Numerical methods for quantum dynamics

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Summary

Quantum dynamics and its approximations

Many-body quantum dynamics

Solving the single-particle Schrödinger equation

Finite-size effects

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Quantum dynamics

$$i\partial_t \psi = H(t)\psi,$$

with H self-adjoint.

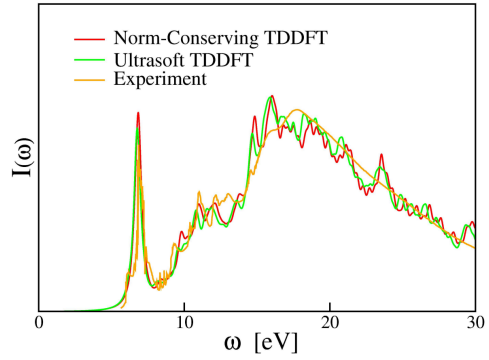
Features:

- The form of all (non-relativistic, non-gravitational) physics
- Non-autonomous
- Linear in ψ
- Strongly non-linear in the Hamiltonian (even in the autonomous case)
- Preserves mass, energy
- Possibly very high-dimensional
- Very rich structure

Applications

Direct simulation is often not needed

- Time-independent Hamiltonian: spectrum usually more informative
- Small parameters: use asymptotic approximation instead



A motivating example: electronic absorption spectrum of benzene

But when no small parameters, no other choices

- Strong fields, nonlinear optics (second harmonic generation, high harmonic generation...)
- Dynamics of light nuclei
- Laser control of chemical reactions
- ...

Asymptotic regimes: semiclassical

Semiclassical: $H(t) = h(t, x, -i\varepsilon\nabla)$; typically,

$$i\varepsilon\partial_t\psi = -\varepsilon^2\Delta\psi + V(x,t)\psi$$

- Flow follows classical trajectories

$$\dot{q} = \frac{\partial h}{\partial p}$$
$$\dot{p} = -\frac{\partial h}{\partial q}$$

- Example: most motion of nuclei

Asymptotic regimes: adiabatic

Adiabatic: $H(t) = H(\varepsilon t)$, with ψ_0 eigenstate of $H(0)$

- If $H(\varepsilon t)$ stays gapped for all $0 \leq t \leq T$, then $\psi(t)$ stays close to an instantaneous eigenstate of $H(\varepsilon t)$
- Example: spin follows magnetic fields, Bloch oscillations...

Asymptotic regimes: perturbative

Perturbative: $H(t) = H_0 + \varepsilon H_1(t)$

- Dyson/Born/interaction picture/Duhamel/variation of constant:

$$\psi(t) = e^{-iH_0 t}\psi_0 - i\int_0^t e^{-iH_0(t-t')}H_1(t')e^{-iH_0 t'}\psi_0 dt' + O(\varepsilon^2)$$

- Eg when ψ_0 is an eigenstate, in finite dimensions, $n \neq 0$:

$$\langle\psi_n|\psi(t)\rangle \approx -i\varepsilon e^{-iE_n t}\int_0^t \langle\psi_n, H_1(t')\psi_0\rangle e^{i(E_n-E_0)t'}dt'$$

  resonates when H_1 has frequency $-(E_n - E_0)$
- Basic to our understanding of quantum systems (transitions, Fermi golden rule...)

Asymptotic regimes: perturbative (2)

Perturbative: $H(t) = H_0 + \varepsilon H_1(t)$

- If $H_1(t) = f(t)H_1$, the first-order mapping

$$f \to \langle O \rangle_{\psi(t)} - \langle O \rangle_{\psi_0}$$

  is linear time-invariant: convolution with an impulse response $K_{OH_1}(t)$
- Linear response function $\widehat{K}(\omega)$ (magnetic susceptibitilites, conductivities, polarizabilities...)

Non-dissipative dynamics:

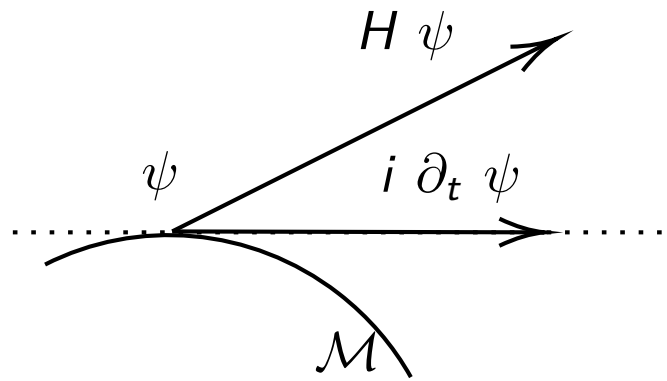
- Validity of linear response non-trivial
- K does not decay: $\widehat{K}(\omega)$?
- Adiabatic switching, regularization, averaging... equivalent to computing $\widehat{K}(\omega)$ in the sense of distributions

The Dirac-Frenkel variational principle

The solution of $i\partial_t\psi = H(t)\psi$ lives on a large space $\mathcal{H}$: seek an approximation inside a manifold $\mathcal{M} \subset \mathcal{H}$, $\dim \mathcal{M} \ll \dim \mathcal{H}$.

How to pick $\psi(t) \in \mathcal{M}$? Dirac-Frenkel:

$$i\partial_t\psi(t) = \operatorname*{arg\,min}_{v \in T_\psi \mathcal{M}} \|H\psi - u\| = P_{T_\psi \mathcal{M}} H\psi$$



- Defines a flow on $\mathcal{M}$, can do all the computations in a lower dimension
- Equivalently, variational form

$$\mathrm{Re}\langle v, i\partial_t\psi - H\psi\rangle = 0 \quad \forall v \in T_\psi \mathcal{M}$$

- Very natural tool, lends itself well to error analysis [Lasser, Lubich]

Examples

Example: $\mathcal{M} = X$, a subspace of $\mathcal{M}$. $T_\psi \mathcal{M} = X$.
Let $\psi(t) = \sum_{i=1}^{N} c_i(t)\phi_i$, with ϕ_i an orthonormal basis of X, then

$$i\partial_t c = \widetilde{H}(t)c, \quad H_{ij}(t) = \langle \phi_i, H(t)\phi_j \rangle$$

Schrödinger equation in reduced dimension

Example: When $H = -\frac{1}{2}\Delta + V$,

$$\mathcal{M} = \{\psi(x) = Ae^{-\alpha(x-q)^2 + ip(x-q) + iAx}\}$$

leads to the semiclassical equations

$$\dot{q} = p, \quad \dot{p} = \langle \psi, -\nabla V \psi \rangle$$

plus differential equations on A, α.

Extension to time-dependent manifolds

Example $\mathcal{M}(t) = \mathrm{Span}(P(t))$, with P projector on the eigenspace corresponding to a gapped eigenvalue $\lambda(t)$ of $H(t)$.
Possible variations of $u \in \mathcal{M}(t)$?

$$P(t)u(t) = u(t) \Rightarrow (1 - P)u = P'(t)u(t)$$

(affine space), so project on it:

$$i\partial_t \psi = PH\psi + P'(t)\psi = \lambda(t)\psi + P'(t)\psi,$$

which is parallel transport on $\mathrm{Span}(P(t))$ (plus dynamical phase)

- Extends to several eigenvectors
- Important because of adiabatic theorem, Berry phase, etc

Summary

Quantum dynamics and its approximations

Many-body quantum dynamics

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Many-body quantum dynamics

Consider N particles with masses m_k, charges q_k. $\mathcal{H} = L^2(\mathbb{R}^{3N})$, and

$$H = \sum_{k=1}^{N} -\frac{1}{2m_k}\Delta_{x_m} + \frac{1}{2}\sum_{k\neq k'} \frac{q_k q_{k'}}{|x_k - x_{k'}|} + V_{\text{ext}}(x)$$

- We ignore spin and indistinguishably for simplicity; in practice, have to treat electrons as fermions
- Contains a huge part of physics and essentially all of chemistry...
- ... $L^2(\mathbb{R}^{3N})$ is **big**!

Several important approximations:

- Born-Oppenheimer to decouple nuclei
- Time-dependent mean-field to decouple the electrons

The Born-Oppenheimer approximation (1)

Consider a quantum system with two particles: $\mathcal{H} = L^2(\mathbb{R}^6)$,

$$H = -\frac{1}{2M}\Delta_R - \frac{1}{2m}\Delta_r + V(R, r)$$

with $M \gg m$. Since the nuclei move slowly, the electrons see a slowly varying electronic Hamiltonian

$$H_{\mathrm{el,R}} = -\frac{1}{2m}\Delta_r + V(R, r)$$

on $L^2(\mathbb{R}^3)$. If $H_{\mathrm{el,R}}$ has a gapped ground state $(\chi_R(r), E_R)$,

$$\psi(R, r) \approx \phi(R)\chi_R(r).$$

This defines an approximation manifold $\mathcal{M}$, and applying the Dirac-Frenkel principle we get

$$i\partial_t\phi = \left(-\frac{1}{2M}\Delta_R + E_R\right)\phi$$

The Born-Oppenheimer approximation (2)

Got decoupled equation for the nuclei:

$$i\partial_t \phi = \left(-\frac{1}{2M}\Delta_R + E_R \right) \phi$$

Can then make a semiclassical approximation to get $\dot{R} = \frac{p}{M}, \dot{p} = -\nabla E_R$

- Two distinct steps: adiabatic then semiclassical
- Need a gap in $H_{\mathrm{el,R}}$
- Often very reasonable, sometimes deviations (eg crossings, photoexcitation, light nuclei)
- Can be improved by including more states:

$$\psi(R, r) \approx \sum_i \phi_i(R)\chi_R^i(r).$$

  gives vector-valued Schrödinger equation
- Involves "vibronic couplings" $\langle \chi_R^i, \nabla_R \chi_R^j \rangle$, blows up when gap closes: expand on non-eigenstates ("diabatic basis")

The many-body electronic problem

In electronic units,

$$H = \sum_{n=1}^{N} -\frac{1}{2}\Delta_{x_m} + \sum_{n \neq n'} \frac{1}{|x_n - x_{n'}|} + V_{\mathrm{nucl}}(x)$$

on $L^2(\mathbb{R}^{3N})$, again ignoring spin and antisymmetry.
Intractably large space, but can use separation of variables:

$$\mathcal{M} = \left\{\psi(x) = \phi_1(x_1)\phi_2(x_2)\ldots\phi_N(x_N), \phi_n \in L^2(\mathbb{R}^3)\right\}$$

and Dirac-Frenkel. Resulting equation:

$$i\partial_t \phi_n = \left(-\frac{1}{2}\Delta + V_{\mathrm{nucl}}(x) + \int \frac{\rho(y)}{|x-y|}dy\right)\phi_n$$

$$\rho(x) = \sum_{n=1}^{N} |\phi_n(x)|^2$$

time-dependent Hartree.

- With antisymmetry: additional nonlocal term (Hartree-Fock)
- Very crude but surprisingly good
- Problem becomes nonlinear

Beyond Hartree(-Fock)

Hartree:

$$i\partial_t \phi_n = \left(-\frac{1}{2}\Delta + V_{\mathrm{nucl}}(x) + \int \frac{\rho(y)}{|x-y|} dy \right) \phi_n$$

- More accuracy: multi-configuration time-dependent Hartree (MCTDH)

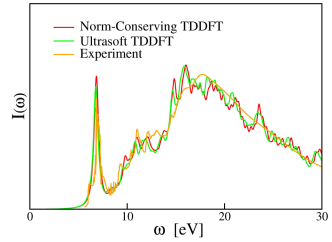
$$\left\{ \psi(x) = \sum_i \alpha_i \phi_1^i(x_1)\phi_2^i(x_2)\dots\phi_N^i(x_N), \phi_n^i \in L^2(\mathbb{R}^3) \right\}$$

- For electrons, adiabatic TDDFT

$$i\partial_t \phi_n = \left(-\frac{1}{2}\Delta + V_{\mathrm{nucl}}(x) + \int \frac{\rho(y)}{|x-y|} dy + V_{\mathrm{xc}}[\rho] \right) \phi_n$$

- But also: coupled cluster, QMC, tensors...

Back to the motivating example: linear response TDDFT



- First, solve ground state, model nuclei classically (Born-Oppenheimer approximation), electrons using DFT:

$$E(R, \phi_1, \ldots, \phi_n) = \underbrace{E_{\mathrm{nucl-nucl}}(R) + E_{\mathrm{elec-nucl}}(\{\phi_n\}, R)}_{\text{electrostatics}} + \underbrace{E_{\mathrm{elec}}(\{\phi_n\})}_{\text{DFT}}$$

- Minimize wrt $\phi_n, R \Rightarrow$ get ground state
- Starting from ground state, solve TDDFT equations

$$i\partial_t \phi_n = \left(-\tfrac{1}{2}\Delta + V_{\mathrm{nucl}} + V_{\mathrm{Hxc}}[\rho] + V_{\mathrm{ext}}(t)\right)\phi_n$$

- Set $V_{\mathrm{ext}}(t) = f(t)x$, apply perturbation theory to get first-order variation of dipole moment $\int \rho(x,t)x dx$ as a convolution of f and K, plot $\widehat{K}(\omega)$

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The single-particle Schrödinger equation

Approximate many-body dynamics reduce to solving single-particle (coupled, nonlinear...) equations

$$i\partial_t \psi = -\frac{1}{2}\Delta\psi + V(t)\psi, \quad \psi \in L^2(\mathbb{R}^3)$$

How to discretize?

- Finite difference methods
- Basis sets methods: $\psi(t) = \sum_i \alpha_i(t)\phi_i$ (finite element, localized basis sets, plane-wave...)
- Moving basis sets: $\psi(t) = \sum_i \alpha_i(t)\phi_i(t)$ (thawed gaussians...)

In most cases, parameters: grid spacing Δx, box size L, timestep Δt, simulation time T

Numerical issues

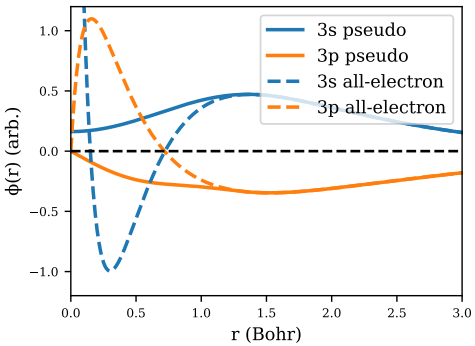
Consider the simplest numerical method: finite differences in space, explicit Euler scheme in time

1. V is not smooth (Coulomb): small Δx
2. CFL condition: small Δt
3. Waves go out of boxes: large L
4. Interesting phenomena might take a long time to appear : large T

Issue 1: V is not smooth, need small Δx

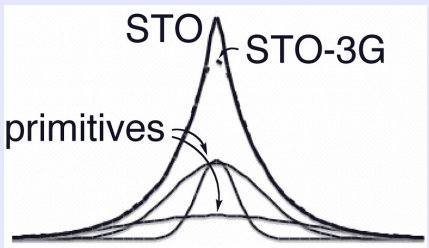
- Already a problem for static computations $H\psi = \lambda\psi$
- Two issues: Coulomb singularities force non-smooth ψ (Kato cusp condition), and orthogonality forces oscillations
- Most physics happens outside of atomic cores

Pseudopotentials (typically condensed matter physics)



Cook up a (nonlocal) potential V_{pseudo} so that atomic orbitals match the actual ones outside some radius, then discretize using standard methods. $\approx$ 1000 dof per atom. "Norm-conserving", "ultrasoft", "PAW"...

Gaussian orbitals (typically quantum chemistry)



Approximate cuspy function by sum of gaussians.
$\approx$ 10 dof per atom

But also: adaptive finite element, wavelets...

Issue 2: CFL condition, need small Δt

- Once discretized, get a system $i\dot{x} = H(t)x$, H hermitian.
- Simplest method: explicit Euler

$$x_{n+1} = x_n - i\Delta t H(t_n)x_n$$

$|(1 - i\Delta t\lambda)^n| = (1 + |\Delta t\lambda|^2)^{n/2}$. If $\Delta t = T/N$, x_N blows up unless

$$\Delta t \ll \frac{1}{\lambda_{\max}^2 T}$$

- With finite differences, $\lambda_{\max} \approx 1/(\Delta x)^2$, so need

$$\Delta t \ll (\Delta x)^4$$

(even more stringent than usual CFL for heat equation, $\Delta t \ll \Delta x^2$)

- Eg $L = 10, \Delta x = 10^{-2}, \Delta t = 10^{-8}, T = 10 \Rightarrow$ at least 10^{18} operations (30 years at 1Ghz)
- Need more clever methods!

CFL condition: implicit methods

- Implicit Euler

$$x_{n+1} = x_n - i\Delta t H x_{n+1}$$

- $\frac{1}{|1+i\Delta t\lambda|} < 1$ for real λ
- Overdamping instead of underdamping: more stable
- Can use larger timesteps
- A miracle: Crank-Nicolson

$$x_{n+1} = x_n - i\Delta t H \frac{x_n + x_{n+1}}{2}$$

$$\frac{|1 - i\frac{\Delta t\lambda}{2}|}{|1 + i\frac{\Delta t\lambda}{2}|} = 1 \quad \forall \lambda \in \mathbb{R}$$

  and so $\|x_{n+1}\| = \|x_n\|$!
- Need to solve a linear system at each step $\Rightarrow$ iterative methods, preconditioning, etc

CFL condition: splitting methods

- Assume that $H(t) = H_1(t) + H_2(t)$ where the propagators $U_{1/2}(t, t')$ of $H_{1/2}$ are known explicitly
- Splitting scheme (Lie/Kato/Suzuki/Trotter):

$$x_{n+\frac{1}{2}} = U_1(t_{n+1}, t_n)x_n$$
$$x_{n+1} = U_2(t_{n+1}, t_n)x_{n+\frac{1}{2}}$$

- Recall Trotter formula

$$e^{A+B} = \lim_{n\to\infty} (e^{A/n}e^{B/n})^n$$

- Respects the natural structure of the problem: norm conservation
- Composition of unitaries: no CFL!
- Splitting methods are very natural in QM (kinetic + potential)
- Particularly pleasant in plane-wave discretizations (kinetic is diagonal in Fourier space, potential is diagonal in real space)

Demo time!

`http://antoine.levitt.fr/quantique/dynamique.html`

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Correlations

Many properties of interest (eg linear response) are computed from correlations

$$C(t) = -i\theta(t)\langle \phi, e^{-iHt}\phi \rangle$$

with localized ϕ, and with $\theta(t)$ the Heaviside function

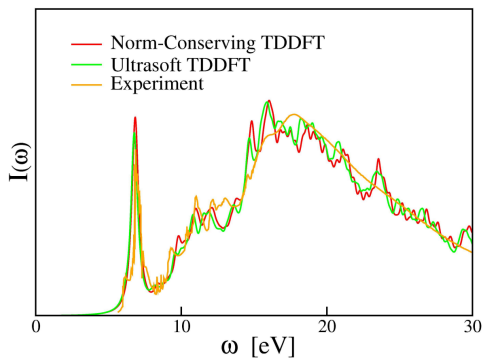
- **Example** atomic polarizability: how does the dipole moment ($\int x\rho = \langle \psi, x\psi \rangle$) move in response to an electric field ($H_1 = x$)?

$$\alpha(t) = -i\theta(t)\langle x\psi_0, e^{-i(H-E_0)t}x\psi_0 \rangle + \text{c.c. (for 1 electron)}$$

- (distributional) Fourier transform

$$\widehat{C}(\omega) = \lim_{\eta\to 0^+} \int_0^\infty e^{-\eta t}e^{i\omega t}C(t)dt \quad \text{(sign weird but standard...)}$$

$$= \lim_{\eta\to 0^+} \left\langle \phi, \frac{1}{\omega + i\eta - H}\phi \right\rangle$$



Boundary values of the resolvent

$$\lim_{\eta\to 0} \left\| \tfrac{1}{\omega+i\eta-H} \right\|_{\mathrm{op}} = \infty,$$

but

$$\lim_{\eta\to 0^+} \frac{1}{\omega+i\eta-E} = \mathrm{p.v.}\frac{1}{\omega-E} - i\pi\delta_E(\omega).$$

so

$$\widehat{C}(\omega) = \mathrm{p.v.}\int \frac{1}{\omega-E} dP_{\phi,H}(E) - i\pi dP_{\phi,H}(\omega)$$

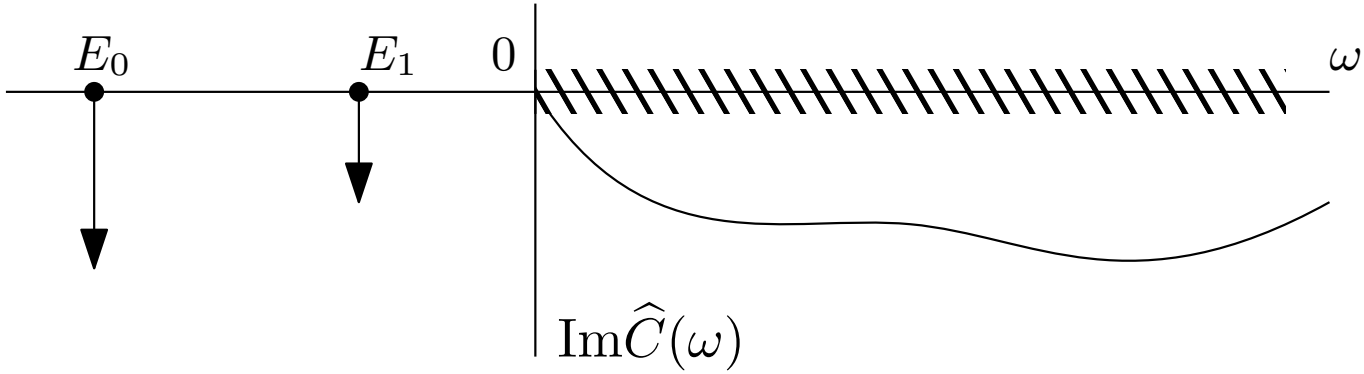
$\left\langle \psi, \tfrac{1}{\omega+i\eta-H}\psi \right\rangle$ doesn't necessarily blow up when $\omega \in \sigma_c(H)$!

Example: Green's function for $H_0 = -\Delta$ in 3D:

$$\frac{1}{\omega+i\eta-H_0}(x,y) = \frac{e^{i\sqrt{\omega+i\eta}|x-y|}}{2i|x-y|}$$

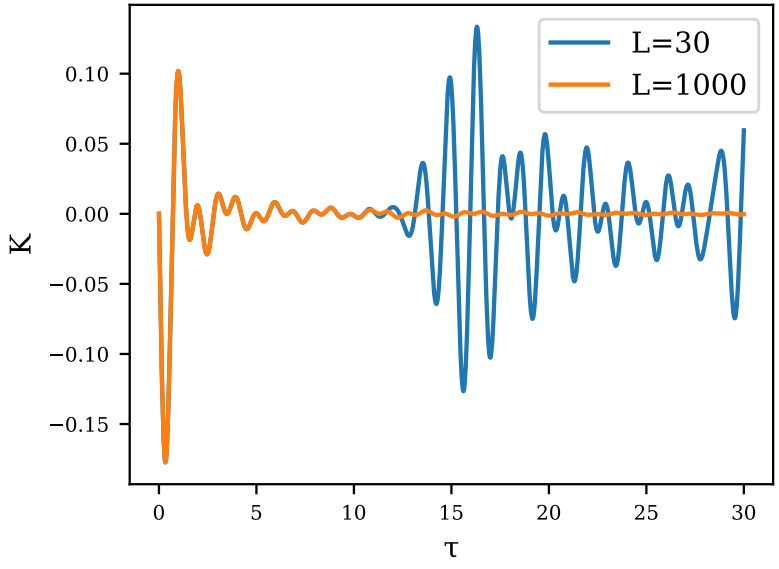
Correlations: how to compute them

Typical correlations of $H = -\Delta + V$

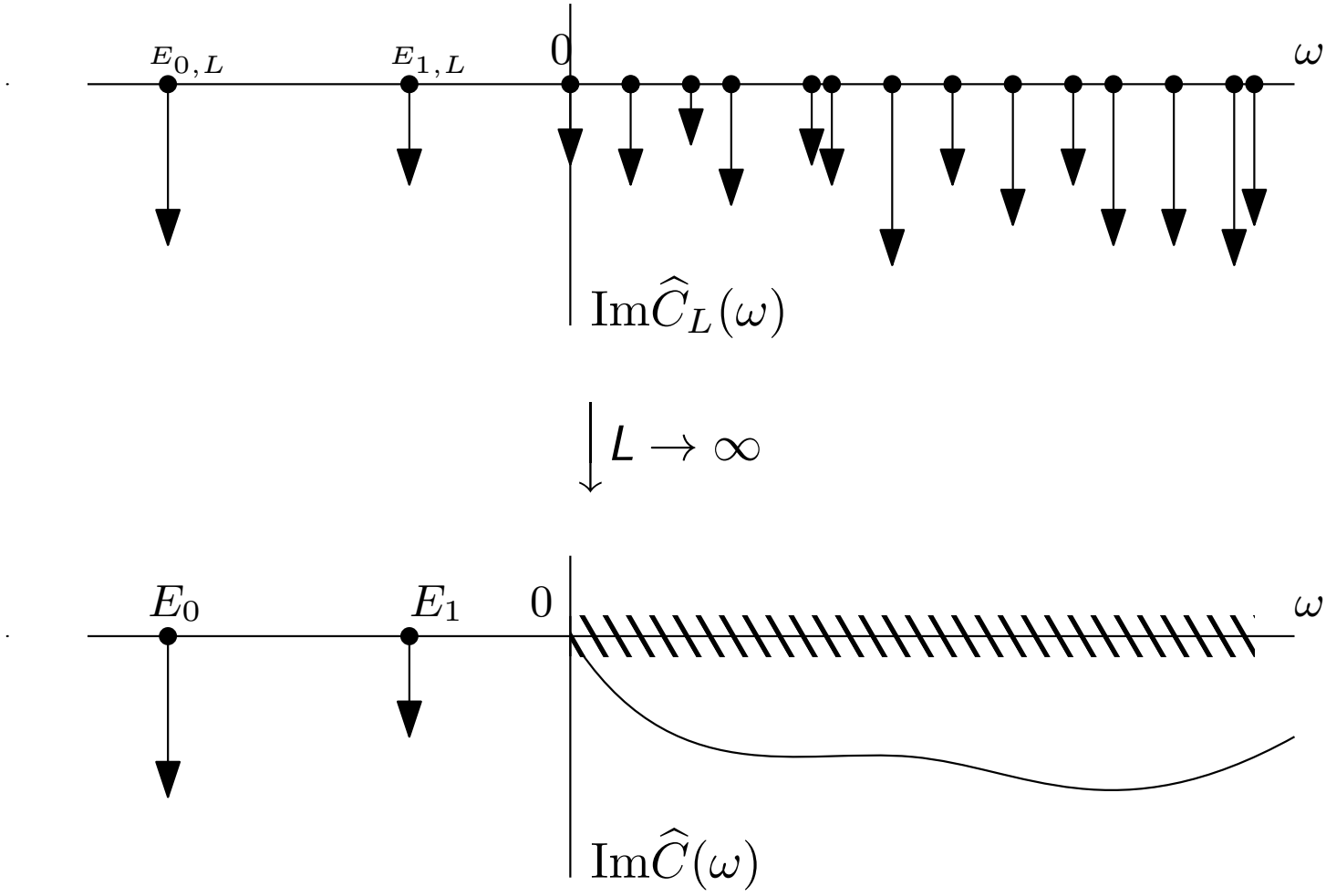


How to compute them in practice?

Simple truncation to a finite basis? Waves bounce back!



Effect of truncation



Under reasonable conditions, $C_L \to C$ in the sense of tempered distributions. Pointwise values?

The artificial dissipation method

Fundamental issue: waves go out of the computational domain.

First solution: add dissipation to the Schrödinger equation $e^{-iHt} \to e^{-\eta t} e^{-iHt}$; equivalently, complex frequency

$$\widehat{C}(\omega) \approx \widehat{C}_L(\omega + i\eta)$$

- Limiting absorption principle: if V decays sufficiently fast, for $\omega > 0$,

$$\widehat{C}(\omega + i\eta) = \widehat{C}(\omega) + O(\eta)$$

- At finite η, resolvents are local (Combes-Thomas):

$$\exists \alpha > 0,\ \widehat{C}(\omega + i\eta) = \widehat{C}_L(\omega + i\eta) + O(e^{-\alpha \eta L})$$

- See [Dupuy/Levitt '21] for details and error control
- Real time picture: need $L \gg$ wave propagation length $\approx \frac{v_g}{\eta}$
- Frequency picture: need $\eta \gg$ eigenvalue spacing $\approx \frac{d\varepsilon/dk}{L}$

Better discretizations

Fundamental issue: waves go out of the computational domain.

A better solution: take care of wave propagation explicitly

- Complex scaling: turn propagation into decay by complex rotation $\widetilde{\psi}(x) = \psi(xe^{i\theta})$
- Complex absorbing potential: add an imaginary potential outside the domain
- Dirichlet-to-Neumann: $d\psi/dn = f(\psi, t, x)$ exact, nonlocal in space and time
- Dyson approaches

All approaches are unsatisfactory in some respects; still an open problem, especially with long-range potentials!

Computing correlations with the Dyson equation

[Duchemin/Genovese/Letournel/Levitt/Ruget '22, Duchemin/Levitt '23]

$$\widehat{C}(z) = \langle \phi, \tfrac{1}{z-(H_0+V)}\phi \rangle$$

but naive truncation ineffective because $\frac{1}{z-(H_0+V)}\phi$ is delocalized.
Need to solve

$$\begin{aligned}(z - H_0 - V)\psi &= f \\ \psi - (z-H_0)^{-1}V\psi &= (z-H_0)^{-1}f \\ (1 - \underbrace{V(z-H_0)^{-1}}_{\text{localizing}}) \underbrace{V\psi}_{\text{localized}} &= \underbrace{V(z-H_0)^{-1}f}_{\text{localized}}\end{aligned}$$

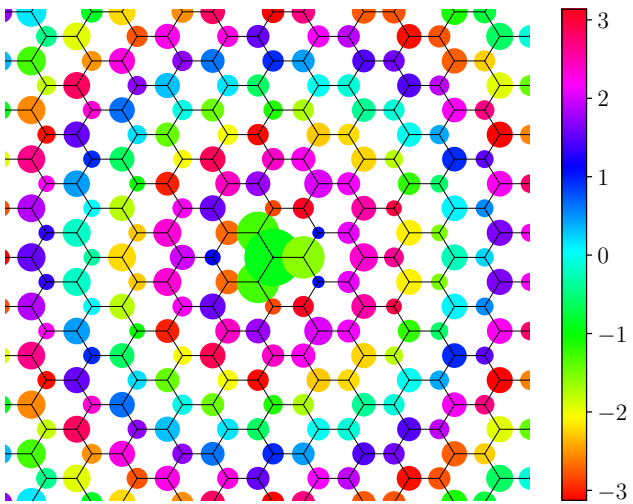
- Discretize $V\psi$, not ψ!
- General methodology flexible; need to known $(z-H_0)^{-1}$
- Can be done in real time (similar to Kaye/Barnett/Greengard/DeGiovanni/Rubio '22)
- Requires V localized...

Bonus: computation of $(z - H_0)^{-1}$ in the periodic setting

If H_0 is periodic, use Bloch transform $H_0 = \int^{\oplus} H_{0,k} dk$

$$(z - H_0)^{-1}(x, y) \propto \int_{\mathrm{BZ}} e^{ik(x-y)} (z - H_{0,k})^{-1}(x, y) dk$$

- When $z = \omega + i\eta$, integral nearly singular on the Fermi surface $\{k \in \mathrm{BZ}, \varepsilon_{nk} = \omega\}$
- Can deform the integral to the complex Brillouin zone to avoid the singularity! $k \to k + ik_i(k)$ (even in $d > 1$!)
- Results in a very efficient numerical scheme, can even compute resonances (poles of analytic continuation to $\eta < 0$)



Example: resonant state induced by a defect on graphene

Conclusion

- Quantum dynamics contains essentially all of physics
- Many-body problem intractable
- Direct numerical simulation is hard: $\Delta x, \Delta t, L, T$

Workflow:

1. Dimensionality reduction (mean field, tensors, perturbation theory...)
2. Asymptotic expansions (adiabatic decoupling, semiclassical approximation, linear response...)
3. Regularization (pseudopotentials, complex absorbing potentials...)
4. Space truncation (plain truncation, absorbing boundary conditions...)
5. Space discretization (plane waves, finite differences, localized basis sets...)
6. Time discretization (symplectic schemes, splitting...)

Not discussed: solids, strongly correlated systems, open quantum systems, classical dynamics, thermodynamics, numerical methods for nonlinear equations, HPC...