QTM Concepts (learning objectives)

1./ Periodic functions

- real and reciprocal lattice; Brillouin zone / Wigner-Seitz cell
- periodic functions

2./ Lattice and Electron Dynamics

- electron/lattice separation
- BO approximation
- binding (van der Waals, ionic, covalent)

3./ Phonons

- harmonic approx; dynamic matrix
- quantisation; ladder ops; commutation
- equations of motion
- phonon dispersion; density of states
- average occupation number

- high/low temp limit
- internal energy; Debye-temp.
- specific heat
- Einstein model
- density of states (def., how to calculate)
- acoustic/optical phonons (what are they, etc.)

4./ Free Electrons

- Bloch theorem;
- effective mass concept
- electronic density of states (free electrons)
- Fermi-energy
- free electrons in semiconductors (→ e/h concept)

5./ Electron-Electron Interaction

- 2nd quantisation
- def.: number ops; field ops;
  occupation number rep.
- Hartree-Fock approx: decoupling
  → effective constit.
- expectation values (grand canonical ensemble)
- plasmons (what are they;
  plasma frequency;
  Drude theory - microscopic
- random phase approx (what does it imply?)
- excitons in semiconductors
  (→ what are they;

6./ Optical Properties

- Maxwell's eqns and complex ref. ind.
- metal optics, skin depth
- opt. prop. of semiconductors
- 2-level system / 2-band system
- semiconductor Bloch equations
  → simple semicond. model
- linear response theory

Imperial College London

BSc/MSci EXAMINATION May 2014

This paper is also taken for the relevant Examination for the Associateship

MOCK-EXAM QUESTIONS: QUANTUM THEORY OF MATTER

For 4th-Year Physics Students

Mock-Exam Questions

A selection of questions
Marks shown on this paper are indicative of those the Examiners anticipate assigning.

General Instructions

Complete the front cover of each of the THREE answer books provided.

If an electronic calculator is used, write its serial number at the top of the front cover of each answer book.

USE ONE ANSWER BOOK FOR EACH QUESTION.

Enter the number of each question attempted in the box on the front cover of its corresponding answer book.

Hand in THREE answer books even if they have not all been used.

You are reminded that Examiners attach great importance to legibility, accuracy and clarity of expression.

1. Many properties of *simple metals* such as Na, K, Mg, Cu, ... can in good approximation be described in terms of the *Sommerfeld model* comprising the following assumptions:

1. Ideal Fermi-gas in a volume $V = L^3$.
2. Periodic boundary conditions on V.
3. Constant lattice potential $V(\mathbf{r}) = \text{const.}$.

(i) Write down the eigenenergies and eigenfunctions. [12 marks]

(ii) Calculate the Fermi-energy and Fermi-wavevector as a function of the electron density $n = N/V$. [6 marks]

(iii) How is the average energy per electron related to the Fermi-energy? [6 marks]

(iv) Calculate the electronic density of states $\rho(E)$. [6 marks]

[Total 30 marks]

2. Consider a d-dimensional crystal (N lattice sites) with one atom (of mass M) per unit cell; $\mathbf{R}_n$ shall denote the lattice vector and $\mathbf{u}_n$ is the elongation of the atom in the n-th unit cell. In harmonic approximation the phonon Hamiltonian may read:

$$H = \sum_{\mathbf{q},j} \hbar\omega_j(\mathbf{q}) \left(b^\dagger_{\mathbf{q}j} b_{\mathbf{q}j} + \frac{1}{2} \right). \tag{1}$$

(i) Show that for the j^{th} component of the elongation vector we have:

$$u_{n,j} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{R}_n} \sqrt{\frac{\hbar}{2M\omega_j(\mathbf{q})}} \left(b_{\mathbf{q}j} + b^\dagger_{-\mathbf{q}j} \right). \tag{2}$$

Hint: Use a cartesian coordinate system such that the dynamic matrix is diagonal.
[8 marks]

(ii) Calculate the average thermal elongation $\langle \mathbf{u} \rangle$. [5 marks]

(iii) Show that

$$\langle \mathbf{u}_n^2 \rangle = \frac{1}{M} \int d\omega \, n(\omega) \frac{1}{\omega} \coth(\beta\hbar\omega), \tag{3}$$

where $n(\omega) = \frac{1}{N} \sum_{\mathbf{q}j} \delta\left(\omega_j(\mathbf{q})\right)$ is the density of phononic states. [12 marks]

(iv) Explain why $\langle \mathbf{u}_n^2 \rangle$ diverges for $d = 1, 2$ but not for $d = 3$. Consequences?
[5 marks]

[Total 30 marks]

3. Consider free electrons described by by the dispersion relation $\mathscr{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$.

(i) Derive a relation between the Fermi-wavenumber k_F and the Fermi-energy E_F with the particle density $n_e = N_e/V$, where N_e is the total number of electrons, V is the volume. [10 marks]

(ii) Calculate the density of states $\rho(E)$. [10 marks]

(iii) In the low-temperature limit ($k_B T \ll E_F$) and using the Sommerfeld expansion for the number of electrons per unit cell

$$Z_e = \int_0^\mu dE \rho(E) + \frac{\pi^2}{6} (k_B T)^2 \rho^2(\mu) + \mathscr{O}\left(T^4\right), \tag{1}$$

with $\rho' = d\rho/dE$, show that for the temperature dependence of the chemical potential $\mu(E)$ the following expression holds:

$$\mu(T) = E_F - \frac{\pi^2}{6} \frac{\rho'(E_F)}{\rho(E_F)} (k_B T)^2 . \tag{2}$$

[10 marks]

[Total 30 marks]

4. In Hartree approximation, the potential for a single electron at position $\mathbf{r}$ of an atom comprising a positively charged nucleus (charge $+Ne$) and a surrounding electron cloud can be written as

$$\Phi(\mathbf{r}) = \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \nu(\mathbf{r}') - \frac{Ne^2}{r}, \tag{1}$$

where $\nu(\mathbf{r})$ is the electron density. Assume further that the potential $\Phi(\mathbf{r})$ varies very slowly with $\mathbf{r}$ (local, homogenous electron gas).

(i) Show that a consequence of these assumptions is:

$$\nu(\mathbf{r}) \sim \frac{(2m(\varepsilon_F - \Phi(\mathbf{r})))^{3/2}}{3\pi^2}, \tag{2}$$

where ε_F denotes the energy of the highest occupied energy level. [12 marks]

(ii) What value does $\varepsilon_F = 0$ hold for a neutral atom? [6 marks]

(iii) Show that the Poisson-equation is a consequence of (1). Hence, using spherical polar coordinates and assuming spherical symmetry for $r > 0$, derive the Thomas-Fermi equations

$$-\frac{3\pi}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Phi(r)}{\partial r}\right) = 4e^2\left[-2m\Phi(r)\right]^{3/2}. \tag{3}$$

[12 marks]

[Total 30 marks]

5. (i) In the grand canonical ensemble use

$$\langle n_\nu \rangle = \frac{1}{\sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha n_\alpha(\varepsilon_\alpha - \mu)}} \sum_{\{n_\alpha\}} n_\nu e^{-\beta \sum_\alpha n_\alpha(\varepsilon_\alpha - \mu)} \tag{1}$$

for a diagonal single-particle Hamiltonian in occupation representation to show

$$\langle n_\nu \rangle = \frac{1}{e^{\beta(\varepsilon_\nu - \mu)} + 1}\,, \tag{2}$$

where μ is the chemical potential and $\beta = \frac{1}{k_B T}$ with Boltzman-constant k_B and temperature T. [10 marks]

(ii) Then explain that for interaction-less Fermions that are described by the (diagonal) Hamiltonian

$$H = \sum_\alpha \varepsilon_\alpha a_\alpha^\dagger a_\alpha . \tag{3}$$

the following relation applies for (grand canonical) expectation values:

$$\begin{aligned} \langle a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger a_{\alpha_3} a_{\alpha_4} \rangle \;=\; & \langle a_{\alpha_1}^\dagger a_{\alpha_4} \rangle \langle a_{\alpha_2}^\dagger a_{\alpha_3} \rangle \delta_{\alpha_1 \alpha_4} \delta_{\alpha_2 \alpha_3} \\ & - \langle a_{\alpha_1}^\dagger a_{\alpha_3} \rangle \langle a_{\alpha_2}^\dagger a_{\alpha_4} \rangle \delta_{\alpha_1 \alpha_3} \delta_{\alpha_2 \alpha_4} . \end{aligned} \tag{4}$$

[10 marks]

(iii) Show then that as a consequence of (ii),

$$\langle a_{n_1}^\dagger a_{n_2}^\dagger a_{n_3} a_{n_4} \rangle = \langle a_{n_1}^\dagger a_{n_4} \rangle \langle a_{n_2}^\dagger a_{n_3} \rangle - \langle a_{n_1}^\dagger a_{n_3} \rangle \langle a_{n_2}^\dagger a_{n_4} \rangle \tag{5}$$

holds for interaction-less Fermions with respect to any other single-particle basis $|\, n \rangle$. [10 marks]

[Total 30 marks]

Question 1 (mock)

this one with some more detailed comments

(i) Schrödinger equation:

$$-\frac{\hbar^2}{2m}\Delta\psi_{\underline{k}}(\underline{r}) = \varepsilon(\underline{k})\,\psi_{\underline{k}}(\underline{r})$$

$$\Delta = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

ansatz: $\psi_{\underline{k}}(\underline{r}) = \alpha\, e^{i\underline{k}\cdot\underline{r}}$

$|\psi_{\underline{k}}(\underline{r})|^2 d^3r$: probability to find electron in volume element d^3r at location $\underline{r}$

normalisation: $1 \doteq \int_V d^3r\, |\psi_{\underline{k}}(\underline{r})|^2$

$$\Rightarrow \quad \alpha = \frac{1}{\sqrt{V}}$$

eigenfunction: $\psi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{V}} e^{i\underline{k}\cdot\underline{r}}$

→ does not yet take on board any boundary conditions:

electrons in crystal: periodic BC

$$\Rightarrow \psi_k(x+L,y,z) \overset{!}{=} \psi_k(x,y+L,z) = \psi_k(x,y,z+L)$$

$$= \psi_k(x,y,z)$$

$$\Rightarrow k_{x,y,z} = \frac{2\pi}{L} n_{x,y,z} \; ; \quad n_{x,y,z} \in \mathbb{Z} .$$

So: $$\Delta k = \frac{(2\pi)^3}{L^3} = \frac{(2\pi)^3}{V} .$$

eigenenergies:

$$\varepsilon(\underline{k}) = \frac{\hbar^2 k^2}{2m}$$

$$= \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$= \frac{2\hbar^2\pi^2}{mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) .$$

(ii) ground state:

electrons occupy all states with

$$\varepsilon(\underline{k}) \leq \varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

k_F: Fermi wavevector

ε_F: Fermi-energy

total number of electrons:

$$N = 2 \sum_{k \leq k_F} 1 .$$

(2: two spins)

and $$N = \frac{2}{\Delta k} \int_{k \leq k_F} d^3k$$

$$= \frac{2V}{(2\pi)^3} \frac{4\pi}{3} k_F^3$$

$$\Rightarrow k_F = (3\pi^2 n)^{1/3}$$

$$\varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

(iii) $\overline{\varepsilon}$ ← average energy

$$= \frac{2}{N} \sum_{k \le k_F} \frac{\hbar^2 k^2}{2m}$$

$$= \frac{2}{N} \frac{\hbar^2}{2m} 4\pi \int_0^{k_F} dk\, k^4 \frac{1}{\Delta k}$$

$$= \frac{2}{N} \frac{4\pi \hbar^2}{2m} \frac{k_F^5}{5} \frac{V}{(2\pi)^3}$$

$$= \frac{2}{N} \frac{4\pi \hbar^2}{2m} \frac{k_F^2}{5} 3\pi^2 n \frac{V}{8\pi^3}$$

$$= \frac{3}{5} \frac{\hbar^2 k_F^2}{2m}$$

$$= \frac{3}{5} \varepsilon_F .$$

(iv) $g(E)\,dE = \frac{2}{\Delta k} \int d^3k$

$\varepsilon(k) \in [E, E+dE]$ ← energy interval from E to E+dE

$$= \frac{2V}{(2\pi)^3} \left(\frac{d\varphi(E)}{dE \, \Delta} \right) dE$$

phase space volume:

$$\varphi(E) = \int_{\varepsilon(k) \le E} d^3k = \frac{4\pi}{3} k^3 \Big|_{\varepsilon(k)=E}$$

$$= \frac{4\pi}{3} \left(\frac{2m}{\hbar} E \right)^{3/2}$$

then:

$$\frac{d\varphi(E)}{dE} = 2\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E}$$

into $$g(E)\,dE = \frac{2V}{(2\pi)^3}\left(\frac{d\varphi(E)}{dE}\right)dE$$

$$\Rightarrow g(E) = \begin{cases} d\sqrt{E} & \text{for } E \geq 0 \\ 0 & \text{otherwise} \end{cases}$$

with $$d = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$$

$$= \frac{3N}{2\,\varepsilon_F^{3/2}}.$$

Quesito 2 (M1)

$$H = \sum_{qj} \hbar\omega_j(q) \left(b^+_{qj} b_{qj} + \frac{1}{2} \right)$$

(i) $$u_{nj} = \frac{1}{\sqrt{N}} \sum_q e^{iq\cdot R_n} \sqrt{\frac{\hbar}{2M\omega_j(q)}} \left(b_{qj} + b^+_{-qj} \right)$$

Reverse def of phonon creation and annihilation ops:

$$b_{qj} = \frac{1}{\sqrt{N}} \sum_R e^{-iq\cdot R} \left(\sqrt{\frac{M\omega_j(q)}{2\hbar}}\, u_{Rj} + i \sqrt{\frac{1}{2M\hbar\omega_j(q)}}\, p_{Rj} \right)$$

$$b^+_{qj} = \frac{1}{\sqrt{N}} \sum_R e^{iq\cdot R} \left(\sqrt{\frac{M\omega_j(q)}{2\hbar}}\, u_{Rj} - i \sqrt{\frac{1}{2M\hbar\omega_j(q)}}\, p_{Rj} \right)$$

M 2.2

(ii) $\langle u_n \rangle = \frac{1}{\sqrt{N}} \sum_q e^{iq \cdot R_n} \sqrt{\frac{\hbar}{2M\omega_j(q)}}$

$$\left(\langle b_{qj} \rangle + \langle b^+_{-qj} \rangle \right)$$

$$= 0$$

as : • equilibrium expectation values to be of harmonic oscillator op

• all diagonal of creation / annihilation ops vanish in eigen-basis (next state is again an eigenstate)

(iii) $\langle \underline{u}_n^2 \rangle = \sum_j \langle u_{nj}^2 \rangle$

$$= \frac{1}{N} \sum_{qq'j} e^{iq R_n + iq' R_n} \frac{\hbar}{2M} \frac{1}{\sqrt{\omega_j(q)\omega_j(q')}}$$

$$\left(\langle b_{qj} b_{q'j} \rangle + \langle b^+_{-qj} b^+_{-q'j} \rangle + \langle b_{qj} b^+_{-q'j} \rangle + \langle b^+_{-qj} b_{qj} \rangle \right)$$

$$= \frac{1}{N} \sum_{qj} \frac{1}{2M\omega_j(q)} \left(2 \langle b^+_{qj} b_{qj} \rangle + 1 \right)$$

$$= \frac{1}{2M} \int d\omega \, n(\omega) \left(2 \frac{1}{e^{\beta\hbar\omega} - 1} + 1 \right) \frac{1}{\omega}$$

$$= \frac{1}{2M} \int d\omega \, n(\omega) \frac{1}{\omega} \coth\left(\frac{\beta\hbar\omega}{2} \right).$$

(iv) for small ω we may write:

$$n(\omega) \sim \omega^{d-1}$$

With $\coth(x) \sim \frac{1}{x}$ for small x we have:

$$\langle \underline{u}_n^2 \rangle \sim \underbrace{\int d\omega\, \omega^{d-1} \frac{2}{\omega^2}}$$

diverges for $d=1,2$ (but not for $d=3$)

$\Rightarrow \langle \underline{u}_n^2 \rangle$ diverges for $d=1,2$

$\Rightarrow$ 1d and 2d crystals will be unstable!

Question 3 (mock)

(i) $\mathcal{E}(\underline{k}) = \dfrac{\hbar^2 k^2}{2m}$

$$N_e = 2 \sum_{k < k_F} 1$$

$$= 2 \frac{V}{(2\pi)^3} \int_{k \le k_F} d^3k$$

$$= \frac{2V}{(2\pi)^3} \frac{4\pi}{3} k_F^3 . \quad = \frac{V}{3\pi^2} k_F^3$$

Thm: $k_F^3 = 3\pi^2 n_e$

$$E_F = \frac{\hbar^2}{2m} k_F^2$$

$$= \frac{\hbar^2}{2m} (3\pi^2 n_e)^{2/3} .$$

(ii) $g(E) = \dfrac{1}{N_e} \sum_{\underline{k}\sigma} \delta\left(E - \dfrac{\hbar^2 k^2}{2m}\right)$

$$= \frac{2V}{N_e (2\pi)^3} \int d^3k \; \delta\left(E - \frac{\hbar^2 k^2}{2m}\right)$$

$$= \ldots -$$

(ii) cont.

$$g(E) = \dots =$$

$$= \frac{V}{4\pi^3 N_e} \cdot 4\pi \int dk\, k^2\, \delta\left(E - \frac{\hbar^2 k^2}{2m}\right)$$

$$= \frac{V}{\pi^2 N_e} \frac{m}{\hbar} \sqrt{\frac{2m}{\hbar^2} E} .$$

(iii) electrons per unit cell:

$$Z_e = \frac{N_e}{N} = \int dE\, g(E)\, f(E)$$

u.c.

Integral : type $\int dE\, \#(E)\, f(E)$

with $Z_e = \int_0^{\mu} dE\, g(E)$

$$+ \frac{\pi^2}{6} (k_B T)^2 \frac{dg(E)}{dE} + \mathcal{O}(T^4)$$

$k_B T \ll E_F$: $\mu(T) \sim E_F$ $\left(\sim \mathcal{O}(k_B T)^2\right)$

Then: $\int_0^{\mu(T)} dE\, g(E) = \int_0^{E_F} dE\, g(E) + (\mu - E_F)\, g(E_F)$

$$= Z_e + (\mu - E_F)\, g(E_F)$$

Term:

$$\mathcal{Z}_e = \mathcal{Z}_e + (\mu - E_F)\, g(E_F) + \frac{\pi^2}{6} (k_B T)^2 g'(E_F)$$

$$\Rightarrow \quad \mu = E_F - \frac{\pi^2}{6} \frac{g'(E_F)}{g(E_F)} (k_B T)^2$$

Question 4 (sketch of solution)

we have: $\phi(\underline{r}) \approx \text{const} = \phi_0$

Thm: local homogeneous electron gas

Setting $\hbar = 1$ (you should NOT do that in the exam unless instructed)

$$\frac{p^2}{2m} \psi_{\underline{k}}(\underline{r}) + \phi_0 \psi_{\underline{k}}(\underline{r}) = E_{\underline{k}} \psi_{\underline{k}}(\underline{r})$$

has solutions $E_{\underline{k}} = \frac{k^2}{2m} + \phi_0$

constant particle density

$$\begin{aligned} \nu_0 &= \sum_{\underline{k}, G, k < k_F} 1 \\ &= \frac{1}{\pi^2} \int_0^{k_F} dk\, k^2 \\ &= \frac{1}{\pi^2} \frac{k_F^3}{3} \\ &= \frac{1}{3\pi^2} \left(2m(\varepsilon_F - \phi_0)\right)^{3/2} \end{aligned}$$

$$\Rightarrow \quad \nu(\underline{r}) \sim \frac{1}{3\pi^2} \left(2m(\varepsilon_F - \phi(\underline{r}))\right)^{3/2}.$$

(iii) • neutral atom

⇒ charge of electron cloud: -Ne

• outside atom: no electron cloud

$$\left.\begin{array}{l} \Rightarrow \rho(r) = 0 \\ \Rightarrow \phi(r) = 0 \end{array}\right\} \Rightarrow \varepsilon_F = 0,$$

(iii) Poisson equation: remember

$$\nabla^2 \phi(r) + \rho(r) = 0$$

and $$\nabla^2 \frac{1}{|r - r'|} = -4\pi \delta(r - r')$$

Then:

$$\nabla^2 \phi(r) = -4\pi e^2 \rho(r) + 4\pi N e^2 \delta(r)$$

Express ∇^2 in terms of spherical polar coordinates to obtain:

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi(r)}{\partial r}\right) = 4\pi e^2 \rho(r)$$

$$= \frac{4e^2}{3\pi} \left(-2m\phi(r)\right)^{3/2}$$

Question 5

M 5.1

(i) $$\langle n_\nu \rangle = \frac{1}{\sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha n_\alpha (\varepsilon_\alpha - \mu)}} \sum_{\{n_\alpha\}} n_\nu e^{-\beta \sum_\alpha n_\alpha (\varepsilon_\alpha - \mu)}$$

$$= -k_B T \frac{\partial}{\partial \varepsilon_\nu} \ln \sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha n_\alpha (\varepsilon_\alpha - \mu)}$$

$$= -k_B T \frac{\partial}{\partial \varepsilon_\nu} \ln Z_{gc}$$

$$= -k_B T \frac{\partial}{\partial \varepsilon_\nu} \ln \left(\prod_\alpha \left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right) \right)$$

$$= -k_B T \frac{\partial}{\partial \varepsilon_\nu} \sum_\alpha \ln \left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right)$$

$$= -k_B T \frac{-\beta e^{-\beta(\varepsilon_\alpha - \mu)}}{\left(1 + e^{-\beta(\varepsilon_\alpha - \mu)}\right)}$$

$$= \frac{1}{e^{\beta(\varepsilon_\nu - \mu)} + 1} .$$

(ii) $H = \sum_{\alpha} \varepsilon_\alpha a_\alpha^+ a_\alpha$

is diagonal

$\Rightarrow$ only diagonal elements in any expectation values

+ have g.c. representation from (1)

$\Rightarrow$ after applying all ops $a_{\alpha_1}^+ a_{\alpha_2}^+ a_{\alpha_3} a_{\alpha_4}$ we have to return to an occupation-number rep similar to the initial state

$\Rightarrow$ all annihilated electrons have to be re-created

$\Rightarrow$ $\alpha_4 = \alpha_1$; $\alpha_2 = \alpha_3$ $\left.\right\}$ $\delta_{\alpha_1\alpha_4}\delta_{\alpha_2\alpha_3}$

or $\alpha_4 = \alpha_2$; $\alpha_4 = \alpha_3$ $\left.\right\}$ $\delta_{\alpha_4\alpha_2}\delta_{\alpha_1\alpha_3}$

(iii) $\langle a^+_{n_1} a^+_{n_2} a_{n_3} a_{n_4} \rangle$

$$= \sum_{\alpha_1}\sum_{\alpha_2}\sum_{\alpha_3}\sum_{\alpha_4} u^*_{n_1\alpha_1} u^{\times}_{n_2\alpha_2} u_{n_3\alpha_3} u_{n_4\alpha_4} \langle a^+_{\alpha_1} a_{\alpha_2} a_{\alpha_3} a_{\alpha_4} \rangle$$

$$= \sum_{\alpha_1}\sum_{\alpha_2}\sum_{\alpha_3}\sum_{\alpha_4} u^*_{n_1\alpha_1} u^{\times}_{n_2\alpha_2} u_{n_3\alpha_3} u_{n_4\alpha_4} \left(\langle a^+_{\alpha_1} a_{\alpha_4} \rangle \langle a^+_{\alpha_2} a_{\alpha_3} \rangle - \langle a^+_{\alpha_1} a_{\alpha_3} \rangle \langle a^+_{\alpha_2} a_{\alpha_4} \rangle \right)$$

$$= \langle a^+_{n_1} a_{n_4} \rangle \langle a^+_{n_2} a_{n_3} \rangle - \langle a^+_{n_1} a_{n_2} \rangle \langle a^+_{n_2} a_{n_4} \rangle .$$