Computational Electron Dynamics

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outline

why?

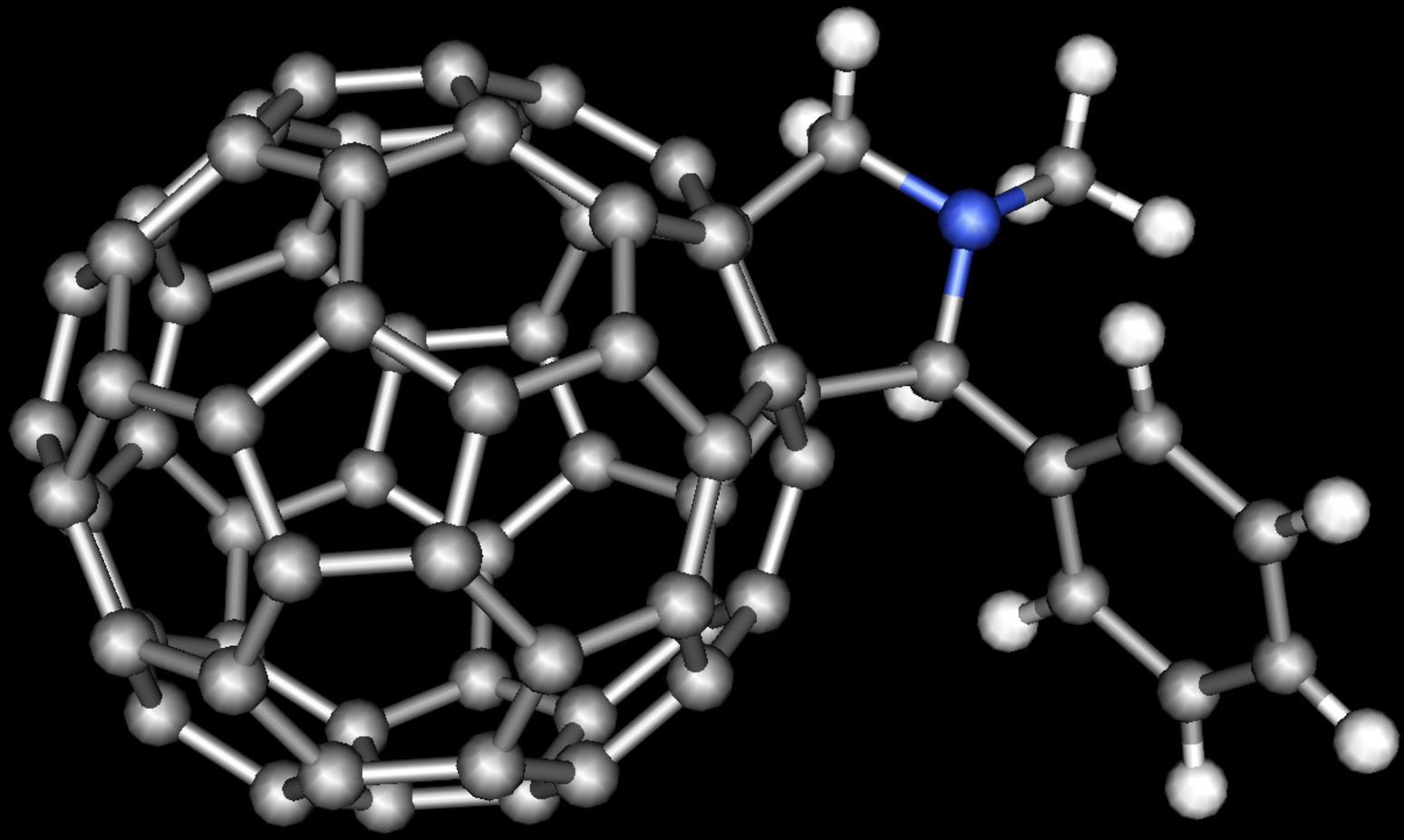
implementation

crystalline systems

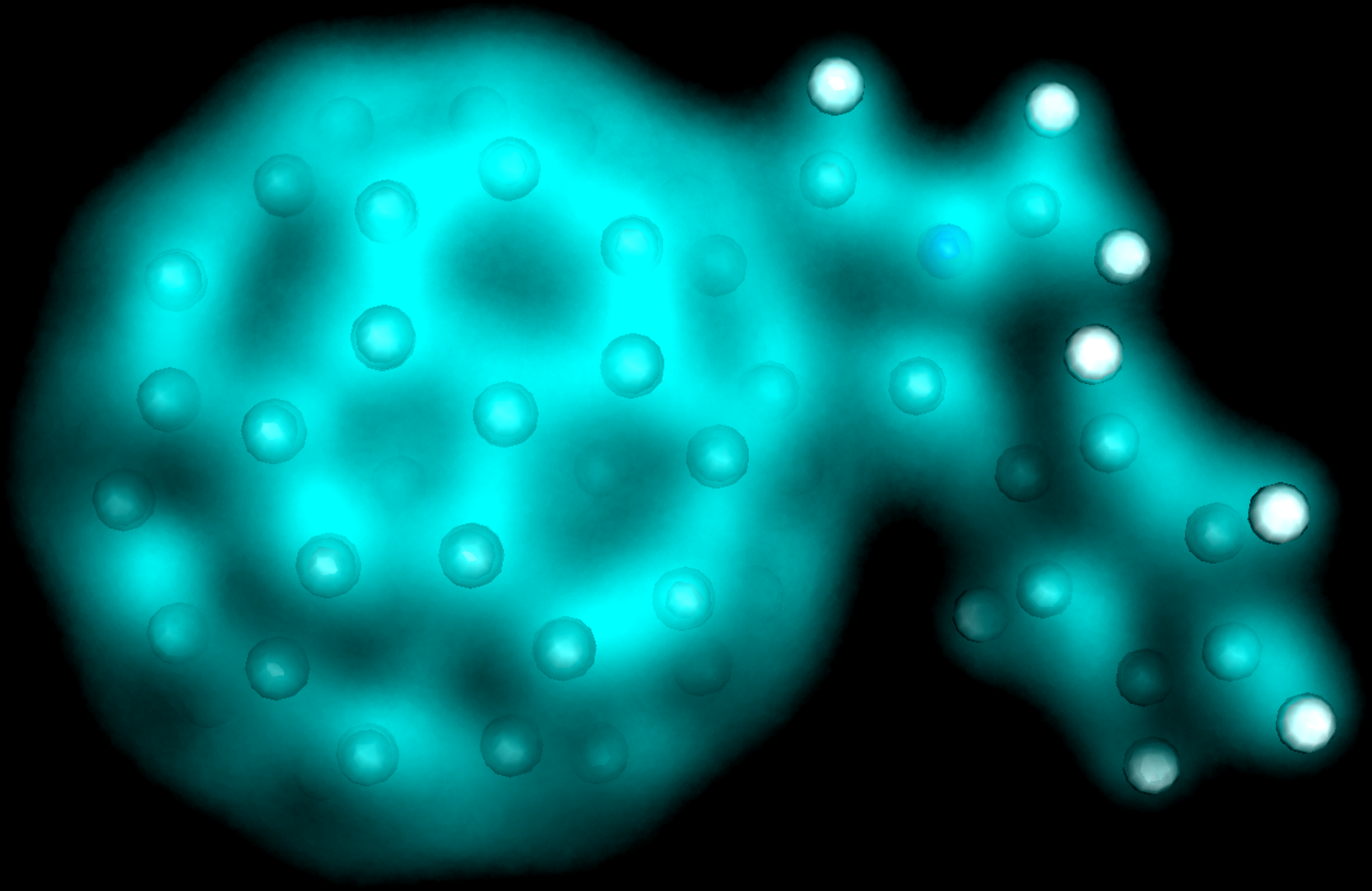
future challenges

why electron dynamics?

atoms

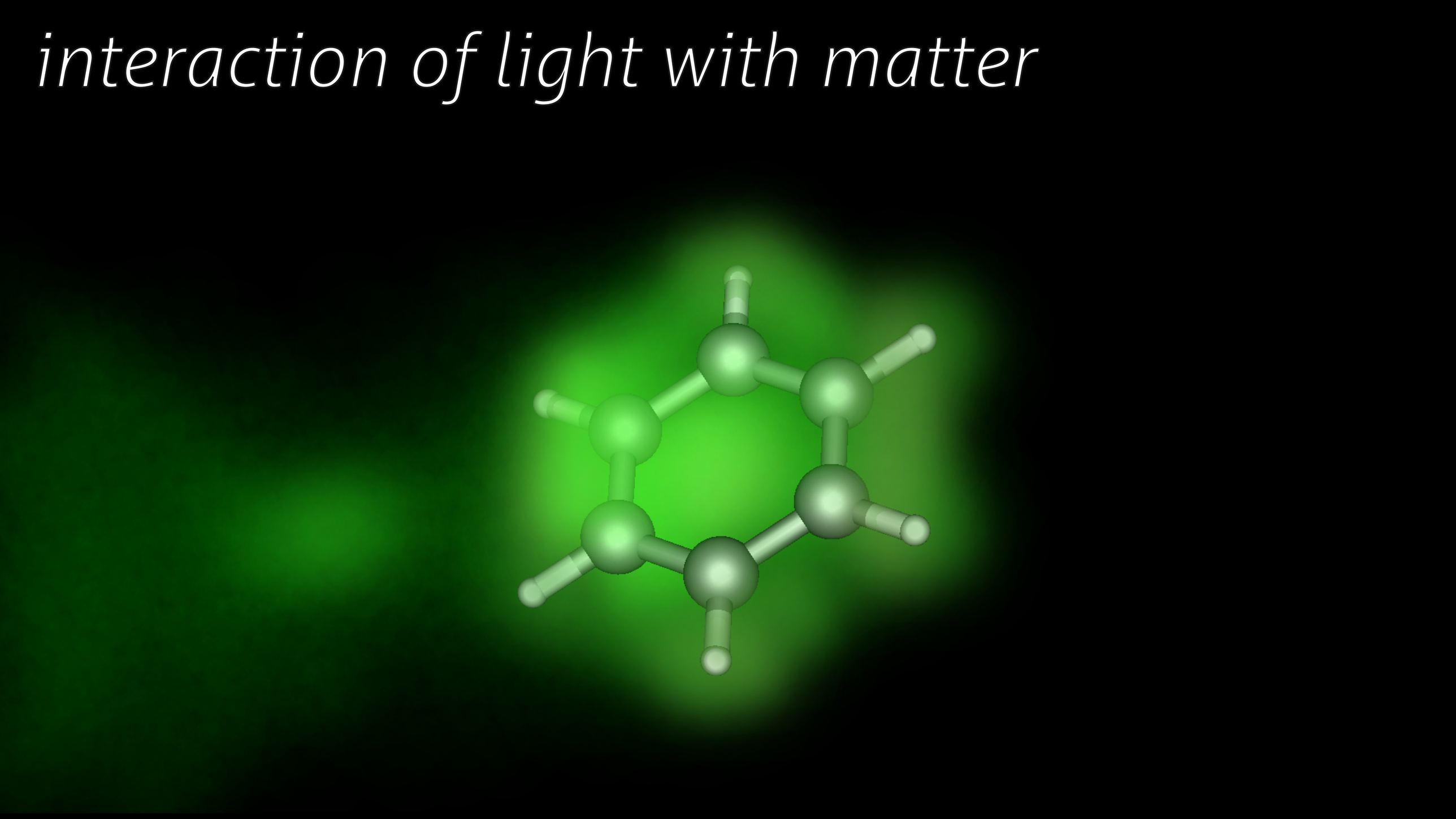


electrons



electron dynamics:
simulate the time-evolution of
electrons as quantum particles

interaction of light with matter

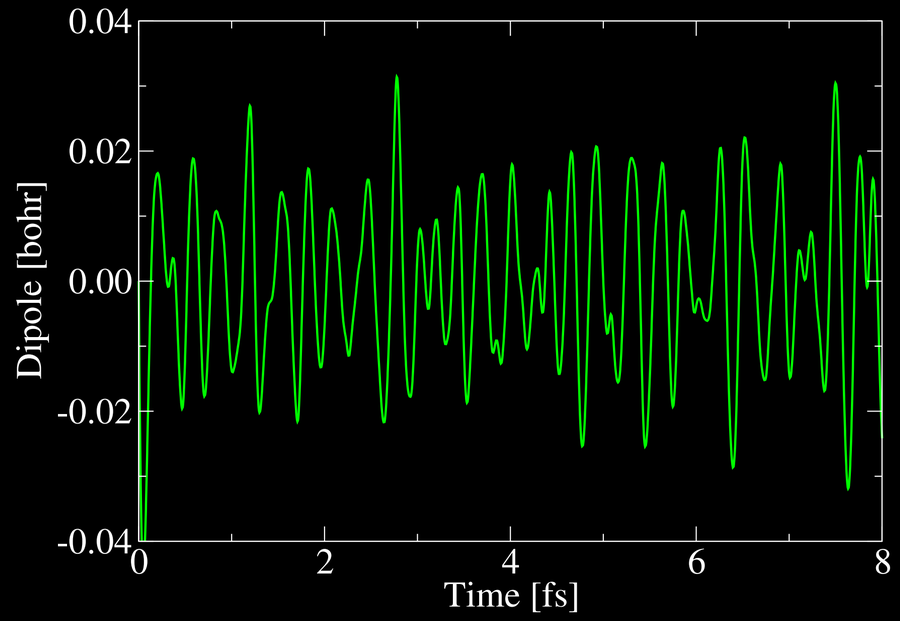


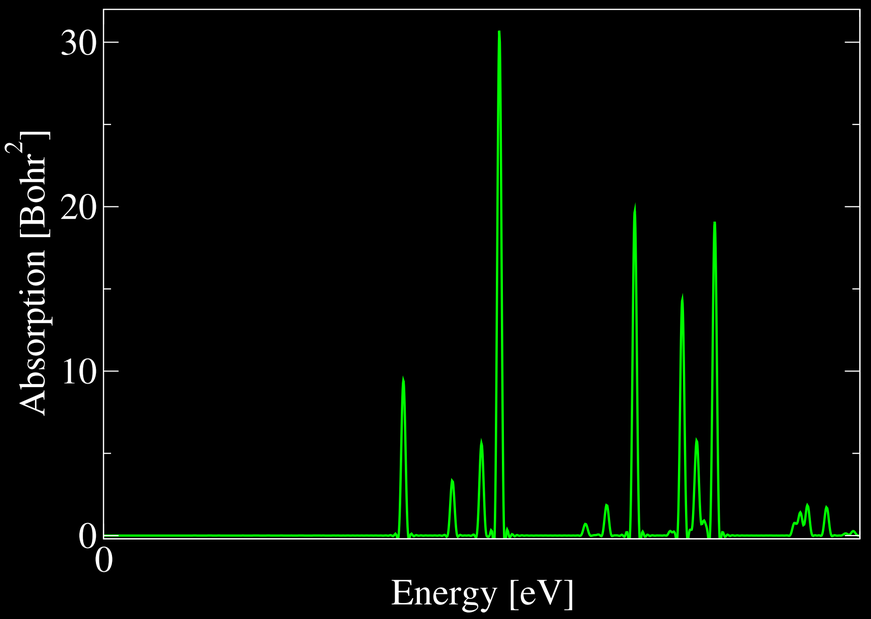
absorption spectrum

$$\boldsymbol{E}(t) = \boldsymbol{E}_0\,\delta(t)$$

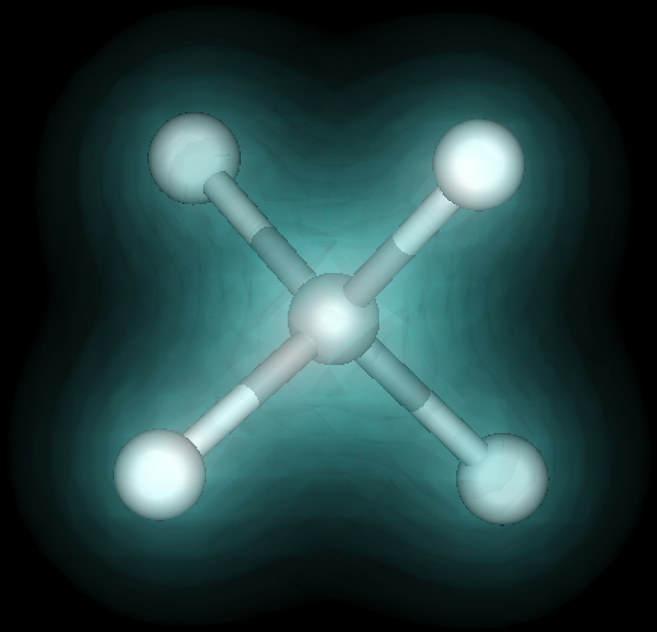
$$\boldsymbol{p}(t) = \int \mathrm{d}\boldsymbol{r}\,\boldsymbol{r}\,n(t)$$

$$\alpha(\omega) = \frac{1}{\boldsymbol{E}_0}\int_0^\infty \mathrm{d}t\,e^{-i\omega t}\boldsymbol{p}(t)$$

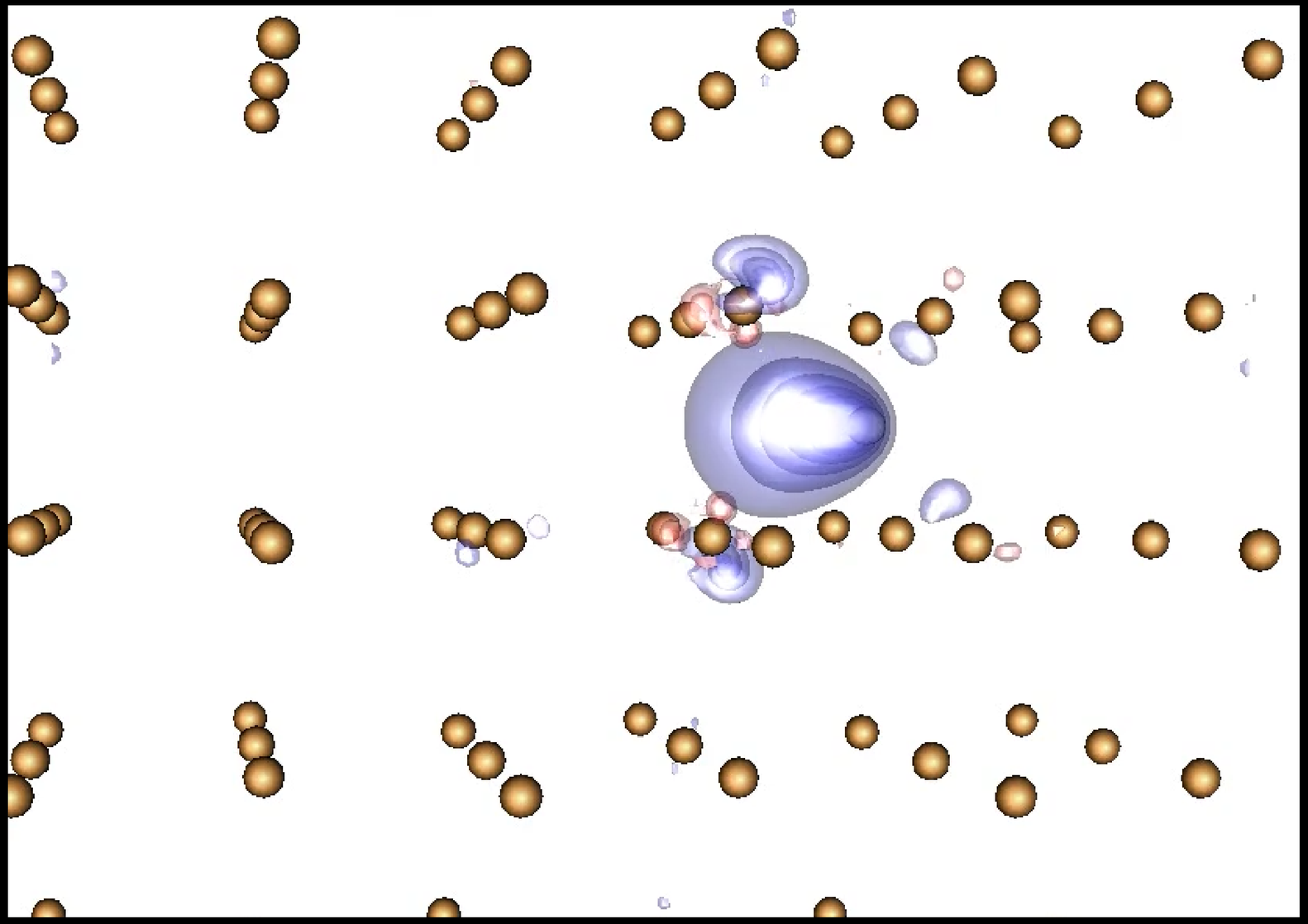




collisions

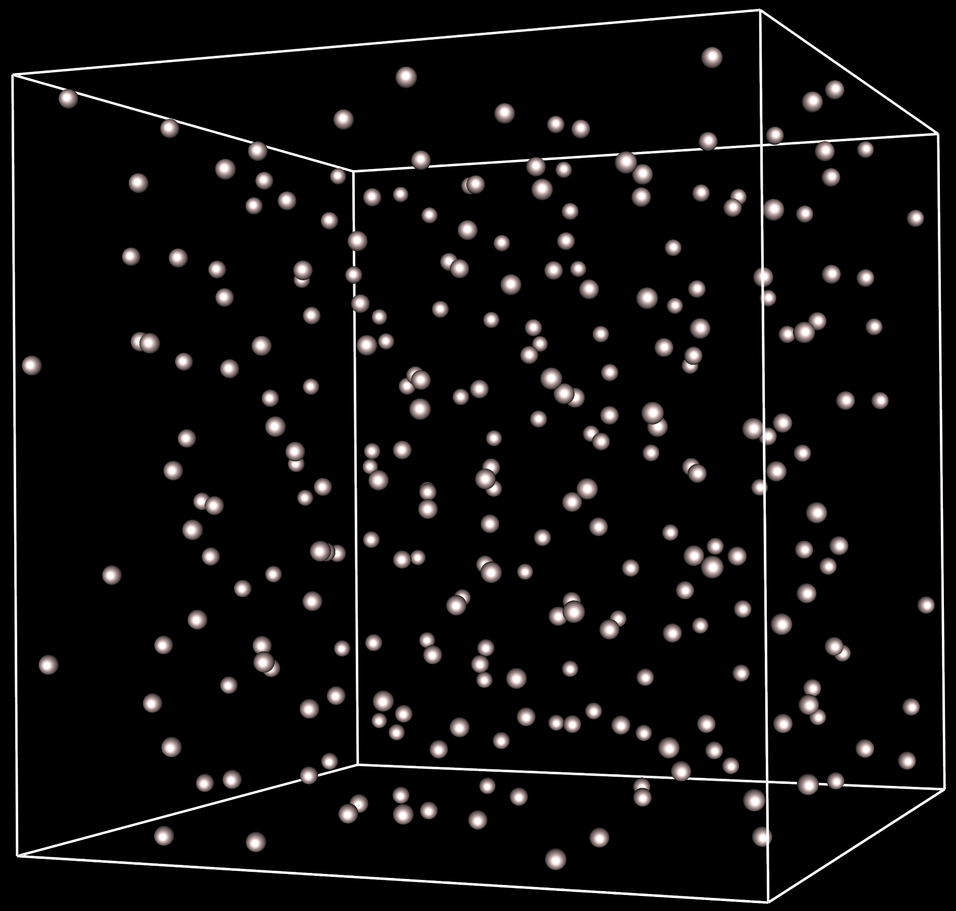


stopping of fast particles in materials

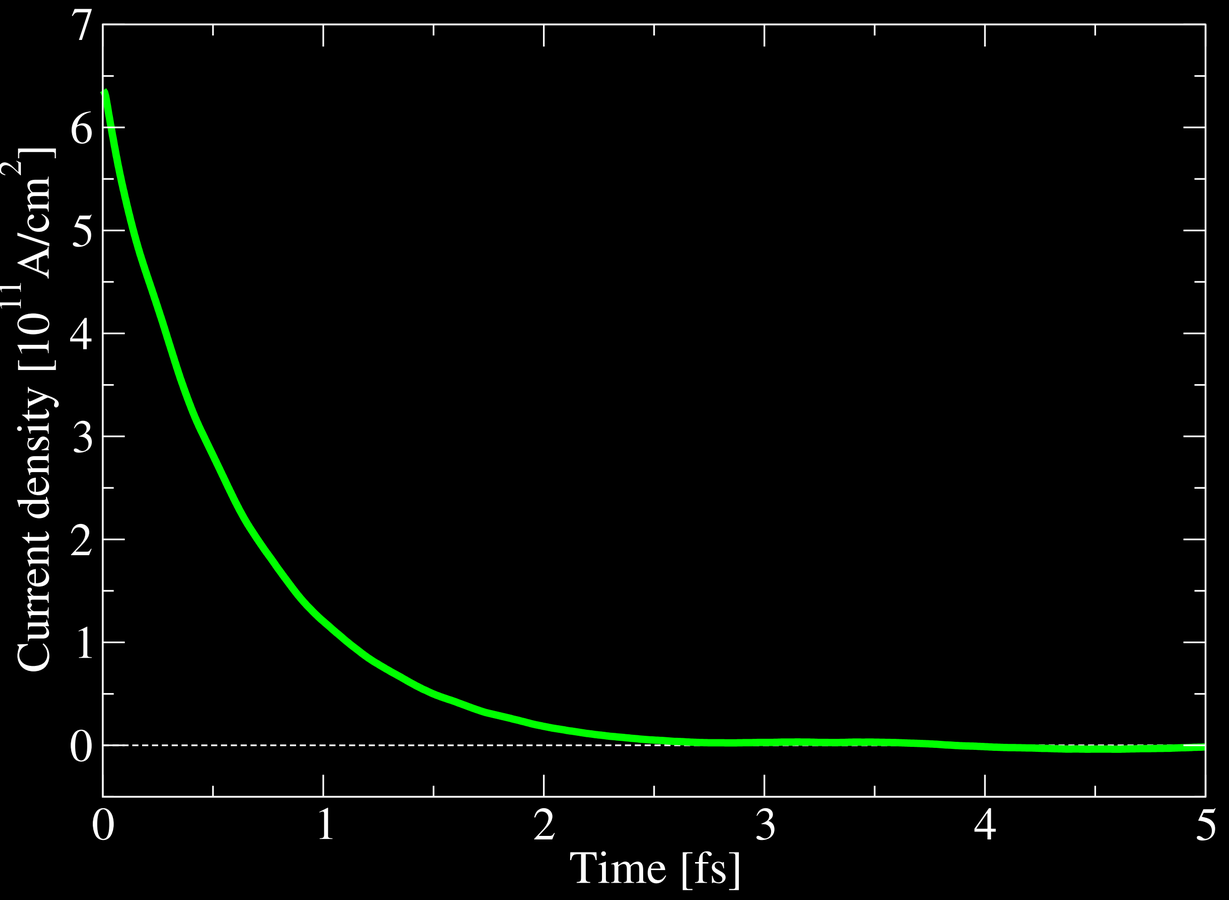


Work by A. Correa, Lawrence Livermore National Laboratory

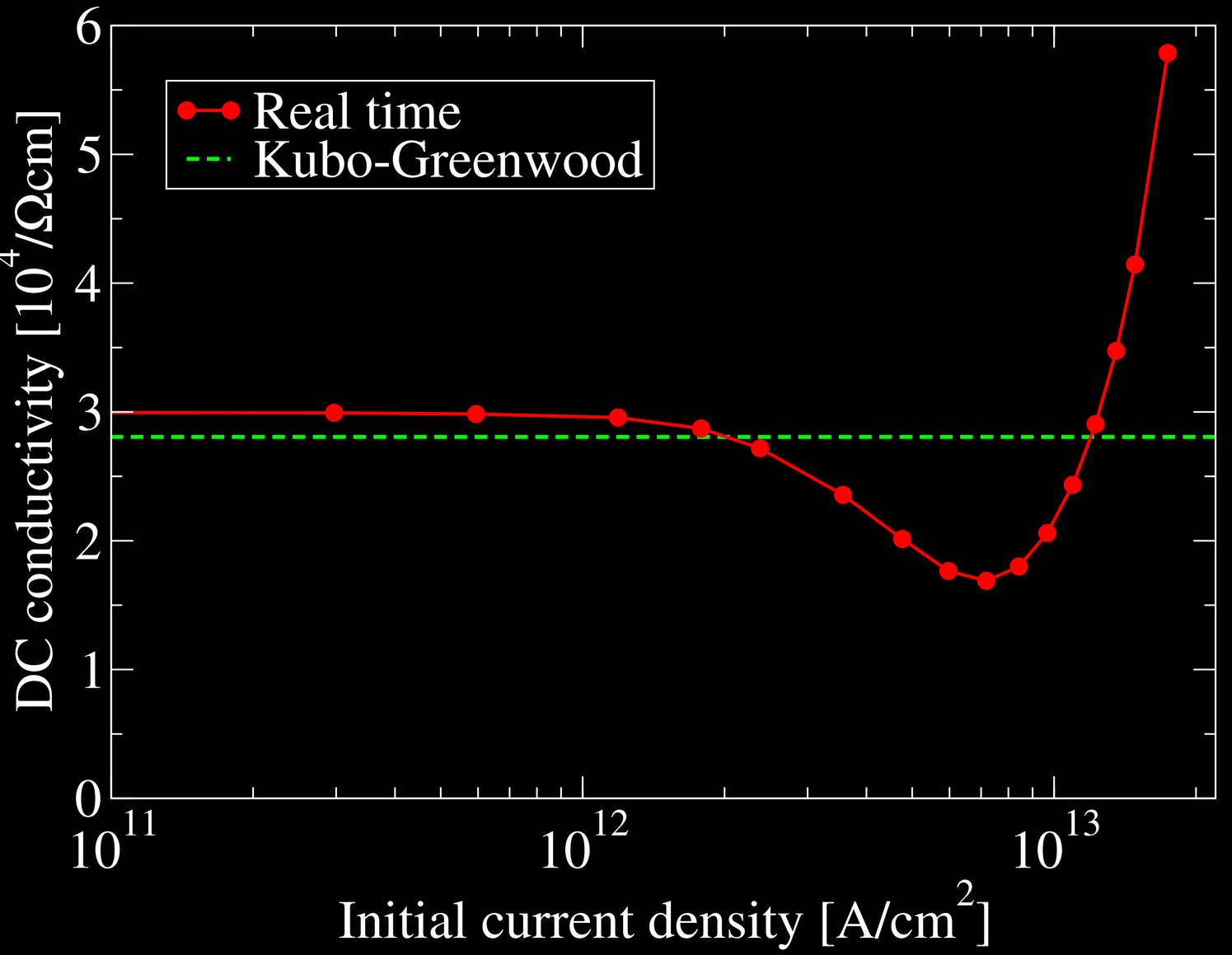
conductivity in metals



liquid aluminum



non-linear conductivity



implementation of electron dynamics

theoretical "back-end"

theoretical "back-end"

real-time tddft

good tradeoff between accuracy and cost

realtively simple implementation

good performance in parallel machines

fundamental in the development of electron dynamics

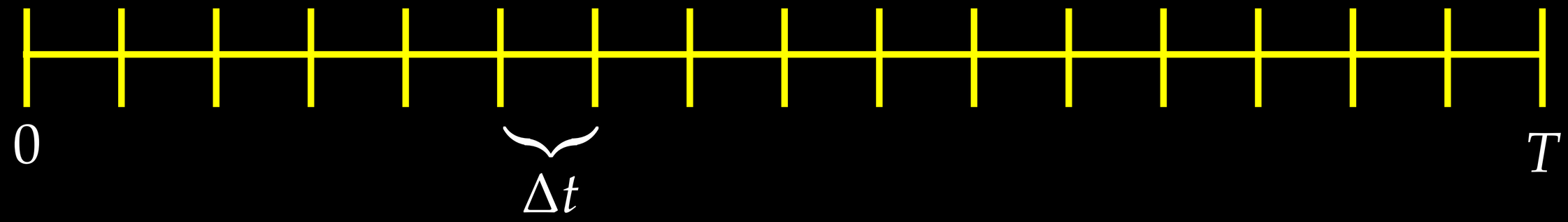
real-time TDDFT equations

$$i\frac{\partial}{\partial t}\varphi_j(\boldsymbol{r},t) = \mathrm{H}[n](t)\,\varphi_j(\boldsymbol{r},t)$$

$$n(\boldsymbol{r},t) = \sum_j \left|\varphi_j(\boldsymbol{r},t)\right|^2$$

$$\varphi_j(\boldsymbol{r},t=0) = \varphi_j^0(\boldsymbol{r})$$

integration in time of tddft equations



propagator

$$\varphi_j(\boldsymbol{r}, t + \Delta t) = \mathrm{U}(t, t + \Delta t)\varphi_j(\boldsymbol{r}, t)$$

enforced time-reversal symmetry propagator

$$\varphi_j(\boldsymbol{r}, t + \Delta t) = \exp\left(i\frac{\Delta t}{2}H(t + \Delta t)\right)\exp\left(i\frac{\Delta t}{2}H(t)\right)\varphi_j(\boldsymbol{r}, t)$$

alternatives:

runge-kutta

explicit methods:
crank-nicholson

propagate over
unoccupied states

exponential of a matrix

taylor expansion

$$\exp(A)\,\varphi(\boldsymbol{r}) \sim \sum_{k=0}^{4} A^k \varphi(\boldsymbol{r})$$

alternatives:

chebyshev

lanczos

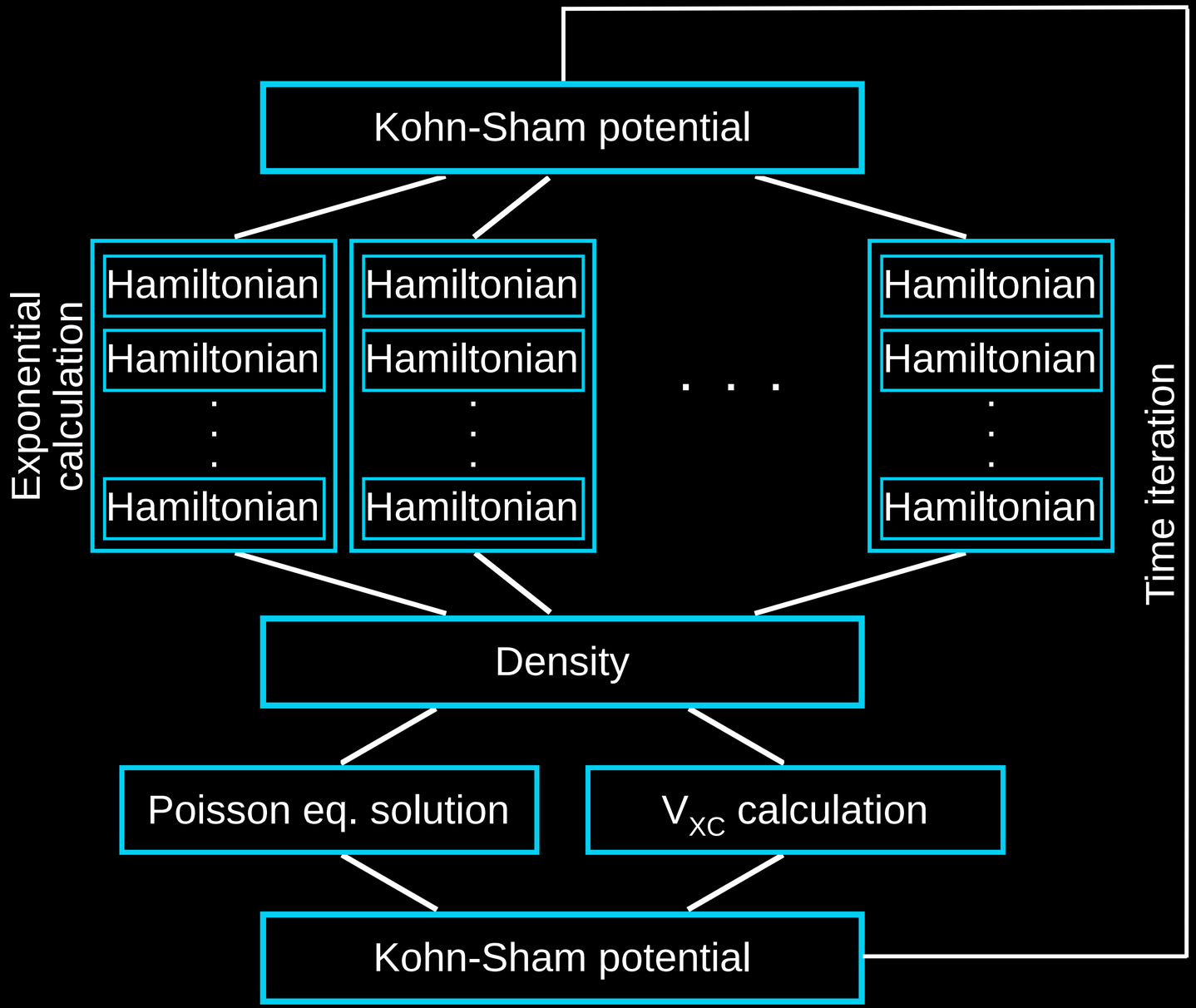
padé

orthogonalization is preserved by the dynamics

no need for orthogonalization procedure

scaling $O(N^2)$ instead of $O(N^3)$

structure of real-time tddft calculation



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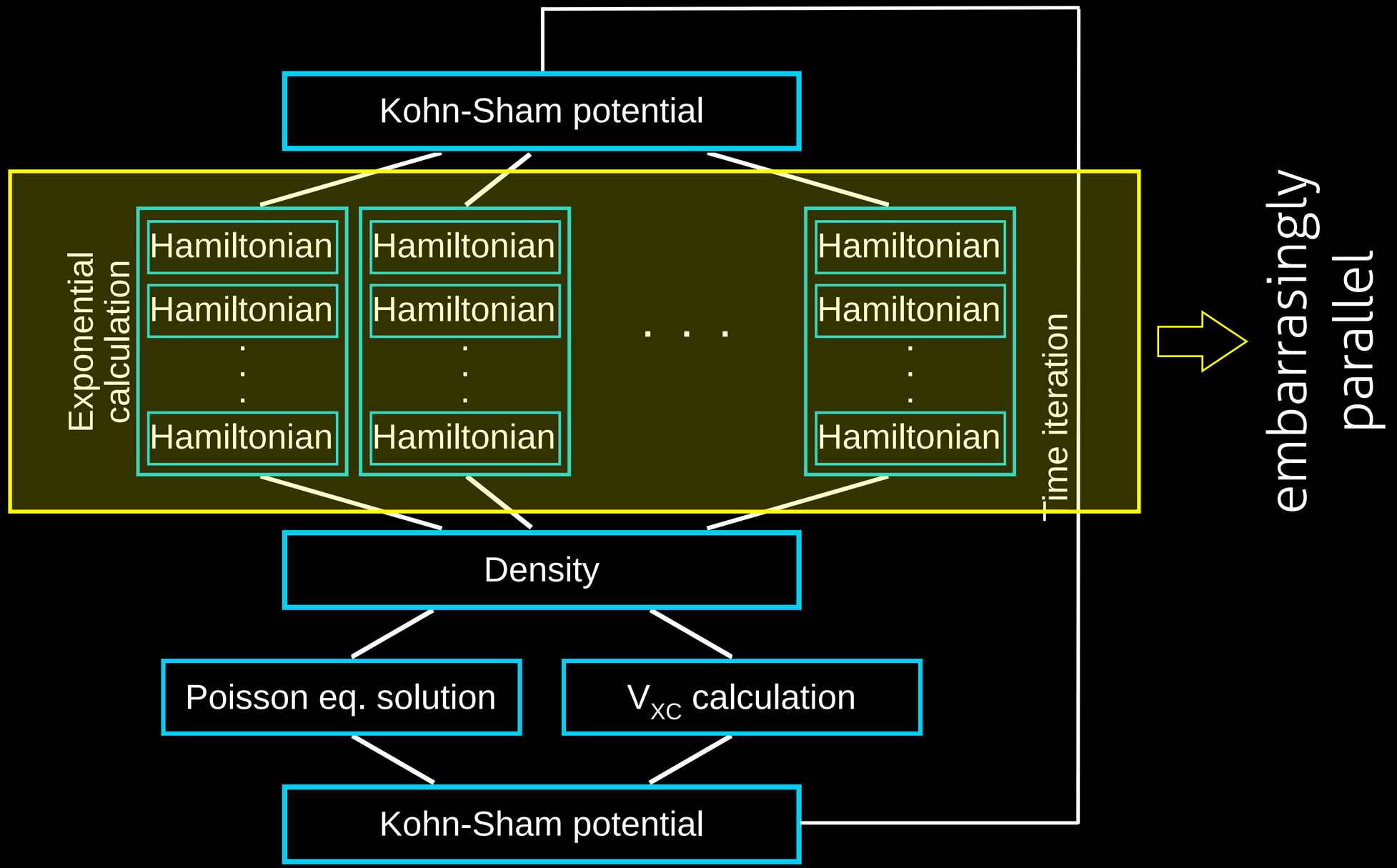


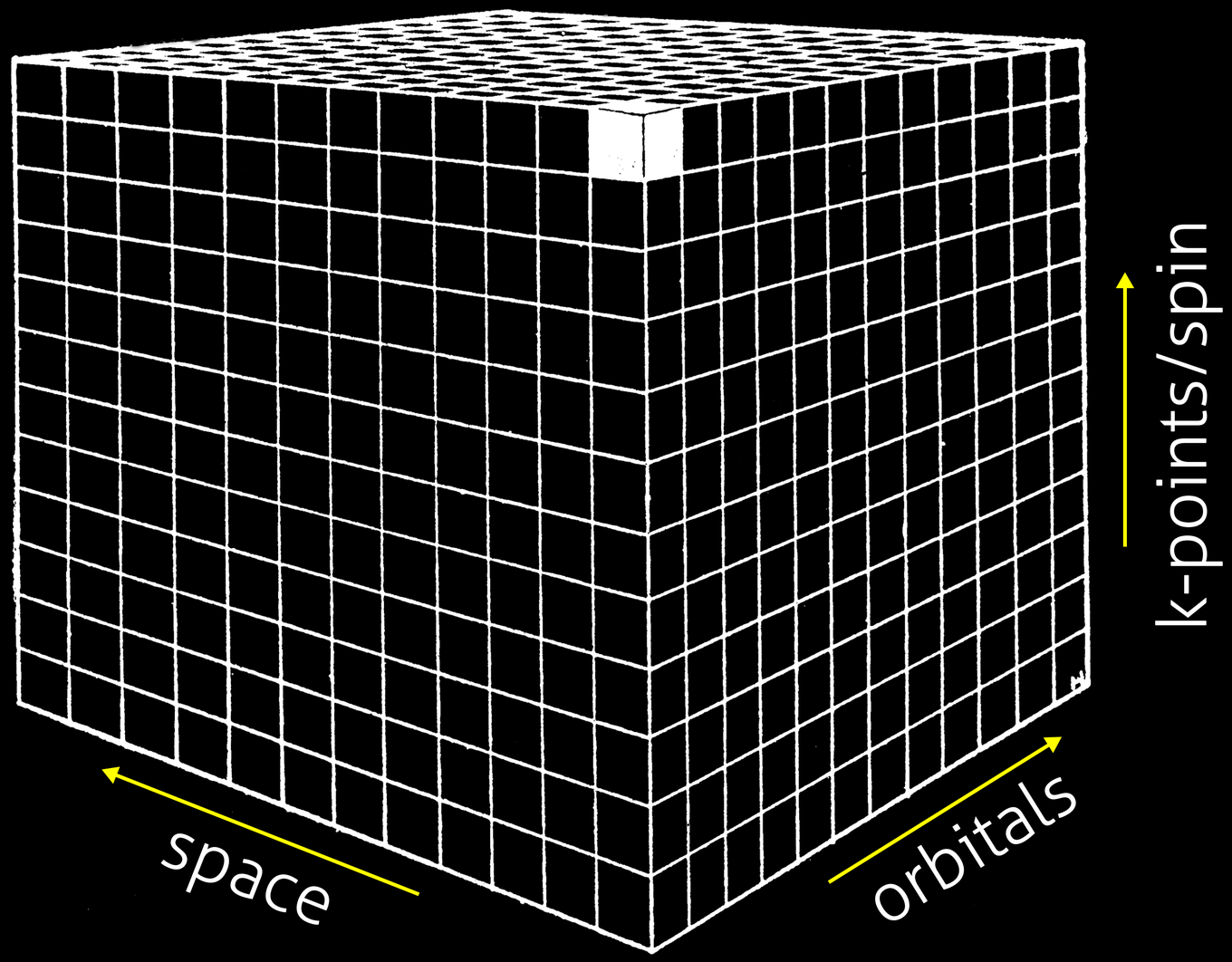
main operation: application of the ks hamiltonian

$$\varphi(\boldsymbol{r},t) \rightarrow \mathrm{H}(t)\varphi(\boldsymbol{r},t)$$

plane-waves

real-space grids

multiple-level parallelization

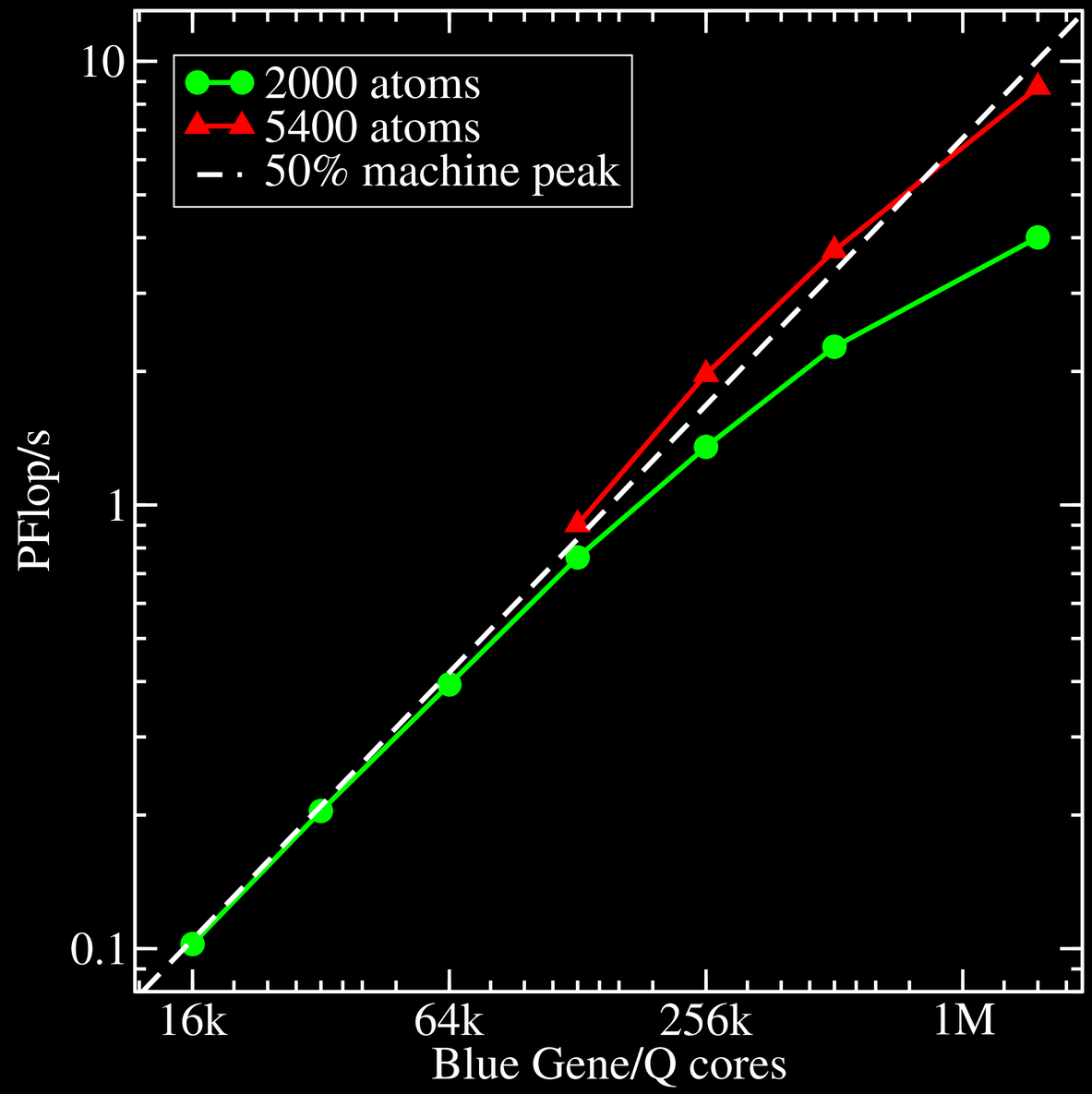


X. Andrade et al, JPCM,126, 184106 (2012)

we can scale electron dynamics up to 1.6 million CPU cores

qb@ll plane-wave code

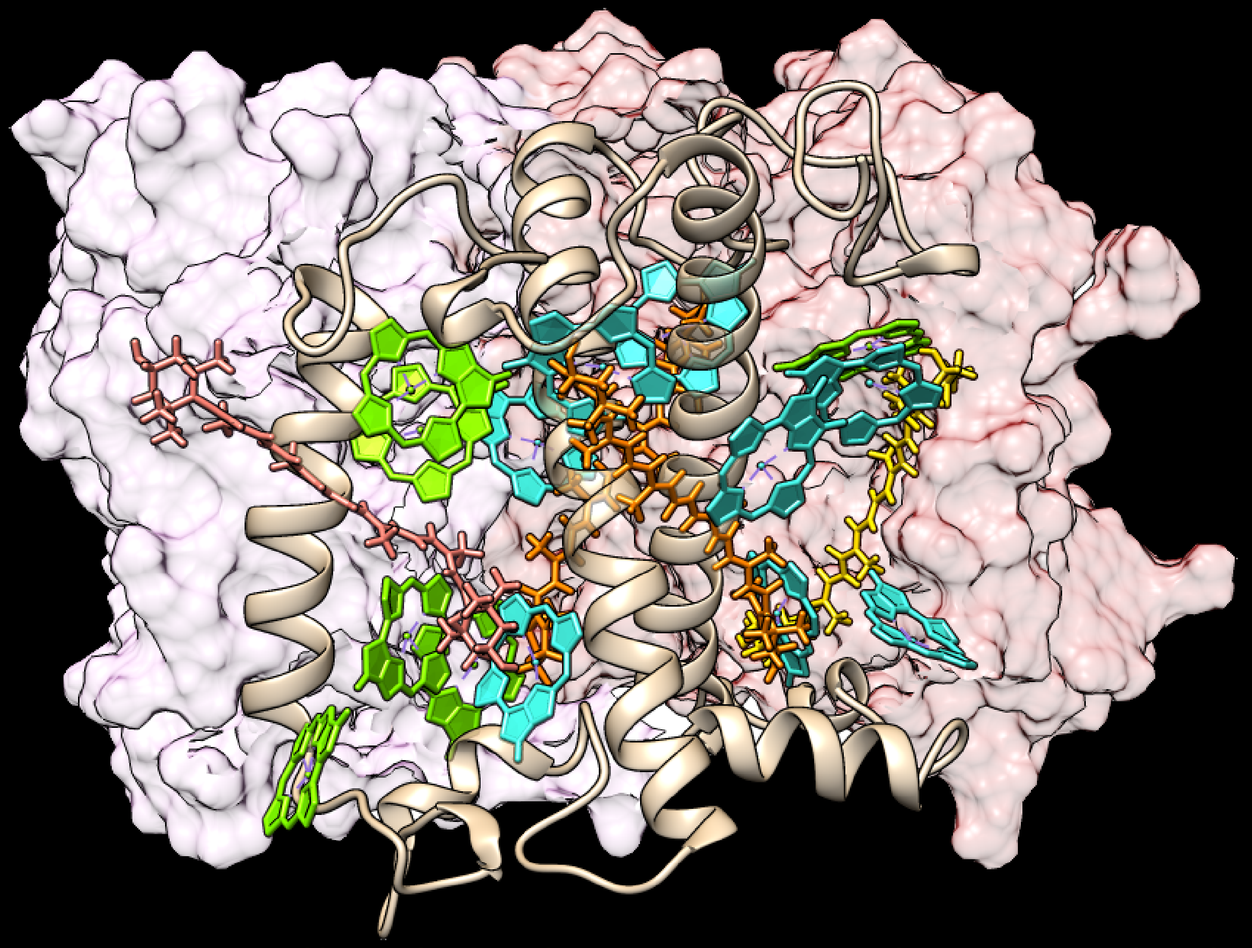
8.8 petaflop/s (44% of peak)

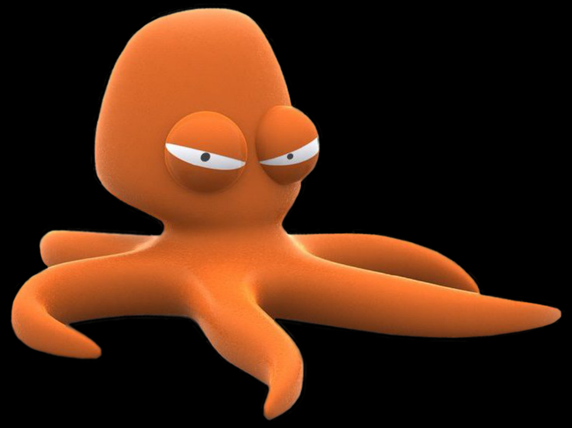


E. W. Draeger, X. Andrade, J.A. Gunnels, A. Bhatele, A. Schleife, A.A. Correa, "Massively parallel first-principles simulation of electron dynamics in materials", best paper IDPDS 2016

simulation of excited state of light harvesting complex II

6075 atoms: largest electron dynamics simulation





J. Jornet-Somoza, J. Alberdi-Rodriguez, B. F. Milne, X. Andrade, M.A.L. Marques, F. Nogueira, M.J.T. Oliveira, J. J. P. Stewart and A. Rubio, PCCP 17 26599 (2015)

electron dynamics in crystalline systems

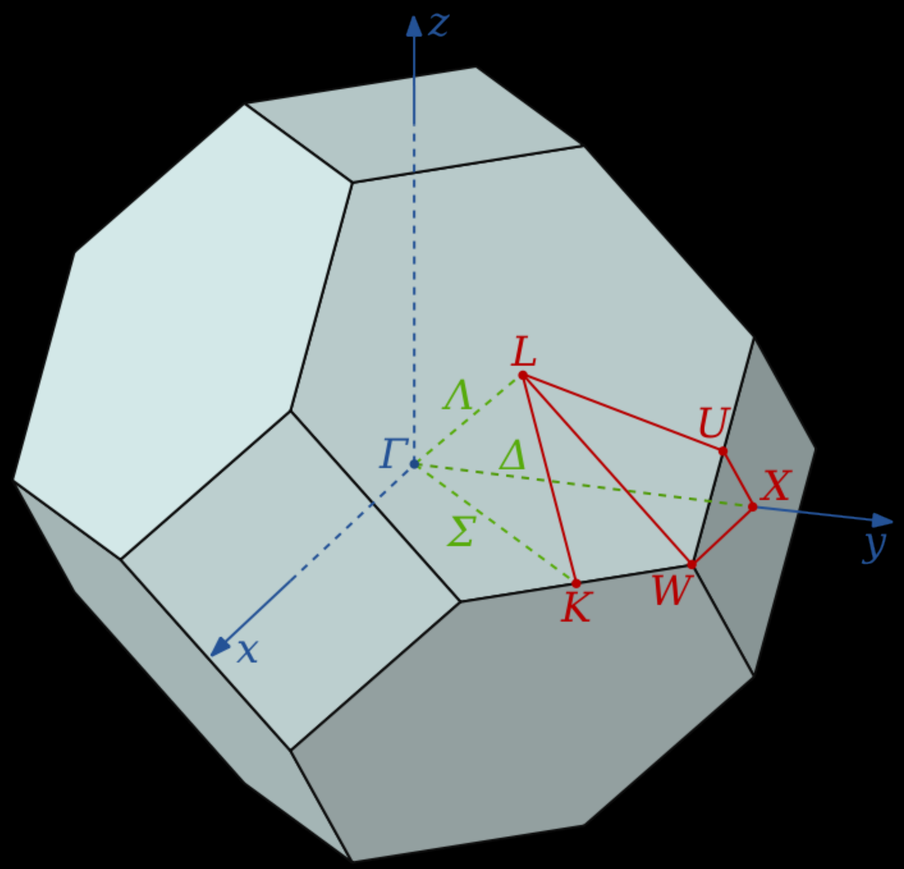
bloch's theorem

in a periodic system, orbitals have the form:

$$\varphi_{n\boldsymbol{k}}(\boldsymbol{r},t) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r},t)$$

k-point

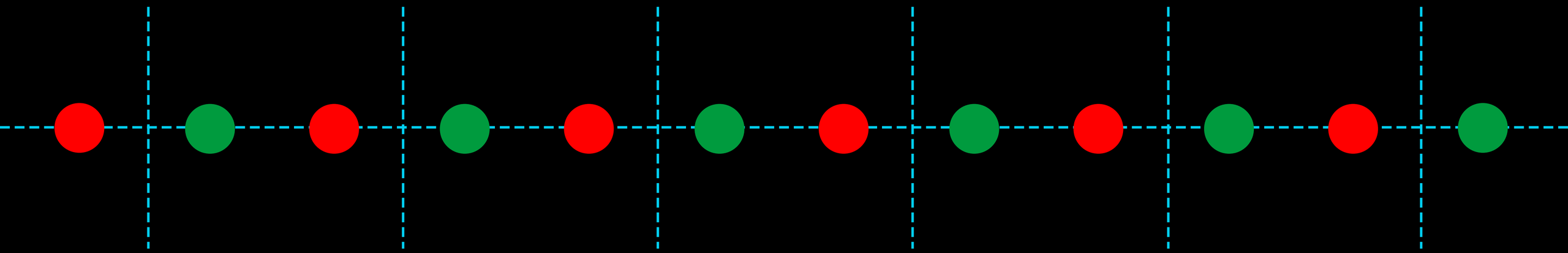
periodic



we can do simulations using periodic quantities

the problem of describing an electric field on a periodic system

$$\boldsymbol{E}(t) \Rightarrow V(\boldsymbol{r},t) = -\boldsymbol{E}\cdot\boldsymbol{r}$$



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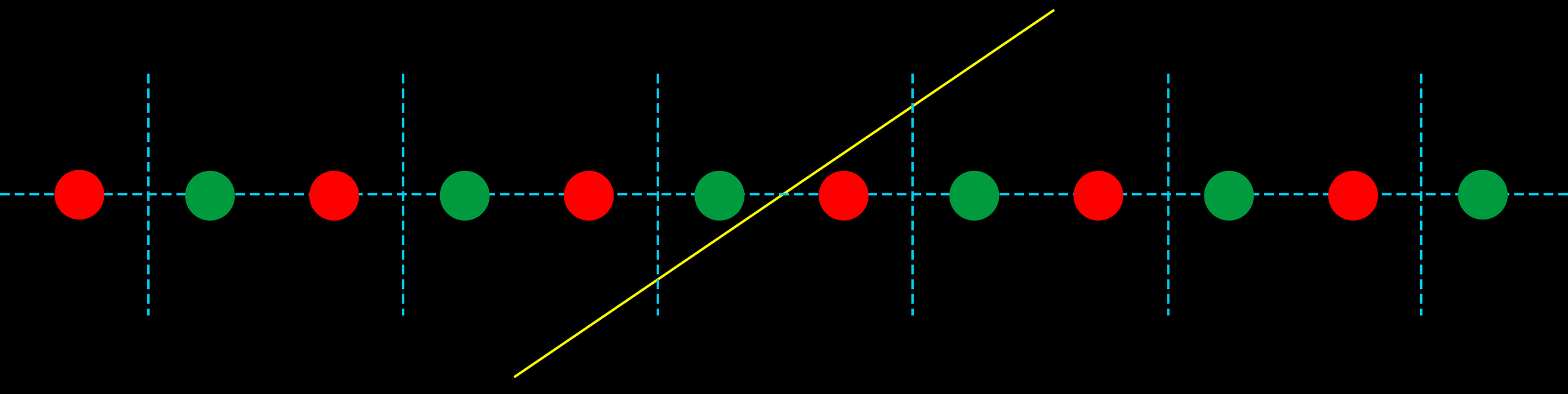

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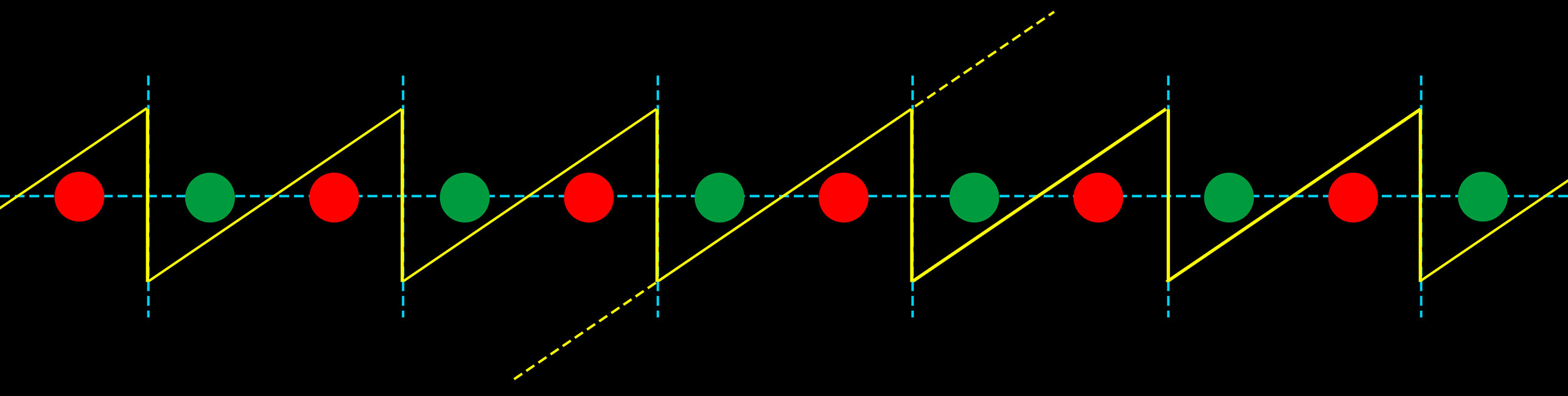
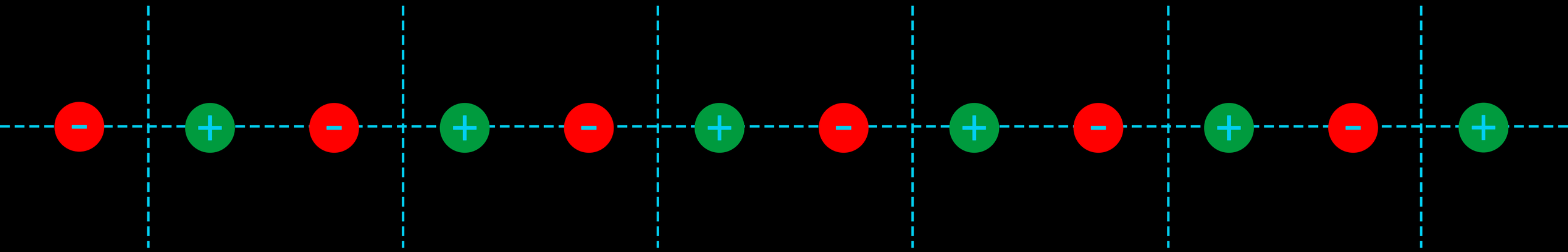


polarization is not properly defined



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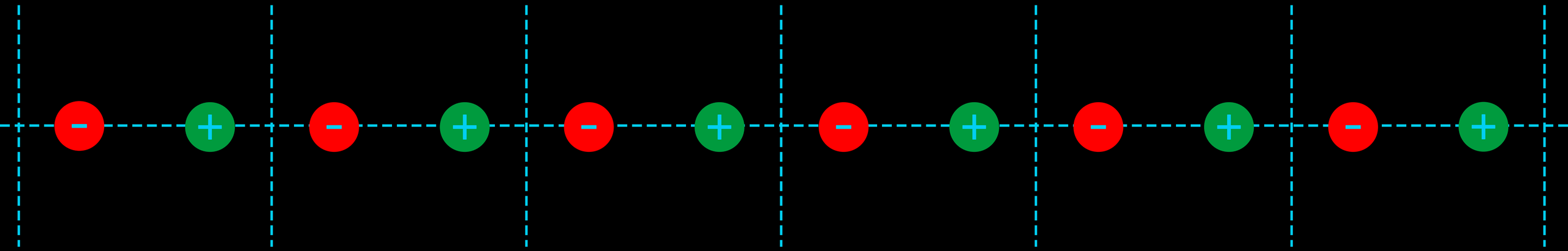


modern polarization theory

only polarization changes are
properly defined in a solid

R. Resta, Rev. Mod. Phys., 66 899 (1994)
N. A. Spaldin, J. Solid State Chem., 195 2 (2012)

how to calculate properties in modern polarization theory

$$\boldsymbol{r} \rightarrow \frac{\partial}{\partial \boldsymbol{k}}$$

in principle, it only applies to perturbation theory

an alternative that can describe finite electric fields

$$\boldsymbol{E}(t) = -\frac{1}{c}\frac{\mathrm{d}\boldsymbol{A}(t)}{\mathrm{d}t}$$

$\boldsymbol{A}(t)$ uniform time-dependent vector potential

G. F. Bertsch, J.-I. Iwata, A. Rubio, and K. Yabana, PRB 62 7998 (2000)

description of an electric field applied to a crystal

$$\boldsymbol{E}(\boldsymbol{r},t) = -\boldsymbol{\nabla} V(\boldsymbol{r},t) - \frac{1}{c}\frac{\mathrm{d}\boldsymbol{A}(t)}{\mathrm{d}t}$$

periodic

uniform electric field

lagrangian for the electron coupled with an electric field

$$L = \int_\Omega \mathrm{d}\boldsymbol{r} \sum_j \frac{1}{2} \left(i\partial^\alpha \varphi_j^* - \frac{1}{c} A^\alpha \varphi_j^* \right) \left(-i\partial^\alpha \varphi_j - \frac{1}{c} A^\alpha \varphi_j \right)$$
$$+ \int_\Omega \mathrm{d}\boldsymbol{r} \sum_j \varphi_j^* V(\boldsymbol{r}) \varphi_j - i \int \mathrm{d}\boldsymbol{r} \sum_j \varphi_j^* \dot{\varphi}_j - \frac{\Omega}{8\pi c^2} \dot{A}^\alpha \dot{A}^\alpha$$

Ω

volume of the unit cell

real-time tddft for solids

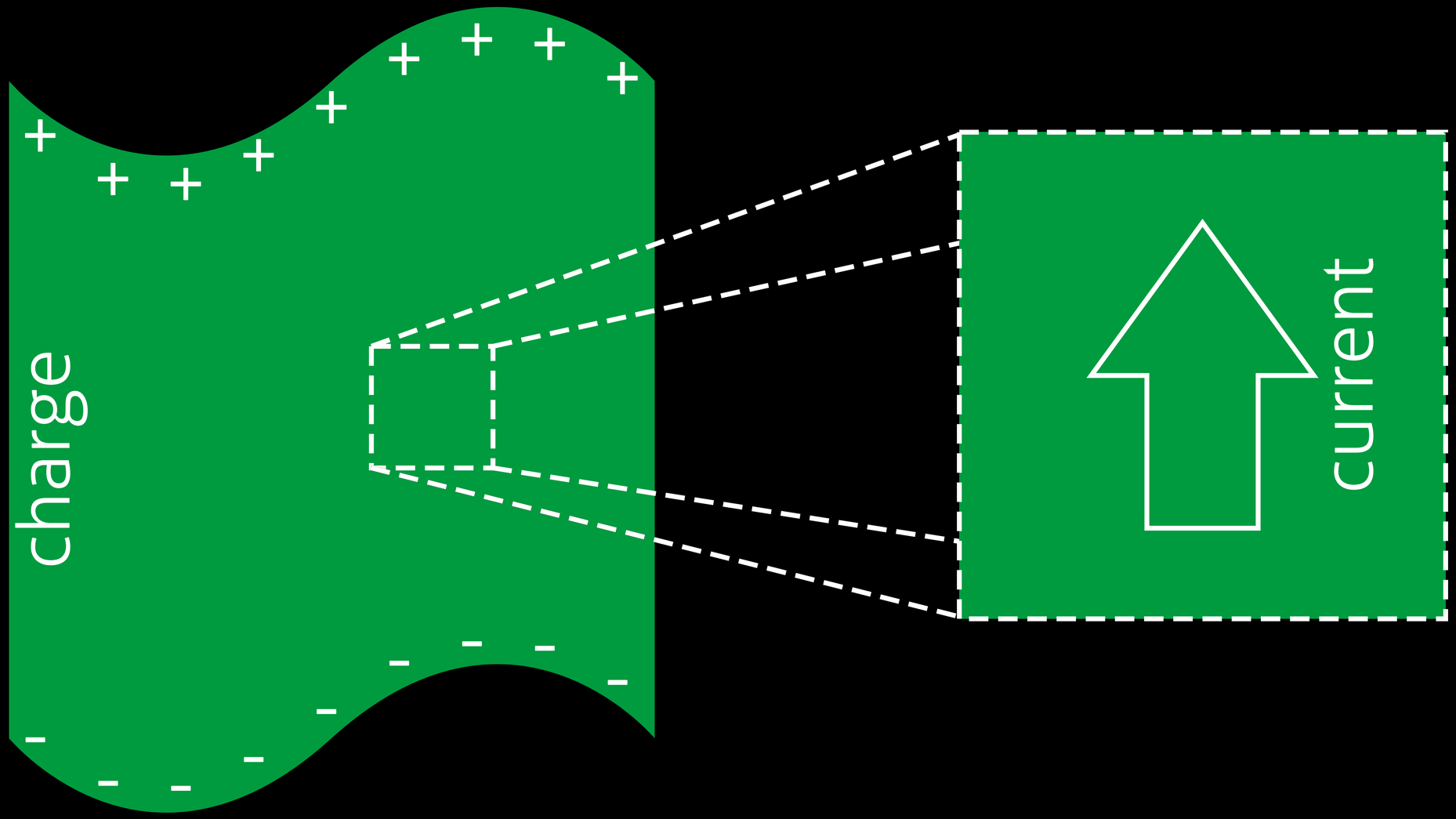
$$i\frac{\partial}{\partial t}\varphi_j(\boldsymbol{r},t) = \left[-\frac{1}{2}\left(\boldsymbol{\nabla} - \frac{i}{c}\boldsymbol{A}(t)\right)^2 + V_{\mathrm{ext}}(\boldsymbol{r},t) + V_{\mathrm{hxc}}[n](\boldsymbol{r},t)\right]\varphi_j(\boldsymbol{r},t)$$

$$n(\boldsymbol{r},t) = \sum_j \left|\varphi_j(\boldsymbol{r},t)\right|^2$$

$$\frac{\partial^2}{\partial t^2}\boldsymbol{A}(t) = 4\pi c\,\boldsymbol{J}(t)$$

general form for the current density

$$\boldsymbol{J}(t) = \frac{i}{\Omega} \int \mathrm{d}\boldsymbol{r} \sum_j \varphi_j^*(\boldsymbol{r}, t) \left[H(t), \boldsymbol{r} \right] \varphi_j(\boldsymbol{r}, t)$$



Macroscopic crystal

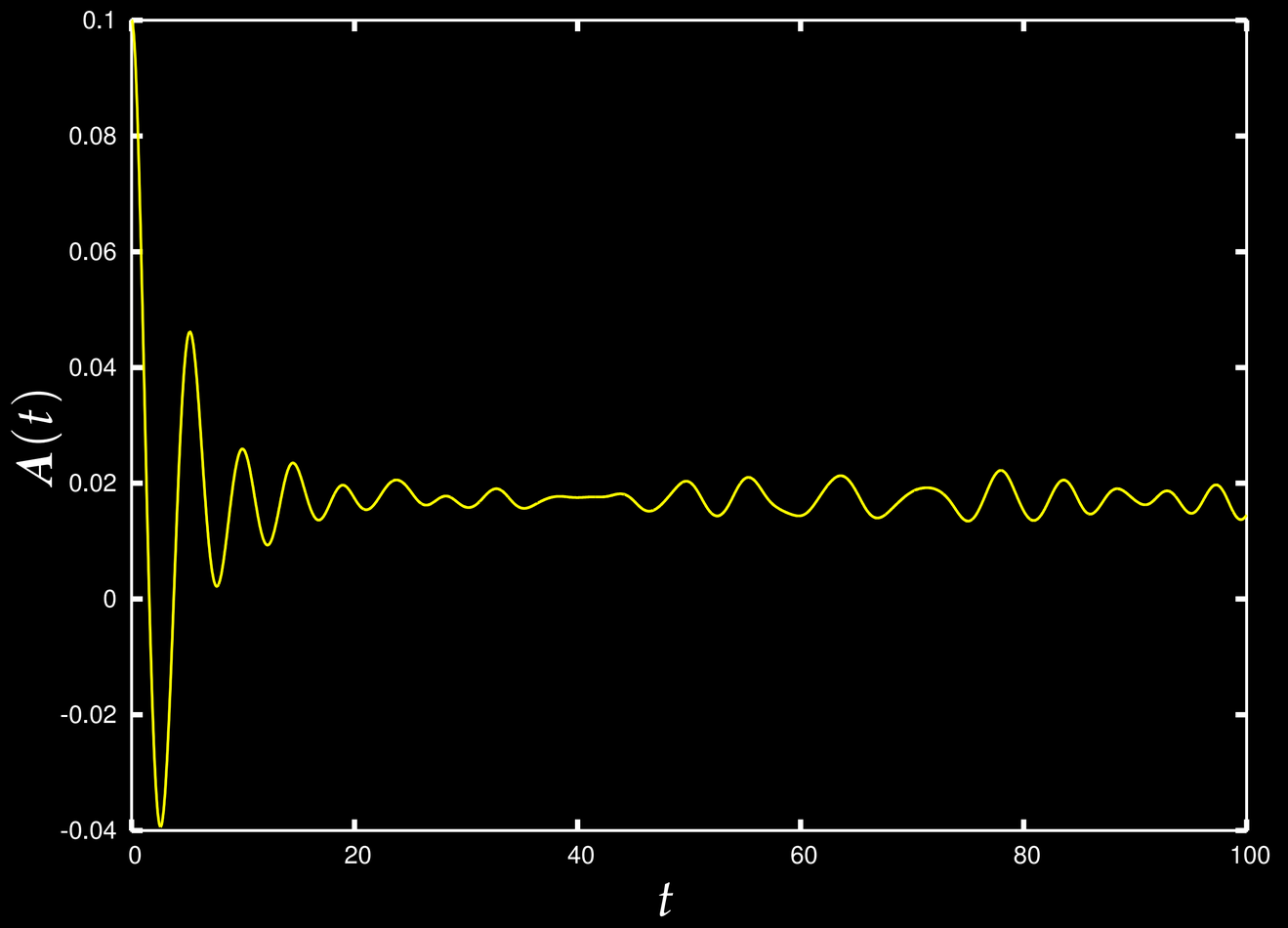
Bulk unit cell

evolution in time of the vector potential

$$\boldsymbol{A}(t) = \boldsymbol{A}_{\mathrm{ext}}(t) + A_{\mathrm{ind}}(t)$$

external field

polarization of the system

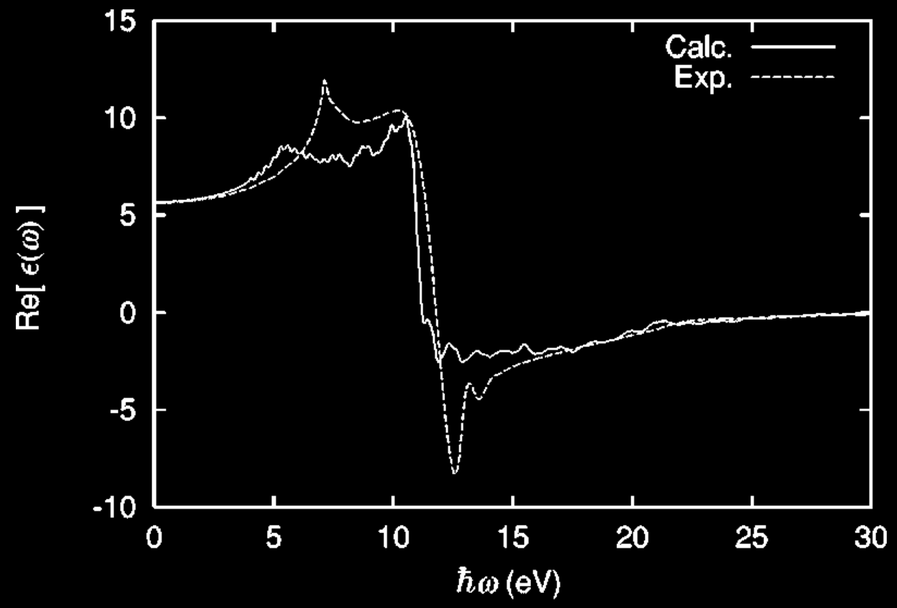


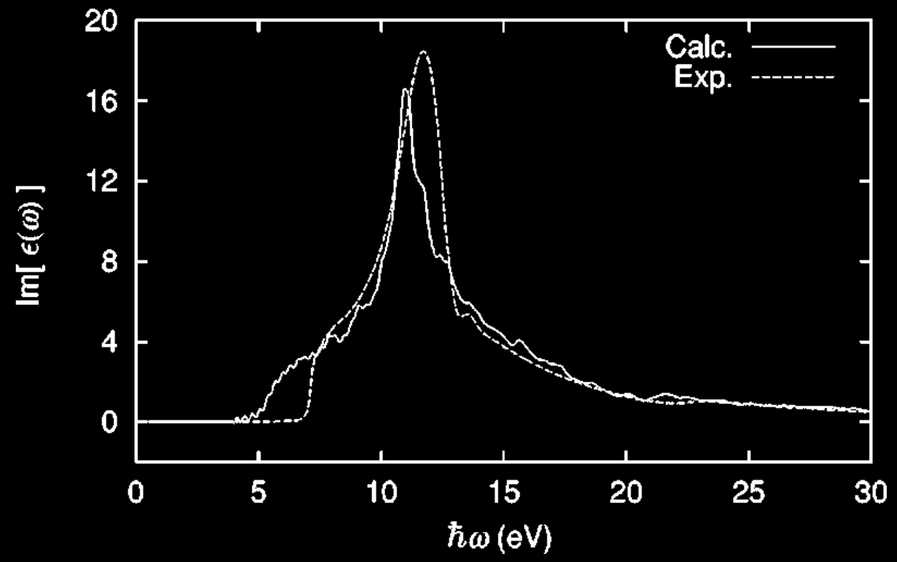
linear response: calculation of the dielectric function

$$\boldsymbol{A}(t=0) = \boldsymbol{A}_0$$

$$\boldsymbol{\epsilon}^{-1}(\omega) = 1 + \frac{1}{A_0}\int_0^\infty e^{-i\omega t}\frac{\partial}{\partial t}\boldsymbol{A}(t)$$

Dielectric function of diamond





G. F. Bertsch, J.-I. Iwata, A. Rubio, and K. Yabana, PRB 62 7998 (2000)

current challenges in computational electron dynamics

long time scales

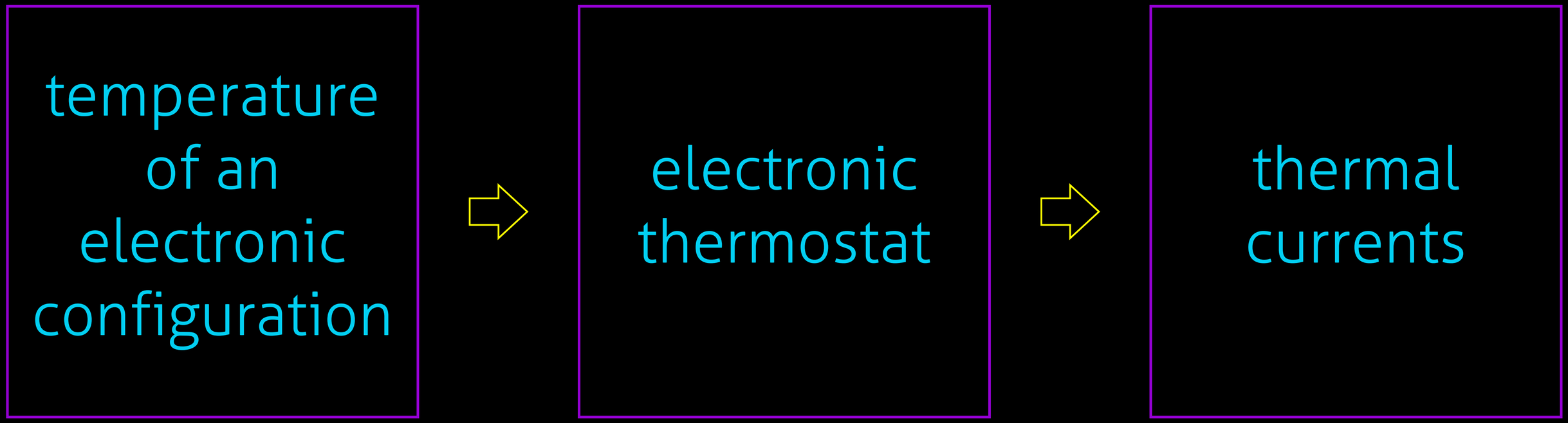
limited by speed of electrons

ionic time scales and beyond

smarter analysis tools*

*X. Andrade, J. N. Sanders, and A. Aspuru-Guzik, "Application of compressed sensing to the simulation of atomic systems", PNAS 109 13928 (2012)

temperature

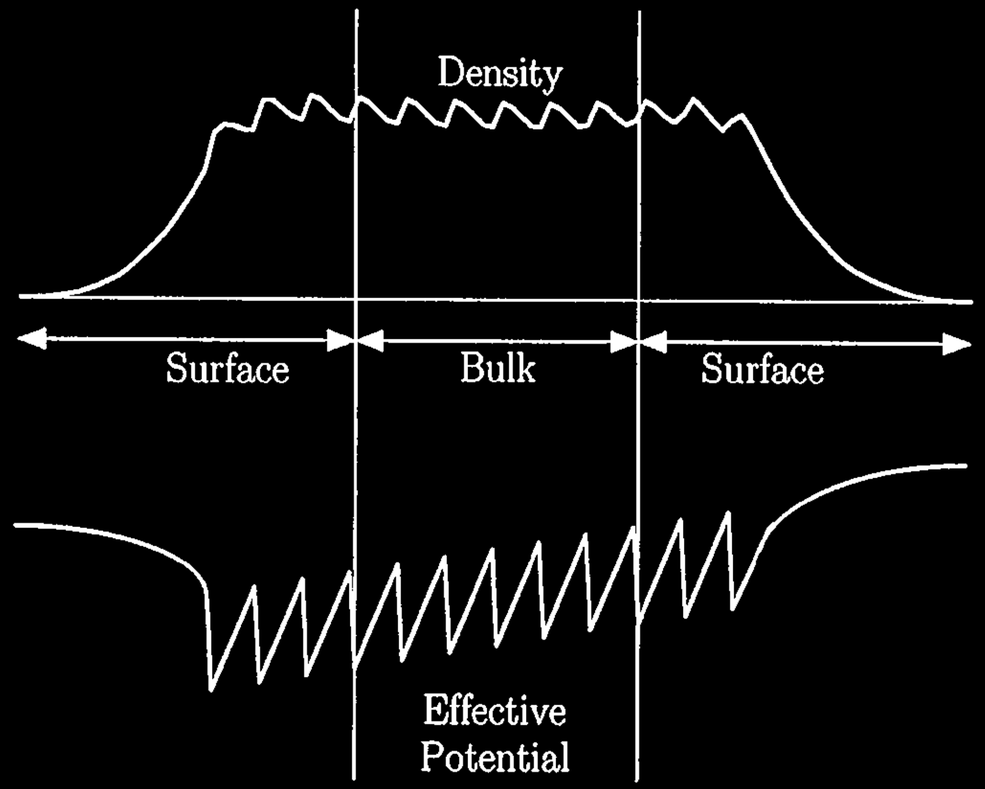


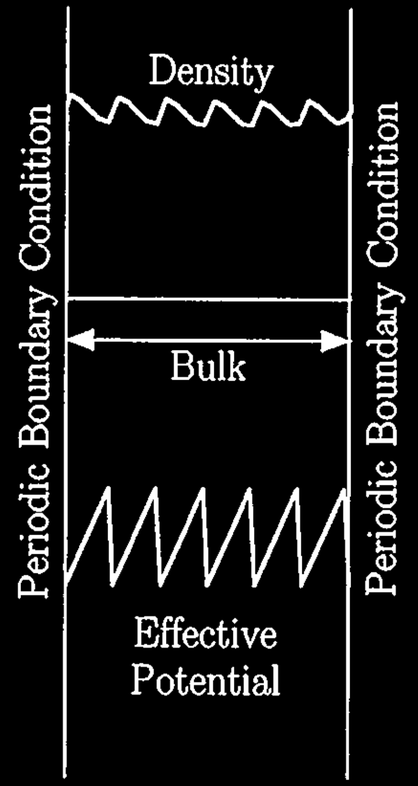
electron - nuclei interaction

beyond
ehrenfest

energy transfer
between ions and
electrons

xc functionals and polarization





X. Gonze, Ph. Ghosez, and R. W. Godby, PRL 74, 4035 (1995)
X. Gonze, Ph. Ghosez, and R. W. Godby, PRL 78, 294 (1997)

conclusions

powerful method to simulate properties of materials

many applications to explore

theory, algorithms, and code development needed