Linear response and Time dependent Hartree-Fock

November 6, 2008

1 General Linear Response Theory

This derivation follows essentially to one found in the book by Pines and Noziéres [1] it is a bit more general because it does not assume translational invariance. In fact, Pines and Nozieres are to some extent misleading.

Assume that our many-body system is subjected to weak, local, time-dependent field

$$\delta H_{\text{ext}}(t) = \sum_i \delta h_{\text{ext}}(r_i, t) = \int d^3r \hat{\rho}(r) \delta h_{\text{ext}}(r, t)$$

Here, $\hat{\rho}(r) = \sum_i \delta(r - r_i)$ is the density operator. We will look at monochromatic external fields, this is best done in frequency space:

$$h_{\text{ext}}(r, \omega) = \int dt e^{-i\omega t} h_{\text{ext}}(r, t)$$

$$\Rightarrow h_{\text{ext}}^*(r, \omega) = \int dt e^{-i\omega t} h_{\text{ext}}(r, t) = h_{\text{ext}}(r, -\omega)$$

since the external field is real. Thus

$$h_{\text{ext}}^*(r, \omega) = h_{\text{ext}}(r, -\omega)$$

and, therefore we have

$$\delta H_{\text{ext}}(t) = \int d^3r \hat{\rho}(r) \left[ h_{\text{ext}}(r, \omega) e^{-i\omega t} + h_{\text{ext}}^*(r, \omega) e^{i\omega t} \right]$$

$$= \delta H_{\text{ext}}(\omega) e^{-i\omega t} + \delta H_{\text{ext}}^*(\omega) e^{i\omega t}.$$  

To preserve causality, we assume that the external field has been turned on very slowly in the distant past, i.e. instead of the above we should have

$$\delta H_{\text{ext}}(t) = \left[ \delta H_{\text{ext}}(\omega) e^{-i\omega t} + \delta H_{\text{ext}}^*(\omega) e^{i\omega t} \right] e^{\eta t}$$
with an infinitesimal parameter $\eta$.

We now want to calculate the induced density fluctuation $\delta \rho(\mathbf{r}, t)$ due to this external field. A priori, the infinitesimal perturbation causes an infinitesimal change in the ground state wave function:

$$|\Psi_0 \rangle \rightarrow |\Psi(t) \rangle = |\Psi_0 \rangle + |\delta \Psi(t) \rangle$$

(6)

The change in density is then, to first order,

$$\delta \rho(t) = \langle \Psi(t)| \hat{\rho}(\mathbf{r}) |\Psi(t) \rangle - \langle \Psi_0| \hat{\rho}(\mathbf{r}) |\Psi_0 \rangle$$

$$\approx \langle \Psi_0| \hat{\rho}(\mathbf{r}) |\delta \Psi(t) \rangle + \langle \delta \Psi(t)| \hat{\rho}(\mathbf{r}) |\Psi_0 \rangle .$$

(7)

This $\delta \rho(t)$ is called the transition density because it is the transition matrix element of the density operator between the ground state $|\Psi_0 \rangle$ and the perturbation $|\delta \Psi(t) \rangle$. The time dependence of the perturbation causes the same time dependence of the density fluctuation,

$$\delta \rho(\mathbf{r}; t) \sim \delta \rho(\mathbf{r}) e^{-i\omega t} e^{\eta t} .$$

(8)

(This is to be taken with a little caution, of course the transition density also must be real.)

The time dependent part of the wave function can be calculated by perturbation theory.

$$i\hbar \frac{\partial}{\partial t} |\Psi(t) \rangle = (H + \delta H_{\text{ext}}(t)) |\Psi(t) \rangle .$$

(9)

Ansatz for the solution

$$|\Psi(t) \rangle = \sum_n a_n(t) e^{-i\omega_nt} |n \rangle$$

(10)

where $\{E_n, |n \rangle \} \equiv \{\hbar \omega_n, |n \rangle \}$ is the energy/eigenfunction pair of the unperturbed Hamiltonian. The initial condition is $a_n(-\infty) = \delta_{n,0}$. Inserting the above in the Schrödinger equation gives

$$\sum_n (i\hbar \dot{a}_n(t) + E_n a_n(t)) e^{-i\omega_nt} |n \rangle = \sum_n (E_n + \delta H_{\text{ext}}(t)) a_n(t) e^{-i\omega_nt} |n \rangle$$

$$\sum_n i\hbar \dot{a}_n(t) |n \rangle = \sum_n \delta H_{\text{ext}}(t) a_n(t) e^{-i\omega_nt} |n \rangle$$

(11)

Now only $a_0(t) = 1$ is 0th order in $\delta H_{\text{ext}}(t)$, all other $a_n(t)$ are first order. We therefore need to keep only the first term on the right hand side. Projecting the equation on a state $|n \rangle$ then gives

$$i\hbar \dot{a}_n(t) = \langle n| \delta H_{\text{ext}}(t) |0 \rangle e^{i(\omega_n - \omega_0)t} \equiv \langle n| \delta H_{\text{ext}}(t) |0 \rangle e^{i\omega_0 t}$$

(12)
with $\omega_{n0} = \omega_n - \omega_0$.

We can now insert the perturbing Hamiltonian

$$\langle n | \delta H_{\text{ext}}(t) | 0 \rangle = \int d^3 r' \langle n | \hat{\rho}(r') | 0 \rangle \left[ h_{\text{ext}}(r') e^{-i\omega t} + h_{\text{ext}}^*(r') e^{i\omega t} \right] e^{\eta t}$$

we can write

$$i\hbar \dot{a}_n(t) = \int d^3 r' \langle n | \hat{\rho}(r') | 0 \rangle \left[ h_{\text{ext}}(r') e^{i(\omega_{n0} - \omega)t + \eta t} + h_{\text{ext}}^*(r') e^{i(\omega_{n0} + \omega)t + \eta t} \right] e^{\eta t}$$

or

$$a_n(t) = \int d^3 r h_{\text{ext}}(r, \omega) \langle n | \hat{\rho}(r) | 0 \rangle \frac{\langle n | \hat{\rho}(r) | 0 \rangle}{\hbar \omega - \hbar \omega_0 + i\eta} e^{i(\omega_{n0} - \omega)t + \eta t}$$

$$- \int d^3 r h_{\text{ext}}^*(r, \omega) \langle n | \hat{\rho}(r) | 0 \rangle \frac{\langle n | \hat{\rho}(r) | 0 \rangle}{\hbar \omega + \hbar \omega_0 - i\eta} e^{i(\omega_{n0} + \omega)t + \eta t}.$$ (15)

(We can redefine $\eta \rightarrow \hbar \eta$ because $\eta$ is infinitesimal.)

Inserting the expansion of $|\delta \Psi(t)|$ into the transition density gives generally

$$\delta \rho(r, t) = \sum_{n>0} a_n(t) \langle 0 | \hat{\rho}(r) | n \rangle e^{-i\omega_{n0} t} + \text{c.c.}$$

$$= \int d^3 r' h_{\text{ext}}(r') \sum_{n>0} \frac{\langle 0 | \hat{\rho}(r) | n \rangle \langle n | \hat{\rho}(r') | 0 \rangle}{\hbar \omega - \hbar \omega_0 + i\eta} e^{-i\omega t + \eta t}$$

$$- \int d^3 r' h_{\text{ext}}^*(r') \sum_{n>0} \frac{\langle 0 | \hat{\rho}(r) | n \rangle \langle n | \hat{\rho}(r') | 0 \rangle}{\hbar \omega + \hbar \omega_0 - i\eta} e^{i\omega t + \eta t} + \text{c.c.}$$

$$= \int d^3 r' h_{\text{ext}}(r') \sum_{n>0} \langle 0 | \hat{\rho}(r) | n \rangle \langle n | \hat{\rho}(r') | 0 \rangle \times$$

$$\times \left[ \frac{1}{\hbar \omega - \hbar \omega_0 + i\eta} - \frac{1}{\hbar \omega + \hbar \omega_0 + i\eta} \right] e^{-i\omega t + \eta t} + \text{c.c.}$$ (17)

We can then define the coordinate space representation of the density-density response function as

$$\chi(r, r'; \omega) = \sum_{n>0} \left[ \frac{\langle 0 | \hat{\rho}(r) | n \rangle \langle n | \hat{\rho}(r') | 0 \rangle}{\hbar \omega - \hbar \omega_0 + i\eta} - \frac{\langle 0 | \hat{\rho}(r) | n \rangle \langle n | \hat{\rho}(r') | 0 \rangle}{\hbar \omega + \hbar \omega_0 + i\eta} \right].$$ (18)

We have already seen the definition of the dynamic structure function. We can immediately read off the relationship, noting that

$$\lim_{\eta \to 0} \frac{1}{\hbar \omega - \hbar \omega_0 + i\eta} = \pi \delta(\hbar \omega - \hbar \omega_0)$$

(19)
and therefore, for $\omega >$  
\[
3m \chi (\mathbf{r}, \mathbf{r}'; \omega) = \pi \sum_{n > 0} \langle 0 \mid \hat{\rho} (\mathbf{r}) \mid n \rangle \langle n \mid \hat{\rho} (\mathbf{r}') \mid 0 \rangle \delta (\hbar \omega - \hbar \omega_{n0})  
\]

(20)  

(The definition of common factors and signs differs in different textbooks !)

In scattering experiments, one observes the momentum transfer, so the 
\[
\chi (\mathbf{q}, \omega) = \int d^3 r d^3 r' e^{i \mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \chi (\mathbf{r}, \mathbf{r}'; \omega) 
\]

\[
= \sum_{n > 0} \left[ \frac{|\langle 0 \mid \hat{\rho}_q \mid n \rangle|^2}{\hbar \omega - \hbar \omega_{n0} + i \eta} - \frac{|\langle 0 \mid \hat{\rho}_q \mid n \rangle|^2}{\hbar \omega + \hbar \omega_{n0} + i \eta} \right].  
\]

(21)  

\[2\] Excited state wave function and the action integral

It comes now to the point where we must some definite model for the excited states of a physical system. This can not be done in general; we must make some approximations. With all the reservations one can have about the Hartree-Fock approximation, we start with that one.  

We approximate the wave function of excited states by 
\[
|\psi(t)\rangle = \frac{1}{N(t)} e^{-i E_{HF} t / \hbar} e^{\frac{1}{2} \sum_{p h} c_{ph}(t) a_p^\dagger a_h} |\phi_{HF}\rangle  
\]

(22)  

where $|\phi_{HF}\rangle$ is a Hartree-Fock ground state. $E_{HF}$ the Hartree-Fock energy expectation value, and the $c_{ph}(t)$ “particle–hole amplitudes”.

\[
N^2(t) = \langle \phi_{HF} | e^{\frac{1}{2} \sum_{p h} c_{ph}(t) a_p^\dagger a_p} e^{\frac{1}{2} \sum_{p h} c_{ph}(t) a_p^\dagger a_p} | \phi_{HF} \rangle  
\]

(23)  

is the normalization integral. Note that states that are labeled with $h, h, h', \ldots$ are understood to be occupied (“hole”) states (i.e. states that are present in the Slater determinant $\phi_{HF}$ and states labeled with $p, p, p', \ldots$ are unoccupied “particle” states. As above, assume that the system is described by a Hamiltonian that is written in coordinate space as

\[H = H_1 + V\]

\[H_1 = \sum_i h (\mathbf{r}_i) = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + U_{\text{ext}} (\mathbf{r}_i) \right]\]

\[V = \sum_{i < j} v (\mathbf{r}_i, \mathbf{r}_j)\]

(24)  

(25)  

(26)
or, in second quantized form
\[
H_1 = \sum_{\alpha\beta} \langle \alpha | h_{\text{ext}} | \beta \rangle a_{\alpha}^\dagger a_{\beta} \tag{27}
\]
\[
V = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | v | \gamma\delta \rangle a_{\alpha}^\dagger a_{\beta}^\dagger a_{\delta} a_{\gamma} . \tag{28}
\]

We furthermore subject the system to a weak, scalar external field
\[
\delta H_{\text{ext}}(t) = \sum_i \delta h_{\text{ext}}(r_i; t) \tag{29}
\]
or, in second quantized form,
\[
\delta H_1(t) = \sum_{\alpha\beta} \langle \alpha | \delta h(t) | \beta \rangle a_{\alpha}^\dagger a_{\beta} . \tag{30}
\]

Similar to the determination of the single-particle wave functions of the Hartree-Fock theory by a variational principle, the “particle-hole amplitudes” are determined by the “Kerman-Koonin” stationarity principle
\[
\delta S = \delta \int_{t_0}^{t_1} dt \mathcal{L}(t) \tag{31}
\]
\[
\mathcal{L}(t) = \langle \psi(t) | H + \delta H_{\text{ext}} - i\hbar \frac{\partial}{\partial t} | \psi(t) \rangle . \tag{32}
\]

We want to derive linear equations of motion, hence we must keep all second order terms in the Lagrangian. The driving quantity is the external perturbing field \( \delta H_1(t) \) which is, by assumption, of first order. Linear equations of motion will lead to \( c_{\text{ph}}(t) \) that are of the same order. Thus, to get linear equations of motion, we must keep the linear terms in \( c_{\text{ph}}(t) \) with the perturbing field, and the quadratic terms in all others.

Thus:
\[
\langle \psi(t) | \delta H_{\text{ext}} | \psi(t) \rangle 
\approx \frac{1}{2} \sum_{p_{\text{ph}}} \left[ c_{\text{ph}}^* \langle \phi_{\text{HF}} | a_{p_{\alpha}}^\dagger a_{p_{\beta}}^\dagger \delta H_{\text{ext}}(t) | \phi_{\text{HF}} \rangle + c_{\text{ph}} \langle \phi_{\text{HF}} | \delta H_{\text{ext}}(t) a_{p_{\beta}}^\dagger a_{p_{\alpha}} | \phi_{\text{HF}} \rangle \right]
\approx \frac{1}{2} \sum_{p_{\text{ph}} \alpha\beta} \langle \alpha | \delta h_{\text{ext}}(t) | \beta \rangle \left[ c_{\text{ph}}^* \langle \phi_{\text{HF}} | a_{p_{\beta}}^\dagger a_{p_{\alpha}}^\dagger a_{p_{\gamma}}^\dagger a_{p_{\delta}} | \phi_{\text{HF}} \rangle + c_{\text{ph}} \langle \phi_{\text{HF}} | a_{p_{\beta}}^\dagger a_{p_{\alpha}}^\dagger a_{p_{\delta}}^\dagger a_{p_{\gamma}} a_{p_{\delta}} | \phi_{\text{HF}} \rangle \right]
\approx \frac{1}{2} \sum_{p_{\text{ph}} \alpha\beta} \langle \alpha | \delta h_{\text{ext}}(t) | \beta \rangle \left[ c_{\text{ph}}^* \delta_{\alpha,p_{\beta}} \delta_{\beta,p_{\delta}} + c_{\text{ph}} \delta_{\beta,p_{\alpha}} \delta_{\alpha,p_{\delta}} \right]
\approx \frac{1}{2} \sum_{p_{\text{ph}}} \left[ c_{\text{ph}}^* \langle p | \delta h_{\text{ext}}(t) | h \rangle + c_{\text{ph}} \langle h | \delta h_{\text{ext}}(t) | p \rangle \right] . \tag{33}
\]
In the time derivative term we must be a bit more careful and keep the normalization $N(t)$.

$$
\langle \psi(t)| i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = E_{HF} + \frac{i\hbar}{2} \langle \psi_0(t)| \sum_{ph} \dot{c}_{ph}(t) a_p^+ a_h |\psi(t)\rangle - \frac{i\hbar N(t)}{2 N(t)}
$$

$$
= E_{HF} + \frac{i\hbar}{4} \sum_{ph} \langle \psi(t)| \dot{c}_{ph}(t) a_p^+ a_h - \dot{c}_{ph}^*(t) c_{ph}'(t) a_h a_p |\psi(t)\rangle
$$

This formula is still exact, we now expand to second order. We can immediately leave out all terms that can be written as a time-derivative. Also, first order terms are zero because $\langle \phi_{HF} | a_p^+ a_h | \phi_{HF} \rangle = 0$. Hence

$$
\langle \psi(t)| i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle
= E_{HF} + \frac{i\hbar}{4} \sum_{php'h'} \langle \phi_{HF} | c_{p'h'}^*(t) \dot{c}_{ph}(t) a_p^+ a_h a_p - \dot{c}_{ph}^*(t) c_{p'h'}(t) a_h a_p a_h a_p |\phi_{HF} \rangle
$$

$$
= E_{HF} + \frac{i\hbar}{4} \sum_{ph} \left[ c_{ph}^*(t) \dot{c}_{ph}(t) - \dot{c}_{ph}^*(t) c_{ph}(t) \right]. \tag{35}
$$

It should also be noted that this term occurs under the time integral in the action (31), hence we can integrate by parts. In other words, the two terms appearing above are the same.

Finally we must expand $\langle \psi(t)| H - E_{HF} |\psi(t)\rangle$ to second order in the $c_{ph}(t)$. The $E_{HF}$ comes from the time-derivative term, it evidently cancels the zeroth order term in our expansion. The normalization integral (23) is to second order

$$
\mathcal{N}^2(t) \approx \langle \phi_{HF} | 1 + \frac{1}{2} \sum_{ph} c_{ph}(t) a_p^+ a_h + \frac{1}{2} \sum_{ph} c_{ph}^*(t) a_h^+ a_p + \mathcal{O}(c_{ph}^2) |\phi_{HF} \rangle
$$

$$
= 1 + \mathcal{O}(c_{ph}^2) \tag{36}
$$

and has therefore no influence.

Now

$$
\langle \psi(t)| H - E_{HF} |\psi(t)\rangle
$$

$$
= \frac{1}{2} \sum_{ph} \left[ c_{ph}^* \langle \phi_{HF} | a_p^+ a_p(H - E_{HF}) |\phi_{HF} \rangle + c_{ph} \langle \phi_{HF} | (H - E_{HF}) a_p^+ a_h |\phi_{HF} \rangle \right]
$$

$$
+ \frac{1}{8} \sum_{pp'h'h'} c_{pp'}^* c_{p'h'}^* \langle \phi_{HF} | a_p^+ a_{p'} a_{h'}^+ a_h(H - E_{HF}) |\phi_{HF} \rangle
$$

$$
+ \frac{1}{8} \sum_{pp'h'h'} c_{ph} c_{p'h'} \langle \phi_{HF} | (H - E_{HF}) a_p^+ a_h a_{p'} a_{h'} |\phi_{HF} \rangle
$$
\[ + \frac{1}{4} \sum_{pp'hh'} c_{pp'h'\ell}^* c_{hh'p} \langle \phi_{HF} | a_{h'}^\dagger a_{p}(H - E_{HF})a_{p}^\dagger a_{h'} | \phi_{HF} \rangle. \]  

(37)

The situation is the same as the usual one in the theory of small oscillations: The first order terms must be zero in order to obtain a sensible second order equation. We must therefore require

\[ \langle \phi_{HF} | a_{h}^\dagger a_{p}(H - E_{HF}) | \phi_{HF} \rangle = \langle \phi_{HF} | (H - E_{HF})a_{p}^\dagger a_{h} | \phi_{HF} \rangle = 0. \]  

(38)

These conditions are called the “Brillouin conditions”. In the case of a Hartree–Fock ground state the condition is identical to the requirement that the single particle orbitals have been obtained by the Hartree-Fock equation.

We can now turn to the evaluation of the second-order terms: In the terms that contain \( c_{pp'h'\ell}^* c_{hh'p} \) or \( c_{pp'h'\ell} c_{hh'p}^* \), the matrix element of \( E_{HF} \) is taken between a \( 2p - 2h \) state and the ground state and is zero because of orthogonality

\[ \langle \phi_{HF} | a_{h'}^\dagger a_{p}^\dagger a_{h} a_{p} | \phi_{HF} \rangle = 0. \]  

Moreover, the matrix element of the one-body part of the Hamiltonian is zero:

\[ \langle \phi_{HF} | a_{h'}^\dagger a_{p}^\dagger a_{h} a_{p} H_1 | \phi_{HF} \rangle = \sum_{\alpha\beta} \langle \alpha | h | \beta \rangle \langle \phi_{HF} | a_{h'}^\dagger a_{p}^\dagger a_{h} a_{p} a_{\alpha}^\dagger a_{\beta} | \phi_{HF} \rangle = 0 \]  

(39)

because, for example \( \alpha = p \) and \( \beta = h \) and then we would have the overlap between a \( 1p-1h \) state and the ground state. Therefore, this term has contributions form the pair potential only:

\[ \langle \phi_{HF} | a_{h'}^\dagger a_{p}^\dagger a_{h} a_{p} V | \phi_{HF} \rangle = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha | v | \gamma \rangle \langle \phi_{HF} | a_{h'}^\dagger a_{p}^\dagger a_{h} a_{p} a_{\alpha}^\dagger a_{\beta} a_{\gamma}^\dagger a_{\delta} | \phi_{HF} \rangle \]

\[ = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha | v | \gamma \rangle \langle \phi_{HF} | a_{h'}^\dagger a_{p}^\dagger a_{h} a_{p} a_{\alpha}^\dagger a_{\beta} a_{\gamma}^\dagger a_{\delta} | \phi_{HF} \rangle \]

\[ = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha | v | \gamma \rangle [\delta_{\alpha p}\delta_{\beta p'} - \delta_{\alpha p'}\delta_{\beta p}] [\delta_{\delta h'}\delta_{\gamma h} - \delta_{\delta h}\delta_{\gamma h'}] \]

\[ = \langle pp' | v | hh' \rangle_a \]  

(40)

Likewise, we get

\[ \langle \phi_{HF} | V a_{p}^\dagger a_{h}^\dagger a_{h'} a_{p} | \phi_{HF} \rangle = \langle hh' | v | pp' \rangle_a. \]  

(41)

Finally we need to work out the last term in Eq. (37). We have to distinguish four cases, namely \( p = p', h = h' \), \( p = p', h \neq h' \), \( p \neq p', h = h' \) and \( p \neq p', h \neq h' \). The case \( p = p', h = h' \) has already been worked out, we have obtained

\[ \langle \phi_{HF} | a_{p}^\dagger a_{h}(H - E_{HF})a_{p}^\dagger a_{h} | \phi_{HF} \rangle = \epsilon_p - \epsilon_h, \]  

(42)
where the $\epsilon_p, \epsilon_h$ are the Hartree-Fock single particle energies.

I calculate only one of the half-off-diagonal terms, $p \neq p', h = h'$. In a uniform system, it is clear that these matrix elements must vanish because the left state has a different momentum as the right state. In an inhomogeneous system, calculate

$$
\langle \phi_{\text{HF}} | a_h^\dagger a_p^\dagger H_1 a_p a_h | \phi_{\text{HF}} \rangle = \sum_{\alpha\beta} \langle \alpha | h | \beta \rangle \langle \phi_{\text{HF}} | a_h^\dagger a_p^\dagger a_\beta a_\alpha a_h | \phi_{\text{HF}} \rangle
$$

$$
= \sum_{\alpha\beta} \langle \alpha | h | \beta \rangle \langle \phi_{\text{HF}} | \delta_{\alpha p} a_h^\dagger a_\beta^\dagger a_h + a_h^\dagger a_\beta^\dagger a_p a_\alpha a_h | \phi_{\text{HF}} \rangle
$$

$$
= \sum_{\alpha\beta} \langle \alpha | h | \beta \rangle \delta_{\alpha p} \delta_{\beta p} = \langle p | h | p' \rangle
$$

(43)

because, to get from the second to the third line, we could use that $p \neq p'$.

The potential term is a little tedious:

$$
\langle \phi_{\text{HF}} | a_h^\dagger a_p V a_p^\dagger a_h | \phi_{\text{HF}} \rangle = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha \beta | v | \gamma \delta \rangle \langle \phi_{\text{HF}} | a_h^\dagger a_p^\dagger a_\delta a_\gamma a_\beta a_\alpha a_h | \phi_{\text{HF}} \rangle
$$

$$
= \frac{1}{2} \sum_{\beta\gamma\delta} \langle p \beta | v | \gamma \delta \rangle \langle \phi_{\text{HF}} | a_h^\dagger a_\beta^\dagger a_\delta a_\gamma a_\beta^\dagger a_h | \phi_{\text{HF}} \rangle
$$

$$
= \sum_{\delta} \langle p \beta | v | p' \delta \rangle a_\delta \langle \phi_{\text{HF}} | a_h^\dagger a_\beta^\dagger a_\delta a_h | \phi_{\text{HF}} \rangle
$$

$$
= \sum_{h'} \langle p h' | v | p'h' \rangle a_\delta .
$$

(44)

The last line (i.e. that we can restrict the sum over the $\delta$ states to occupied states follows because of $\delta$ were a particle state it would destroy the ground state $|\phi_{\text{HF}}\rangle$).

Thus, the result is

$$
\langle \phi_{\text{HF}} | a_h^\dagger a_p^\dagger H a_p a_h | \phi_{\text{HF}} \rangle = \langle p | h | p' \rangle + \sum_{h'} \langle p h' | v | p'h' \rangle a_\delta
$$

(45)

In the above, we recover the matrix element of the Hartree-Fock operator. Thus, if all states are generated by the Hartree-Fock equation, then these “half-off-diagonal” term vanish. Since this is a reasonable assumption (how else would one generate the particles wave functions?) we can go on and assume either $p = p', h = h'$ or $p \neq p', h \neq h'$.

In the latter case, we can have only contributions from the interaction:

$$
\langle \phi_{\text{HF}} | a_h^\dagger a_p^\dagger V a_p a_h | \phi_{\text{HF}} \rangle = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha \beta | v | \gamma \delta \rangle \langle \phi_{\text{HF}} | a_h^\dagger a_p^\dagger a_\beta^\dagger a_\alpha a_\gamma a_\beta^\dagger a_\delta a_\gamma^\dagger a_h | \phi_{\text{HF}} \rangle
$$
= \frac{1}{2} \sum_{\beta\gamma\delta} \langle p\beta | v | \gamma\delta \rangle \langle \phi_{HF} | a_{\beta}^\dagger a_{\gamma}^\dagger a_{\delta} a_{\delta}^\dagger a_{\nu} \rangle \langle \phi_{HF} \rangle \\
= \sum_{\beta\delta} \langle p\beta | v | p'\delta \rangle \langle \phi_{HF} | a_{\beta}^\dagger a_{\beta}^\dagger a_{\delta} \rangle \langle \phi_{HF} \rangle \\
= -\langle ph' | v | p'\delta \rangle = \langle ph' | v | hp' \rangle_a.
\tag{46}

This derivation deviates from the previous one only in the last line: Now we can not have \( \beta = \delta \) because that would imply \( h = h' \) which contradicts our assumption.

With these manipulations, we have derived our Lagrangian (32) to second order:

\[ L(t) = \sum \left[ c_{ph} \langle p | \delta h(t) | h \rangle + c_{ph} \langle h | \delta h(t) | p \rangle \right] + \frac{i\hbar}{2} \sum \left[ c_{ph}^* \langle t | c_{ph}(t) - c_{ph}^* \langle t | c_{ph}(t) \right] \\
+ \frac{1}{2} \sum_{pp'hh'} \left[ c_{ph}^* c_{p'hh'}^{\dagger} \langle pp' | v | hh' \rangle_a + c_{ph} c_{p'hh'} \langle hh' | v | pp' \rangle_a \right] \\
+ \sum_{pp'hh'} c_{ph}^* c_{p'hh'} \left[ (\epsilon_p - \epsilon_h) \delta_{pp'} \delta_{hh'} + \langle ph' | v | hp' \rangle_a \right]
\tag{47}

3 \quad \text{Equations of Motion}

We are now ready to derive the equations of motion. The action integral (47) has been expanded to second order in the particle–hole amplitudes \( c_{ph} \) and \( c_{ph}^* \). The linear equations of motion are now obtained from the stationarity principle

\[ \delta S \left[ c_{ph}(t), c_{ph}^*(t) \right] = 0. \tag{48} \]

Recall that the Lagrangian (47) appears under the time integral, we can therefore integrate the time coordinate by parts. Doing the variation with respect to \( c_{ph} \) and \( c_{ph}^* \) gives two equations:

\[ 0 = i\hbar \dot{c}_{ph} + \langle p | \delta h_{ext}(t) | h \rangle \\
+ \sum_{p'hh'} \left[ \langle pp' | v | hh' \rangle c_{p'hh'}^* + [(\epsilon_p - \epsilon_h) \delta_{pp'} \delta_{hh'} + \langle ph' | v | hp' \rangle_a] c_{p'hh'} \right] \]

\[ 0 = -i\hbar \dot{c}_{ph}^* + \langle p | \delta h_{ext}(t) | h \rangle \\
+ \sum_{p'hh'} \left[ \langle pp' | v | hh' \rangle c_{p'hh'} + [(\epsilon_p - \epsilon_h) \delta_{pp'} \delta_{hh'} + \langle ph' | v | hp' \rangle_a] c_{p'hh'}^* \right]
\tag{49} \]
A convenient representation of the resulting equations is a “supermatrix” form, considering sets of states $ph$ as row/column indices of a “supermatrix”.

$$H \equiv \begin{bmatrix} A & B \\ B^\dagger & A^\dagger \end{bmatrix}, \quad M \equiv \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (50)$$

$$c(t) \equiv \begin{bmatrix} c(t) \\ c^*(t) \end{bmatrix}, \quad h(t) \equiv \begin{bmatrix} h(t) \\ h^*(t) \end{bmatrix} \quad (51)$$

where $A$ and $B$ are particle–hole matrices of the form

$$A = (A_{ph,p'h'}) \equiv ((\epsilon_p - \epsilon_h) \delta_{pp'} \delta_{hh'} + \langle ph' | v | hp' \rangle) \quad (52)$$

$$B = (B_{ph,p'h'}) \equiv \langle pp' | v | hh' \rangle \quad (53)$$

and

$$c(t) \equiv (c_{ph}(t)) \quad h(t) \equiv \langle p | \delta h_{ext}(t) | h \rangle \quad (54)$$

In terms of these quantities, the linearized equations of motion assume the form

$$Hc(t) + h(t) = i\hbar \frac{\partial}{\partial t} M c(t). \quad (55)$$

It is always convenient to rewrite the equations in terms of frequencies. To that end, write

$$\delta h_{ext}(r; t) = \delta h_{ext}(r; \omega) \left[ e^{i\omega t} + e^{-i\omega t} \right] e^{\eta t} \quad (56)$$

and also split the $c_{ph}(t)$ into components with positive and negative frequency:

$$c(t) = \left[ xe^{-i\omega t} + y^* e^{i\omega t} \right] e^{\eta t} \quad (57)$$

Insert these in the time-dependent equation and collect the terms with positive and negative frequency gives the final form

$$\begin{bmatrix} A & B \\ B^\dagger & A^\dagger \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} + \begin{bmatrix} h \\ h^* \end{bmatrix} = \hbar(\omega + i\eta) \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}. \quad (58)$$

These are the general “time-dependent Hartree-Fock” equations. Solving these equations is quite common in nuclear and atomic physics. A derivation may be found, for example, in the book by Thouless [2].

4 TDHF for the density-density response function

The above equation gives, for the case of zero external field, the eigenfrequencies of the system. To get a density-density response, one must calculate, to
first order in the particle-hole amplitudes, the density fluctuation

\[ \delta \rho(\mathbf{r}, t) = \langle \psi(t)| \hat{\rho}(\mathbf{r})|\psi(t)\rangle - \langle \phi_{HF}| \hat{\rho}(\mathbf{r})|\phi_{HF}\rangle \]

\[ = \sum_{ph} \left[ c_{ph}^* \langle \phi_{HF}| a_h^\dagger a_p \hat{\rho}(\mathbf{r})|\phi_{HF}\rangle + c_{ph} \langle \phi_{HF}| \hat{\rho}(\mathbf{r}) a_h a_p|\phi_{HF}\rangle \right] \]

\[ = \sum_{ph} \left[ c_{ph}^* \varphi_p(\mathbf{r}) \varphi_h^*(\mathbf{r}) + c_{ph} \varphi_p^*(\mathbf{r}) \varphi_h(\mathbf{r}) \right] \]

\[ = \sum_{ph} \left[ x_{ph} \varphi_p(\mathbf{r}) \varphi_h^*(\mathbf{r}) + y_{ph} \varphi_p^*(\mathbf{r}) \varphi_h(\mathbf{r}) \right] e^{i\omega t + \eta t} + c.c. \]

\[ = [x(\mathbf{r}) + y(\mathbf{r})] e^{-i\omega t + \eta t} + [x^*(\mathbf{r}) + y^*(\mathbf{r})] e^{i\omega t + \eta t} \]

where

\[ x(\mathbf{r}) \equiv \sum_{ph} \varphi_h^*(\mathbf{r}) \varphi_p(\mathbf{r}) x_{ph} \quad \text{and} \quad y(\mathbf{r}) \equiv \sum_{ph} \varphi_h(\mathbf{r}) \varphi_p^*(\mathbf{r}) y_{ph} \tag{59} \]

In principle, one can solve the TDHF equation for any external potential, obtain the \( x_{ph} \) and \( y_{ph} \), and insert these in the density fluctuation. But this does not lead to the beloved form of the density-density response function that is fancied by the condensed matter community. To get such a form, one must first omit all exchange terms. Using this simplification, the explicit forms of \( A \) and \( B \) are

\[ A_{ph,p'h'} = \left[ e(p) - e(h) \right] \delta_{pp'} \delta_{hh'} + \int d^3 r d^3 r' \varphi_p^*(\mathbf{r}) \varphi_{p'}^*(\mathbf{r'}) V(\mathbf{r}, \mathbf{r'}) \varphi_h(\mathbf{r}) \varphi_{h'}(\mathbf{r'}) \]

\[ B_{ph,p'h'} = \int d^3 r d^3 r' \varphi_p^*(\mathbf{r}) \varphi_{p'}^*(\mathbf{r'}) V(\mathbf{r}, \mathbf{r'}) \varphi_h(\mathbf{r}) \varphi_{h'}(\mathbf{r'}) \tag{61} \]

Then we can write Eq. (58)

\[ x_{ph} + \frac{\langle p | \delta h_{ext} | h \rangle}{\epsilon_p - \epsilon_h - \hbar \omega - i\eta} + \int d^3 r d^3 r' \varphi_p^*(\mathbf{r}) \varphi_h(\mathbf{r}) \frac{\varphi_{p'}^*(\mathbf{r}) \varphi_{h'}(\mathbf{r'}) V(\mathbf{r}, \mathbf{r'}) [x(\mathbf{r'}) + y(\mathbf{r'})]}{\epsilon_p - \epsilon_h - \hbar \omega - i\eta} = 0 \]

\[ y_{ph} + \frac{\langle h | \delta h_{ext} | p \rangle}{\epsilon_p - \epsilon_h + \hbar \omega + i\eta} + \int d^3 r d^3 r' \varphi_p(\mathbf{r}) \varphi_{p'}^*(\mathbf{r'}) \frac{\varphi_{h'}^*(\mathbf{r'}) V(\mathbf{r}, \mathbf{r'}) [x(\mathbf{r'}) + y(\mathbf{r'})]}{\epsilon_p - \epsilon_h + \hbar \omega + i\eta} = 0, \tag{62} \]

where the small imaginary parts have been introduced to maintain causality.

Now we multiply the first equation \( \varphi_h^*(\mathbf{r''}) \varphi_p(\mathbf{r''}) \) and the second equation with \( \varphi_h(\mathbf{r''}) \varphi_p^*(\mathbf{r''}) \) and sum over the indices \( p, h \) to obtain after the renaming \( \mathbf{r} \rightarrow \mathbf{r''} \)

\[ x(\mathbf{r}) = \int d^3 r' \chi_0^{(+)}(\mathbf{r}, \mathbf{r'}, \omega) \left\{ \delta h_{ext}(\mathbf{r'}) + \int d^3 r'' V(\mathbf{r'}, \mathbf{r''}) [x(\mathbf{r''}) + y(\mathbf{r''})] \right\} \tag{63} \]

\[ y(\mathbf{r}) = \int d^3 r' \chi_0^{(-)}(\mathbf{r}, \mathbf{r'}, \omega) \left\{ \delta h_{ext}(\mathbf{r'}) + \int d^3 r'' V(\mathbf{r'}, \mathbf{r''}) [x(\mathbf{r''}) + y(\mathbf{r''})] \right\} \]
with
\[
\chi_0^{(+)}(r, r', \omega) = \sum_{p,h} \frac{\varphi_p(r)\varphi_h^*(r')\varphi_h(r')}{\hbar \omega - \epsilon_p + \epsilon_h + i\eta},
\]
\[
\chi_0^{(-)}(r, r', \omega) = \sum_{p,h} \frac{\varphi_p^*(r)\varphi_h(r)\varphi_p(r')}{\hbar \omega + \epsilon_p - \epsilon_h + i\eta}.
\] (64)

Noting that
\[
\delta \rho(r; \omega) = [x(r) + y(r)]
\] (65)

and defining the Lindhard function for an inhomogeneous system as
\[
\chi_0(r, r'; \omega) = \chi_0^{(+)}(r, r'; \omega) - \chi_0^{(-)}(r, r'; \omega)
\] (66)

we get, by adding the two equations (63)
\[
\delta \rho(r; \omega) - \int d^3r'd^3r'' \chi_0(r, r''; \omega)V(r'', r')\delta \rho(r'; \omega) = \int d^3r' \chi_0(r, r'; \omega)\delta h_{\text{ext}}(r'; \omega).
\] (67)

This is the desired result. It is known as the “Random Phase approximation”. Since there are about 25 derivations of this result, I refrain from explaining what that has to do with “random phase”.

5 Homogeneous system

In the limit of a homogeneous system, the potential is a function of the distance
\[
V(r, r') = V(|r - r'|)
\] (68)

We define the Fourier transform with a density factor
\[
\widetilde{V}(q) = \rho \int d^3r e^{iqr}V(r).
\] (69)

The single-particle wave functions are just plane waves, i.e.
\[
\chi_0^{(+)}(r, r', \omega) = \frac{1}{\Omega^2} \sum_{p,h} \frac{e^{i(p-h)\cdot(r-r')}}{\hbar \omega - \epsilon_p + \epsilon_h + i\eta}
\]
\[
= \frac{\rho}{\Omega} \sum_q e^{iq\cdot(r-r')} \frac{1}{N} \sum_h \frac{n(h)\hat{n}(h + q)}{\hbar \omega - \epsilon_h + i\eta}
\]
\[
= \frac{\rho}{(2\pi)^3} \int d^3q e^{iq(r-r')} \widehat{\chi}_0^{(+)}(q, \omega),
\] (70)
\[ \chi_0^{(-)}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\Omega^2} \sum_{ph} \frac{e^{i(p-h) \cdot (\mathbf{r}'-\mathbf{r})}}{\hbar \omega + \epsilon_p - \epsilon_h + i\eta} \]

\[ = \frac{\rho}{\Omega} \sum_q e^{i\mathbf{q} \cdot (\mathbf{r}'-\mathbf{r})} \frac{1}{N} \sum_h \frac{n(h)\bar{n}(\mathbf{h} + \mathbf{q})}{\hbar \omega + \epsilon_{h+\mathbf{q}} - \epsilon_h + i\eta} \]

\[ \equiv \frac{\rho}{(2\pi)^3} \int d^3q e^{i\mathbf{q} \cdot (\mathbf{r}'-\mathbf{r})} \chi_0^{(-)}(q, \omega). \quad (71) \]

Since the functions \( \chi_0^{(+)}(q, \omega) \) and \( \chi_0^{(-)}(q, \omega) \) are invariant under \( \mathbf{q} \rightarrow -\mathbf{q} \), we can add the two functions to the coordinate form of the full response function of the non-interacting system and write

\[ \chi_0(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\rho}{(2\pi)^3} \int d^3q e^{i\mathbf{q} \cdot (\mathbf{r}'-\mathbf{r})} \chi_0(q, \omega) \quad (72) \]

If, furthermore, we approximate the Hartree-Fock spectrum by the free single-particle spectrum, we obtain the familiar Lindhard function. This is actually consistent with the approximation to leave out the exchange matrix elements in the matrices \( \mathbf{A} \) and \( \mathbf{B} \). We finally transform the full equation (67) in momentum space and solve

\[ \delta \rho(q, \omega) = \frac{\chi_0(q, \omega)}{1 - V(q)\chi_0(q, \omega)} \delta \bar{h}(q, \omega), \quad (73) \]

or

\[ \chi(q, \omega) = \frac{\chi_0(q, \omega)}{1 - V(q)\chi_0(q, \omega)}. \quad (74) \]

This is the beloved “RPA” equation for the density-density response function.

The present derivation is perhaps a bit complicated, but it shows very well what kinds of approximations have been made. These are

- Assume a local, translationally invariant (effective) interaction
- Omit exchange
- Assume a free single particle spectrum

References
