Quantum kinetic equations
Lecture #3

Michael Bonitz, Karsten Balzer

Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

December 5, 2008
Outline

1  Numerical procedure
   - Basic concepts
   - Equilibrium—Dyson equation
   - Nonequilibrium—real-time KBE

2  Application to homogeneous Coulomb systems
   - Plasmas and correlated electron gases

3  Application to localized systems
   - Quantum dots
   - Atoms and small molecules

4  Conclusion
   - Conclusion
Basic numerical concepts I

Question of representation:

(a) Homogeneous systems (e.g. plasmas, correlated electron gases)

\[ G(r_{1t_1}, r_{\bar{t}}t_{\bar{1}}) \rightarrow G(p; t_{1}, t_{\bar{1}}) \text{ or } G(k; t_{1}, t_{\bar{1}}) \]

- \( G \) depends on a single momentum or wave vector
  \[ \Rightarrow \text{Numerically, solve KBE on a } p- \text{ or } k-\text{grid} \]

(b) Inhomogeneous finite systems (e.g. particles in traps, quantum dots, atoms)

\[ G(r_{1t_1}, r_{\bar{t}}t_{\bar{1}}) \rightarrow g_{mn}(t_{1}, t_{\bar{1}}) \]

Definition:

\[ G(r_{1t_1}, r_{\bar{t}}t_{\bar{1}}) = \sum_{m,n=0}^{n_b-1} \phi_m^*(r_1) \phi_n(r_{\bar{1}}) g_{mn}(t_{1}, t_{\bar{1}}) \]

- \( \{ \phi_m(r) \}, m = 0, 1, \ldots, n_b - 1 \), denotes a complete orthonormal set of (effective) one-particle states
- Solve KBE in basis representation: Each element \( G^{\geq,M,\bar{M}}/\Gamma \) of \( G \)
  becomes a \( n_b \times n_b \)-matrix
Basic numerical concepts II

**Initial/boundary conditions:**

*Either*

- Build up of correlations or specify initial correlation contributions including an initial self-energy $\Sigma^{IN}(1, \bar{1})$, see Ref. 1

*or*

- Apply Kubo-Martin-Schwinger (KMS) boundary conditions to start from a equilibrium Green’s function, which on the same approximate level (as its nonequilibrium counterpart) accounts for the amount of correlations initially in the system.

**Most complete and systematical picture:** Consider the boundary problem → starting from a self-consistent equilibrium Green’s function $G^M(r_1, r_{\bar{1}}; \tau)$.

1. **Apply equilibrium theory:** Solve *Dyson’s equation* for $G^M(r_1, r_{\bar{1}}; \tau)$

2. **Extension to nonequilibrium situations:** Propagate the initial state characterized by $G^M(r_1, r_{\bar{1}}; \tau)$ in time according to the *two-time KBE*
A closed equation for $G^M(1, \bar{1})$ is obtained by taking the difference of both KBEs, evaluating all Green’s functions at $1 = t_0 - i\tau_1$ and $\bar{1} = t_0 - i\bar{\tau}_1$

Dyson equation: $\tau \in [-\beta, +\beta]$

\[
\left[ -\partial_\tau - H^1(r_1) \right] G^M(r_1, r_{\bar{1}}; \tau) = \delta(\tau) + \int d^3\bar{r} \int_0^{\beta} d\bar{\tau} \Sigma^M \left[ G^M \right](r_1, \bar{r}; \tau - \bar{\tau}) G^M(\bar{r}, r_{\bar{1}}; \bar{\tau}) .
\]

- $G^M(1, \bar{1})$ and $\Sigma^M(1, \bar{1})$ only depend on the time-difference $\tau = \tau_1 - \tau_{\bar{1}}$
  \Rightarrow consider the quantities

  \[
  X^M(r_1, r_{\bar{1}}; \tau) = -i X^M(r_1 t_0 - i\tau_1, r_{\bar{1}} t_0 - i\bar{\tau}_{\bar{1}}) , \quad X = G, \Sigma
  \]

- need self-consistent solution for a given self-energy approximation
- KMS boundary conditions for $\tau$-arguments: $G(\tau) = \pm G(\tau - \beta)$
Dyson equation: Time-discretization

Without interaction (\(\Sigma \equiv 0\)) the Dyson equation reads

\[
\left[ -\partial_\tau - H^1(\mathbf{r}_1) \right] G^M(\mathbf{r}_1, \mathbf{r}_{\bar{1}}; \tau) = \delta(\tau)
\]

Thus, typical solution for \(G(\tau)\) has exponential-like character being peaked around \(\tau = 0, \pm \beta\).

Due to KMS conditions restrict solution to interval \([-\beta, 0]\). Compare with one-particle density matrix: \(\rho(\mathbf{r}_1, \mathbf{r}_{\bar{1}}) = G(\mathbf{r}_1, \mathbf{r}_{\bar{1}}; 0^-)\).

- Apply uniform power mesh (UPM) which is dense around the end-points \(\tau = -\beta, 0\).
- \(p\): # of 'power' divisions
- \(u\): # of equidistant subdevisions

1. total # of mesh points: \(M = 2up + 1\)
2. largest mesh-spacing \(\Delta \tau_{\text{max}} = \beta/(4u)\)
3. smallest mesh-spacing \(\Delta \tau_{\text{min}} = \frac{1}{2} \beta/(2^{p-1} u)\)
Numerical scheme—Dyson equation

- Expand $G(1,\bar{1})$ in terms of precomputed Hartree-Fock (HF) orbitals $\phi_m^0(r)$, $m = 0, 1, \ldots, n_b - 1$, with eigenenergies $\epsilon_m^0$ and a chemical potential $\mu^0$. HF Green’s function with self-energy $\Sigma_{ij}^0$:

$$G^0(r_1, r_{\bar{1}}; \tau) = \sum_{m,n} \phi_m^0(r_1)^* \phi_n^0(r_{\bar{1}}) g_{mn}^0(\tau), \quad g_{mn}^0 = \delta_{mn} \frac{\exp(-\tau[\epsilon_i^0 - \mu^0])}{\exp(\beta[\epsilon_i^0 - \mu^0]) + 1}$$

- Dyson equation in integral form $\Leftrightarrow$ Re-interpretation as a set of $n_b$ independent (but typically large-scale) linear systems of the form

$$A \chi^{(j)} = B^{(j)},$$

with $(\chi^{(j)})_{ip} = g_{ij}^M(\tau_p)$, $(B^{(j)})_{ip} = g_{ij}^0(\tau_p)$ and coefficient matrix $(A)_{ip,jq} = \alpha_{ij}(\tau_p, \tau_q)$ is defined by the convolution integral

$$\alpha_{ij}(\tau, \bar{\tau}) = \delta_{ij} \delta(\tau - \bar{\tau}) - \sum_{k=0}^{n_b-1} \int_0^\beta d\bar{\tau} g_{ik}^0(\tau - \bar{\tau}) \Sigma_{kj}^r(\bar{\tau} - \bar{\tau})$$

$$\Sigma_{ij}^r[g^M](\tau) = \Sigma_{ij}^M[g^M](\tau) - \delta(\tau) \Sigma_{ij}^0[g^0(0^+)]$$

- Eq. (1) has to be iterated! But allows for a numerically fast and accurate implementation $\rightarrow$ Result: self-consistent correlated $G^M$
For the time-propagation, we consider (without loss of generality) $t_0 = 0$.

Initial conditions:\(^1\):

\[
\begin{align*}
g^< (0, 0) &= i \mathbf{g}^M (0^-), & g^> (0, 0) &= i \mathbf{g}^M (0^+), \\
g^\parallel (0, -i\tau) &= i \mathbf{g}^M (-\tau), & g^\perp (-i\tau, 0) &= i \mathbf{g}^M (\tau).
\end{align*}
\]

**Time-stepping procedure:**

- Due to symmetry properties $[g^\geq (t, t')]^\dagger = -g^\geq (t', t)$ and $g^> (t, t) = -i + g^< (t, t)$ on the time-diagonal, restrict to propagate $g^<$ on the red triangle and $g^>$ on the blue triangle.

- Propagate $g^\parallel/\perp$ on time-axes $t, t'$.

- Each step requires to update r.h.s. of KBE (collision integrals $l^\geq(t, t')$ and $l^\parallel/\perp(t, t')$) to be performed over the expanding square $[0, T] \times [0, T]$.

---

\(^1\)use matrix notation $(\mathbf{g}^M)_{ij} = g_{ij}^M$.
Sub-femtosecond energy relaxation in dense plasma

**Dense hydrogen plasma:** \( T = 10000 \text{ K}, \ n = 10^{21} \text{ cm}^{-3}, \ k = 0.6/a_B \)

- Solution of the KBE equations conserves total energy
  \[ E(t) = T(t) + U(t) = E(t_0) \]

- Initial state uncorrelated:
  zero correlation energy \( U \rightarrow \) correlations build up \( \rightarrow \) increase of \( |U| \rightarrow \) increase of kinetic energy \( T \)

\[ \Rightarrow \text{Preparing the system in an over-correlated initial state leads to cooling} \]

[D. Semkat et al, Phys. Rev. E 59, 1557 (1999)]
**Plasmon spectrum of the correlated electron gas**

**Solution of the KBE for short monochromatic excitation** $U(t) = U_0(t) \cos(q_0 r)$

Periodic density fluctuation, with Landau plus correlation damping

Fourier transform yields dynamic structure factor $S(q, \omega)$

- Conservation properties of the KBE guarantee exact sum rule preservation of plasmon spectrum $S(q, \omega)$
- Simple approximations for the self-energy (such as 2nd Born approximation) give high-level correlation effects, including vertex corrections, in $S(q, \omega)$

[Kwong/Bonitz, Phys. Rev. Lett. 84, 1768 (2000)]
Application of NEGFs to quantum dot (QD) systems

\( N \)-electron quantum dot:

\[ \hat{H}_e = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{m_e}{2} \omega_0^2 r_i^2 \right) + \sum_{i<j}^{N} \frac{e^2}{4\pi \epsilon r_{ij}}, \]  

(2)

- Using the replacement rules \( \{r_i \rightarrow r_i/l_0^*, E \rightarrow E/E_0^*\} \), Hamiltonian (2) transform to dimensionless form:

\[ \hat{H}_\lambda = \frac{1}{2} \sum_{i=1}^{N} (-\nabla_i^2 + r_i^2) + \sum_{i<j}^{N} \frac{\lambda}{r_{ij}}, \quad \lambda = \frac{E_C}{E_0^*} = \frac{e^2}{4\pi \epsilon l_0^* \hbar \omega_0} = \frac{l_0^*}{a_B} \]

\[ l_0^* = \sqrt{\frac{\hbar}{m_e \omega_0}}, \quad E_0^* = \hbar \omega_0, \quad E_C = \frac{e^2}{4\pi \epsilon l_0^*} \]

- \( \lambda \) is coupling parameter (tunable via confinement frequency \( \omega_0 \)) → measures the relative e\(^-\)-e\(^-\) interaction strength.

- \( m_e^* \): effective electron mass in the environment of dielectric constant \( \epsilon \),

- \( l_0^* \): characteristic single-electron extension in the QD,

- \( a_B \): effective electron Bohr radius,

- \( E_0^* \): oscillator energy,

- \( E_C \): Coulomb energy
Example: Strongly correlated QD

\( N = 3 \) electrons (1D parabolic confinement): \( \lambda = 2 \) and \( \beta = 2 \)

c) \( \rho(x) \): one-electron density
\( \rightarrow \) ideal (dotted), \( \lambda = 0 \)
\( \rightarrow \) Hartree-Fock (solid)
\( \rightarrow \) second Born (dashed)
Correlations lead to weakening of density modulations

a) \( f_i^0 = g_{ii}^0(0^-) \): HF (Fermi-Dirac) distribution function

b) \( n_i - f_i^0 = g_{ii}^M(0^-) - g_{ii}^0(0^-) \):
development of the second Born result from the HF distribution function in %
One-particle spectral function $a_k(\omega)$

**Spectral function**: Obtained from KBE time-evolution without external disturbance

- Orbital-resolved carrier spectral function

$$a(\tau) = i \{ g^>(T - \tau, T + \tau) - g^<(T - \tau, T + \tau) \}$$

- Identify the diagonal (offdiagonal) elements of matrix $a(\tau)$ with the intraband (interband) spectral functions

$$a_k(\tau) = a_{kk}(\tau)$$ for three electrons in a 1D quantum dot

**Inverse hyperbolic cosine model (IHC)**

$$a_k(\tau) = e^{i\omega_k\tau} \frac{1}{\cosh \eta_k(\nu_k\tau)}$$

with fit parameters $\{\omega_k, \eta_k, \nu_k\}$, damping $\gamma_k = \eta_k\nu_k$

[H. Haug, L. Banyai, Solid State Comm. 100, 303 (1998)]

$^a$Matrix notation $(a(\tau))_{mn} = a_{mn}(\tau)$
Correlated one-particle spectral function \( a(\omega) = \sum_k a_k(\omega) \)

- Fourier transform of \( a_k(\tau) \rightarrow \) single peaks \( a(\omega) \) (black dotted lines), sum of all \( a_k(\omega) \) gives whole spectral function (blue dashed lines filled gray), discrete HF levels (vertical solid lines)

3 electrons in a 1D quantum dot
Correlated dipole excitation \( V(r, t) = V_0 r \exp\left(-\frac{(t - t)^2}{\Delta t^2}\right) \cos(\omega t) \)

Figure: 4 e\(^-\) in a 1D trap—\( \lambda = 1 \) and \( \beta = 3 \): Evolution of \( \text{Im} g_{ii}^{<}(t_1, t_2) \) in the external field \( V(r, t) \) centered at \( t_{1,2} = 4 \), levels \( i = 0 \) to \( i = 3 \).
Correlated dipole excitation

\[ V(r, t) = V_0 r \exp(- (t - t)^2 / \Delta t^2) \cos(\omega t) \]

**Figure:** 4 e\(^-\) in a 1D trap—\( \lambda = 1 \) and \( \beta = 3 \): Evolution of \( \text{Im} \ g_{ii}^{<}(t_1, t_2) \) in the external field \( V(r, t) \) centered at \( t_{1,2} = 4 \), levels \( i = 4 \) to \( i = 7 \).
Ionization potentials (IP) of atoms and molecules


<table>
<thead>
<tr>
<th></th>
<th>Second Born</th>
<th>HF</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.53</td>
<td>24.98</td>
<td>24.59</td>
</tr>
<tr>
<td>Be</td>
<td>8.52</td>
<td>8.39</td>
<td>9.32</td>
</tr>
<tr>
<td>Ne</td>
<td>20.17</td>
<td>23.14</td>
<td>21.56</td>
</tr>
<tr>
<td>Mg</td>
<td>6.93</td>
<td>6.88</td>
<td>7.65</td>
</tr>
<tr>
<td>H$_2$</td>
<td>16.11</td>
<td>16.18</td>
<td>15.43</td>
</tr>
<tr>
<td>LiH</td>
<td>7.84</td>
<td>8.20</td>
<td>7.90</td>
</tr>
</tbody>
</table>

**Table:** Ground state Matsubara Green’s function in second Born approx., IPs (in eV) are calculated using the *Extended Koopmans Theorem* (EKT).

- Form $N - 1$ optimized states as a linear combination of the states formed by annihilation of one electron from the ground state: $|\phi_{i}^{N-1}\rangle = \int dx \; u_{i}(x) \hat{\phi}(x)|\phi_{0}^{N}\rangle$
  where $|\phi_{i}^{N-1}\rangle$ is normalized and $u_{i}(x)$ is determined by the condition

  $$\frac{\delta E}{\delta u_{i}} = 0 , \quad E^{N-1}[u_{i}] = \frac{\langle \phi_{i}^{N} | \hat{H} | \phi_{i}^{N-1}\rangle}{\langle \phi_{i}^{N-1} | \phi_{i}^{N-1}\rangle}$$

- Eigenvalue equation $\int dx' \; \Delta(x, x') u_{i}(x') = (E_{0}^{N} - E_{i}^{N-1} - \mu) \int dx' \; \rho(x, x') u_{i}(x')$
  where $\Delta = -\partial_{\tau} G^{M}(\tau)|_{\tau=0^{-}}$ and the density matrix is given by $\rho = G^{M}(0^{-})$. 
Atomic spectral function in an external field


Figure: Below: Trace of $\text{Im } G^\gamma(t_1, t_2)$ for the $H_2$ molecule (25 molecular orbitals) in its ground state (left) and in an applied electric field (right): $E(t) = \theta(t)E_0$ where $E_0 = 0.14$ a.u. Above: the same for a fixed value of $T = (t_1 + t_2)/2$ compared with TDHF (1 a.u. = $2.418884 \cdot 10^{-17}$s)
Time-dependent dipole moment of a Be atom


\[ \alpha(\omega) = -\frac{1}{E_0} \int_0^T dt \, e^{i\omega t} \, d(t) \] with dipole moment \( d(t) = -i \int d^3r \, z \, n(r, t) \), propagated for various times \( T \) (using 28 basis functions).

**Left:** Peak positions (for \(^1\)S \( \rightarrow \) \(^1\)P excitation energy): TDHF = 0.178 a.u., KBE-2nd Born = 0.189 a.u., Experiment = 0.194 a.u. (1 a.u. = 27.2 eV)

**Right:** Time dependent dipole moment calculated within HF and second Born approx., obtained with a non-perturbative ”kick” \( E(t) = E_0 \delta(t) \), \( E_0 = 1.0 \) a.u.

**Figure:** Polarizability \( \alpha(\omega) \) and time dependent dipole moment \( d(t) \)
(Ultra-)fast dynamics of Coulomb correlations. Correlation build up ⇒ Requires non-Markovian kinetic treatment

Real-time nonequilibrium Green’s functions (Keldysh/Kadanoff-Baym)
→ Self-consistent non-perturbative treatment of strong fields
→ Total energy conservation, exact spin statistics

Numerical applications: propagation of NEGF in two-time plain
→ Semiconductors, dense plasmas, electron gas
→ Dynamics of trapped charge carriers
→ Atoms, molecules in strong fields

Text books, reviews:


Announcement: Interdisciplinary conference Progress in Nonequilibrium Green Functions IV, August 17-22 2009, Glasgow, Scotland

Web page: www.theo-physik.uni-kiel.de/~bonitz
Kadanoff-Baym/Keldysh equations:

- In a given basis representation $G(r_t, r'_{t'}) \rightarrow g_{mn}(t, t')$ can be rewritten in the form

\[
i \partial_t g^>(t, t') = h(t) g^>(t, t') + I^>_{1}(t, t')
\]
\[
- i \partial_t g^<(t', t) = g^<(t', t) h(t) + I^<_{2}(t', t)
\]
\[
i \partial_t g^\dagger(t, -i\tau) = h(t) g^\dagger(t, -i\tau) + I^\dagger(t, -i\tau)
\]
\[
- i \partial_t g^\rceil(-i\tau, t) = g^\rceil(-i\tau, t) h(t) + I^\rceil(-i\tau, t)
\]

- In $h(t) = h^0(t) + \Sigma^{HF}(t)$ the Hartree-Fock self-energy and the time-dependent contribution from the single-particle Hamiltonian are collected.

- The collision integrals $I^>_{1}$, $I^<_{2}$ and $I^\dagger/\rceil$ are defined on the next slide!
Summary of all relevant right hand sides of the two-time KBE:

\[ I_1^> (t, t') = \int_0^t d\tilde{t} \left[ \Sigma^> (t, \tilde{t}) - \Sigma^< (t, \tilde{t}) \right] g^> (\tilde{t}, t') + \int_0^{t'} d\tilde{t} \Sigma^> (t, \tilde{t}) \left[ g^< (\tilde{t}, t') - g^> (\tilde{t}, t') \right] \]

\[ -i \int_0^\beta d\bar{\tau} \Sigma^\downarrow (t, -i\bar{\tau}) g^\uparrow (-i\bar{\tau}, t') \]

\[ I_2^< (t', t) = \int_0^{t'} d\tilde{t} \left[ g^> (t', \tilde{t}) - g^< (t', \tilde{t}) \right] \Sigma^< (\tilde{t}, t) + \int_0^t d\tilde{t} g^< (t', \tilde{t}) \left[ \Sigma^< (\tilde{t}, t) - \Sigma^> (\tilde{t}, t) \right] \]

\[ -i \int_0^\beta d\bar{\tau} g^\downarrow (t', -i\bar{\tau}) \Sigma^\uparrow (-i\bar{\tau}, t) \]

\[ I^\downarrow (t, -i\tau) = \int_0^t d\tilde{t} \left[ \Sigma^> (t, \tilde{t}) - \Sigma^< (t, \tilde{t}) \right] g^\downarrow (\tilde{t}, -i\tau) + \int_0^\beta d\bar{\tau} \Sigma^\downarrow (t, -i\bar{\tau}) g^M (\bar{\tau} - \tau) \]

\[ I^\uparrow (-i\tau, t) = \int_0^t d\tilde{t} g^\uparrow (-i\tau, \tilde{t}) \left[ \Sigma^< (\tilde{t}, t) - \Sigma^> (\tilde{t}, t) \right] + \int_0^\beta d\bar{\tau} g^M (\tau - \bar{\tau}) \Sigma^\uparrow (-i\bar{\tau}, t) \]