Numerical approaches to solving the Schrödinger equations

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Outline

- time-independent Schrödinger eqs.

  - discretization schemes, tight binding

  - finding the ground state and few excited states for quantum wells

  - Lanczos method for exact diagonalization

- time-dependent Schrödinger eqs.

  - Chebyshev propagation method
  - wave-packet propagation
  - electric field (Bloch-Zener oscillations)

Exact Diagonalization: basic idea

$$\mathcal{H}|\psi\rangle = E|\psi\rangle$$

- Solve the Schrödinger equation numerically: matrix formulation

- The Hamiltonian is usually a sparse matrix:
  - discretization of the Laplacian
  - tight binding formalism

- Still, this is a computationally intensive problem
  - quantum many body systems (electrons, spins)
  - the vector space grows exponentially

Exact Diagonalization: applications

- Quantum magnets: Ising model, Heisenberg model in 1D and 2D
  - nature of the ground state, quantum phase transitions
  - quantum computing, entanglement

- Fermionic models: Hubbard and t-J models
  - ground states, gaps, pairing properties

- Fractional quantum Hall states:
  - gaps, testing analytical ground states

- Full configuration interaction in quantum dots or quantum chemistry
  - single particle states + interactions

Exact Diagonalization: world records

- Spin S=1/2 models: 2^n scaling
  40 sites on a square lattice

- Hubbard models: 4^n scaling
  20 sites on a square lattice at half-filling
  20 sites quantum dot structure

- t-J models (no double occupancy): 3^n scaling
  32 sites on a square lattice with 4 holes

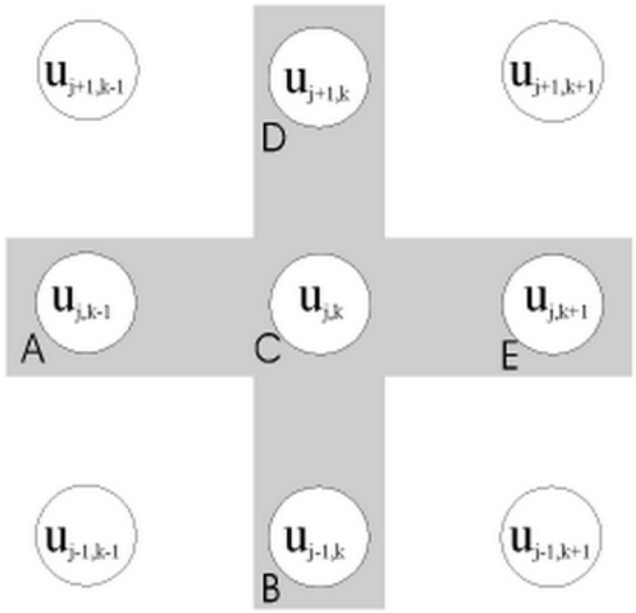
Number of states on the order of $\sim 10^{10}$

Single electron states - continuum

$$\mathcal{H}(r) = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

- Discretize the spatial coordinates
- Use finite differences to approximate the Laplacian on a grid
- 1D approx. $$\nabla^2 u = \frac{1}{h^2}(u_{i-1} - 2u_i + u_{i+1}) + \mathcal{O}(h^2)$$
- 2D approx. $$\nabla^2 u = \frac{\partial^2}{\partial x^2}u + \frac{\partial^2}{\partial y^2}u$$

$$\approx \frac{1}{h^2}(u_{i,j-1} - 2u_{i,j} + u_{i,j+1} + u_{i-1,j} - 2u_{i,j} + u_{i+1,j}) + \mathcal{O}(h^2)$$



$$\frac{1}{h^2} \times \begin{array}{ccc} & 1 & \\ 1 & -4 & 1 \\ & 1 & \end{array}$$

5-point

$$\frac{1}{6h^2} \times \begin{array}{ccc} 1 & 4 & 1 \\ 4 & -20 & 4 \\ 1 & 4 & 1 \end{array}$$

9-point

13-point $$\frac{1}{h^4} \times \begin{array}{ccccc} & & 1 & & \\ & 2 & -8 & 2 & \\ 1 & -8 & 20 & -8 & 1 \\ & 2 & -8 & 2 & \\ & & 1 & & \end{array}$$

$n^2 \times n^2$
Hamiltonian is now a sparse matrix

$$\mathrm{T}_{\mathrm{kinetic}} = \begin{bmatrix} -4 & 1 & 0 & 1 & & & & & \\ 1 & -4 & 1 & 0 & 1 & & & & \\ 0 & 1 & -4 & 0 & 0 & 1 & & & \\ 1 & 0 & 0 & -4 & 1 & 0 & 1 & & \\ & 1 & 0 & 1 & -4 & 1 & 0 & 1 & \\ & & 1 & 0 & 1 & -4 & 0 & 0 & 1 \\ & & & 1 & 0 & 0 & -4 & 1 & 0 \\ & & & & 1 & 0 & 1 & -4 & 1 \\ & & & & & 1 & 0 & 1 & -4 \end{bmatrix}$$

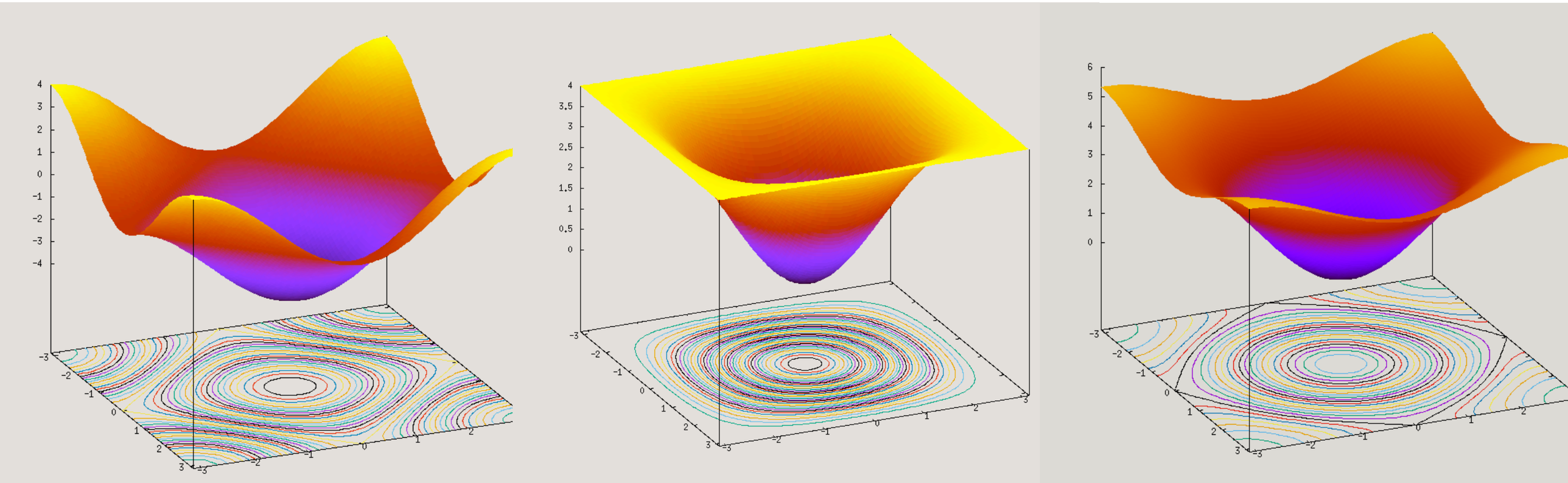
V(r) appears only on the diagonal

9-point stencil

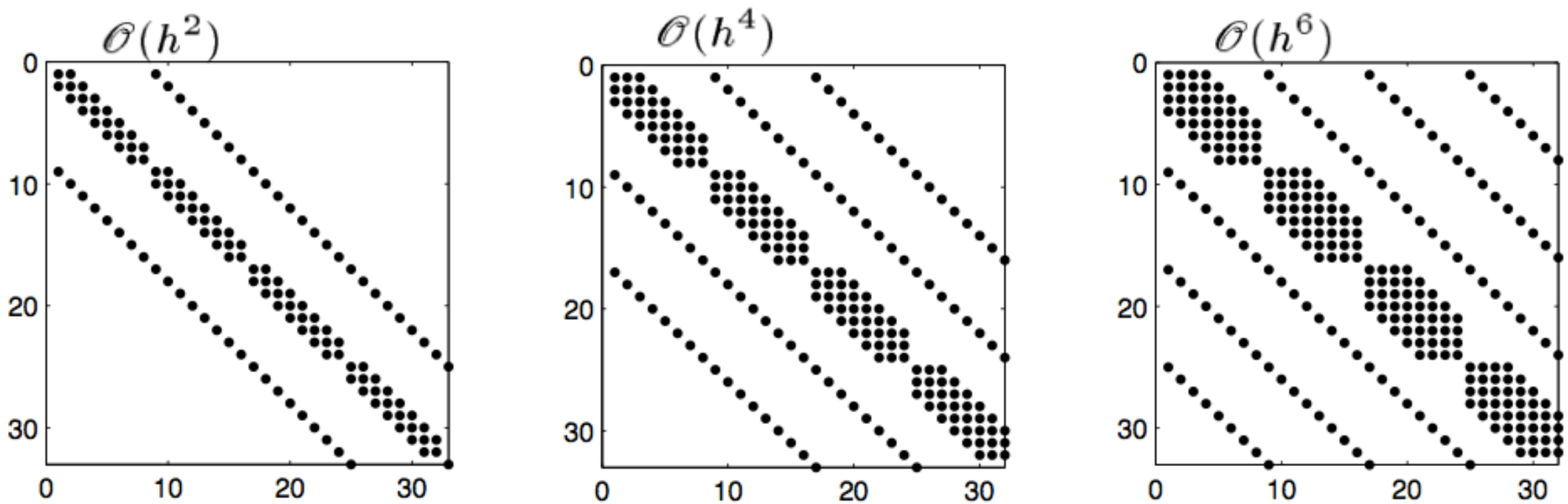
$$F_9 = \gamma \begin{bmatrix} 0 & 1 & 0 \\ 1 & -4 & 1 \\ 0 & 1 & 0 \end{bmatrix} + (1-\gamma) \begin{bmatrix} 1/2 & 0 & 1/2 \\ 0 & -2 & 0 \\ 1/2 & 0 & 1/2 \end{bmatrix}$$

$$E(k_x, k_y) = 2(1-\gamma)(cosk_x cosk_y - 1) + 2\gamma(cosk_x + cosk_y - 2)$$

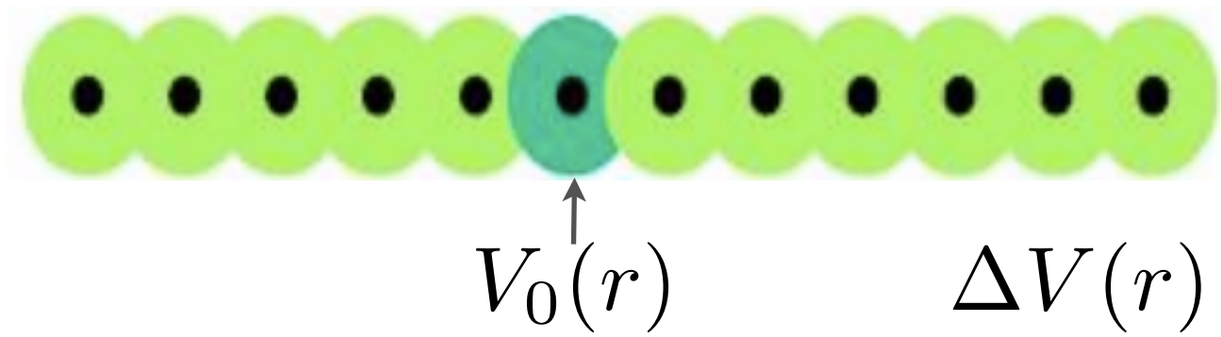
$\gamma = 1$ $\gamma = 0.5$ $\gamma = 2/3$



- trade-off between the grid size and the precision of the finite difference approximation
- an important factor is also the scaling of the diagonalization procedure vs. grid size



Atomistic tight- binding theory, LCAO



- Consider a solid comprised of a periodic lattice of atoms
- Electrons will move in the potential V(r) generated by the atoms

$$[-\frac{\hbar^2}{2m}\nabla^2 + V(r)]\psi_l = E_l\psi_l \longrightarrow [\underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V_0(r)}_{\text{atomic part}} + \Delta V(r)]\psi_l = E_l\psi_l$$

$$\Delta V(r) = \sum_{R\neq 0} V_0(r+R) \longrightarrow V(r) = \sum_{R} V_0(r+R)$$

- define localized atomic orbitals, bound to each atom:

$$[-\frac{\hbar^2}{2m}\nabla^2 + V_0(r)]\phi_i = E_i\phi_i$$

- then the total wave-function is a linear combination of atomic orbitals

different atomic orbitals

$$\psi(r) = \sum_{\alpha}\sum_{R_n} c_{\alpha[R_n]}\phi_\alpha(r - R_n)$$

- for a 1D chain with one orbital/atom: $\psi(r) = \sum_{n=-\infty}^{\infty} c_{[n]}\phi(r - na_x)$

- we arrive at a generalized eigenvalue problem

$$\boxed{\sum_m \tilde{H}(n,m)c_{[m]} = E\sum_p \tilde{S}(n,p)c_{[p]}}$$

- the tight-binding parameters are:

$$\tilde{H}(n,m) = \langle \phi(r - na_x) | \mathcal{H} | \phi(r - ma_x) \rangle \quad \text{with} \quad \tilde{H}(n,n) = \epsilon_n$$

hopping amplitude — on-site energy

$$\tilde{S}(n,p) = \langle \phi(r - na_x) | \phi(r - pa_x) \rangle \quad \text{with} \quad \tilde{S}(n,n) = 1$$

overlap integral — normalization

- both the hopping amplitudes and the overlap integrals are small, unless the atoms are close (nearest or next-nearest neighbor)

- the discrete lattice is now given by the atomic lattice

- example: for one s-orbital/atom and a square lattice, the tight-binding Hamiltonian matrix is identical to the finite-differences one

$$\epsilon_k = \epsilon_s + 2t_{nn}\cos(k_x a) + 2t_{nn}\cos(k_y a) + 2t_{nnn}\cos(k_x a)\cos(k_y a)$$

- the evaluation of the hopping terms involves three-center integrals
- a commonly used approximation is the two-center approx.

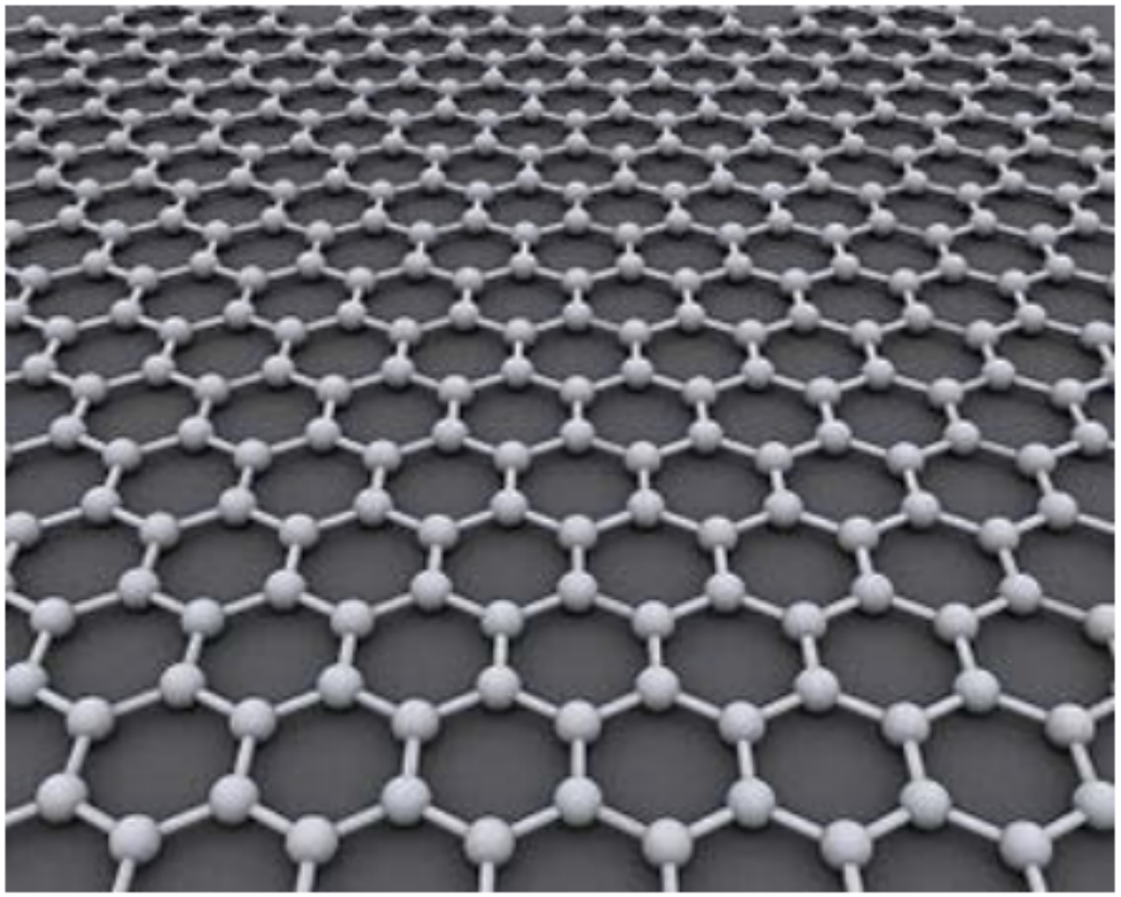
J. C. Slater, G. F. Koster, Phys. Rev. 94, 1498 (1954)

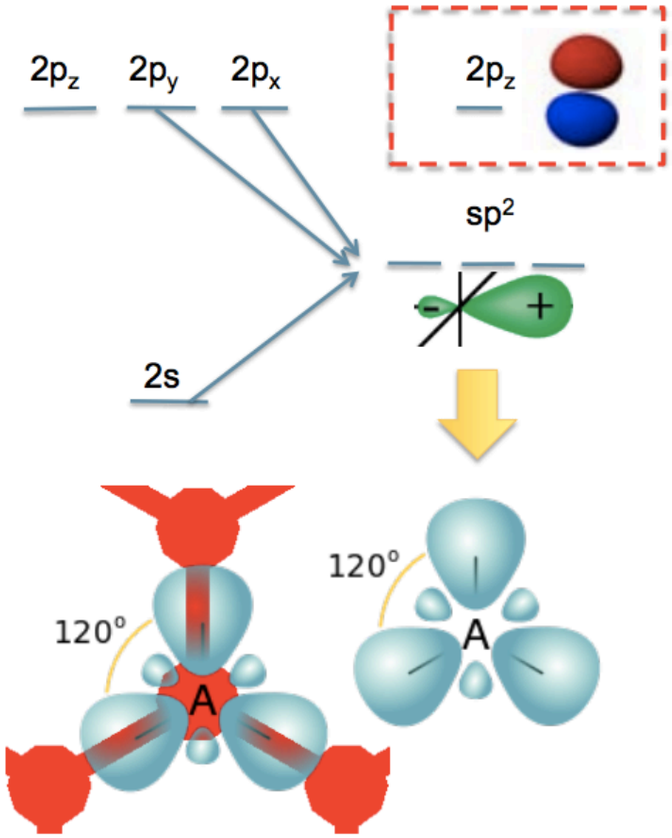
- two-center parameters: $t_{ss\sigma}, t_{sp\sigma}, t_{pp\sigma}, t_{pp\pi}, t_{sd\sigma}, etc.$

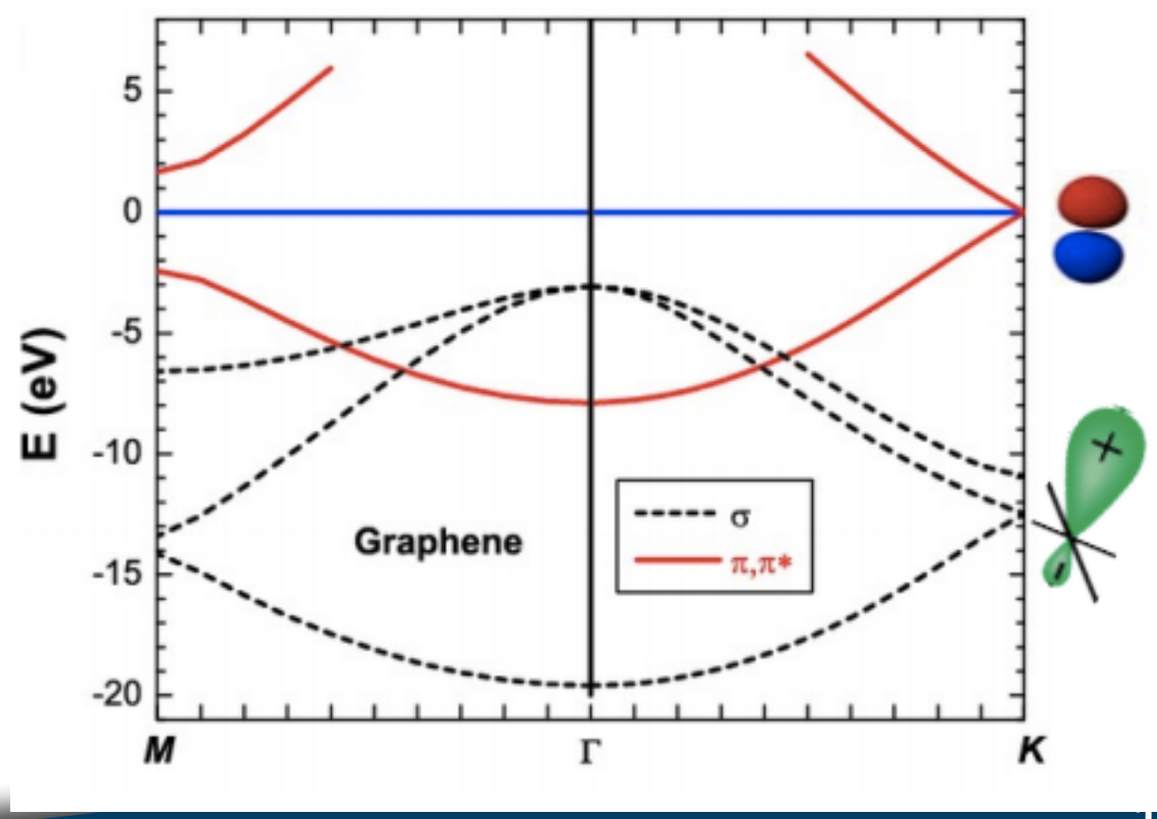
- they are usually obtained by fitting DFT results and are specific for each material due to different lattice constants and symmetries

- example: the low energy band-structure of graphene is well described by a single orbital/atom, ppπ

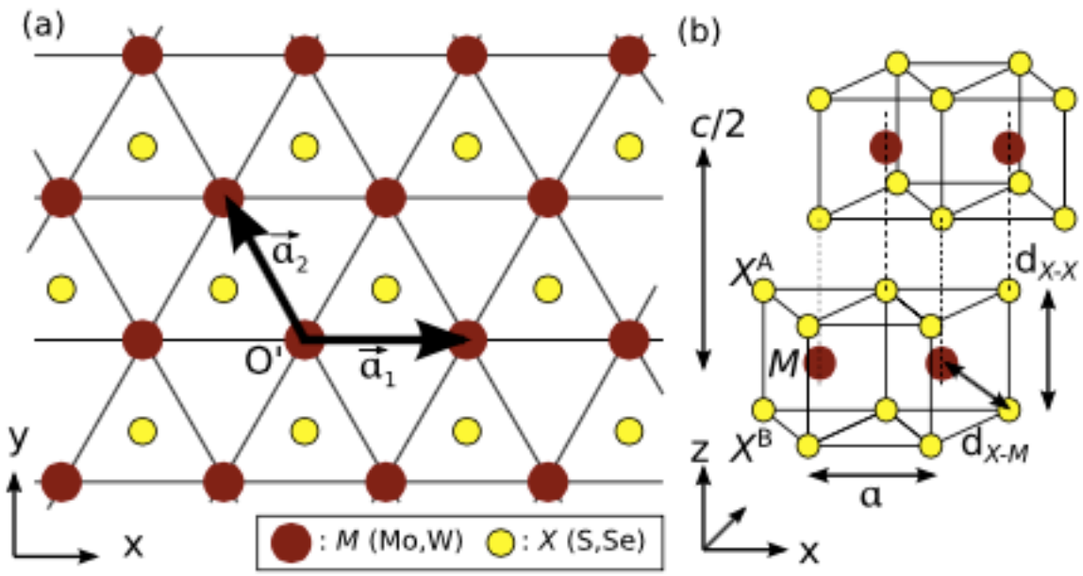
Graphene band-structure



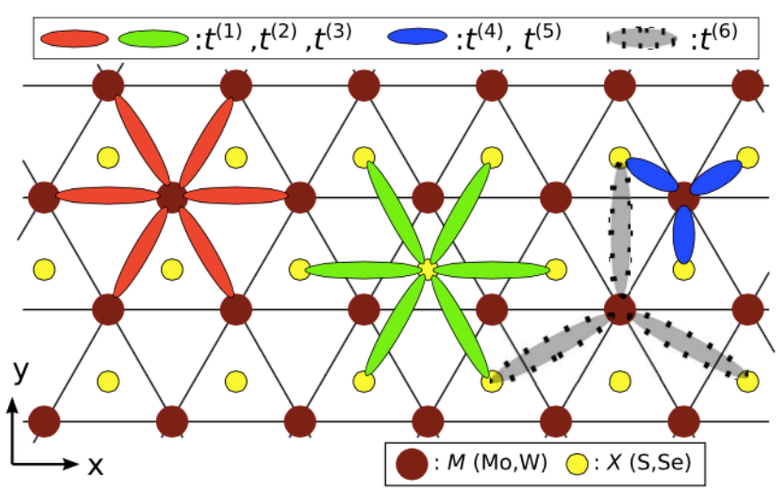


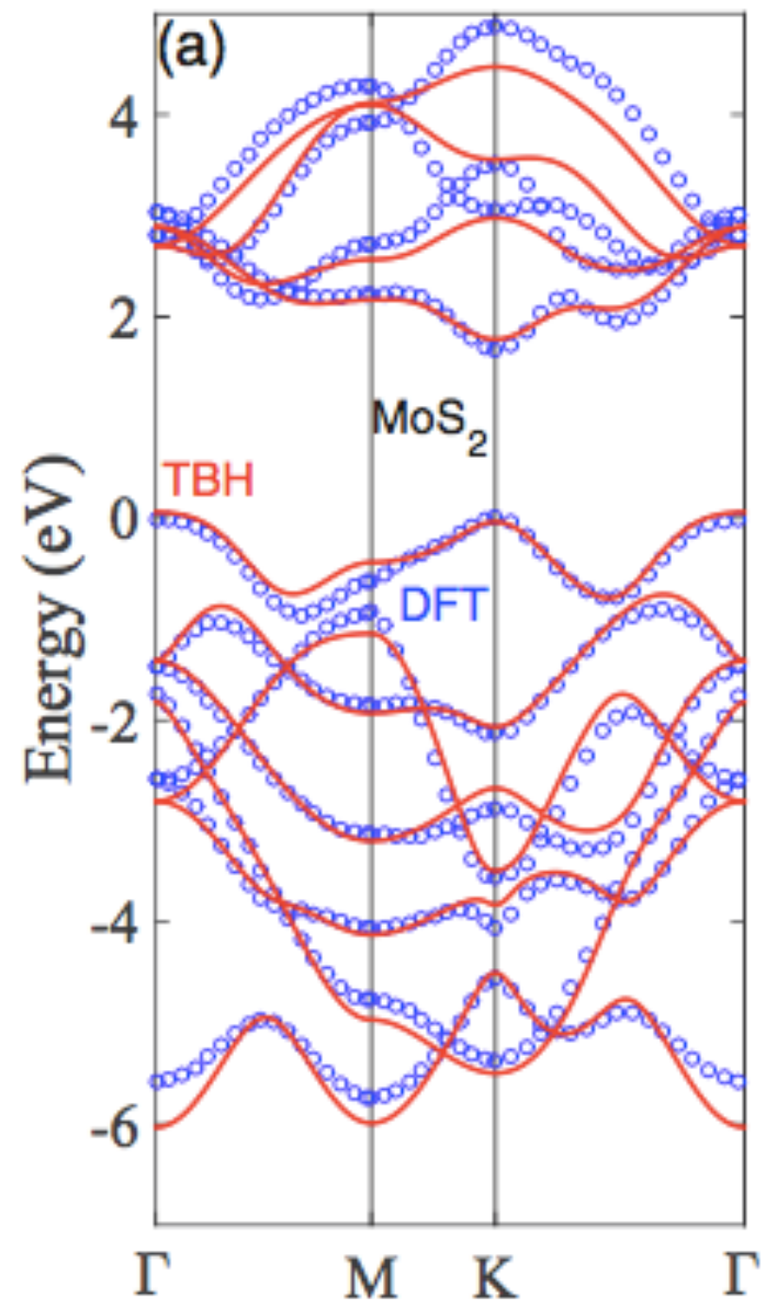


MoS_2 band-structure (transition metal dichalcogenide)



$$\hat{\psi}^{\dagger}_{pd} = [\hat{d}^{\dagger}_{z^2}, \hat{d}^{\dagger}_{xy}, \hat{d}^{\dagger}_{x^2-y^2}, \hat{d}^{\dagger}_{xz}, \hat{d}^{\dagger}_{yz}, \hat{p}^{A\dagger}_{x}, \hat{p}^{A\dagger}_{y}, \hat{p}^{A\dagger}_{z}, \hat{p}^{B\dagger}_{x}, \hat{p}^{B\dagger}_{y}, \hat{p}^{B\dagger}_{z}].$$





Löwdin orthogonalization

Generalized eigenvalue eq: $\mathcal{H}b = \epsilon \mathcal{S} b$

use: $\mathcal{S}^{-1/2}\mathcal{S}^{1/2} = 1$ $\mathcal{S}^{1/2}\mathcal{S}^{1/2} = \mathcal{S}$

Conventional eigenvalue eq: $\bar{\mathcal{H}}\bar{b} = \epsilon \bar{b}$

where: $\bar{\mathcal{H}} = \mathcal{S}^{-1/2}\mathcal{H}\mathcal{S}^{1/2}$ and $\bar{b} = \mathcal{S}^{1/2} b$

- could be potentially very cumbersome to find $\mathcal{S}^{1/2}$
- using that $\delta\mathcal{S} = \mathcal{S} - 1$ is small:

$$\mathcal{S}^{1/2} \approx 1 + \frac{1}{2}\delta\mathcal{S} + \frac{1}{8}(\delta\mathcal{S})^2 \longrightarrow \text{still sparse}$$

Numerical diagonalization

Full diagonalization

- Householder transformation, reduction to tridiagonal form
- diagonalization of tridiagonal matrices
- both are of order $\mathcal{O}(n^3)$ and the matrix needs to be stored
- useful for dense matrices, simple problems, many eigenstates are needed

Iterative methods

- project on a cleverly chosen subspace with reduced dimension
- power method, Lanczos and Arnoldi(ARPACK) methods
- very powerful for sparse matrices and if the matrix is not stored
- allows the calculation of few extreme eigenvalues/vectors

The power method

- assume that A is a diagonalizable matrix, with eigenvalues

  $\lambda_1, \lambda_2, \cdots, \lambda_n$ and $|\lambda_1| > |\lambda_j|$ is the largest one

- any vector can be expanded in the eigenbasis: $v_0 = \sum_i c_i x_i$

$$A^k v_0 = \sum_i c_i A^k x_i = \sum_i c_i \lambda_i^k x_i = c_1 \lambda_1^k \left[x_1 + \sum_{i>1} \frac{c_i}{c_1} \left(\frac{\lambda_i}{\lambda_1} \right)^k x_i \right]$$

$$v_k = \frac{A^k v_0}{||A^k v_0||} \xrightarrow[k\to\infty]{} x_1 \qquad \frac{v_k^T A v_k}{v_k^T v_k} \xrightarrow[k\to\infty]{} \lambda_1$$

- geometric convergence with ratio $\left| \frac{\lambda_2}{\lambda_1} \right|$ large gap is beneficial

- very fast for sparse matrices, only stores 2 vectors

The Lanczos method

Cornelius Lanczos (1893–1974)
born in Budapest
assistant of Einstein

- use the subspace (Krylov) spanned by $\{v_k\} = \{A^k v_0\}$
- Lanczos procedure, finds $T = V^T A V$ with $V = [v_1 v_2 \cdots v_m]$

$$T_m = \begin{bmatrix} a_1 & b_1 & & \\ b_1 & \ddots & \ddots & \\ & \ddots & \ddots & b_{m-1} \\ & & b_{m-1} & a_m \end{bmatrix}$$

$$AV = VT \longrightarrow \qquad Av_k = \beta_{k-1} v_{k-1} + \alpha_k v_k + \beta_k v_{k+1}$$

Lanczos iteration

$$Av_k = \beta_{k-1}v_{k-1} + \alpha_k v_k + \beta_k v_{k+1}$$

$$AV_k = V_k T_k + re_k^T$$

- sparse matrix-vector multiplication
- need to keep only 3 vectors
- orthogonality is mathematically ensured, in practice this becomes a problem because of numerical precision

$$\begin{aligned}
&\text{for } k = 1, 2, \cdots, m \\
&\quad \text{if } k = 1 \text{ then} \\
&\quad\quad r = Av_k \\
&\quad \text{else} \\
&\quad\quad r = Av_k - \beta_{k-1}v_{k-1} \\
&\quad \text{end} \\
&\quad \alpha_k = v_k^T r \\
&\quad r = r - \alpha_k v_k \\
&\quad \beta_k = ||r|| \\
&\quad v_{k+1} = r/\beta_k \\
&end
\end{aligned}$$

Convergence and orthogonality

- the Lanczos iteration should be coupled with the diagonalization of T

$$T = V^T A V = S \Lambda S^T$$

$$A = (VS)\Lambda(VS)^T$$

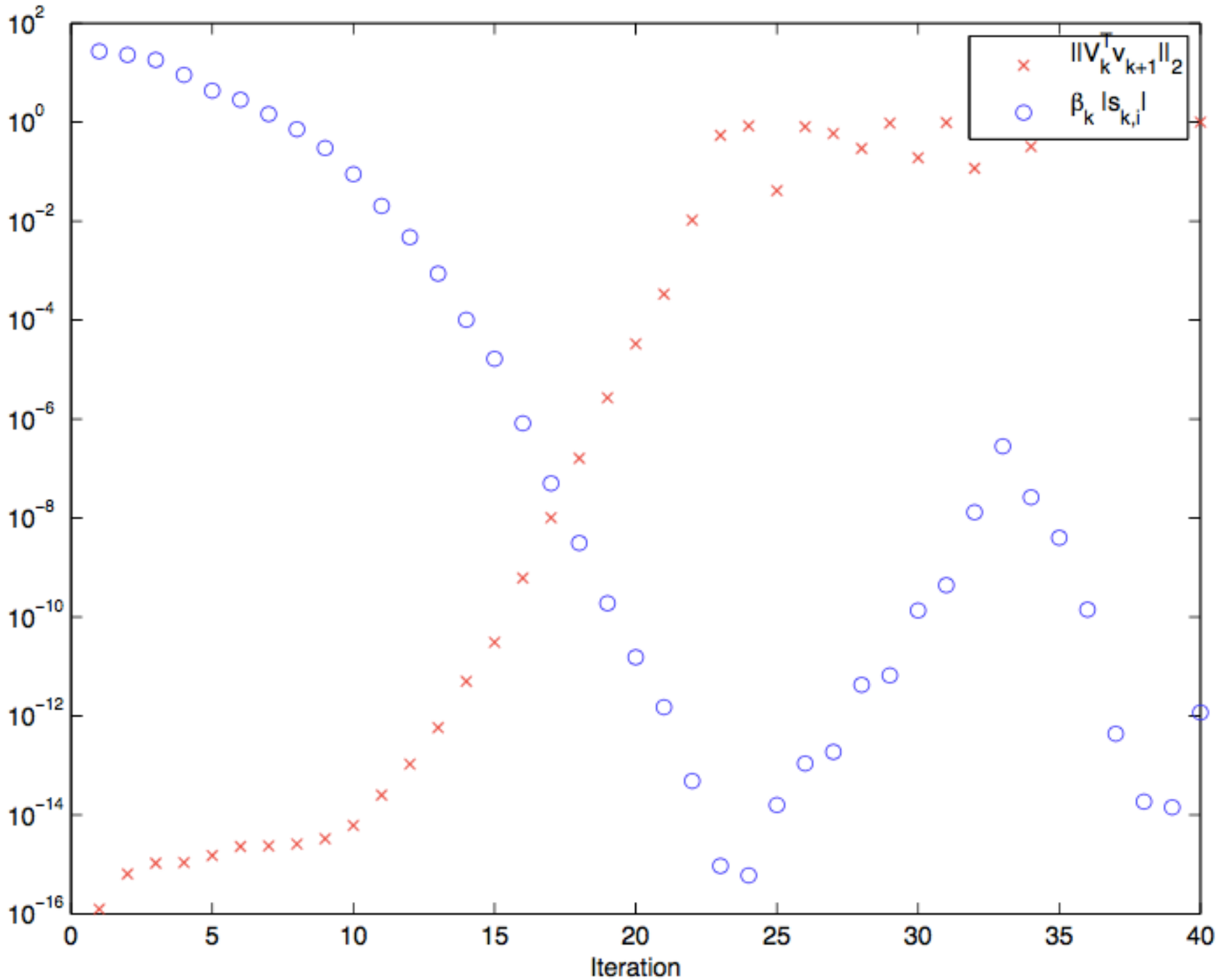
- eigenvalues of T (Ritz values) are also eigenvalues of A, with corresponding eigenvectors given by $X = VS$

- test for convergence of eigenpair $(\theta_i, x_i = V s_i)$

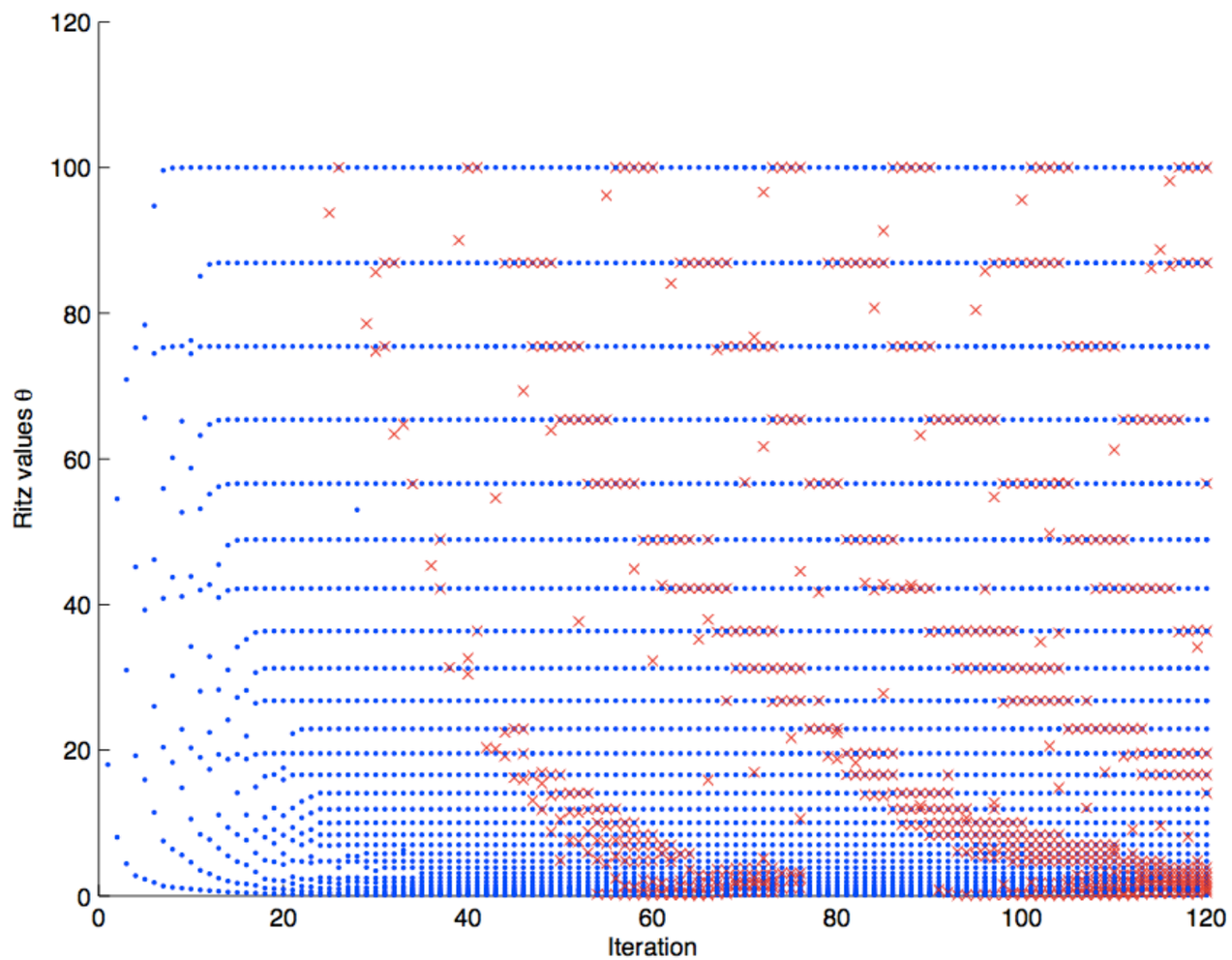
$$\begin{aligned} ||Ax_k - \theta_k x_k||_2 &= ||AV_m s_k - \theta_k V_m s_k||_2 \\ &= ||(AV_m - V_m T_m) s_k||_2 \\ &= ||r e_m^T s_k||_2 = \beta_m |s_{m,k}| \end{aligned}$$

$$|v_{m+1}^T v_i| \approx \frac{|r^T v_i| + \epsilon_{mach}||A||_2}{|\beta_m|} \qquad |v_{m+1}^T x_i| \approx \frac{\epsilon_{mach}||A||_2}{|\beta_m||s_{m,i}|}$$

C. C. Paige, *J. Appl. Math.*, 18:341–349, 1976

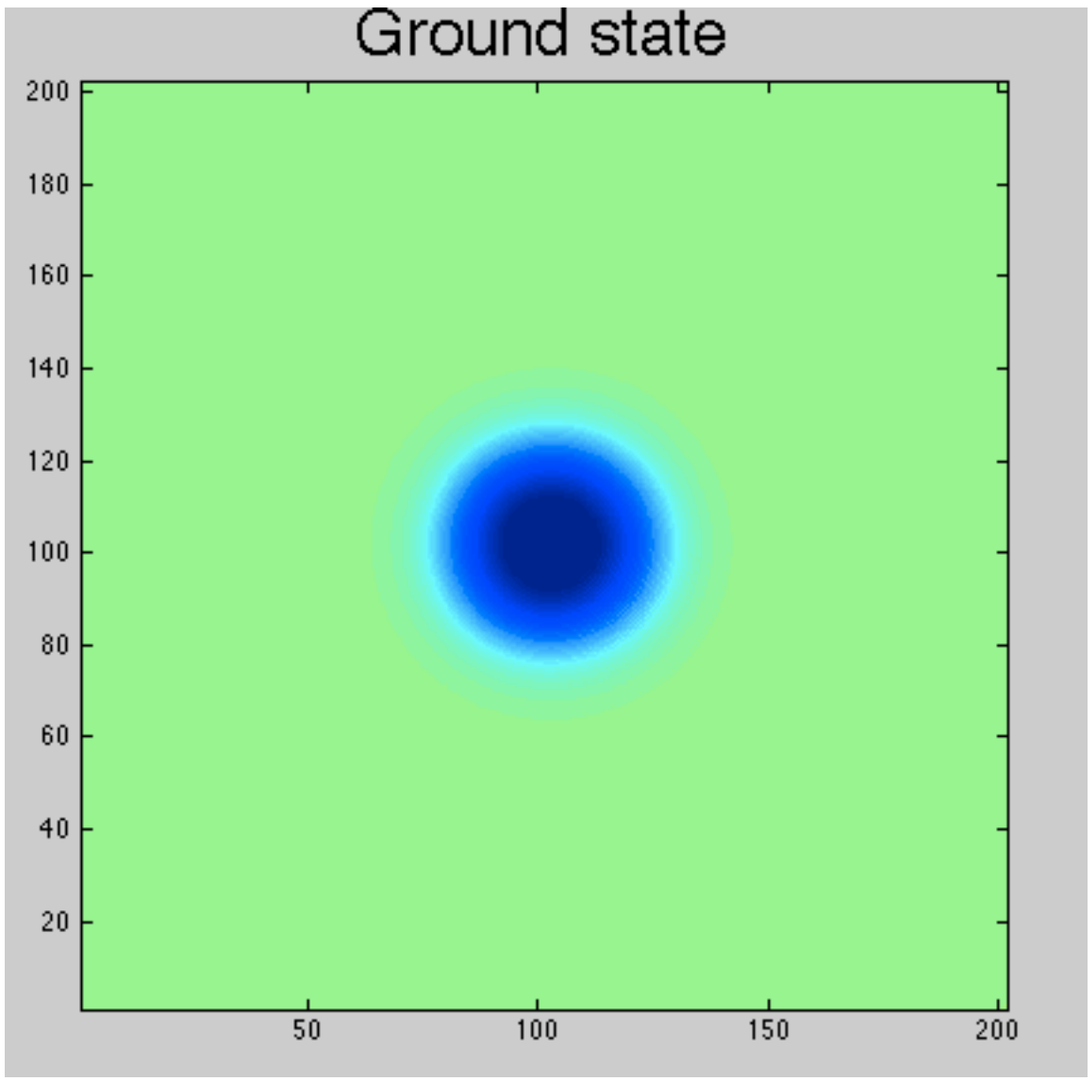

10^{2}
10^{0}
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
0
5
10
15
20
25
30
35
40
Iteration
$\|V_k^T v_{k+1}\|_2$
$\beta_k |s_{k,i}|$

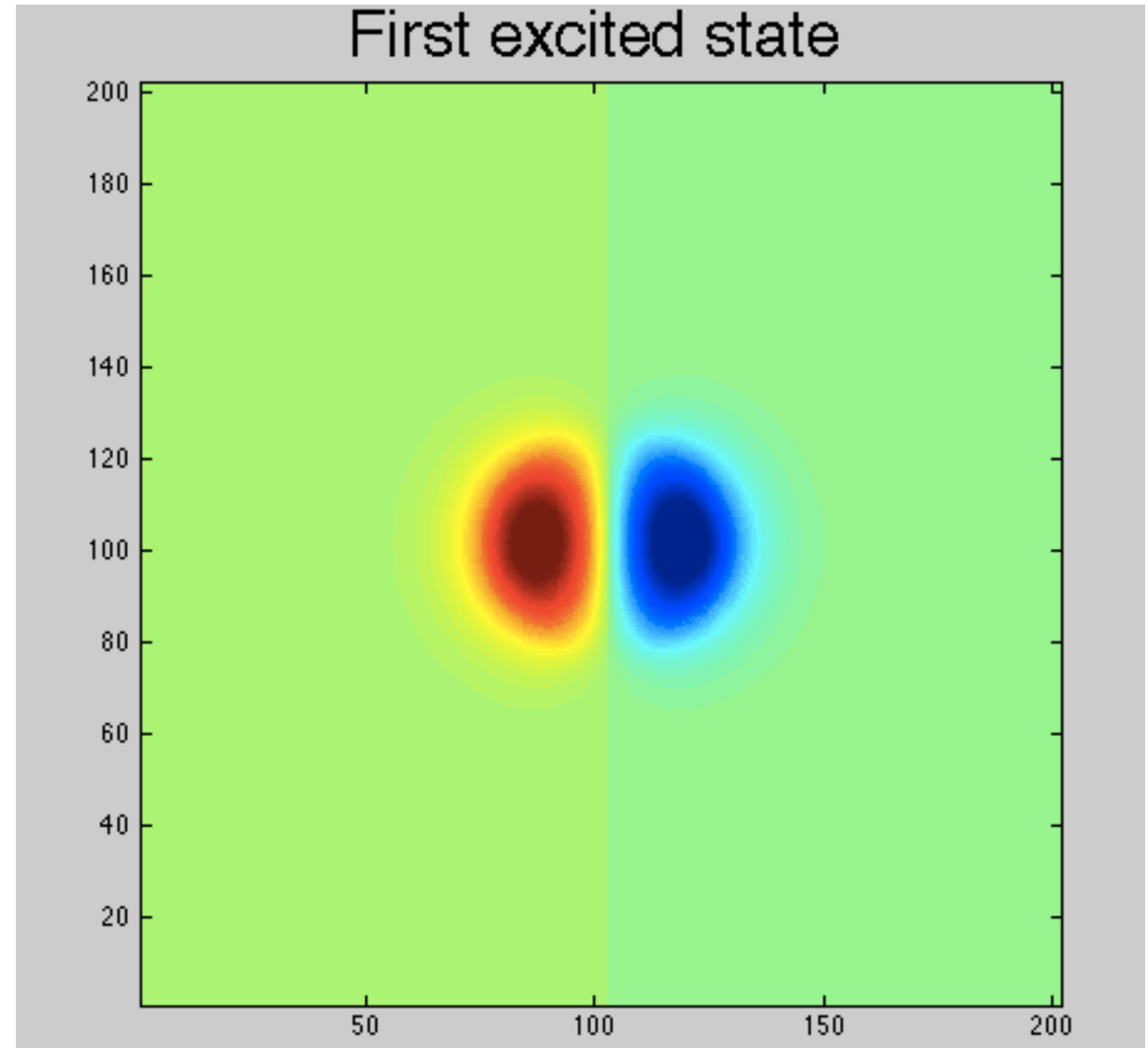
- Lanczos without reorthogonalization? not in real life
- loss of orthogonality when an eigenpair converges
- spurious eigenvalues appear and converge towards already converged Ritz values



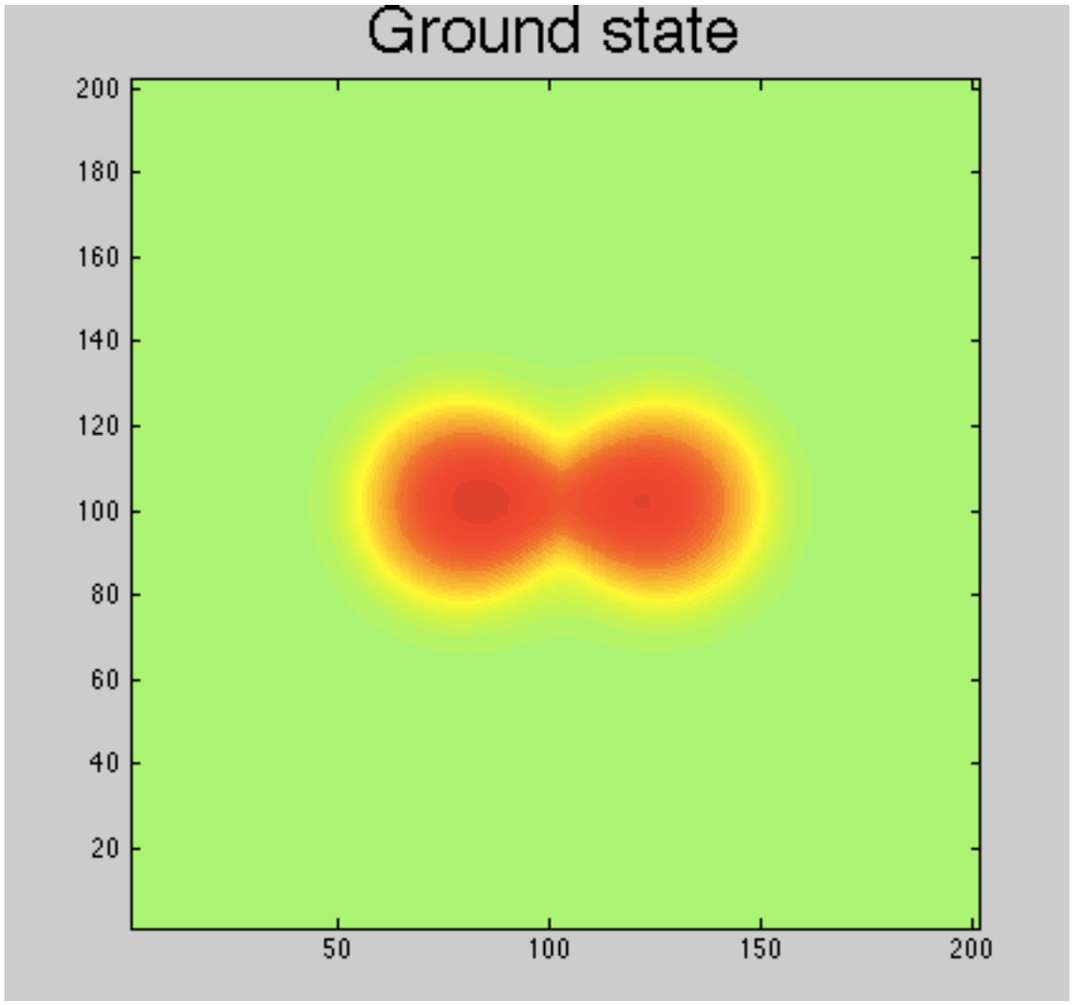
Application: quantum well

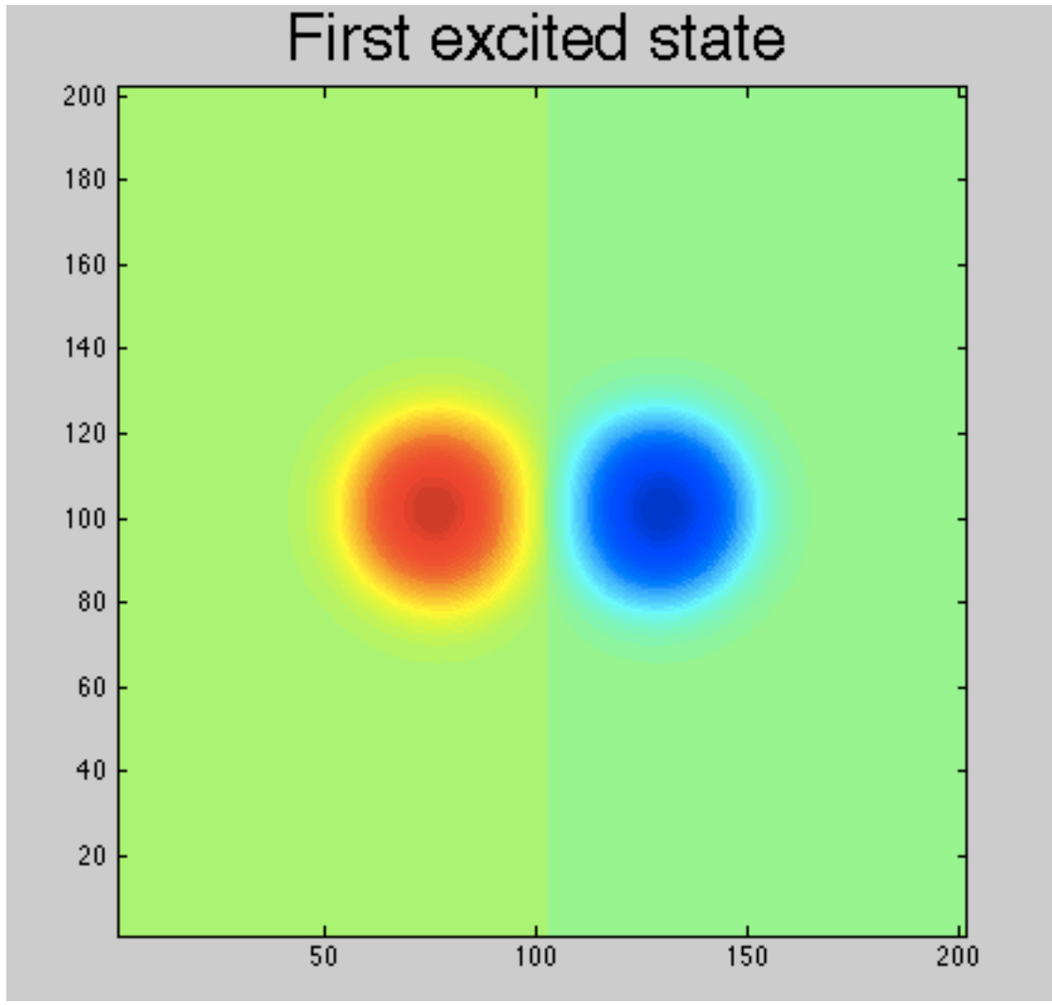
- consider a square lattice, discretized square grid
- use Lanczos to find the bound states of circular regions that have negative potential (quantum wells)



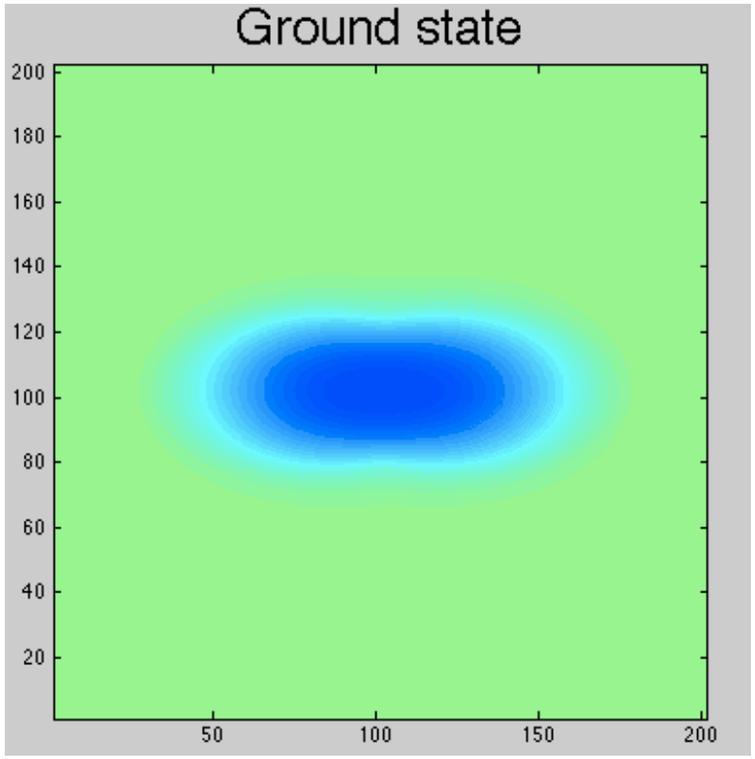


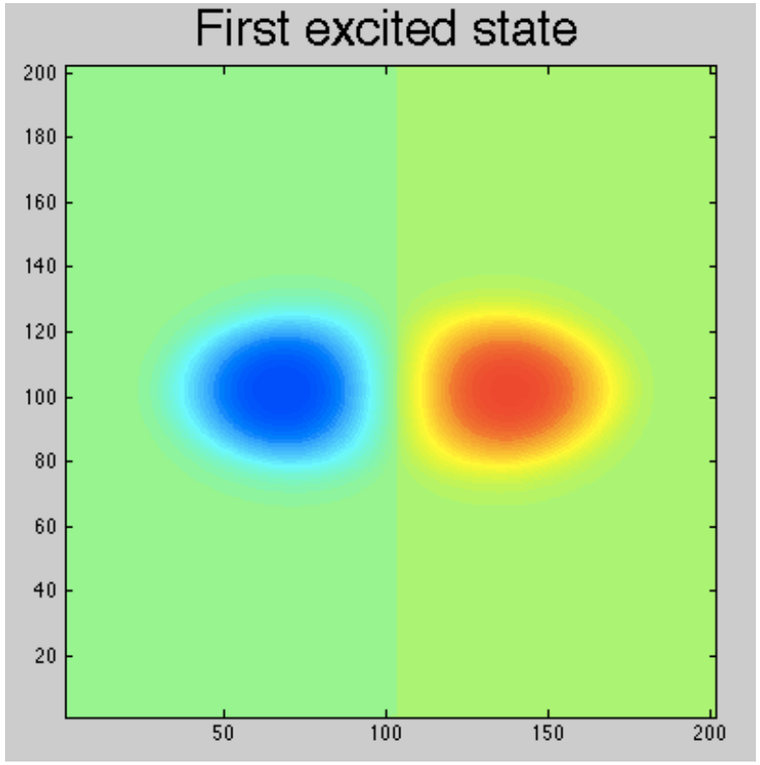
- Coupling of bound states from two separate wells
- Bonding and anti-bonding

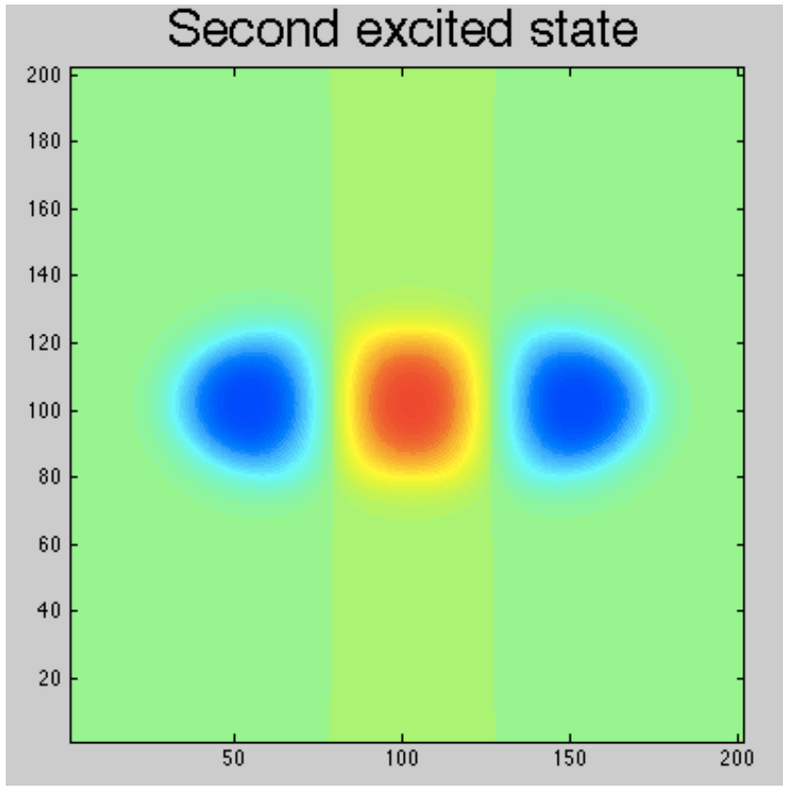


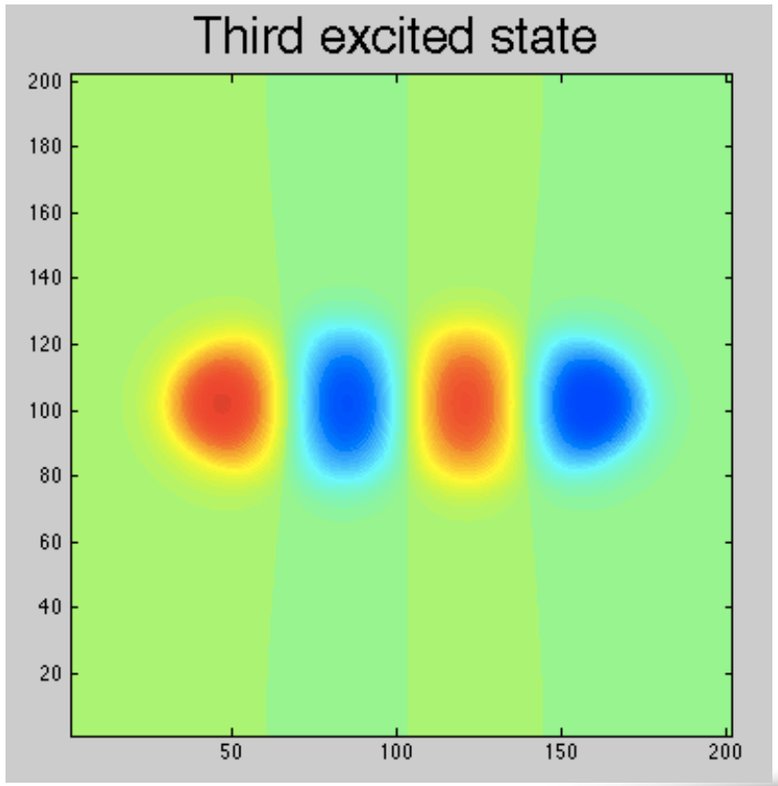


- states with p-wave symmetry (ellipsoidal wells)



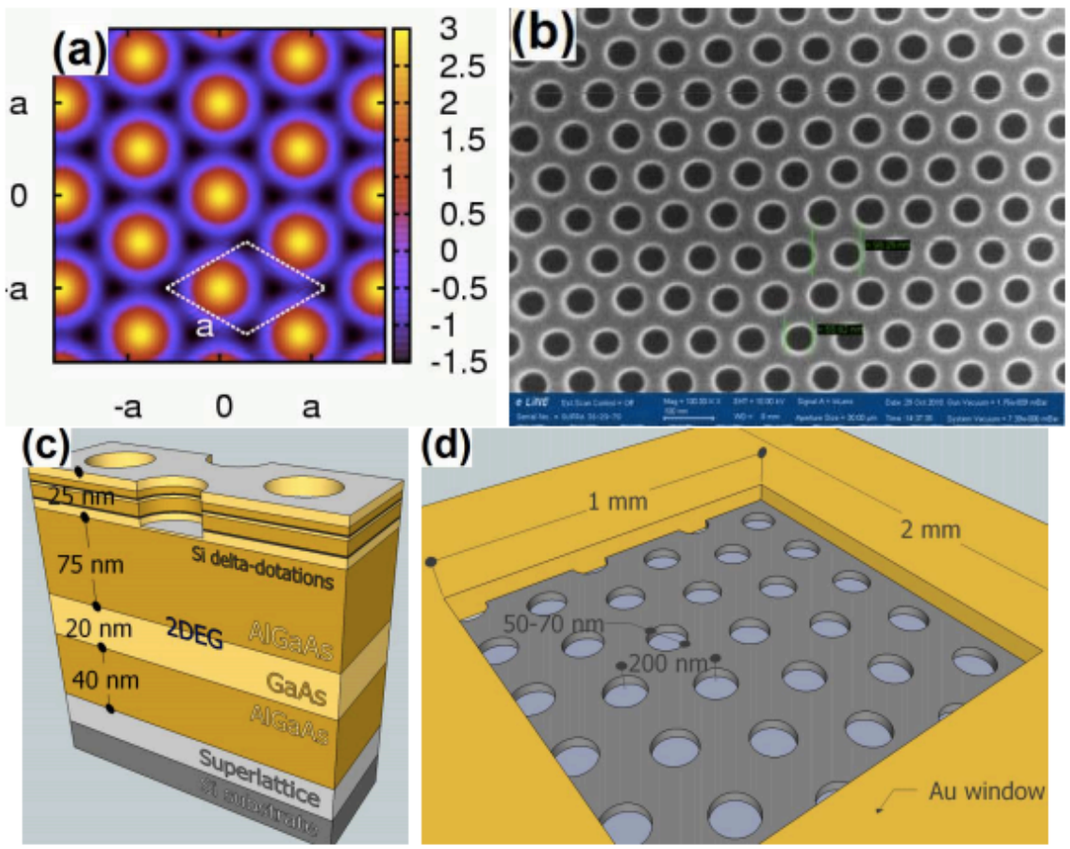


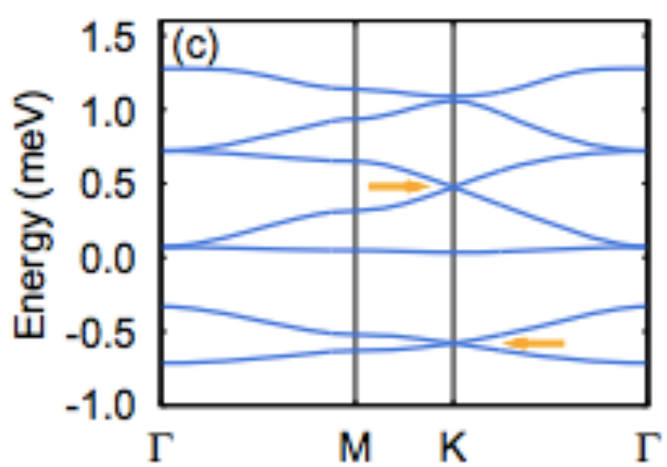




Artificial graphene

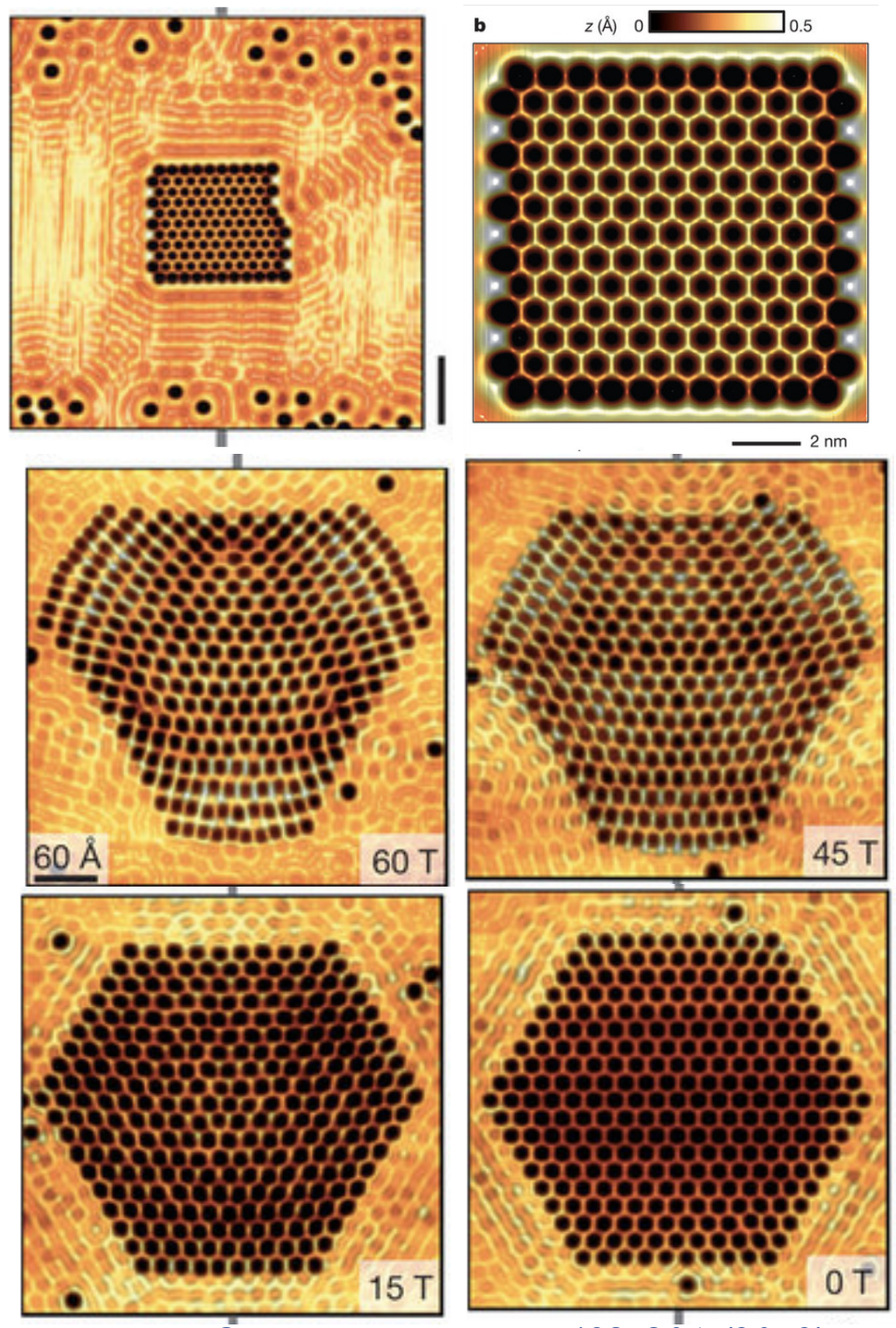
2DEG





L. Nadvornik et al., New J Phys 14, 053002 (2012)

CO molecules on Cu



K.K. Gomes et al. Nature 483, 306 (2012)

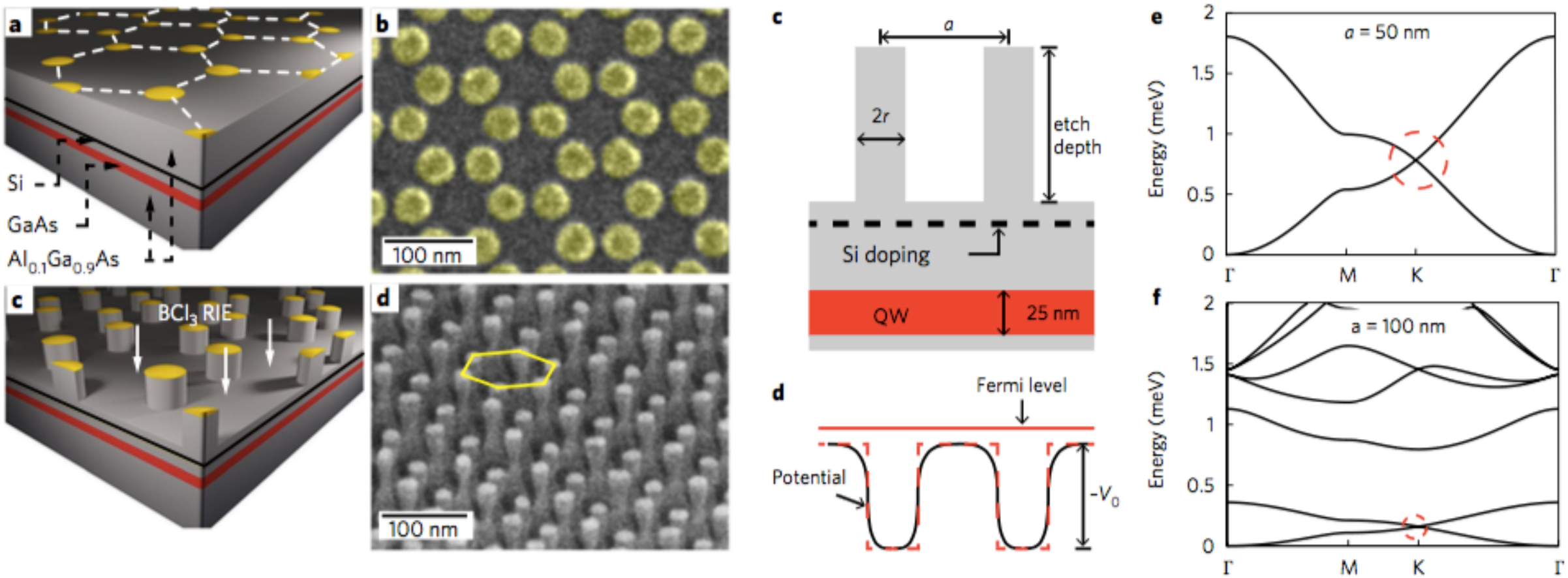
nature nanotechnology

LETTERS

https://doi.org/10.1038/s41565-017-0006-x

Observation of Dirac bands in artificial graphene in small-period nanopatterned GaAs quantum wells

Sheng Wang[1], Diego Scarabelli[1,6], Lingjie Du[1*], Yuliya Y. Kuznetsova[2], Loren N. Pfeiffer[3], Ken W. West[3], Geoff C. Gardner[4], Michael J. Manfra[4], Vittorio Pellegrini[5], Shalom J. Wind[1] and Aron Pinczuk[1,2]



Time dependent Schrodinger eq.

$$\mathcal{H}(t)|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle$$

- time-dep. of the potential $\mathcal{H}(t) = -\frac{\hbar^2}{2m}\nabla^2 + V(t)$
- formal solution in terms of evolution operator U(t,t'):

$$|\psi(t)\rangle = U(t,0)\psi(0)\rangle \qquad U(t,0) = \mathcal{T}e^{-i/\hbar\int_0^t \mathcal{H}(s)ds}$$

- time-independent case: $U(t,0) = e^{-i/\hbar\mathcal{H}t}$

$$|\psi(t)\rangle = U(t,0)\sum_n c_n|v_n\rangle = \sum_n c_n e^{-i/\hbar E_n t}|v_n\rangle$$ (not feasible)

Chebyshev polynomial expansion

Let $f : [-1 : 1] \rightarrow \mathcal{R}$;integrable function

Set of orthogonal functions: $$\phi_n = \frac{T_n(x)}{\pi\sqrt{1-x^2}}$$

$$\langle \phi_n | \phi_m \rangle = \int_{-1}^{1} \pi\sqrt{1-x^2}\phi_n(x)\phi_m(x)dx \qquad \langle \phi_n | \phi_m \rangle = \frac{1+\delta_{n0}}{2}\delta_{n,m}$$

Chebyshev polynomials:

$$T_n(x) = cos[n\, arccos(x)]$$
$$T_0(x) = 1$$
$$T_1(x) = x$$
$$T_{n+1} = 2xT_n(x) - T_{n-1}$$

$$U_n(x) = \sin[(n+1)\, arccos(x)]/\sin[n\, arccos(x)]$$
$$U_0(x) = 1$$
$$U_1(x) = 0$$
$$U_{n+1} = 2xU_n(x) - U_{n-1}$$

$$\mathcal{P}\int_{-1}^{1} \frac{T_n(y)}{(y-x)\sqrt{1-y^2}}dy = \pi U_{n-1}(x)$$

Then any integrable function f(x), can be expressed as:

$$f(x) = \frac{1}{\pi\sqrt{1-x^2}}[\mu_0 + 2\sum_{n=1}^{\infty}\mu_n T_n(x)]; \qquad \mu_n = \int_{-1}^{1} f(x)T_n(x)\, dx$$

- for a time-indep. Hamiltonian: $|\psi(t)\rangle = e^{-i\mathcal{H}t}|\psi(0)\rangle$

- expand the evolution operator

$$e^{-i\mathcal{H}t} = c_0 + 2\sum_{n=1}^{\infty} c_n T_n(\mathcal{H}) \qquad c_n = \int_{-1}^{1} \frac{T_n(x)e^{-ixt}}{\pi\sqrt{1-x^2}} = (-i)^n J_n(t)$$

- iterative scheme for the wave-function

$$\begin{aligned} \text{if } |\psi_n\rangle &= T_n(\mathcal{H})\,|\psi(0)\rangle \\ \text{then: } |\psi_0\rangle &= |\psi(0)\rangle \\ |\psi_1\rangle &= \mathcal{H}\,|\psi(0)\rangle \\ |\psi_{n+1}\rangle &= 2\mathcal{H}\,|\psi_n\rangle - |\psi_{n-1}\rangle \end{aligned}$$

$$|\psi(t)\rangle = c_0(t)|\psi_0\rangle + 2\sum_{n=1}^{N} c_n(t)|\psi_n\rangle$$

Efficiency of the expansion

$$J_k(x) = \frac{1}{\sqrt{2\pi k}} \left(\frac{ex}{2k}\right)^k \text{ for } k \to \infty$$

- the propagation can be truncated safely since

$$J_k \to 0 \text{ for } k \gg ex/2$$

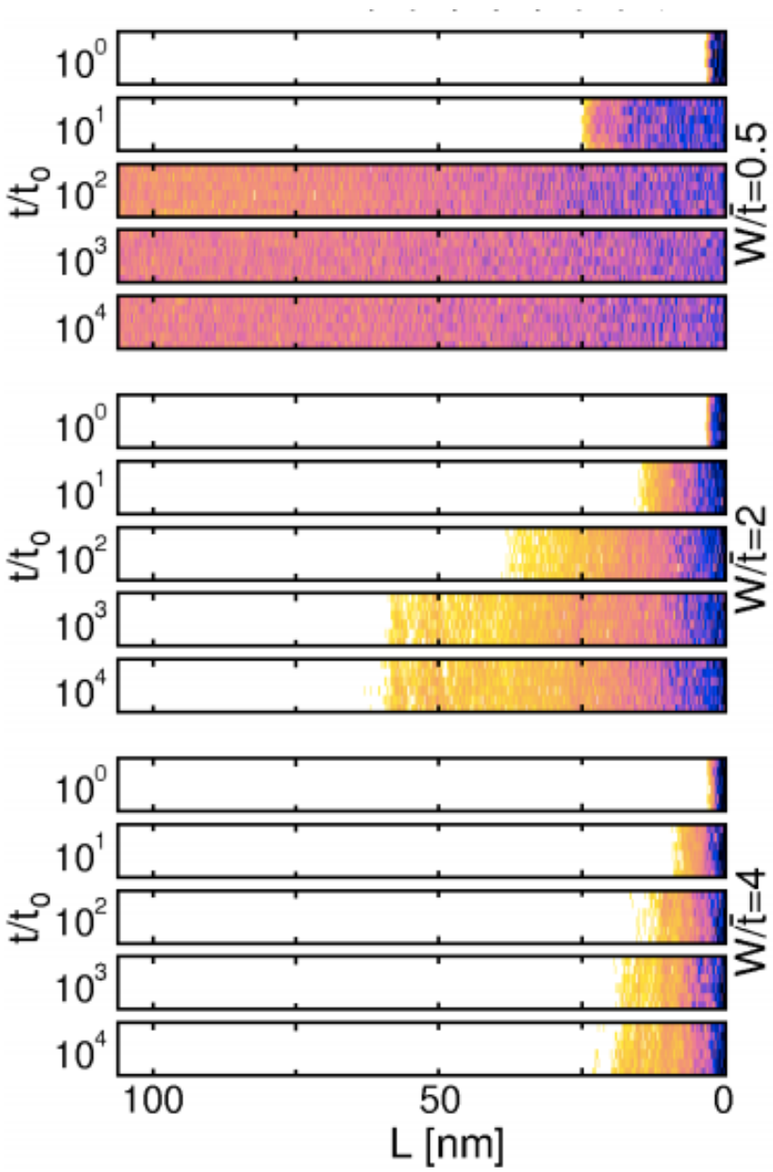
- quasi-exact method, which allows for arbitrarily large time-steps

- well suited for fast computations on GPUs or CPU clusters

Wave-packet localization in graphene

$$\mathcal{H} = -t \sum_{\langle i,j \rangle} (c_i^\dagger c_j + h.c) + \sum_j \epsilon_j c_j^\dagger c_j \qquad \epsilon_j \in [-W/2, W/2]$$

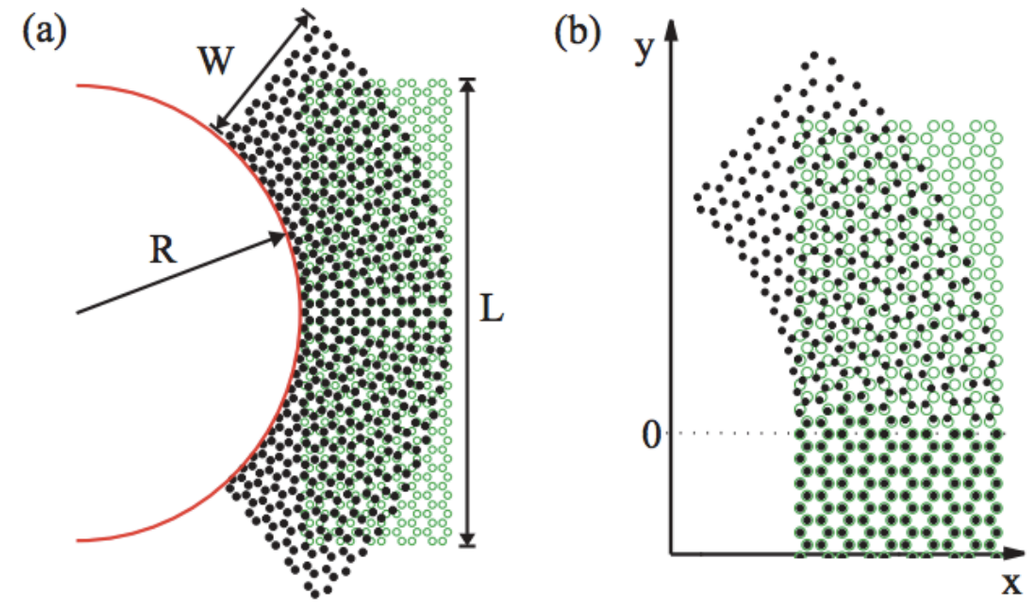
- single orbital tight-binding on honeycomb lattice

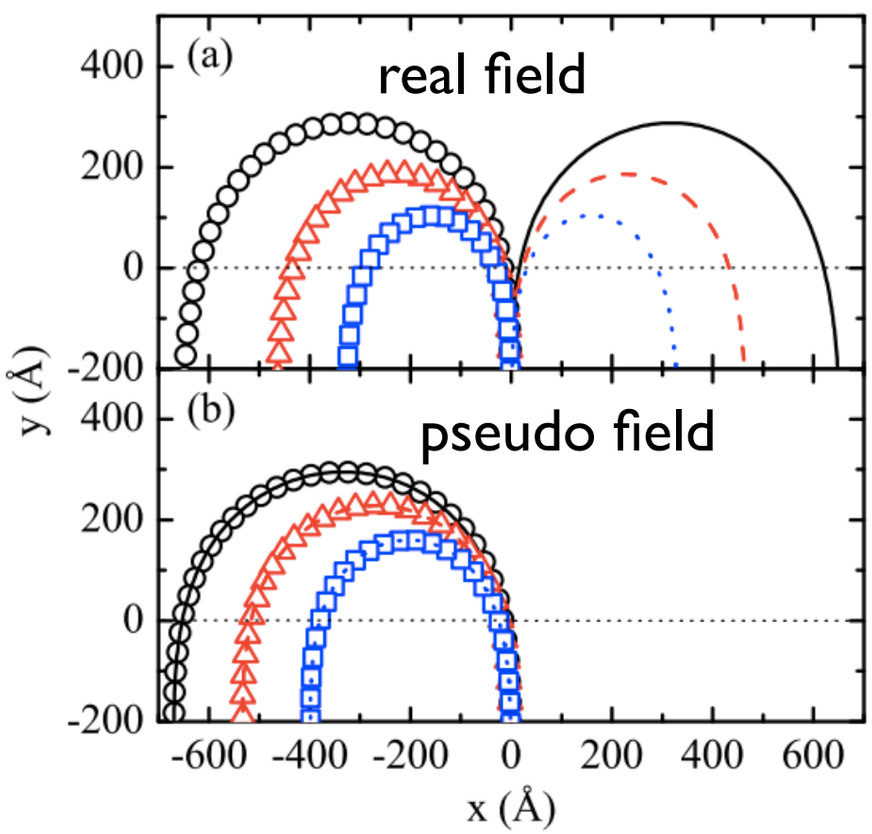


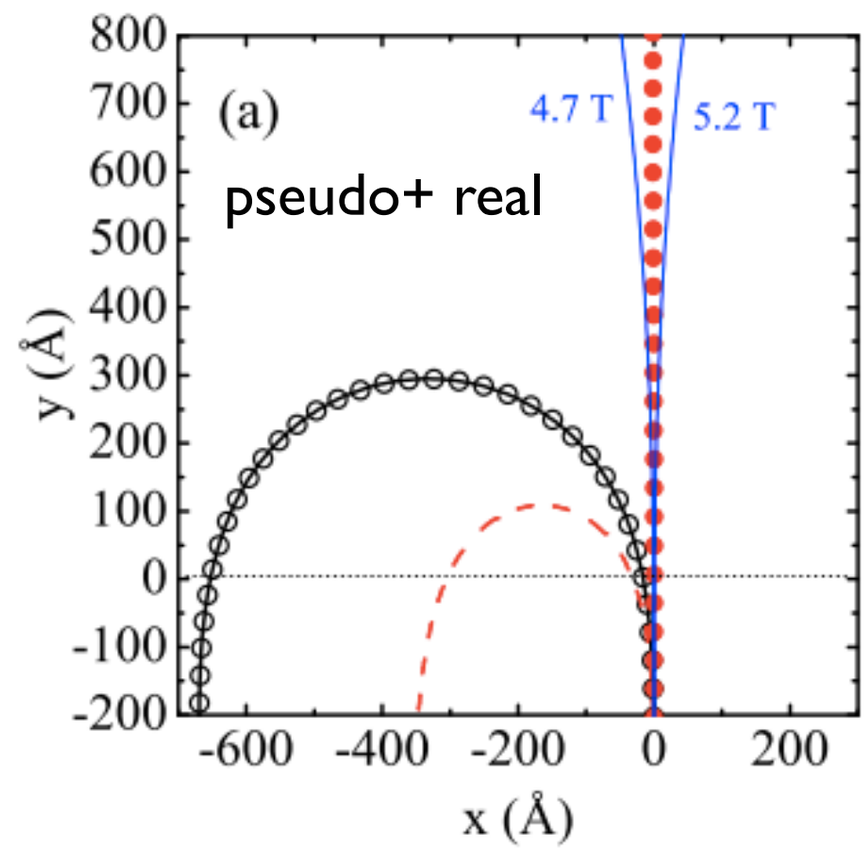
	C			CN	ED
$\Delta t/t_0$	1	10	100	10^{-3}	∞
M	104	264	1210	–	–
$T_{\text{run}}[s]$	378	97	45	$> 10^7$	1278

Wave packet propagation: strain valley filtering

- bend graphene ribbon into arc of circle
- K and K' feel magnetic fields with opposite signs
- combination of real and pseudo-magnetic fields will induce valley filtering







A. Chaves, L. Covaci, K.Y. Rakhimov, G.A. Farias, and F. M. Peeters, Phys. Rev. B 82, 205430 (2010)

Time-dependent Hamiltonian

- break the time evolution into smaller steps, consider the Hamiltonian to be time-indep. during each time-steps

$$U(t,0) \approx \prod_{i}^{N} e^{-i\hbar\mathcal{H}(t_i)\delta t}$$

$$|\psi(t_i + \delta t)\rangle = e^{-i\hbar\mathcal{H}(t_i)\delta_t}|\psi(t_i)\rangle$$

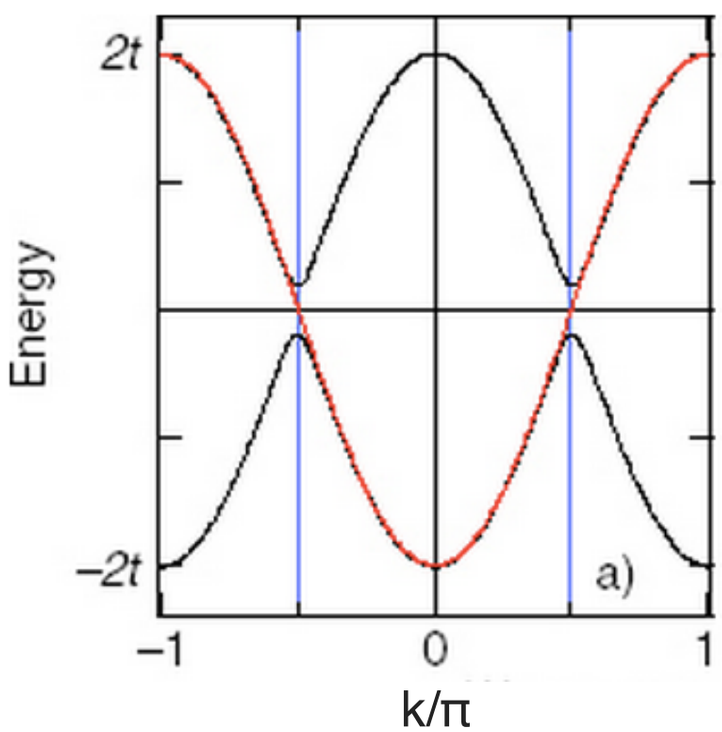
- the number of Chebyshev iterations is drastically reduced due to the small time step, therefore still very efficient

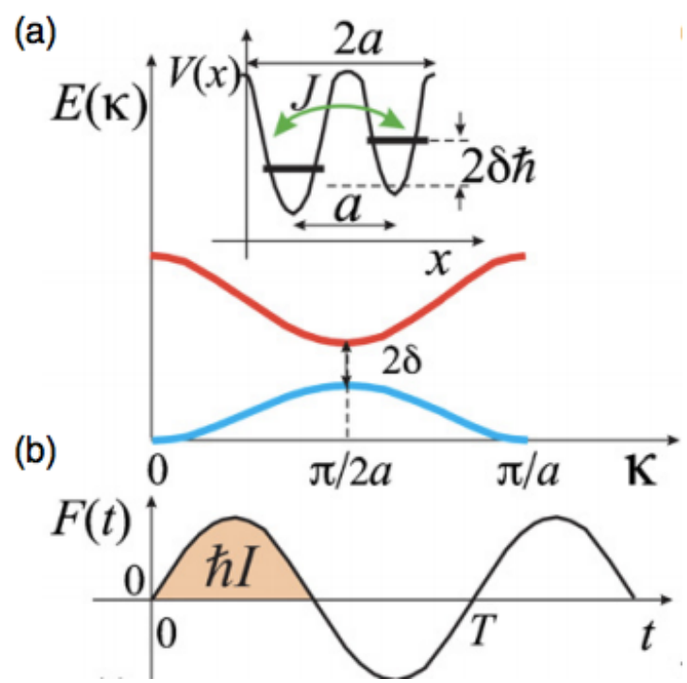
Bloch-Zener quantum walk

- Bloch oscillations: electric field + periodic potential

$$E(k) = 2t\cos(ka) \rightarrow v(k) = \partial E/\partial k = -2ta\sin(ak)$$

- 1D chain and dimerization in order to induce gaps
- finite electric field → linear potential drop across the chain

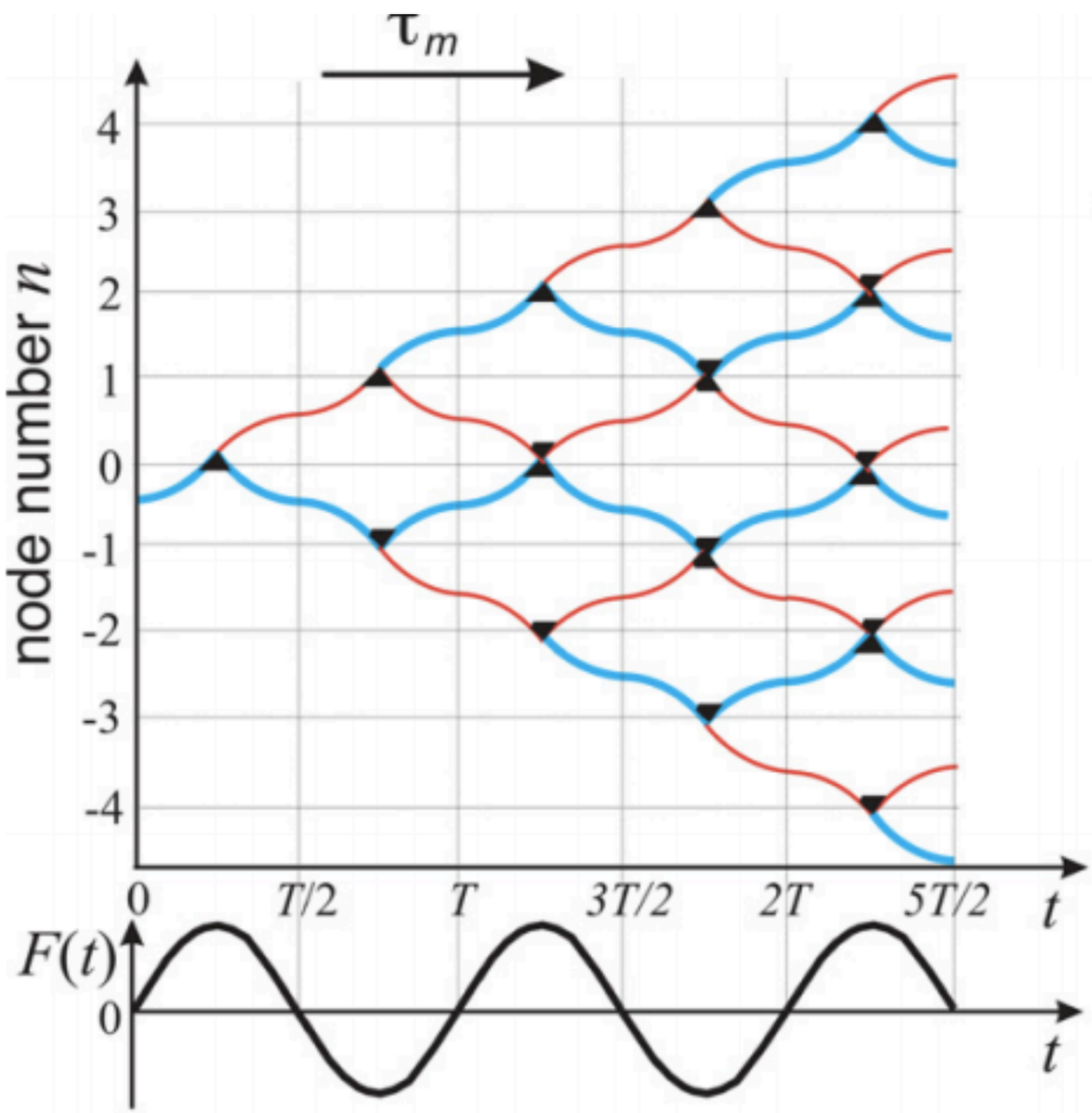


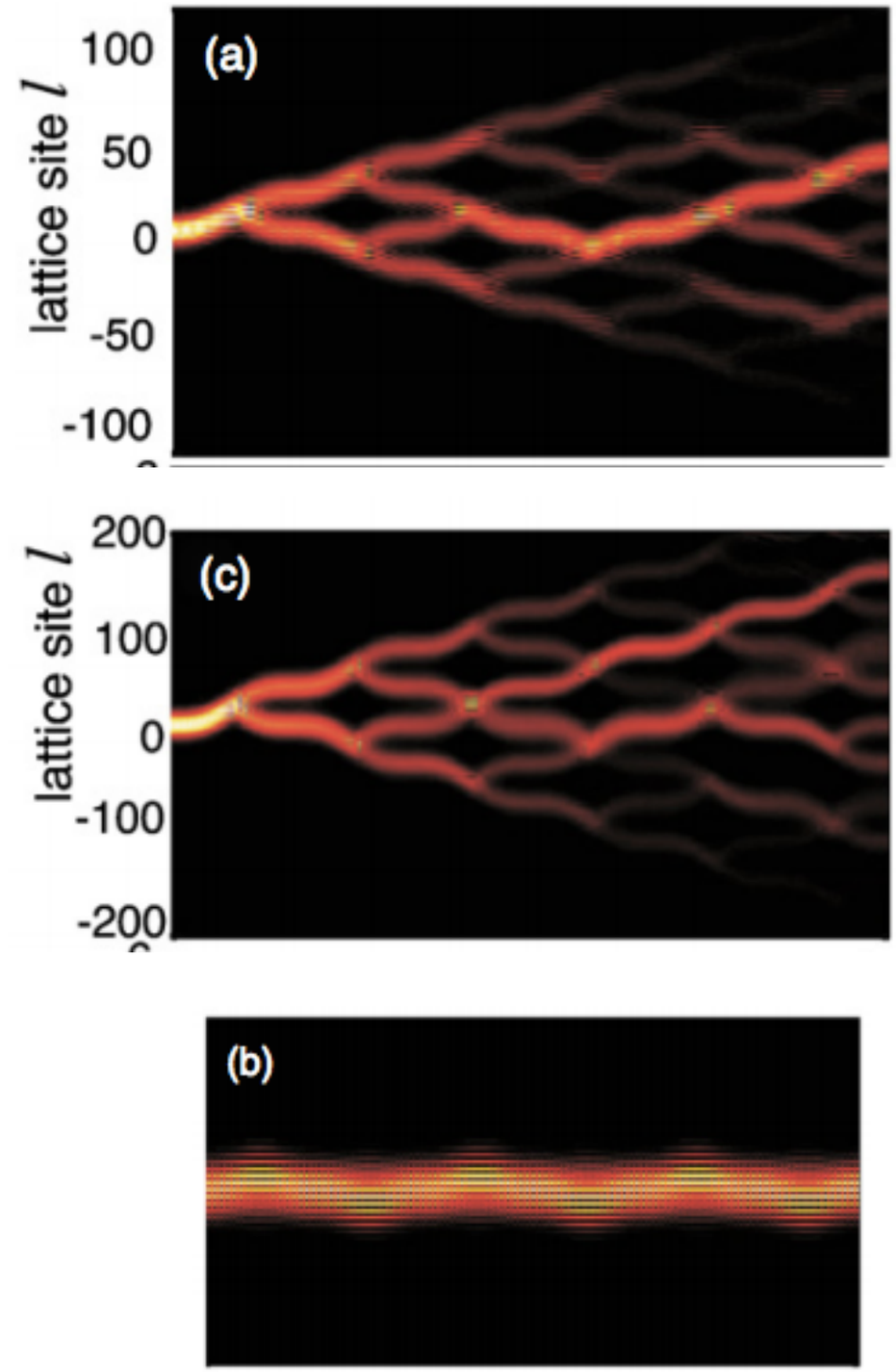


Landau-Zener transition prob.

$$P \sim E^{-\delta^2/|\partial F/\partial t|}$$

S. Longhi, J. Phys. B: At. Mol. Opt. Phys. 45 (2012) 225504





Realization of a Quantum Walk with One and Two Trapped Ions

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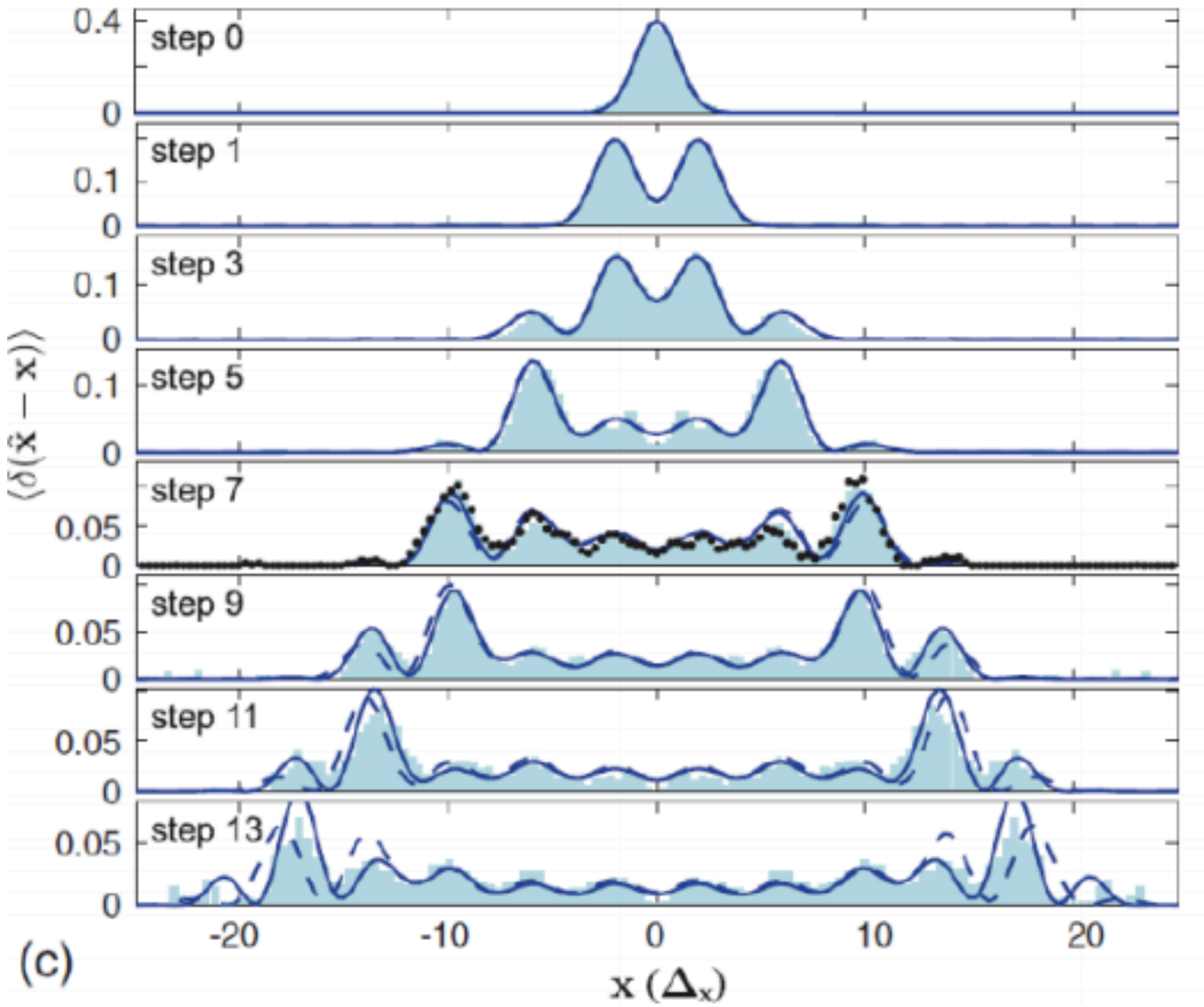
- realised exp.
  - trapped ions
  - cold atoms
  - photons



Project

- Chebyshev wave-packet propagation in 1D chains
  - investigate the balance: time step vs. number of Chebyshev terms
  - study the effect of dc and ac electric fields in a binary chain
  - study effect of multiple bands/gaps by increasing the unit cell