

Problem Set 4
Physics 481 / Fall 1994
Professor Klaus Schulten

Problem 1: Two-Fermion Operators

- (a) Exercise 9.3.1 of class notes.
- (b) Exercise 9.3.2 1 of class notes.
- (c) Exercise 9.3.3 1 of class notes.

Problem 2: Ethylene π -Electron States

The molecule ethylene C_2H_4 has two electrons that move in two $2p_z$ atomic orbitals, one $2p_z$ orbital on either of its carbons. Denoting the atomic orbitals (including spin) by $|j, \sigma\rangle$, $j = 1, 2$; $\sigma = \pm \frac{1}{2}$ assume that the Hamiltonian for the system is

$$H = -t \sum_{\sigma} \left(c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma} \right) + U \left(c_{1\alpha}^\dagger c_{1\alpha} c_{1\beta}^\dagger c_{1\beta} + c_{2\alpha}^\dagger c_{2\alpha} c_{2\beta}^\dagger c_{2\beta} \right). \quad (1)$$

Here α, β denote spin-up ($|\frac{1}{2}, \frac{1}{2}\rangle$) and spin-down ($|\frac{1}{2}, -\frac{1}{2}\rangle$) states, respectively.

- (a) State all possible 2-electron states of the system in the given basis of single electron states (there are six states).
- (b) Determine the Hamiltonian matrix in the basis of 2-electron states determined in (a).
- (c) Assume $t = 2.5$ eV and $U = 3$ eV and diagonalize the Hamiltonian using *Mathematica*. State the energies for all states of the system. Identify singlet and triplet states.
- (d) Determine the energies in (c) for variable U . Plot the energies as a function of U/t . Discuss the result.

Problem 3: SCF Approximation for 2N Electron System

Let us consider a system of $2N$ ($N \in \mathbb{N}^*$) electrons which move in a set of one electron states $|r, \sigma\rangle$, $r = 1, \dots, S$ ($S > N$). The spatial separation

between these states is such that

1. an electron can jump from a given state $|r, \sigma\rangle$ only into states $|r \pm 1, \sigma\rangle$;
2. the Coulomb repulsion between two electrons acts only if they occupy one and the same orbital state, i.e. $|r, \sigma\rangle$ and $|r, -\sigma\rangle$.

Hence, the model Hamiltonian reads

$$H = H_0 + V, \quad (2)$$

where

$$H_0 = - \sum_{\substack{rs \\ \sigma}} t_{rs} c_{r\sigma}^\dagger c_{s\sigma}, \quad (3)$$

with

$$t_{rs} = \begin{cases} I_r & \text{if } r = s \\ \beta_{rs} & \text{if } |r, \sigma\rangle \text{ and } |s, \sigma\rangle \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

and

$$V = \frac{v}{2} \sum_{\substack{r \\ \sigma, \sigma'}} c_{r\sigma}^\dagger c_{r\sigma'}^\dagger c_{r\sigma'} c_{r\sigma}. \quad (5)$$

The physical meaning of the newly introduced quantities are: I_r is the ionization energy of state $|r, \sigma\rangle$; β_{rs} is the interaction energy connecting states $|r, \sigma\rangle$ and $|s, \sigma\rangle$ and v is the “on site” Coulomb repulsion energy between electrons and it is the same for each state $|r, \sigma\rangle$.

(a) Following the notations and the procedure of the lecture notes (Sec. 9.5, 9.6) prove that the Hamiltonian (2), in the Self Consistent Field (SCF) approximation is given by ¹

$$H_{mf} = H_0 + V_{mf}, \quad (6)$$

where

$$V_{mf} = v \sum_{\sigma}^S \left[\sum_{m=1}^N U_{rm}^* U_{rm} \right] c_{r\sigma}^\dagger c_{r\sigma}. \quad (7)$$

¹Corresponding to the reference state specified by Eq.(9.145) in the lecture notes.

(b) For the benzene molecule C_6H_6 the matrix form of H_0 , in the basis of the six $2p_z$ atomic orbitals of carbon atoms, denoted by $|r\rangle$ ($r = 1, \dots, S = 6$), reads

$$H_0 = \sum_{r,s,\sigma} t_{rs} c_{r\sigma}^\dagger c_{s\sigma} \quad (8)$$

where t_{rs} are the elements of the matrix defined through

$$t = - \begin{pmatrix} I & \beta & 0 & 0 & 0 & \beta \\ \beta & I & \beta & 0 & 0 & 0 \\ 0 & \beta & I & \beta & 0 & 0 \\ 0 & 0 & \beta & I & \beta & 0 \\ 0 & 0 & 0 & \beta & I & \beta \\ \beta & 0 & 0 & 0 & \beta & I \end{pmatrix}. \quad (9)$$

In the case of the benzene molecule determine analytically the exact eigenvalues of the Hamiltonian (6). (Hint: The translational symmetry dictates the form of the wave function.) The values for I , β and v above are really not explicitly needed, but you may use $I = v = 11$ eV and $\beta = 2.5$ eV.

Problem 4: 2D Hubbard Model in the Weak Coupling Approximation

Consider a two dimensional square lattice with $N \times N$, ($N \in \mathbb{N}$), sites and lattice spacing a . Assume that each site contains a single atomic orbital which can accommodate, according to Pauli principle, at most two electrons corresponding to the two different spin orientations $\sigma = \alpha$ ($= \frac{1}{2}$) and $\sigma = \beta$ ($= -\frac{1}{2}$). Further, assume that one has \mathcal{N} ($\leq N^2$) electrons in the system and that

- (i) an electron can move through the lattice only by *hopping* from one site to one of the nearest sites; and
- (ii) electrons interact via a repulsive Coulomb interaction only when they share the same orbital, i.e., they are located at the same lattice site.

The model Hamiltonian of the many-particle system described above can be written, in the second quantization form, as

$$H = H_0 + H_1, \quad (10)$$

where

$$H_0 = -t \sum_{\substack{(\vec{r}, \vec{r}') \\ \sigma}} \left(c_\sigma^\dagger(\vec{r}) c_\sigma(\vec{r}') + c_\sigma^\dagger(\vec{r}') c_\sigma(\vec{r}) \right), \quad (11)$$

and

$$H_1 = U \sum_{\vec{r}} n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) . \quad (12)$$

The Hamiltonian (10–12) is known in the literature as the (one band) Hubbard model (HM). Above, H_0 describes the kinetic energy of the electrons; t is the so called *hopping* amplitude (assumed to be real), $c_{\sigma}^{\dagger}(\vec{r})$ ($c_{\sigma}(\vec{r})$) creates (destroys) an electron with spin σ at lattice site $\vec{r} = (ia, ja)$, ($i, j = 1, \dots, N$) and $\langle \vec{r}, \vec{r}' \rangle$ means that \vec{r} and \vec{r}' label two nearest lattice sites. On the other hand, H_1 describes the on site Coulomb interaction between electrons; U is the Coulomb repulsion energy between two electrons located at a same site, while

$$n_{\sigma}(\vec{r}) = c_{\sigma}^{\dagger}(\vec{r}) c_{\sigma}(\vec{r}) , \quad (\sigma = \alpha, \beta) \quad (13)$$

gives the occupation number of the one particle state $|\vec{r}, \sigma\rangle$ and, obviously, it can take only two values, namely 0 and 1.

The 2D Hubbard model cannot be solved (i.e., diagonalized) exactly. Nevertheless, one can obtain “exact” solutions of the HM if one employs extra approximations. The purpose of this problem is to solve the HM in the so called *weak coupling* limit, when $U \ll t$ holds, and when, as a 0th order approximation we can drop H_1 in Eq.(10) retaining only the kinetic energy term H_0 . The spectrum of H_0 can be calculated exactly and then, the term H_1 can be treated as a small perturbation. So our ultimate goal in this problem is to determine the ground state of H_0 .

(a) For convenience consider that N is a large even number and that one has periodic boundary conditions, i.e., the sites $\vec{r} + N(\pm a, \pm a)$ and \vec{r} are equivalent. Now for an arbitrary function $f(\vec{r})$ we can introduce the following discrete Fourier transforms

$$f(\vec{r}) = \sum_{\vec{k}} \tilde{f}(\vec{k}) e^{i\vec{k}\vec{r}} , \quad (14)$$

and

$$\tilde{f}(\vec{k}) = \frac{1}{N^2} \sum_{\vec{r}} f(\vec{r}) e^{-i\vec{k}\vec{r}} , \quad (15)$$

where

$$\left(-\frac{N}{2} + 1 \right) \frac{\pi}{a} \leq k_{\mu} \leq \frac{N}{2} \frac{\pi}{a} , \quad (\mu = x, y) \quad (16)$$

Prove that in the thermodynamic limit ($N \rightarrow \infty$) Eq.(14) becomes

$$f(\vec{r}) = A \iint \frac{d^2 k}{(2\pi)^2} \tilde{f}(\vec{k}) e^{i\vec{k}\vec{r}} , \quad (17)$$

where $A = (Na)^2$ is the “volume” of the 2D square lattice, $-\frac{\pi}{a} \leq k_\mu \leq \frac{\pi}{a}$, ($\mu = x, y$), and k_μ now is a continuous variable.

(b) Show that by employing the Fourier transform (17), H_0 can be diagonalized as

$$H_0 = A \sum_{\sigma} \iint \frac{d^2 k}{(2\pi)^2} \epsilon(\vec{k}) \tilde{c}_{\sigma}^{\dagger}(\vec{k}) \tilde{c}_{\sigma}(\vec{k}) , \quad (18)$$

where

$$\epsilon(\vec{k}) = -4t (\cos(k_x a) + \cos(k_y a)) . \quad (19)$$

So, in the *weak coupling* approximation the 2D Hubbard model is equivalent with a system of \mathcal{N} non-interacting, spin 1/2, particles with dispersion law (i.e., the energy of a particle for a given value of \vec{k}) given by Eq.(19). Note that $\epsilon(\vec{k})$ can take values only within the range of a finite interval known as the *energy band width*.

(c) The ground state $|Gnd\rangle$ of a non-interacting many-fermion system is obtained by filling up the Fermi sea, i.e., by distributing the fermions in the one-particle quantum states (according to Pauli’s exclusion principle a certain quantum state can accommodate one and only one fermion at a time) corresponding to energy values less or equal to the so called *Fermi energy* ϵ_F .

Prove that we have the following expressions for the

(i) ground state

$$|Gnd\rangle = \prod_{\substack{\vec{k}, \sigma \\ \epsilon(\vec{k}) \leq \epsilon_F}} \tilde{c}_{\sigma}(\vec{k}) |0\rangle , \quad (20)$$

where $|0\rangle$ denotes the *vacuum*, i.e., the state without any particle present;

(ii) ground state energy

$$E_0 = 2A \iint_{\epsilon(\vec{k}) \leq \epsilon_F} \frac{d^2 k}{(2\pi)^2} \epsilon(\vec{k}) , \quad (21)$$

(iii) total number of particles

$$\mathcal{N} = 2A \iint_{\epsilon(\vec{k}) \leq \epsilon_F} \frac{d^2 k}{(2\pi)^2} . \quad (22)$$

Now all we left to do is to determine the Fermi energy ϵ_F as a function of t , a and \mathcal{N}/N^2 .

(d) Eq.(22) allows us to calculate ϵ_F in terms of the so called *filling factor* defined through

$$n \equiv \frac{\mathcal{N}}{N^2} \left(= \frac{\text{total number of particles}}{\text{total number of lattice sites}} \right). \quad (23)$$

Argue that $0 \leq n \leq 2$ and then prove that n and ϵ_F are related through the following equation

$$n = \frac{a^2}{2\pi^2} \mathcal{A}(\epsilon_F), \quad (24)$$

where

$$\mathcal{A}(\epsilon_F) = \iint_{\epsilon(\vec{k}) \leq \epsilon_F} d^2k \quad (25)$$

is the area enclosed in the k -plane by the iso-energy curve $\epsilon(\vec{k}) = \epsilon_F$. Eq.(24) gives ϵ_F as an implicit function of n .

(e) By employing the `ContourPlot` feature of *Mathematica* (or by any other means) plot the iso-energy curves $\epsilon(\vec{k}) = \epsilon_F$ in the (k_x, k_y) plane. In your plot single out the curve corresponding to $\epsilon_F = 0$. Indicate on the same plot the location of the curves corresponding to $\epsilon_F < 0$ and $\epsilon_F > 0$ respectively.

(f) Using Eq.(24), prove that

(i) $\epsilon_F(n = 1) = 0$, and

(ii) $\epsilon_F(2 - n) = \epsilon_F(n)$, $0 \leq n \leq 1$.

(This last equation has to do with the *particle-hole* symmetry of the model.)

(g) By evaluating numerically the area $\mathcal{A}(\epsilon_F)$ for $\epsilon_F \in [-8t, 8t]$ and by using Eq.(24) determine the functional dependence $\epsilon_F(n)$; provide your answer as a plot of $\epsilon_F/8t$ vs. n .

(h) Proceeding similarly as at part (g), determine numerically the ground state energy density $\mathcal{E}_0 \equiv E_0/A$ as a function of the filling factor n . Present your results as a plot of \mathcal{E}_0/t vs. n .

(i) Analogue to the one-particle density operator (see lecture notes) one can define the so called one-particle density of states (DOS) through

$$\rho(\epsilon) = \iint \frac{d^2k}{(2\pi)^2} \delta(\epsilon - \epsilon(\vec{k})), \quad (26)$$

where $\delta(x)$ is the *Dirac–delta* functional. $\rho(\epsilon)d\epsilon$ gives us the number of one-particle states (with a definite spin orientation) corresponding to energies $\epsilon \in]\epsilon, \epsilon + d\epsilon[$.

Show that the following relations hold

$$\mathcal{E}_0 = 2A \int_{-8t}^{\epsilon_F} \epsilon \rho(\epsilon) d\epsilon , \quad (27)$$

and

$$n = 2a^2 \int_{-8t}^{\epsilon_F} \rho(\epsilon) d\epsilon . \quad (28)$$

Try to obtain an analytic expression for $\rho(\epsilon)$ and then plot $\rho(\epsilon)$ vs. ϵ . Note that $\rho(\epsilon)$ can be evaluated numerically even if you are not able to find an analytical expression for it. Notice that $\rho(\epsilon)$ has an *integrable singularity* for $\epsilon = 0$ (the so called *van Hove* singularity). The simplest (but not necessarily the best) way of dealing with this singularity during your numerical calculations (by using *Mathematica* or anything else) is to eliminate a small interval around $\epsilon = 0$ (say $-10^5 < \epsilon/t < 10^5$) from the spectrum $-8t < \epsilon < 8t$.

Due Tuesday, March 21 in mail box of Gheorghe-Sorin Paraoan.