Linear response and resonances in adiabatic time-dependent density functional theory

Antoine Levitt
Laboratoire de mathématiques d'Orsay, Université Paris-Saclay

August 21 2024, ICERM workshop

Joint with Mi-Song Dupuy, Eloïse Letournel

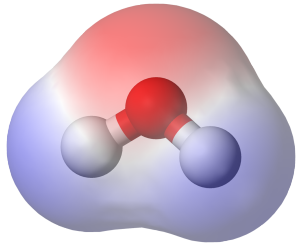
Summary

Linear response

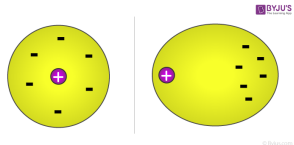
TDDFT

Resonances

Polarizability



Permanent dipole



Dipole induced by a field

Static response

Physical systems are characterized by their **response properties**

Mathematically: **perturbation theory** for $F(X, \varepsilon)$ around equilibrium

$$F(X_*, 0) = 0$$

Equilibrium perturbation:

$$F(X(\varepsilon), \varepsilon) = 0.$$

Implicit function theorem:

$$X(\varepsilon) = X_* - \varepsilon(\partial_X F)^{-1}\partial_\varepsilon F + O(\varepsilon^2)$$

derivatives evaluated at $(X_*, 0)$.

- Expansion of observables to first order provide response coefficients (mechanical, electrical, thermal, magnetic, optical...)
- $\partial_X F$ also determines the mathematical structure (error control, sensitivity, convergence of numerical methods...)

Dynamical response

Time-dependent:

$$\dot{X} = F(X, \varepsilon f(t)), \quad X(0) = X_*$$
$$\dot{X} \approx \partial_X F(X - X_*) + \varepsilon f(t) \partial_\varepsilon F$$

Duhamel formula: (Dyson/variation of constant/interaction picture/perturbation theory/...)

$$X(\varepsilon, t) = X_* + \varepsilon \int_0^t \underbrace{e^{\partial_X F (t-t')} (\partial_\varepsilon F)}_{K(t-t')} f(t') dt' + O_t(\varepsilon^2)$$
$$= X_* + \varepsilon (K * f)(t) + O_t(\varepsilon^2)$$

by extending K and f to zero for negative times (causal functions).

- For physically stable systems (eg damped oscillator), $e^{\partial_X F t} \to 0$
  - Validity of linear response clear (O independent on time)
  - $\widehat{K}(\omega)$ well-defined (AC response)
- Quantum mechanics is purely oscillatory: $e^{\partial_X F t}$ unitary
  - Validity of linear response much more subtle
  - K does not decay: $\widehat{K}(\omega)$?

Dynamical polarizability

Consider a **single electron** in a localized potential (e.g. hydrogen atom)

$$H = -\tfrac{1}{2}\Delta + V$$
$$\sigma(H) = \{\lambda_0, \lambda_1, \dots\} \cup \mathbb{R}^+$$

Start in ground state:

$$\psi(0) = \psi_0, \quad H\psi_0 = \lambda_0\psi_0$$

turn on a small dynamical electric field

$$\boxed{i\partial_t\psi = H\psi + \varepsilon f(t) V_{\mathcal{P}}\psi}$$

and observe the result

$$\boxed{\langle V_{\mathcal{O}}\rangle(t) = \langle \psi(t), V_{\mathcal{O}}\psi(t)\rangle.}$$

Eg dynamical polarizability

$$V_{\mathcal{O}} = x_\alpha, \quad V_{\mathcal{P}} = x_\beta$$

Directly observable experimentally by light absorption (dipole approximation)

Linear response theory

Duhamel:

$$i\partial_t \psi = H\psi + \varepsilon f(t) V_{\mathcal{P}} \psi$$

$$\psi(t) = e^{-iHt}\psi_0 - \varepsilon i \int_0^t U(t,t') f(t') V_{\mathcal{P}} e^{-iHt'} \psi_0 dt'$$

and therefore linear response: (Kubo, Green-Kubo...)

$$\langle V_{\mathcal{O}} \rangle(t) = \langle \psi_0, V_{\mathcal{O}} \psi_0 \rangle + \varepsilon \int_0^\infty K(t-t') f(t') dt' + O_t(\varepsilon^2)$$

$$K(\tau) = -i\theta(\tau) \left\langle \underbrace{V_{\mathcal{O}}\psi_0}_{\text{observe}}, \underbrace{e^{-i(H-\lambda_0)\tau}}_{\text{propagate}} \underbrace{V_{\mathcal{P}}\psi_0}_{\text{perturb}} \right\rangle + \text{c.c.},$$

θ the Heaviside function

Response is dictated by correlations/fluctuations

$K(\tau)$ and $\widehat{K}(\omega)$

$$K(\tau) = -i\theta(\tau)\left\langle V_{\mathcal{O}}\psi_0, e^{-i(H-\lambda_0)\tau}V_{\mathcal{P}}\psi_0\right\rangle + \text{c.c.},$$

K does not decay, but Fourier transform defined in the distributional sense

$K(\tau) = 0$ for $\tau < 0$: K is **causal**, Fourier transform can be computed as a limit:

$$\begin{aligned}\widehat{K}(\omega) &= \lim_{\eta\to 0^+}\int_0^\infty e^{i(\omega+i\eta)\tau}K(\tau)d\tau \\ &= \lim_{\eta\to 0^+}\left\langle \psi_0, V_{\mathcal{O}}\Big(\omega + i\eta - (H-\lambda_0)\Big)^{-1}V_{\mathcal{P}}\psi_0\right\rangle \\ &\qquad - \left\langle \psi_0, V_{\mathcal{P}}\Big(\omega + i\eta + (H-\lambda_0)\Big)^{-1}V_{\mathcal{O}}\psi_0\right\rangle,\end{aligned}$$

in the sense of distributions.

(unusual sign of Fourier transform, to match Schrödinger's e^{-iEt})

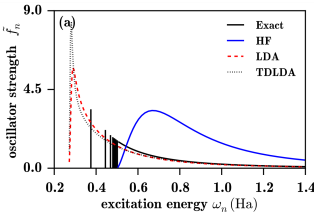
The response function

$$\widehat{K}(\omega) = \lim_{\eta\to 0^+} \left\langle \psi_0, V_{\mathcal{O}} \Big(\omega + i\eta - (H-\lambda_0)\Big)^{-1} V_{\mathcal{P}}\psi_0 \right\rangle - \left\langle \psi_0, V_{\mathcal{P}} \Big(\omega + i\eta + (H-\lambda_0)\Big)^{-1} V_{\mathcal{O}}\psi_0 \right\rangle$$

- At pole at each excitation energy $\lambda_n - \lambda_0$, with λ_n eigenvalues of H, $n > 0$
- Nothing at $\omega = 0$ (transition $\psi_0 \to \psi_0$ corresponds to a gauge mode $\psi_0 e^{-i\alpha(t)}$)
- Plemelj formula

$$\lim_{\eta\to 0^+} \frac{1}{\omega + i\eta - \lambda} = \text{p.v.}\frac{1}{\omega - \lambda} - i\pi\delta(\omega - \lambda)$$

When $\omega > -\lambda_0$, $\mathrm{Im}\widehat{K}(\omega)$ is continuous: ionization cross-section



Several **non-interacting** electrons

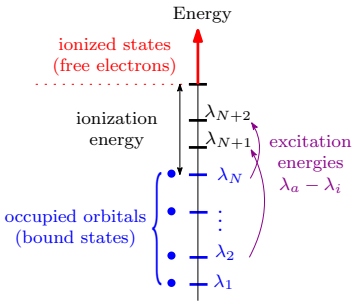
Start with N eigenfunctions $\psi_1(0), \ldots, \psi_N(0)$ of H, and solve

$$i\partial_t \psi_n = H\psi_n + \varepsilon f(t) V_{\mathcal{P}} \psi_n$$

$$\langle V_{\mathcal{O}} \rangle(t) = \sum_{n=1}^{N} \langle \psi_n(t), V_{\mathcal{O}} \psi_n(t) \rangle.$$

$$\widehat{K}(\omega) = \sum_{n=1}^{N} \lim_{\eta \to 0^+} \left\langle \psi_n, V_{\mathcal{O}} \Big(\omega + i\eta - (H - \lambda_n) \Big)^{-1} V_{\mathcal{P}} \psi_n \right\rangle$$

$$- \left\langle \psi_n, V_{\mathcal{P}} \Big(\omega + i\eta + (H - \lambda_n) \Big)^{-1} V_{\mathcal{O}} \psi_n \right\rangle$$



- Pole at each transition energy $\lambda_a - \lambda_i$, $i \leq N$, $a > N$
- Occupied-occupied transitions $\psi_i \to \psi_j$, $i, j' \leq N$ don't count (gauge modes)

Summary

Linear response

TDDFT

Resonances

Electron interaction: Kohn-Sham density functional (DFT)

Quantum N-body problem intractable, replace with mean-field model.

Static problem (ground state)

$$H_\rho \psi_n = \lambda_n \psi_n, \quad \langle \psi_m, \psi_n \rangle = \delta_{mn}$$

$$H_\rho = -\tfrac{1}{2}\Delta + V_{\text{nuclei}}(x) + \int_{\mathbb{R}^3} \frac{\rho(y)}{|x-y|}\, dy + v_{\text{xc}}[\rho](x)$$

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

- $v_{\text{xc}}[\rho]$ exchange-correlation potential, e.g. Local Density Approximation $v_{\text{xc}}[\rho](x) = v_{\text{xc}}(\rho(x))$
- Also admits a variational formulation

$$\min_{\langle \psi_m | \psi_n \rangle = \delta_{mn}} E(\Psi)$$

  with λ_n as Lagrange multipliers
- $E(\Psi R) = E(\Psi)$ if R is unitary: $U(N)$ symmetry group of the equation

Assumptions

$d = 3$. Assumptions:

1. V_{nuclei} is $L^2 + L^\infty_\varepsilon$
2. LDA, $v_{\text{xc}} = e'_{\text{xc}}$, e_{xc} C^2, $e_{\text{xc}}(0) = e'_{\text{xc}}(0) = 0$
3. There is $\Psi^0 \in (H^2)^N$, $\langle \psi^0_m | \psi^0_n \rangle = \delta_{mn}$, non-degenerate local minimizer up to rotation, in the sense that, for all $\Psi \in (H^2)^N$ with $\langle \psi_m | \psi_n \rangle = \delta_{mn}$,

$$\boxed{E(\Psi) - E(\Psi^0) \geq \gamma \min_{R \in U(N)} \|\Psi - \Psi^0 R\|^2}$$

(independent of Aufbau principle)

- Existence of (possibly degenerate) minimizer from [Anantharaman-Cancès '09] (under additional hypotheses on e_{xc})
- Restriction to particular model for the functional analysis, but method general:
  - Works for magnetic fields (does not use specific real structure)
  - Works for Hartree-Fock exchange (does not use the fact that H depends only on ρ, unlike Dyson methods)

The Stiefel manifold

$$\mathfrak{M}_N = \{\Psi \in (L^2)^N, \langle \psi_m | \psi_n \rangle = \delta_{mn}\}$$

Tangent space:

$$T_\Psi \mathfrak{M}_N = \{U \in (L^2)^N, \langle \psi_m | u_n \rangle + \langle u_m | \psi_n \rangle = 0\}$$

$$(L^2)^N = \underbrace{\underbrace{(\mathrm{Ran}(\Psi)^\perp)^N}_{\text{excitations}} + \underbrace{\Psi\mathcal{A}}_{\text{gauge modes}}}_{T_\Psi \mathfrak{M}_N} + \underbrace{\Psi\mathcal{S}}_{\text{growth modes}}$$

with $\mathcal{S}$ and $\mathcal{A}$ the set of Hermitian and skew-Hermitian matrices ($N = 1 \Rightarrow \mathbb{R}\psi$ and $i\mathbb{R}\psi$)

$$E(\Psi) - E(\Psi^0) \geq \gamma \min_{R \in U(N)} \|\Psi - \Psi^0 R\|^2$$

for all $\Psi \in (H^2)^N \cap \mathfrak{M}_N$ implies that the hessian M of the energy is positive on $(\mathrm{Ran}(\Psi^0)^\perp)^N$

Time-dependent density functional theory (TDDFT)

Adiabatic TDDFT:

$$i\partial_t \psi_n = H_\rho \psi_n + \varepsilon V_{\mathcal{P}} f(t) \psi_n$$

Linearize near equilibrium:

$$\psi_n = e^{-i\lambda_n t}(\psi_n^0 + \varepsilon u_n(t))$$

$$i\partial_t u_n = \underbrace{(H_{\rho^0} - \lambda_n)u_n + \left(\frac{dH}{d\rho}\frac{d\rho}{d\Psi}U\right)\psi_n^0}_{(M_{\mathrm{dyn}}U)_n} + \varepsilon f(t) V_{\mathcal{P}} \psi_n^0 + O(U^2 + \varepsilon U)$$

$$\left(\frac{d\rho}{d\Psi}U\right)(x) = \sum_{n=1}^{N} \overline{\psi_n^0(x)} u_n(x) + \psi_n^0(x)\overline{u_n(x)}$$

M_{dyn} is not $\mathbb{C}$-linear; $iM_{\mathrm{dyn}} \neq M_{\mathrm{dyn}} i$

Time-dependent density functional theory (TDDFT)

Adiabatic TDDFT:

$$J\partial_t \psi_n = H_\rho \psi_n + \varepsilon V_{\mathcal{P}} f(t) \psi_n$$

Linearize near equilibrium:

$$\psi_n = e^{-J\lambda_n t}(\psi_n^0 + \varepsilon u_n(t))$$

$$J\partial_t u_n = \underbrace{(H_{\rho^0} - \lambda_n)u_n + \left(\frac{dH}{d\rho}\frac{d\rho}{d\Psi}U\right)\psi_n^0}_{(M_{\mathrm{dyn}}U)_n} + \varepsilon f(t) V_{\mathcal{P}} \psi_n^0 + O(U^2 + \varepsilon U)$$

$$\left(\frac{d\rho}{d\Psi}U\right)(x) = \sum_{n=1}^{N} \overline{\psi_n^0(x)} u_n(x) + \psi_n^0(x)\overline{u_n(x)}$$

M_{dyn} is not $\mathbb{C}$-linear; $JM_{\mathrm{dyn}} \neq M_{\mathrm{dyn}}J$

Well-posedness

Theorem (DLL '24)

Assume that f is continuous, and $V_{\mathcal{P}} \in H^2$. Then, for any $T > 0$, there is $\varepsilon_0 > 0$ such that, for all $\varepsilon \leq \varepsilon_0$,

$$J\partial_t \psi_n = H_\rho \psi_n + \varepsilon V_{\mathcal{P}} f(t) \psi_n, \quad \psi_n(0) = \psi_n^0$$

is well-posed in $(H^2(\mathbb{R}^3, \mathbb{C}))^N$ for times $\leq T$.

- Suboptimal both in regularity and in existence time, but sufficient to define and study linear response
- Strategy of proof: fixed-point in the Duhamel form of

  $$J\partial_t u_n = (M_{\mathrm{dyn}} U)_n + \varepsilon f(t) V_{\mathcal{P}} \psi_n^0 + O(U^2 + \varepsilon U)$$

  in H^2.
- Sufficient to study the linear equation

  $$J\partial_t U = M_{\mathrm{dyn}} U$$

  and prove bounds like

  $$\|U(t)\|_{H^2} \leq C(t) \|U(0)\|_{H^2}$$

The linearized equation

$$J\partial_t U = M_{\mathrm{dyn}} U$$

- M_{dyn} is not $\mathbb{C}$-linear (let alone skew-adjoint), so this is non-trivial
- "Realify" the space: $((L^2)^N, \mathbb{C}_J) \to ((L^2)^N, \mathbb{R})$
- But we need complex vector space structure to do spectral theory, so complexify: $((L^2)^N, \mathbb{R}) \to (((L^2)^N)^2, \mathbb{C}_i)$, introducing new imaginary unit i
- Different possible explicit representation of vectors and operators in $(((L^2)^N)^2, \mathbb{C}_i)$; splitting real and imaginary parts not necessarily best one, especially when Ψ^0 is not real
- In quantum chemistry, Casida representation mostly used

The linearized equation

$$J\partial_t U = M_{\mathrm{dyn}} U$$

- M_{dyn} is not $\mathbb{C}$-linear (let alone skew-adjoint), so this is non-trivial
- "Realify" the space: $((L^2)^N, \mathbb{C}_J) \to ((L^2)^N, \mathbb{R})$
- But we need complex vector space structure to do spectral theory, so complexify: $((L^2)^N, \mathbb{R}) \to (((L^2)^N)^2, \mathbb{C}_i)$, introducing new imaginary unit i
- Different possible explicit representation of vectors and operators in $(((L^2)^N)^2, \mathbb{C}_i)$; splitting real and imaginary parts not necessarily best one, especially when Ψ^0 is not real
- In quantum chemistry, Casida representation mostly used

	Casida representation	Real/imaginary representation
$U + iV$ for $U, V \in (L^2(\mathbb{R}^3, \mathbb{C}))^N$	$\begin{pmatrix} U + iV \\ \overline{U} + i\overline{V} \end{pmatrix} \in (L^2(\mathbb{R}^3, \mathbb{C}))^{2N}$	$\begin{pmatrix} U_{\mathrm{r}} + iV_{\mathrm{r}} \\ U_{\mathrm{j}} + iV_{\mathrm{j}} \end{pmatrix} \in (L^2(\mathbb{R}^3, \mathbb{C}))^{2N}$
J	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$
$U \mapsto AU + B\overline{U}$	$\begin{pmatrix} A & B \\ \overline{B} & \overline{A} \end{pmatrix}$	$\begin{pmatrix} A_{\mathrm{r}} + B_{\mathrm{r}} & -A_{\mathrm{j}} + B_{\mathrm{j}} \\ A_{\mathrm{j}} + B_{\mathrm{j}} & A_{\mathrm{r}} - B_{\mathrm{r}} \end{pmatrix}$

The linearized equation

$$J\partial_t U = M_{\mathrm{dyn}} U$$

M_{dyn} $\mathbb{C}$-linear on $(L^2)^{2N}$

- Still not a Schrödinger structure, but now a Hamiltonian structure
- Stability depends on positive definiteness of M_{dyn} (like in classical mechanics)
- If M_{dyn} is positive definite, then

$$e^{-JM_{\mathrm{dyn}}t} = M_{\mathrm{dyn}}^{-1/2}\, e^{-M_{\mathrm{dyn}}^{1/2} J M_{\mathrm{dyn}}^{1/2} t}\, M_{\mathrm{dyn}}^{1/2}$$

  with $M_{\mathrm{dyn}}^{1/2} J M_{\mathrm{dyn}}^{1/2}$ skew-adjoint
- M_{dyn} is not positive definite on L^2 (only on $(\mathrm{Ran}(\Psi^0)^\perp)^N$), but the non-positive-definite part is in $(\mathrm{Ran}(\Psi^0))^N$, finite-dimensional
- Conclude using standard functional analysis tools (norm equivalences, interpolation)

$$\|U(t)\|_{H^2} \leq C(t)\|U(0)\|_{H^2}$$

  with C polynomial (needed for distributional Fourier transforms)

Linear response

Refining the proof,

$$\rho(t) = \rho_{\Psi^0(t)+\varepsilon U(t)} = \rho_0 + \varepsilon \int_0^t \chi(t-t') V_P f(t') dt' + O_t(\varepsilon^2)$$

$$\chi(t) V_P = -\theta(t) \frac{d\rho}{d\Psi} \left(e^{-tJM} J (1-P_0) V_P \Psi^0 \right)$$

with P_0 projector on $(\mathrm{Ran}(\Psi^0))$, and $M = (1-P_0) M_{\mathrm{dyn}} (1-P_0)$.

Frequency response:

$$\hat{\chi}(\omega) V_P = \lim_{\eta \to 0^+} -\frac{d\rho}{d\Psi} \left(\frac{1}{M + i(\omega + i\eta) J} (1-P_0) V_P \Psi^0 \right).$$

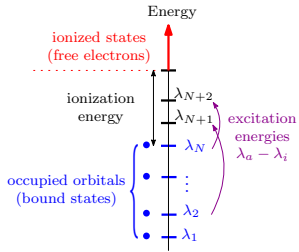
Excitation energies are poles of $(M + i(\omega + i\eta)J)^{-1}$ (spectrum of $-JM$)

Back to independent electrons

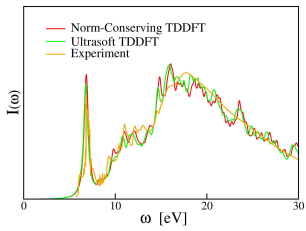
$$\hat{\chi}(\omega)V_P = \lim_{\eta\to 0^+} -\frac{d\rho}{d\Psi}\left(\frac{1}{M + i(\omega + i\eta)J}(1 - P_0)V_P\Psi^0\right).$$

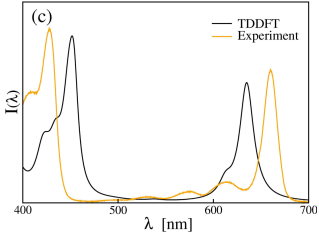
When independent electrons, in the Casida representation,

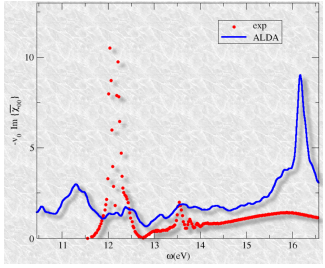
$$J \overset{\text{Casida}}{\simeq} \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}, \quad M \overset{\text{Casida}}{\simeq} \begin{pmatrix} \Omega & 0 \\ 0 & \Omega \end{pmatrix}, \quad (\Omega U)_n = H_{\rho_0} u_n - \lambda_n u_n$$



Accuracy of TDDFT







Absorption spectrum of benzene (C_6H_6)and chlorophyll ($C_{55}H_{72}O_5N_4Mg$), D. Rocca '07; Solid Argon, F. Sottile et al (2007)

Summary

Linear response

TDDFT

Resonances

Beryllium

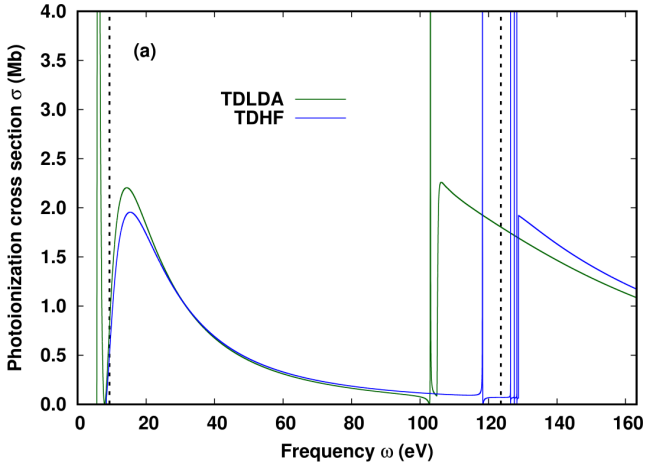
Be $1s^2 2s^2$: two electrons in ψ_{1s}, two in ψ_{2s}.

- $\lambda_{1s}, \lambda_{2s}, \lambda_{2p} < 0$
- $\lambda_{2p} - \lambda_{1s} = \lambda_{\mathrm{scatt}} - \lambda_{2s}$, $\lambda_{\mathrm{scatt}} > 0$
- Eigenvalue $i(\lambda_{2p} - \lambda_{1s})$ embedded in continuous spectrum of non-interacting $-JM$

Beryllium

Be $1s^2 2s^2$: two electrons in ψ_{1s}, two in ψ_{2s}.

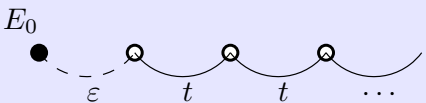
- $\lambda_{1s}, \lambda_{2s}, \lambda_{2p} < 0$
- $\lambda_{2p} - \lambda_{1s} = \lambda_{\mathrm{scatt}} - \lambda_{2s}$, $\lambda_{\mathrm{scatt}} > 0$
- Eigenvalue $i(\lambda_{2p} - \lambda_{1s})$ embedded in continuous spectrum of non-interacting $-JM$



Fermi's golden rule: example

Generically, eigenvalue embedded in continuous spectrum turn into resonances upon perturbation: Feshbach resonances ($\neq$ shape resonances)

Elementary example



$E_0 \notin [-2t, 2t] \Rightarrow$ bound state

$E_0 \in [-2t, 2t] \Rightarrow$ resonance

- The bound state at $\varepsilon = 0$ pumps energy to the propagating waves through resonant coupling
- Mathematically nontrivial phenomenon, derivations in the physical literature often "incomplete"
- In time, exponential decay of $\langle \psi_0 | e^{-iHt} | \psi_0 \rangle$ in a special regime (Davies, Orth, Sofer-Weinstein, ...)
- In frequency, pole in the analytic continuation of the resolvent (Simon, ...)

Fermi's golden rule: assumptions

Let $H = H_0 + \varepsilon H_1$, H_0 with simple eigenvalue at E_0:

$$H_0 = E_0 |\psi_0\rangle\langle\psi_0| + \int_{\mathbb{R}} \lambda dP_\lambda.$$

Assume there is $X \subset \mathcal{H}$ sub-Hilbert such that

$$dP_\lambda = p(\lambda) d\lambda$$

near E_0, with $p(\lambda)$ analytic from X to X^*. Also assume $\psi_0 \in X$, H_1 bounded from $\mathcal{H}$ to $\mathcal{H}$ and from X to X^*

Exemple: $X =$ exponentially localized functions, H_0 local perturbation of Laplacian, H_1 multiplication by exponentially localized function

Fermi's golden rule: result

Theorem (Classical)

1. *The Green function*

$$G(z) = \langle \psi_0 | \frac{1}{z - (H_0 + \varepsilon H_1)} | \psi_0 \rangle$$

defined for $\mathrm{Im}(z) > 0$ *extends to a meromorphic function near* E_0 *for* ε *small enough, and has a simple pole at* $E(\varepsilon) = E_0 + \varepsilon \langle \psi_0 | H_1 | \psi_0 \rangle + \varepsilon^2 \Delta E + O(\varepsilon^3)$*, with*

$$\Delta E = \mathrm{p.v.} \int \frac{\langle \psi_0 | H_1 p_\lambda H_1 | \psi_0 \rangle}{E_0 - \lambda} d\lambda - i\pi |\langle \psi_0 | H_1 p_{E_0} H_1 | \psi_0 \rangle|^2$$

2. *The time evolution satisfies*

$$\langle \psi_0 | e^{-i(H_0 + \varepsilon H_1)t} \psi_0 \rangle = e^{-iE(\varepsilon)t} + o_{\mathrm{unif}}(1)$$

Proof: 1 by Schur complement, 2 by 1 + spectral concentration

Many applications and extensions

Fermi's golden rule: interpretation

- Resonance = long-lived unbound state, with decay rate (to second order)

$$\Gamma = \pi |\langle \psi_0 | H_1 p_{E_0} H_1 | \psi_0 \rangle|^2$$

- In physics literature:

$$\Gamma = \pi |\langle \psi_0 | H_1 | \psi_f \rangle|^2 D(E_0)$$

with ψ_f the "final states", and $D(E_0)$ the density of such states at energy E_0

- Correct upon proper interpretation (normalization of continuum eigenstates, average over all possible eigenstates):

$$p(E_0) = \int dk \delta(\lambda(k) - E_0) |\psi_k\rangle\langle\psi_k| = \underbrace{\int_{\lambda(k)=E_0} dk \frac{1}{|\nabla \lambda(k)|}}_{D(E_0)} |\psi_k\rangle\langle\psi_k|$$

with $\langle \psi_k | \psi_{k'} \rangle = \delta(k - k')$ (in the sense of distributions)

Application to TDDFT

$$\hat{\chi}(\omega)V_P = \lim_{\eta\to 0^+} -\frac{d\rho}{d\Psi}\left(\frac{1}{M+i(\omega+i\eta)J}(1-P_0)V_P\Psi^0\right).$$

$$J \overset{\text{Casida}}{\simeq} \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$$

$$M \overset{\text{Casida}}{\simeq} \begin{pmatrix} \Omega & 0 \\ 0 & \Omega \end{pmatrix} + \underbrace{\left(\frac{dH}{d\rho}\,\frac{d\rho}{d\Psi}\cdot\right)\Psi^0}_{K}$$

$$(\Omega U)_n = H_{\rho_0}u_n - \lambda_n u_n$$

Assume

1. There is a simple transition $\lambda_{a_0} - \lambda_{i_0}$ at the same energy as a ionization $\lambda_{\text{scatt}} - \lambda_{j_0}$, $i_0, j_0 \leq N$, λ_{a_0} eigenvalue, $a_0 > N$, $\lambda_{\text{scatt}} > 0$
2. Total (Kohn-Sham potential) is exponentially localized (eg atoms)

Resonances in TDDFT

Theorem (DLL '14)

$\hat{\chi}(z)$ admits an analytic continuation in a neighborhood of $\lambda_{a_0} - \lambda_{i_0}$. If $\|K\|$ is small enough, it has a simple pole at distance $O(\|K\|^2)$ of $\lambda_{a_0} - \lambda_{i_0}$ with a non-positive imaginary part given by a Fermi golden rule expression.
(in the appropriate topologies)

Ideas of the proof:

- X: exponentially localized functions
- Need to continue (essentially) the resolvent of

$$M = \underbrace{-\tfrac{1}{2}\Delta + \text{shift}}_{M_0} + \underbrace{V + K}_{M_1}$$

- Resolvent of M_0 extends analytically as a delocalizing operator (from X to X^*)
- V and the electron-electron interaction part $K = \left(\frac{dH}{d\rho}\,\frac{d\rho}{d\Psi}\cdot\right)\Psi^0$ localize (map X^* to X)
-

$$(z - M)^{-1} = (z - M_0)^{-1}(1 - M_1(z - M_0)^{-1})^{-1}$$

and $1 - M_1(z - M_0)^{-1}$ Fredholm on X

Extensions, perspectives

- Numerics
  - What happens in a finite basis [Dupuy-Levitt '21]
  - How to compute resonances [Toulouse et. al. '22, Duchemin-Levitt '23]
  - Periodic background [Duchemin et al. '22]
  - Non-perturbative dynamics
- Resonance structure instance of a general notion of effective dynamics of $x' = (A + \varepsilon B)x$ with $x(0) \in \mathrm{Null}(A)$
- Coulomb interaction (hybrids)