

Using Green's functions to couple a finite region to an infinite one

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The aim here is to figure out how to compute the Green's function for an infinite system consisting of a finite subsystem such as a quantum dot or a molecule that is coupled to an infinite subsystem such as a carbon nanotube, graphene sheet, or a generic surface. The aim is to find a computationally tractable method that gives the correct Green's function and thus time evolution for such a system with no assumption of periodic boundary conditions.

We are going to assume that the infinite subsystem prior to coupling is “nice” in that we can solve for its Green's function effectively and with low computational cost. For example, graphene has only two atoms per cell so once can compute its Green's function with very little work and to very high precision. This infinite periodic system is coupled locally to a single finite system. The problem is how to deal with this total system which lacks periodicity.

The type of matrix element we are interested in look like

$$i\mathcal{G}(t)_{ab} = \langle a | \exp(-it\hat{H}) | b \rangle$$

for $t > 0$. Here H is the Hamiltonian of the whole system and states $|a\rangle, |b\rangle$ are localized on the finite system. So this might represent the amplitude for remaining in the finite system after time t and not tunneling out into the infinite bath. Thus $|\mathcal{G}(t)_{aa}|^2$ is the probability of staying in state $|a\rangle$ after time t — i.e. not tunneling out to the infinite subsystem and “getting lost” there.

1 Green's function of frequency in resolvent form

First we do some formal rearrangements of Greens's functions in time and frequency. The main results are equations (1) and (2) below. In what follows, we assume the Hamiltonian

and (any overlap operators) are real-valued matrices. This means time-reversal invariance and real-valued eigenfunctions $\psi_n(x) = \psi_n(x)^*$. So the Green's function is given by

$$i\mathcal{G}(x, x', t) = \sum_n \psi_n(x)\psi_n(x') \exp(-i\epsilon_n t)$$

where $H\psi_n = \epsilon_n\psi_n$. The Fourier transform of \mathcal{G} is then

$$iG(x, x', \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} i\mathcal{G}(x, x', t) = \sum_n \psi_n(x)\psi_n(x') \int_{-\infty}^{\infty} dt e^{i(\omega - \epsilon_n)t}$$

Since the ϵ_n are real, the only way we can make this absolutely convergent for $t > 0$ is to have a positive imaginary part to ω . Letting $\omega = \omega_r + i\eta$ where ω_r and η are real and $\eta > 0$ is a fixed small number, we perform the contour integral over ω_r to get

$$G(x, x', \omega) = \sum_n \frac{\psi_n(x)\psi_n(x')}{\omega_r + i\eta - \epsilon_n}$$

or in operator form

$$\hat{G}(\omega) = [\omega_r + i\eta - \hat{H}]^{-1}$$

The inverse transform is

$$i\mathcal{G}(x, x', t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} iG(x, x', \omega) = \int_{-\infty}^{\infty} \frac{d\omega_r}{2\pi} e^{-i\omega_r t + \eta t} iG(x, x', \omega_r + i\eta)$$

or in explicit form

$$i\mathcal{G}(x, x', t) = i \sum_n \psi_n(x)\psi_n(x') \int_{-\infty}^{\infty} \frac{d\omega_r}{2\pi} \frac{\exp(-i\omega_r t + \eta t)}{\omega_r + i\eta - \epsilon_n}$$

The integral can be done via contour methods by closing over the lower complex half plane of ω_r and is $-i \exp(-i\epsilon_n t)$ as expected.

Next, we notice that the imaginary part of $G(x, x', \omega)$ is nice

$$\text{Im } G(x, x', \omega) = \sum_n \psi_n(x)\psi_n(x') \cdot \frac{-\eta}{(\omega_r - \epsilon_n)^2 + \eta^2}$$

The function $-\eta/(u^2 + \eta^2)$ is a Lorentzian with area $-\pi$ under it. In the limit $\eta \rightarrow 0^+$ it turns into $-\pi\delta(u)$, although we won't be taking this limit. We can also evaluate the integral

$$\int_{-\infty}^{\infty} \frac{d\omega_r}{2\pi} \frac{\exp(-i\omega_r t + \eta t) \cdot (-\eta)}{(\omega_r - \epsilon_n)^2 + \eta^2} = -\frac{\exp(-i\epsilon_n t - \eta t)}{2}$$

This means we can write a first key result

$$\langle x | \exp(-i\hat{H}t) | x' \rangle = - \int_{-\infty}^{\infty} \frac{d\omega_r}{\pi} \text{Im} \langle x | (\omega_r + i\eta - \hat{H})^{-1} | x' \rangle \exp(-i\omega_r t + \eta t). \quad (1)$$

For a complex number z we can define

$$G(x, x', z) = \langle x | (z - \hat{H})^{-1} | x' \rangle \quad (2)$$

So if we have some efficient way of computing $G(x, x', z)$ then we can use this Fourier formula to get the time-evolution easily.

2 Tight-binding and overlap matrices

The above derivations are in terms of real space and Hilbert space operators which is not so useful for a practical computation. In practice, it is more useful to use some basis set localized in real space to deal with the finite subsystem and its coupling to the infinite subsystem in an effective manner. We will assume in general that the basis functions are not orthonormal so we have an overlap matrix S to deal with in addition to the Hamiltonian H . This section is mainly standard material on what various computed quantities look like in such a situation.

The localized basis is given by the localized functions $\{\chi_\alpha(r)\}$ and thus our matrices are

$$H_{\alpha\beta} = \langle \alpha | \hat{H} | \beta \rangle, \quad S_{\alpha\beta} = \langle \alpha | \beta \rangle.$$

A ket $|\phi\rangle$ has expansion in coefficients ϕ_α

$$|\phi\rangle = \sum_{\alpha} |\alpha\rangle \phi_{\alpha}.$$

So the inner product is given by

$$\langle \phi | \psi \rangle = \phi^\dagger S \psi$$

where we put the coefficients into vectors. Next, the Schrödinger equation looks like

$$HV = SVE$$

where V is the matrix of normalized eigenvectors in the columns, E is a diagonal matrix of eigenvalues $E_{n,m} = \epsilon_n \delta_{n,m}$, and the vectors are normalized as

$$V^\dagger S V = I.$$

Here are a bunch of identities that follow:

$$V V^\dagger S = I, \quad V^\dagger = V^{-1} S^{-1}, \quad V^{-1} = V^\dagger S, \quad E = V^\dagger H V = V^{-1} S^{-1} H V.$$

The most powerful is the last one which shows that E and $S^{-1}H$ are related by a change of basis. It generalizes to

$$E^n = V^{-1} [S^{-1}H]^n V.$$

So for an analytic function $f(x)$ with a convergent Taylor expansion, we have

$$f(E) = V^{-1} f(S^{-1}H) V. \tag{3}$$

The last general fact we need is the resolution of identity. Notice that the basis is not orthonormal so blind substitution makes for wrong results: for example

$$S_{\alpha\beta} = \langle \alpha | \beta \rangle \neq \sum_{\gamma} \langle \alpha | \gamma \rangle \langle \gamma | \beta \rangle = S^2_{\alpha\beta}.$$

The resolution of the identity is

$$\hat{1} = \sum_{\alpha\beta} |\alpha\rangle S^{-1}_{\alpha\beta} \langle\beta| \quad (4)$$

which as an example gives us the proper way to compute a trace of some operator \hat{O} :

$$\text{trace}\{\hat{O}\} = \text{trace}\{\hat{1} \cdot \hat{O}\} = \text{trace}\{S^{-1}O\} \quad (5)$$

where $O_{\alpha\beta} = \langle\alpha|\hat{O}|\beta\rangle$ is the matrix representation of \hat{O} .

Now consider some analytic function $f(x)$ with a convergent Taylor series. Our first job is to compute a matrix element of the sort

$$\langle\alpha|f(\hat{H})|\beta\rangle = \sum_n \langle\alpha|\psi_n\rangle f(\epsilon_n) \langle\psi_n|\beta\rangle.$$

One example would be $\alpha = \beta$ and $f(x) = \delta(\omega - x)$ to give the local density of states projected onto state α . Substituting in from the Schrödinger equation: $|\psi_n\rangle = \sum_\alpha |\alpha\rangle V_{\alpha n}$ gives

$$\langle\alpha|f(\hat{H})|\beta\rangle = \sum_n (SV)_{\alpha n} f(\epsilon_n) (V^\dagger S)_{n\beta} = (SVf(E)V^\dagger S)_{\alpha\beta}$$

and using our above result for $f(E)$ we get as well

$$\langle\alpha|f(\hat{H})|\beta\rangle = \left(Sf(S^{-1}H) \right)_{\alpha\beta}.$$

Hence the correct mnemonic for replacement of Hilbert space operators to matrices is

$$f(\hat{H}) \longrightarrow SVf(E)V^\dagger S = Sf(S^{-1}H). \quad (6)$$

As an application, the total density of states is

$$D(\omega) = \sum_n \delta(\omega - \epsilon_n) = \text{trace}\{\delta(\omega I - E)\} = \text{trace}\{\delta(\omega I - S^{-1}H)\}.$$

Since $V^\dagger S V = I$ then $V^\dagger = V^{-1} S^{-1}$ so $E = V^\dagger H V = V^{-1} S^{-1} H V$ and

$$D(\omega) = \text{trace}\{\delta(\omega I - V^{-1} S^{-1} H V)\} = \text{trace}\{\delta(\omega I - S^{-1} H)\}$$

where we used the cyclicity of the trace to get rid of the V and V^{-1} .

3 Computing the Green's function efficiently

We now turn to our actual system to put this result to use. We will throughout assume a localized basis in real-space (otherwise the problem is hard to define or think about sensibly).

We will be general and assume the basis functions — e.g., tight-binding atomic-like orbitals — may not be orthonormal so we have an overlap matrix S to worry about as well.

To make progress, let us define a finite patch of the system surrounding the finite system as F . This could be a molecule or quantum dot coupled to graphene, and we cut out a section of the graphene + molecule that is “large enough” (defined below). The rest of the infinite system we will call B (for bath). We can thus write the Hamiltonian and overlap in a 2×2 block representations as

$$H = \begin{pmatrix} H_{FF} & H_{FB} \\ H_{FB}^T & H_{BB} \end{pmatrix} \quad , \quad S = \begin{pmatrix} S_{FF} & S_{FB} \\ S_{FB}^T & S_{BB} \end{pmatrix}$$

Again, these are real-valued symmetric matrices. We can also define H^0 and S^0 as the matrices when we don’t couple the molecule to the infinite system (e.g., the infinite system itself with no molecule or the infinite system with molecule but not matrix elements between them):

$$H^0 = \begin{pmatrix} H_{FF}^0 & H_{FB}^0 \\ H_{FB}^0{}^T & H_{BB}^0 \end{pmatrix} \quad , \quad S^0 = \begin{pmatrix} S_{FF}^0 & S_{FB}^0 \\ S_{FB}^0{}^T & S_{BB}^0 \end{pmatrix}$$

The main assumption is that the region F is large enough so the matrix elements H_{FB} and S_{FB} are identical to high accuracy to the same matrix elements for the idealized system. Namely we assume

$$H_{FB}^0 = H_{FB} \quad , \quad S_{FB}^0 = S_{FB} \quad , \quad H_{BB}^0 = H_{BB} \quad , \quad S_{BB}^0 = S_{BB}$$

This is what we mean by the finite system F must be “big enough” so its edges don’t interact via matrix elements with the molecule in the center.

We now write H and S as perturbations off H^0 and S^0 :

$$H = H^0 + \begin{pmatrix} \Delta H & 0 \\ 0 & 0 \end{pmatrix} \quad , \quad S = S^0 + \begin{pmatrix} \Delta S & 0 \\ 0 & 0 \end{pmatrix}$$

so the perturbations are only non-zero in the finite region F . This is the key that makes everything work.

In this basis, the Green’s function in frequency space is given by

$$G(z)^{-1} = zS - H = zS^0 - H^0 + \begin{pmatrix} z\Delta S - \Delta H & 0 \\ 0 & 0 \end{pmatrix} = G^0(z)^{-1} + \begin{pmatrix} z\Delta S - \Delta H & 0 \\ 0 & 0 \end{pmatrix}$$

which we compactify to

$$G(z)^{-1} = G^0(z)^{-1} - \Delta(z) \quad \text{where} \quad \Delta(z) \equiv \begin{pmatrix} z\Delta S - \Delta H & 0 \\ 0 & 0 \end{pmatrix}$$

so when we invert to get $G(z)$ we get the standard infinite series and Dyson’s equation

$$\begin{aligned} G(z) &= G^0(z) + G^0(z)\Delta(z)G^0(z) + G^0(z)\Delta(z)G^0(z)\Delta(z)G^0(z) + \dots \\ &= G^0(z) + G^0(z)\Delta(z)G(z) \end{aligned}$$

The second line is the Dyson equation. We now write G and G^0 in 2×2 form (suppressing the z argument)

$$G = \begin{pmatrix} G_{FF} & G_{FB} \\ G_{BF} & G_{BB} \end{pmatrix}, \quad G^0 = \begin{pmatrix} G_{FF}^0 & G_{FB}^0 \\ G_{BF}^0 & G_{BB}^0 \end{pmatrix}$$

and plug into the Dyson equation to find for the upper left G_{FF} part

$$G_{FF} = G_{FF}^0 + G_{FF}^0(z\Delta S - \Delta H)G_{FF}$$

which only involves the finite system itself. Solving this for G_{FF} gives a key result

$$G_{FF} = [I - G_{FF}^0(z\Delta S - \Delta H)]^{-1} G_{FF}^0 \quad (7)$$

This is what we want: a system of equations for finding the Green's function of the finite system alone using quantities only in the finite system and of its size. It assumes we can compute G_{FF}^0 for the unperturbed system.

Thus, given two vectors of coefficients a and b that are non-zero only in the finite system, the matrix element we want is

$$\begin{aligned} \langle a | \exp(-i\hat{H}t) | b \rangle &= a^T S \exp(-itS^{-1}H)b \\ &= - \int_{-\infty}^{\infty} \frac{d\omega_r}{\pi} \text{Im} a^T S(\omega_r + i\eta - S^{-1}H)^{-1} b \exp(-i\omega_r t + \eta t) \\ &= - \int_{-\infty}^{\infty} \frac{d\omega_r}{\pi} \text{Im} a^T S([\omega_r + i\eta]S - H)^{-1} S b \exp(-i\omega_r t + \eta t) \\ &= - \int_{-\infty}^{\infty} \frac{d\omega_r}{\pi} \text{Im} a^T S [([\omega_r + i\eta]S - H)^{-1}]_{FF} S b \exp(-i\omega_r t + \eta t) \\ &= - \int_{-\infty}^{\infty} \frac{d\omega_r}{\pi} \text{Im} a^T S G(\omega_r + i\eta)_{FF} S b \exp(-i\omega_r t + \eta t) \end{aligned}$$

where we used the fact that a and b are non-zero only in F so we only need G_{FF} in this integral.

So the algorithm to compute the matrix element of the evolution operator between states a and b localized in the subsystem F that we want $U(t)_{ab} = \langle a | \exp(-it\hat{H}) | b \rangle$ is

1. Zero out the matrix elements $U(t_j)_{ab}$ for all times t_j we are computing
2. Loop over values of ω_r along the real axis
3. Get $G_{FF}^0(\omega_r + i\eta)$ by lookup or matrix inversion $G_{FF}^0(z) = [(zS^0 - H^0)^{-1}]_{FF}$
4. Compute $G_{FF} = [I - G_{FF}^0(z\Delta S - \Delta H)]^{-1} G_{FF}^0$.
5. Compute $a^T S G_{FF} S b$.

6. For each t_j , compute product $-Im a^T S G_{FF} S b \cdot \exp(-i\omega_r t_j + \eta t_j)$ and multiply by $\Delta\omega_r/\pi$ and accumulate into $U(t_j)_{ab}$.

Some basic considerations on choosing η and grid size $\Delta\omega_r$:

- We are relying on the Lorentzian of width η in frequency space to have a good normalization. To ensure this, our frequency grid better be smaller than this so $\Delta\omega_r < \eta$ is required.
- If η is too big, our integration range over ω_r will have to be very large to make sure we are again normalizing the Lorentzian properly. So there is a tradeoff: large η means large $\Delta\omega_r$ but also a grid of frequencies going to large negative and positive values of ω_r just to ensure that the tails of the Lorentzians are well integrated.
- Probably the most stringent requirement comes from Nyquist's theorem. If we want to get the long-time evolution correctly, then this imposes constraints on $\Delta\omega_r$. Namely, to correctly describe the integral for times from zero up to T , we must have $\Delta\omega_r T < \pi$ as an upper limit. So $\Delta\omega_r < \pi/T$.

4 Further practical considerations

Some final practical considerations regarding the specific type of system we have been talking about follow. In what went above, F is a finite system including the molecule and the patch of the infinite system. So to be very clear about what the matrices look like in F , let us further subdivide F into a molecular segment M and the patch P that comprise F . So we have a further 2×2 subdivision this time inside of F :

$$H_{FF} = \begin{pmatrix} H_{MM} & H_{MP} \\ H_{MP}^T & H_{PP} \end{pmatrix}$$

and similarly for S_{FF} . One way of defining the unperturbed matrices is

$$H_{FF}^0 = \begin{pmatrix} H_{MM}^0 & 0 \\ 0 & H_{PP}^0 \end{pmatrix}$$

and similarly for S_{FF}^0 . Here we have turned off the $M - P$ coupling and set the matrices to their uncoupled values.

However, we instead can define $H_{MM}^0 = H_{MM}$ and $H_{PP}^0 = H_{PP}$ with no error since in the end we add back what was missing (the coupling) inside of F when we do our computations. Thus we can work with the following matrices as an alternative

$$H = \begin{pmatrix} H_{MM} & H_{MP} & 0 \\ H_{MP}^T & H_{PP} & H_{PB} \\ 0 & H_{PB}^T & H_{BB} \end{pmatrix}$$

and

$$H^0 = \begin{pmatrix} H_{MM} & 0 & 0 \\ 0 & H_{PP} & H_{PB} \\ 0 & H_{PB}^T & H_{BB} \end{pmatrix}$$

and similarly for S and S^0 .

Looking at this, it is tempting to say that one could actually redo the above derivation but take the smaller M system as the finite system F and the larger $P + B$ becomes the bath. However, this is only correct if $H_{PP} = H_{PP}^0$ is a good approximation. Namely, only in this case will the patch P form a continuous part of the periodic unperturbed “bath” for which we can compute the Green’s function easily. If instead, the actual matrix elements of H_{PP} are different than the corresponding ones in the bath B (e.g., due to charge transfer from/to the molecule M or any other important physical effect of the $M - P$ connection on the Hamiltonian of P), then we will have a hard time computing the “unperturbed” Green’s function for $P + B$ easily since we will have a defective P connected to a bath B that differs from it and this is the difficult problem that we were trying to solve from the start.

However, if $H_{PP} = H_{PP}^0$ is in fact a good approximation, then we can directly compute everything in the smaller M subspace using the above methods by relabeling $F \rightarrow M$ and $B \rightarrow B + P$ and thus achieve computational savings.