Time-dependent adiabatic *GW*

Jinyuan Wu

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1 From Keldysh formalism to quantum master equation

Existing researches [1] utilizing TD-aGW carry out the calculation within the framework of quantum master equation (QME)

$$\dot{\rho} + \mathrm{i}[\rho, H] = \int_{-\infty}^{t} \mathrm{d}t' \, F[\rho(t')] \tag{1}$$

which is the equation of motion of the reduced single-electron density matrix

$$\rho(\boldsymbol{r}, \boldsymbol{r}', t) = \left\langle \psi^\dagger(\boldsymbol{r}')\psi(\boldsymbol{r}) \right\rangle = -\mathrm{i}G^<(\boldsymbol{r}, t; \boldsymbol{r}', t). \tag{2}$$

QME can be derived heuristically when the system contains well-defined quasiparticles. The generality of QME and the flow from the most generalized Keldysh formalism to quantum kinetic theories is discussed in [2, 3, 4, 5]. In this section we give a brief summary of the derivation and coverage as well as possible simplifications of QME.

In Keldysh formalism we still have the Dyson equation

$$G = G_0 + G_0 \Sigma G = G_0 + G \Sigma G_0, \tag{3}$$

although now G, G_0 and Σ are 2×2 matrices due to the need of anti-time-ordered, lesser and greater Green functions besides the time-ordered Green function in deriving a diagrammatic perturbation theory for non-equilibrium Green functions [6]; alternatively they can be defined on the Keldysh contour [7]. Note that the choice of H_0 has some arbitrariness at this point: we may split the full many-body self-energy correction Σ^{full} into an "effective field" which has no retardation and is inserted into H_0 and a "real" interaction part Σ. By Langreth's rules (also known as Lengreth's rules or theorem – note the spelling) [7], we reduce (3) on the Keldysh contour into the following equation on the physical time axis:

$$G^< = G_0^< + G_0^{\mathrm{R}} \Sigma^{\mathrm{R}} G^< + G_0^{\mathrm{R}} \Sigma^< G^{\mathrm{A}} + G_0^< \Sigma^{\mathrm{A}} G^{\mathrm{A}}, \quad G^{\mathrm{A,R}} = G_0^{\mathrm{A,R}} + G_0^{\mathrm{A,R}} \Sigma^{\mathrm{A,R}} G^{\mathrm{A,R}}. \tag{4}$$

By applying

$$\overleftarrow{G}_0^{-1} = -\mathrm{i}\overleftarrow{\partial}_t - H_0, \quad \overrightarrow{G}_0^{-1} = \mathrm{i}\overrightarrow{\partial}_t - H_0 \tag{5}$$

to the left and right hand sides of the equation about $G^<$ and utilizing the fact that $G_0^< \overleftarrow{G}_0^{-1} = \overrightarrow{G}_0^{-1} G_0^< = 0$, we obtain the so-called Kadanoff-Baym equation (KBE); a similar equation can be obtained for $G^>$.

The KBE is not the only way to calculate the lesser Green function. By inserting $G^<$ iteratively to the RHS of (4), we find

$$G^< = (1 + G^{\mathrm{R}}\Sigma^{\mathrm{R}}) G_0^< (1 + \Sigma^{\mathrm{A}} G^{\mathrm{A}}) + G^{\mathrm{R}} \Sigma^< G^{\mathrm{A}}. \tag{6}$$

Note that the first factor of the first term is just $G^{\mathrm{R}} \overrightarrow{G}_0^{-1}$ (note the direction of the arrow: by multiplying G_0^{R} to the end of both expressions we'll find it's alright), and therefore we eventually get

$$G^< = G^{\mathrm{R}} \Sigma^< G^{\mathrm{A}}. \tag{7}$$

This is known as the Keldysh equation of non-equilibrium Green functions (see e.g. [8]).

Here I present a form of Kadanoff-Baym equation [7] that is closer to what is often seen in equilibrium Green function theory:

$$[G_0^{-1} - U - \Sigma, A] - [\Gamma, G] = 0, \tag{8}$$

where and A, Γ, G, and Σ are defined as

$$\Sigma = \frac{1}{2}\left(\Sigma^{\mathrm{R}} + \Sigma^{\mathrm{A}}\right), \quad G = \frac{1}{2}\left(G^{\mathrm{R}} + G^{\mathrm{A}}\right), \quad A = \mathrm{i}\left(G^{\mathrm{R}} - G^{\mathrm{A}}\right), \quad \Gamma = \mathrm{i}\left(\Sigma^{\mathrm{R}} - \Sigma^{\mathrm{A}}\right). \tag{9}$$

The quantities A and G is the generalization of its equilibrium counterpart, namely the spectral function; Σ and Γ are generalizations of $\mathrm{Re}\,\Sigma$ and $\mathrm{Im}\,\Sigma$ in the equilibrium formalism, respectively; note that in the most general case there is no guarantee that Σ is predominantly a real number. The form of (8) also shows that the division of labor between Σ and U_0 is only artificial, and with no further approximation done, different divisions give the same EOM for A, as is expected. The Kadanoff-Baym equation about $G^<$ can be written in to the following more readable form

$$\mathrm{i}\partial_T G^< - [H_0, G^<] = \Sigma^{\mathrm{R}} G^< + \Sigma^< G^{\mathrm{A}} - G^{\mathrm{R}}\Sigma^< - G^<\Sigma^{\mathrm{A}}, \tag{10}$$

where we have redefined the time variables as

$$T = \frac{t_1 + t_2}{2}, \quad t = t_1 - t_2. \tag{11}$$

Roughly speaking, T is related to the time variance of the external driving field or the relaxation of the system, while t corresponds to the time variable in equilibrium Green function, and often Fourier transform is done in t, and thus $G^< = G^<(T, \omega)$.

The "precursor" equation (10) is already very close to QME, its left hand side being the left hand side of QME after integrating over ω. Three approximations are needed however to close the equation: the explicit form of $\Sigma[G]$, representation of $G^{\mathrm{A,R}}$ with $G^<$ and $\Sigma^{\mathrm{A,R}}$, and reconstruction of $G^<$ using $\rho(T)$ i.e. $G^<(t_1 = t_2 = T)$. It can be proved that the last is always possible [3], with the lowest order approximation being the Generalized Kadanoff–Baym Ansatz (GKBA), and a closed QME can therefore be obtained [4, 7]. Note that in principle this procedure does not require the system to have well-defined electron-like quasiparticle. Note that we may be able to adjust the division of labor between H_0 and Σ, as is said above, and if we want to place as much content as we want into H_0, there is no guarantee that it stays real, as is seen in the Lindblad equation widely used in quantum optics.

QME can be used to study higher-order correlations in a system without explicitly constructing the relevant Green functions. The linear response, for example, reveals $G^{(4)}$, since the first order response can be diagrammatically obtained by choosing an arbitrary propagator and plant an external field line into it (Figure 1 (a)). Since the single-electron self-energy can always be written into the convolution of the two-electron kernel function and the renormalized Green function (Figure 1 (b)), the letter containing its own self-energy correction and hence a two-electron kernel function, by taking the linear response i.e. breaking a propagator in a single-electron self-energy, we get a two-electron kernel function with the same level of accuracy (Figure 1 (c, d)).

Two further approximations reduce QME to quantum Boltzmann equation (QBE) [2, 7]. Under the assumption that well-defined quasiparticles always exist (this approximation is known as Kadanoff-Baym ansatz) and hence we have

$$G^<(\boldsymbol{X}, \boldsymbol{p}, T, \omega) = 2\pi\delta(\omega - E_{\boldsymbol{p}}(\boldsymbol{X}))f(\boldsymbol{X}, \boldsymbol{p}, T), \tag{12}$$

where Wigner transform has been applied. Using the condition of smooth external driving force, by gradient expansion, the left hand side of QME becomes the usual form of collisionless Boltzmann equation. With both the quasiparticle assumption the right hand side of QME becomes the Fermi golden rule, which is prevalently used as the collision integral [9]. Deviations from the quasiparticle approximation, e.g. strong electron-phonon interaction-induced renormalization, may still lead to QBE, although with modified collision integral [2, 10]. The two approximations are rather severe: it is possible to break them into combinations of "smaller" approximations and apply the latter one by one. (12), for example, implies that the kinetic of the system is Markovian, or in more physical words, that collision almost takes no time; this condition of course can applied on its own without assuming that well-defined quasiparticles always exist, usually by taking up the generalized Kadanoff-Baym ansatz, where the "duration" of $\Sigma^<(t_1, t_2)$ is ignored [5]. Note that the collision duration time is not the same as the quasiparticle lifetime, and is not only about the interaction vertex, but also the internal properties of the quasiparticles. TODO: $\tau_{\mathrm{c}} \sim l_{\text{force range}}/v$?

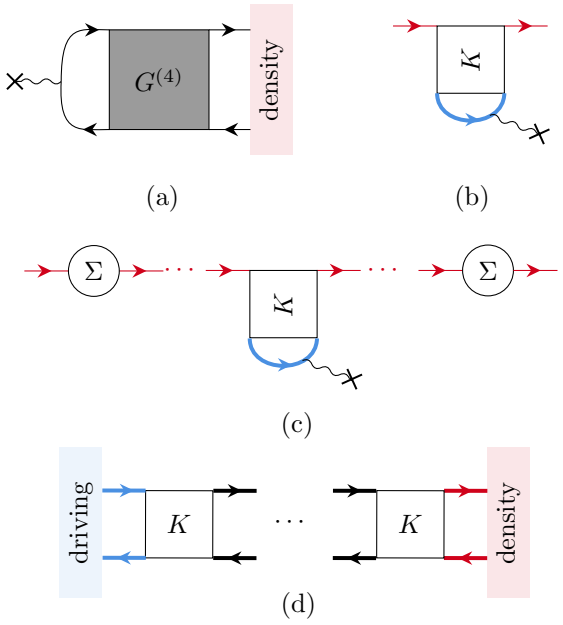

Figure 1: Feynman diagrams representing linear response. (a) Linear response of electron density (red rectangle) is given by plating a line representing the external field into one bare propagator. (b) Single-electron self-energy, rewritten as a convolution between the four-point kernel function (i.e. self-energy of renormalized electron-hole pair) and the renormalized Green function (thick blue line) with the influence of the driving field. The electron lines that are connected to the external legs in (a) are colored red. Note that the blue line has its own self-energy correction, and the external field line is connected to one bare propagator within the thick blue line. (c) Inserting (b) into (a). (d) The diagram we get after evaluating the derivative with respect to the external field i.e. after removing the external field line. Since the thick blue line in (b) and (c) has its own self-energy correction which is also represented by (b), we get accurately diagrams representing renormalized electron-hole pair; note that K can be obtained by removing a renormalized Green function from Σ.

2 The COHSEX approximation

3 Experimental characterization: tr-ARPES

Time-resolved ARPES (tr-ARPES) is done by driving the material with a pulse ("pump") and then use another following pulse ("probe") to drive out electrons that are driven to excited states by the pump; by measuring the direction and the energy of the outgoing electron jet, we are able to reconstruct the dynamic spectral function; in this section I discuss how this is achieved and how it is related to TD-aGW.

References

[1] Yang-Hao Chan et al. "Giant exciton-enhanced shift currents and direct current conduction with subbandgap photo excitations produced by many-electron interactions". In: *Proceedings of the National Academy of Sciences* 118.25 (2021), e1906938118.

[2] Jørgen Rammer and H Smith. "Quantum field-theoretical methods in transport theory of metals". In: *Reviews of modern physics* 58.2 (1986), p. 323.

[3] Václav Špička, Bedřich Velickỳ, and Anděla Kalvová. "Long and short time quantum dynamics: I. Between Green's functions and transport equations". In: *Physica E: Low-dimensional Systems and Nanostructures* 29.1-2 (2005), pp. 154–174.

[4] Václav Špička, Bedřich Velickỳ, and Anděla Kalvová. "Long and short time quantum dynamics: II. Kinetic regime". In: *Physica E: Low-dimensional Systems and Nanostructures* 29.1-2 (2005), pp. 175–195.

[5] Václav Špička, Bedřich Velickỳ, and Anděla Kalvová. "Long and short time quantum dynamics: III. Transients". In: *Physica E: Low-dimensional Systems and Nanostructures* 29.1-2 (2005), pp. 196–212.

[6] EM Lifschitz and LP Pitajewski. "Physical kinetics". In: *Textbook of theoretical physics. 10*. 1983.

[7] Hartmut Haug, Antti-Pekka Jauho, et al. *Quantum kinetics in transport and optics of semiconductors*. Vol. 2. Springer, 2008.

[8] Antti-Pekka Jauho, Ned S Wingreen, and Yigal Meir. "Time-dependent transport in interacting and noninteracting resonant-tunneling systems". In: *Physical Review B* 50.8 (1994), p. 5528.

[9] Hsiao-Yi Chen, Davide Sangalli, and Marco Bernardi. "First-principles ultrafast exciton dynamics and time-domain spectroscopies: Dark-exciton mediated valley depolarization in monolayer WSe 2". In: *Physical Review Research* 4.4 (2022), p. 043203.

[10] Michael Wais et al. "Quantum Boltzmann equation for strongly correlated systems: Comparison to dynamical mean field theory". In: *Physical Review B* 98.13 (2018), p. 134312.