_i| < \infty$$

If Q is trace-class then

$$\rho_Q(\mathbf{r}) = Q(\mathbf{r},\mathbf{r}) = \sum_{i=1}^{+\infty} \lambda_i |\phi_i(\mathbf{r})|^2 \in L^1(\mathbb{R}^3)$$

and for any orthonormal basis $(e_n)_{n\in\mathbb{N}}$ of $L^2(\mathbb{R}^3)$,

$$\int_{\mathbb{R}^3} \rho_Q = \mathbf{Tr}(Q) = \sum_{i=1}^{+\infty} \lambda_i = \sum_{n\in\mathbb{N}} \langle e_n|Q|e_n\rangle = \textbf{ charge of } Q$$

• **A self-adjoint operator Q on $L^2(\mathbb{R}^3)$ is called Hilbert-Schmidt if**

$$Q = \sum_{i=1}^{+\infty} \lambda_i |\phi_i\rangle\langle\phi_i| \qquad \textbf{with} \qquad \langle\phi_i|\phi_j\rangle = \delta_{ij}, \qquad \sum_{i=1}^{+\infty} |\lambda_i|^2 < \infty$$

3. $\rho_{\mathrm{sc},L}^{m,\varepsilon_{\mathrm{F}}} - \rho_{\mathrm{sc},L}^{0}$ **converges to** $\rho^{m,\varepsilon_{\mathrm{F}}} \in L^2(\mathbb{R}^3)$

4. $\gamma_{\mathrm{sc},L}^{m,\varepsilon_{\mathrm{F}}} - \gamma_{\mathrm{sc},L}^{0}$ **converges to some Hilbert-Schmidt operator** $Q^{m,\varepsilon_{\mathrm{F}}}$ **(u.t.e.)**

5. $\rho^{m,\varepsilon_{\mathrm{F}}}$ **is the density associated with** $Q^{m,\varepsilon_{\mathrm{F}}}$ **in some weak sense**

Theorem (EC and Lewin, ARMA '10). As a consequence of the long-range of the Coulomb potential

- $Q^{m,\varepsilon_{\mathrm{F}}}$ **is not trace-class (except possibly when** $\displaystyle\int_{\mathbb{R}^3} m = 0$**)**

  Reminiscent of the renormalization problem in QED

  (see Gravejat, Lewin, Séré for a mathematical analysis)

- $\rho^{m,\varepsilon_{\mathrm{F}}}$ **is not an integrable function for anisotropic crystals**

There exist two orthonormal bases $(\phi_n)_{n\in\mathbb{N}}$ **and** $(\psi_n)_{n\in\mathbb{N}}$ **of** $L^2(\mathbb{R}^3)$ **such that**

$$\sum_{n=0}^{+\infty} \langle \phi_n | Q^{m,\varepsilon_{\mathrm{F}}} | \phi_n \rangle \quad \neq \quad \sum_{n=0}^{+\infty} \langle \psi_n | Q^{m,\varepsilon_{\mathrm{F}}} | \psi_n \rangle \quad \neq \quad \lim_{R\to+\infty} \int_{|\mathbf{r}|<R} \rho^{m,\varepsilon_{\mathrm{F}}}(\mathbf{r})\, d\mathbf{r}$$

How to define the electronic charge of the defect?

Definitions of the "bare" and "renormalized" charges of the defect

There exists

- **an orthonormal basis** $(\phi_i^-)_{i>N_-}$ **of** $\mathcal{H}_- = \mathbf{Ran}(\gamma^0_{\rm per})$
- **an orthonormal basis** $(\phi_i^+)_{i>N_+}$ **of** $\mathcal{H}_+ = \mathbf{Ran}(1-\gamma^0_{\rm per})$

such that in the orthonormal basis $((\phi_i^-),(\phi_i^+))$ **of** $L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+$

$$\gamma^0_{\rm per} = \left(\begin{array}{c||c} I & 0 \\ \hline\hline 0 & 0 \end{array}\right) \qquad Q^{m,\varepsilon_{\rm F}} = \left(\begin{array}{c|c||c|c} -I_{N_-} & 0 & 0 & 0 \\ \hline 0 & \mathbf{diag}(-a_1,-a_2,\cdots) & 0 & \mathbf{diag}(b_1,b_2,\cdots) \\ \hline\hline 0 & 0 & I_{N_+} & 0 \\ \hline 0 & \mathbf{diag}(b_1,b_2,\cdots) & 0 & \mathbf{diag}(a_1,a_2,\cdots) \end{array}\right)$$

with

$$0 \le a_i < 1, \qquad \sum_{i=1}^{+\infty} a_i < +\infty, \qquad b_i = \sqrt{a_i(1-a_i)}$$

$$\boxed{\mathbf{Tr}_0(Q^{m,\varepsilon_{\rm F}}) := \mathbf{Tr}\big([Q^{m,\varepsilon_{\rm F}}]^{++} + [Q^{m,\varepsilon_{\rm F}}]^{--}\big) = N_+ - N_- = \text{"bare" charge of } Q^{m,\varepsilon_{\rm F}}}$$

We can prove that for an isotropic crystal, there exist $\varepsilon_\mu > \varepsilon_{\mathrm{M}} > 1$ (ε_{M}: macroscopic dielectric permittivity of the host crystal) such that if the Coulomb energy of m is small enough, then

- **$\mathbf{Tr}_0(Q^{m,\varepsilon_{\mathrm{F}}}) = 0$ so that the "bare" charge of the defect is**

$$q_{\text{"bare"}} = \int_{\mathbb{R}^3} m - \mathbf{Tr}_0(Q^{m,\varepsilon_{\mathrm{F}}}) = \int_{\mathbb{R}^3} m$$

- **if $\rho_{Q^{m,\varepsilon_{\mathrm{F}}}} \in L^1(\mathbb{R}^3)$, then $\displaystyle\int_{\mathbb{R}^3} \rho_{Q^{m,\varepsilon_{\mathrm{F}}}} = \frac{\varepsilon_\mu - 1}{\varepsilon_\mu} \int_{\mathbb{R}^3} m$, and the "observed" or "renormalized" charge of the defect is**

$$q_{\text{"renormalized"}} = \int_{\mathbb{R}^3} m - \int_{\mathbb{R}^3} \rho_{Q^{m,\varepsilon_{\mathrm{F}}}} = \frac{1}{\varepsilon_\mu} \int_{\mathbb{R}^3} m$$

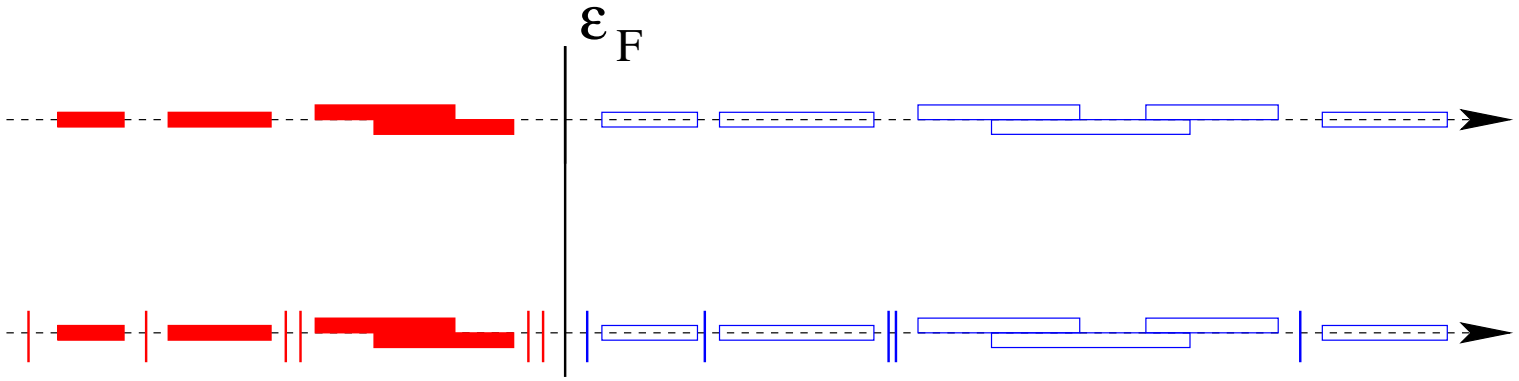
Characterization of $Q^{m,\varepsilon_{\mathrm{F}}}$

Let $\widetilde{H}_{\rho^{m,\varepsilon_{\mathrm{F}}}}$ be the Hartree Hamiltonian of the crystal with the local defect

$$\widetilde{H}_{\rho^{m,\varepsilon_{\mathrm{F}}}} = H^0_{\mathrm{per}} - V^{\mathrm{Coulomb}}_m + V^{\mathrm{Coulomb}}_{\rho^{m,\varepsilon_{\mathrm{F}}}}$$

$Q^{m,\varepsilon_{\mathrm{F}}}$ satisfies the Dyson-like self-consistent embedding equation

$$Q^{m,\varepsilon_{\mathrm{F}}} = 1_{(-\infty,\varepsilon_F]}(\widetilde{H}_{\rho^{m,\varepsilon_{\mathrm{F}}}}) - 1_{(-\infty,\varepsilon_F]}(H^0_{\mathrm{per}})$$



Can we obtained $Q^{m,\varepsilon_{\mathrm{F}}}$ by minimizing some energy functional on some variational set?

Variational characterization of $Q^{m,\varepsilon_{\rm F}}$

Let $\mathcal{H}_- = \mathbf{Ran}(\gamma^0_{\rm per})$ and $\mathcal{H}_+ = \mathbf{Ran}(1-\gamma^0_{\rm per})$. Then $L^2(\mathbb{R}^3) = \mathcal{H}_- \oplus \mathcal{H}_+$ and

$$\gamma^0_{\rm per} = \left(\begin{array}{c||c} I & 0 \\ \hline\hline 0 & 0 \end{array}\right) \qquad H^0_{\rm per} - \varepsilon_{\rm F} = \left(\begin{array}{c||c} [H^0_{\rm per} - \varepsilon_{\rm F}]^{--} \leq 0 & 0 \\ \hline\hline 0 & [H^0_{\rm per} - \varepsilon_{\rm F}]^{++} \geq 0 \end{array}\right)$$

$Q^{m,\varepsilon_{\rm F}}$ is a minimizer (and $\rho^{m,\varepsilon_{\rm F}}$ is the unique minimizing density) to

$$\inf\left\{\mathcal{E}^m_{\varepsilon_{\rm F}}(Q),\ Q \in \mathcal{Q}\right\}$$

$$\mathcal{E}^m_{\varepsilon_{\rm F}}(Q) = \mathbf{Tr}_0((H^0_{\rm per} - \varepsilon_{\rm F})Q) - \int_{\mathbb{R}^3} \rho_Q V^{\rm Coulomb}_m + \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_Q(\mathbf{r})\,\rho_Q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$

$$Q = \left(\begin{array}{c||c} Q^{--} \leq 0 & Q^{-+} \\ \textbf{trace-class} & \textbf{Hilbert-Schmidt} \\ \hline\hline Q^{+-} & Q^{++} \geq 0 \\ \textbf{Hilbert-Schmidt} & \textbf{trace-class} \end{array}\right), \qquad \begin{array}{l} Q^* = Q \\ 0 \leq \gamma^0_{\rm per} + Q \leq 1 \\ |\nabla|Q^{++}|\nabla|,\ |\nabla|Q^{--}|\nabla| \ \textbf{trace-class} \end{array}$$

Wannier Functions

The Bloch decomposition $\mathcal{H}_- =$ "Span"$(\phi_{n,\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}})_{1\leq n\leq z,\, \mathbf{k}\in \mathrm{BZ}}$ is not optimal for expanding localized functions

There exists an orthonormal basis $(\phi_{i,\mathbf{R}})_{1\leq i\leq z,\, \mathbf{R}\in\mathcal{R}}$ of $\mathcal{H}_-$ such that

$$\forall 1 \leq i \leq z,\ \mathbf{R} \in \mathcal{R}, \qquad \phi_{i,\mathbf{R}} \in L^2(\mathbb{R}^3), \qquad \phi_{i,\mathbf{R}}(\mathbf{r}) = \phi_{i,0}(\mathbf{r} - \mathbf{R})$$

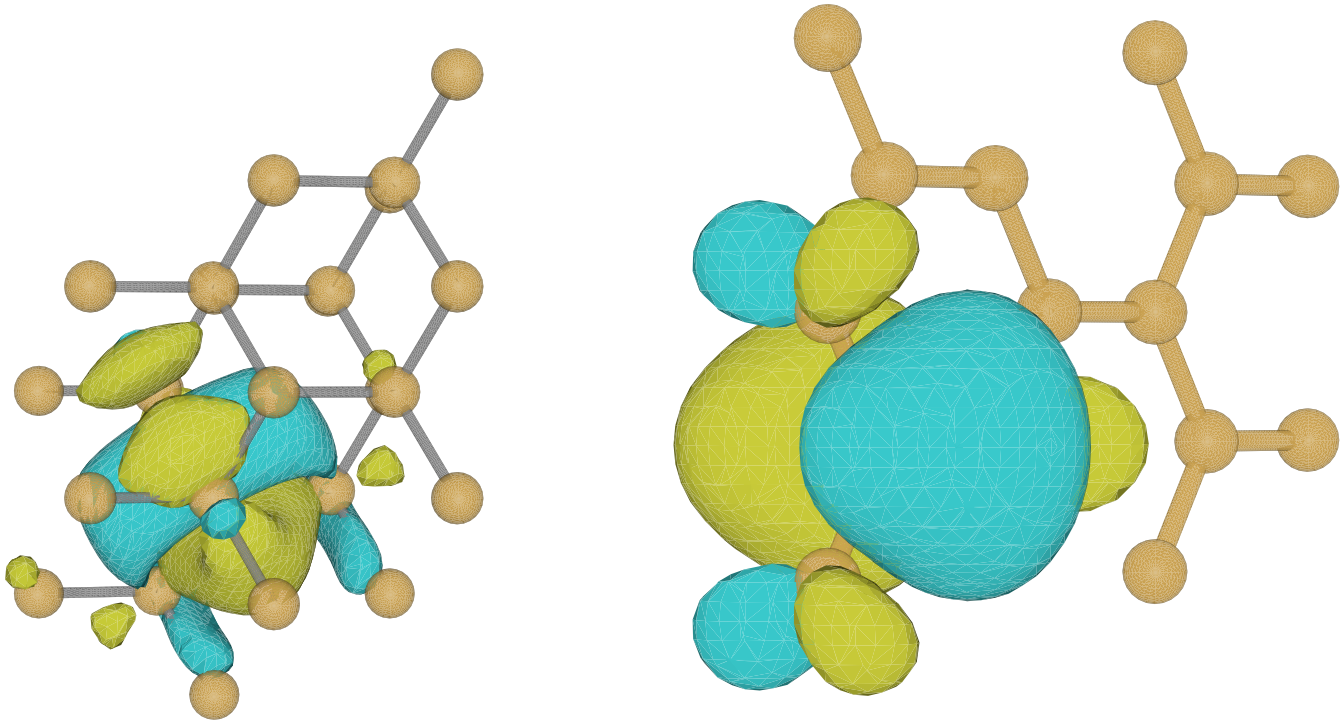
If the host crystal is an insulator with vanishing Chern numbers, the $\phi_{i,\mathbf{R}}$ can be chosen exponentially decreasing (Panati '07)

Maximally Localized Wannier Functions (Marzari-Vanderbilt '97) are Wannier functions minimizing the spread (variance of the position)

$$\sum_{i=1}^{z} \left(\langle \phi_{i,0} | |\mathbf{r}|^2 | \phi_{i,0} \rangle - |\langle \phi_{i,0} | \mathbf{r} | \phi_{i,0} \rangle|^2 \right)$$

Wannier functions depend only on the host crystal, not on the defect

Examples: **Wannier functions of diamond Silicon (left) and graphene (right)**



A hierarchical family of variational approximations V_-^h of $\mathcal{H}_-$ can be obtained by

- **computing z Maximally Localized Wannier Functions $(\phi_{i,0})_{1\leq i\leq z}$ associated with the occupied space of the host crystal**

- **considering**

$$V_-^h = \textbf{Span}(\phi_{i,\mathbf{R}})_{1\leq i\leq z,\ \mathbf{R}\in\mathcal{R}_h}$$

  where $\mathcal{R}_h$ is a finite set of points of the lattice in the vicinity the defect

Note that the $(\phi_{i,0})_{1\leq i\leq z}$ only depend on the host crystal, not on the defect. They are universal basis functions, that can be computed once and for all, and stored in databases. The basis sets $(\phi_{i,\mathbf{R}})_{1\leq i\leq z,\ \mathbf{R}\in\mathcal{R}_h}$ are local and minimal

There is more flexibility in the design of variational approximations V_+^h of $\mathcal{H}_+$

- **consider Maximally Localized Wannier Functions associated with the lowest virtual bands of the host crystal**

- **enrich the so-obtained space by adding projected atomic orbitals of the atoms and ghost atoms involved in ν (using the functions $(\phi_{i,\mathbf{R}})_{1\leq i\leq z,\, \mathbf{R}\in\mathcal{R}}$ to project out the $\mathcal{H}_-$ component does not kill the locality)**

The Wannier Functions are well-localized and are obtained by translating a small number of mother Wannier functions (one mother Wannier function per band of the host crystal). Better localization can be obtained using non-orthogonal generalized Wannier functions

$\longrightarrow$ **Toward efficient linear scaling algorithms?**

Up to a change of variable, the discretized minimization problem to be solved is of the form

$$\inf \left\{ \widetilde{\mathcal{E}}^h(P^h), \quad P^h \in \mathcal{P}^h \right\}$$

$$\mathcal{P}^h = \left\{ P^h \in \mathbb{R}^{N_b \times N_b}, \quad P^h = [P^h]^T, \quad 0 \leq P^h \leq 1, \quad \mathbf{Tr}(P^h) = N^h \right\}$$

$\longrightarrow$ **Relaxed Constrained Algorithms**

- **EC and Le Bris, IJQC '00**
- **EC, J. Chem. Phys. 114 '01**
- **Kudin, Scuseria and EC , J. Chem. Phys. '02**

Conclusions of this part

1. **Using rigorous bulk limit arguments, we have obtained a (non-trivial) variational model for computing the electronic ground state of insulating and semiconducting crystals with local defects.**

   This model takes into account the screening effect in insulators and semi-conductors in an implicit (but exact) way.

2. **Hierarchical variational approximations of the modification $Q^{m,\varepsilon_{\mathrm{F}}}$ of the density matrix can be computed using a (possibly enriched) basis of Maximally Localized Wannier Functions of the host crystal (EC, Deleurence and Lewin, J. Phys.: Cond. Mat. '08)**

   $\longrightarrow$ **Accurary? - Linear scaling? - Sublinear scaling?**