561 F 2005 Lecture 4

Second Quantization and Elementary Excitations: Phonons and Electrons
References: Second quantization: Mahan 1.1,1.2,1.3A, Pines p. 18, p. 67; Fetter and Walecka; Phillips Ch 3; many other texts.

Elementary Excitations Condensed Matter I: Nuclear Vibrations - Phonons
References: Phillips, Sec. 10.1, 10.2; Pines, Ch. 2; Doniach, Ch. 1; class notes.

In the Adiabatic Approximation, we have shown the equation for nuclear motion can be written:

$$\hat{H}_N \chi_m(\{R_I\}) = [\sum_I \frac{\hbar^2}{2M_I} \boldsymbol{\nabla}_I^2 + E_0(\{R_I\})]\chi_m(\{R_I\}) = E_m \chi_m(\{R_I\}) \tag{1}$$

Define displacements of the atoms from their equilibrium positions, $R_I = R_I^0 + u_I$, and expand the potential energy in powers of u_I,

$$E_0(\{R_I\}) = E_0(\{R_I^0\}) + \frac{1}{2} \sum D_{IJ}^{\alpha\beta} u_I^\alpha u_J \beta + \dots \tag{2}$$

where the linear terms vanish, the D's are second derivatives, etc. The exact eigenstates can be written as $\chi_m(\{u_I\})$.

Harmonic Approximation
In the harmonic approximation, where we neglect all higher order derivatives, the equations are exactly soluble as independent oscillators, even though it is a strongly coupled system of nuclei. This is a very good approximation at low temperatures for all solids except H and He, where zero point motion is large. (Note that the Lindeman criterion for melting is $\sqrt{\langle u^2 \rangle} \approx 0.2a$, where a is a typical interatomic distance, so the harmonic approximation is often good for many purposes up to the melting temperature.

The quantum system can be treated by solving the classical equations of motion for the classical oscillator eigenmodes and quantizing the oscillators. From the Bloch theorem the eigenmodes can be classified by the **k**, e.g., for one atom per cell, (considering a normalization to a volume of N unit cells)

$$u_I = \frac{1}{\sqrt{N}} \sum_k u_k e^{ikR_I^0} \; ; \; p_I = M \frac{du_I}{dt} = \frac{1}{\sqrt{N}} \sum_k p_k e^{ikR_I^0}, \tag{3}$$

The classical hamiltonian becomes

$$H = \sum_k \left[\frac{1}{2M} p_k^* p_k + \frac{M}{2} \omega_k^2 u_k^* u_k \right]. \tag{4}$$

where

$$M\omega_k^2 \equiv \sum_J D_{IJ} e^{ik(R_I^0 - R_J^0)}. \tag{5}$$

Defining new operators

$$Q_k = \left(\frac{M\omega_k}{2\hbar} \right)^{1/2} u_k, \quad P_k = \left(\frac{1}{2\hbar M\omega_k} \right)^{1/2} u_k, \tag{6}$$

the hamiltonian becomes

$$H = \sum_k \hbar\omega_k \left[P_k^* P_k + Q_k^* Q_k \right]. \tag{7}$$

Quantizing the independent oscillators, the creation and annihilation operators are

$$a_k^\dagger = (Q_k^* - iP_k), \quad a_k = (Q_k + iP_k^*), \tag{8}$$

and the hamiltonian becomes

$$H = \frac{1}{2} \sum_k \hbar\omega_k \left[a_k^\dagger a_k + a_k a_k^\dagger \right] = \sum_k \hbar\omega_k \left[a_k^\dagger a_k + \frac{1}{2} \right]. \tag{9}$$

Note that the order of the operators is crucial!

The state of the nuclei in the harmonic approximation is fully specified by the number of quanta in each of the eigenmodes modes of vibration. Since the quantized modes are bosons, the many body state is the symmetrized combination, which is simply a product wavefunction.

It is straightforward to show that in d dimensions there are d modes that have frequency ω that vanishes as $k \to 0$.

This is the first example of "elementary excitations". This gives the exact many-body description in the harmonic approximation, and it defines a complete set of eigenstates which are a convenient basis for describing the system even when anharmonic interactions are included.

Collective Excitation

A phonon at a particular k, ω is a *collective excitation* in which all the nuclei move in unison. The harmonic case is the special case where the equations for this collective excitation are easily solved to find non-interacting excitations (phonons). In general this is not the case!

Qualitative examples of phonons

See Phillips Ch. 10 for the example of a chain of atoms.

Since the nuclei are charged, long ranged Coulomb interactions lead to longitudinal plasma modes with ω that is finite as $k \to 0$ – unless the electrons "screen" the long range interactions. This happens in a metal, and a homework problem is to derive the qualitative result that the phonons properly have accoustic modes with $\omega \propto k$, and qualitatively relate the sound velocity to the Fermi velocity.

Anharmonic Interactions

In the presence of anharmonic interactions, the problem is no longer exactly soluble. The energy can always be written in an expansion

$$E_0(\{R_I\}) = E_0(\{R_I^0\}) + \frac{1}{2!} \sum_{IJ} D_{IJ} u_I u_J + \frac{1}{3!} \sum_{IJK} D_{IJK} u_I u_J u_K + \ldots, \tag{10}$$

where we have dropped the vector index for simplicity. It is most advantageous to work in the basis of the elementary excitations, (the phonons) since the harmonic terms are diagonal in this basis. Since the $u's$ are simply related to the creation and annihilation operators, it is straightforward to write the cubic term in terms of the a_k^+ and a_k. This is left as an exercise (not required) to develop the perturbation expressions, and to interpret the terms as the various possible ways for a phono to scatter while creating or destroying another phonon. Finally, one can write down the temperature dependent factors that show the general trends.

Elementary Excitations Condensed Matter II: Electronic Excitations
References: Phillips Ch. 4,5; Mahan, ch 1.2, Pines Ch 3; class notes.
Second Quantized Form of Hamiltonian

$$\hat{H} = \sum_{p\sigma} \epsilon_p c_{p\sigma}^+ c_{p\sigma} + \frac{1}{2} \sum_k V_k \sum_{p\sigma p'\sigma'} c_{p+k\sigma}^+ c_{p'-k\sigma'}^+ c_{p'\sigma'} c_{p\sigma} \tag{11}$$

$$= \sum_{p\sigma} \epsilon_p c_{p\sigma}^+ c_{p\sigma} + \frac{1}{2} \sum_k V_k (\rho_{-k}\rho_k - N), \tag{12}$$

where $V_k = \frac{1}{\Omega}\frac{4\pi e^2}{k^2}$ and $\rho_k = \sum_{p\sigma} c_{p+k\sigma}^+ c_{p\sigma}$. In general one always has sums of the form $\frac{1}{\Omega}\sum_k \to \frac{1}{(2\pi)^D}\int d^D k$, where D is the dimension. (We will sometimes set the normalization volume $\Omega = 1$.)

This hamiltonian is valid only for homogeneous Jellium because we have assumed the single particle terms are diagonal in momentum index p. However, a general form can be made for for atoms, crystals, and molecules if one changes only the single particle part, since the electron-electron interactions always have the Coulombic form shown.

For example, the exchange energy can be derived as

$$E_x = \frac{1}{2} \sum_k V_k \sum_{p\sigma p'\sigma'} \langle 0|c_{p+k\sigma}^+ c_{p'-k\sigma'}^+ c_{p'\sigma'} c_{p\sigma}|0\rangle \tag{13}$$

$$= -\frac{1}{N}(-\frac{1}{2}\sum_{k,k',\sigma} V_{k'})\langle \rho_{k+k',\sigma}\rho_{k,\sigma}\rangle \tag{14}$$

$$= \frac{1}{N}(-\frac{1}{2}\sum_{k,k'<k_F} V_{k-k'}) = -\frac{0.916}{r_s} \; Ryd. \tag{15}$$

Hartree-Fock Theory for Jellium

We have previously derived the form of exchange in the first-quantized notation. The key ingredients were the pair distribution function defined by

$$g(r,r') = \frac{1}{\rho(r)}\frac{1}{\rho(r')}p(r,r') \tag{16}$$

where

$$p(r,r') = \langle \Psi|\sum_{i\neq j}\delta(r-r_i)\delta(r-r_j)|\Psi\rangle \tag{17}$$

is the joint probability of simultaneously finding an electron at points r and r'.

In second quantized form in terms of the elementary excitations (plane waves) it is most convenient to work in k-space. For a homogeneous system one can define the static structure factor $S(k)$ (see Pines and Fulde)

$$S(k) = \int d^3 r p(r) exp(ikr) \tag{18}$$

$$= \frac{1}{N} \langle \Psi | \sum_{i,j} exp(-ik(r_i - r_j)) | \Psi \rangle \tag{19}$$

$$= \frac{1}{N} \langle \Psi | \rho_{-k} \rho_k | \Psi \rangle \tag{20}$$

which includes the self-term. In terms of creation and annihilation operators, this may be written

$$S(k) = \frac{1}{N} \langle 0 | \sum_{p\sigma} c_{p-k\sigma}^\dagger c_{p\sigma} \sum_{p'\sigma'} c_{p'+k\sigma'}^\dagger c_{p'\sigma'} | 0 \rangle, \tag{21}$$

which after some algebra can be shown to be

$$S(k) = N\delta_{k=0} + \frac{1}{N} \sum_{p\sigma} (1 - n_{p-k\sigma}) n_{p\sigma}, \tag{22}$$

where is the occupation $n_{p\sigma} = 1$ for $k < k_F$ and 0 for $k > k_F$. (See Pines p 75 and class notes.)

Thus the Hartree-Fock structure factor is very simple in k space (See Pines p 75 and class notes.) For $k \neq 0$, define $x = \frac{k}{2k_F}$, in which case

$$S(k) = \frac{3}{2}x - \frac{1}{2}x^3, x < 1 \tag{23}$$

$$S(k) = 1, x > 1 \tag{24}$$

A main point is that $S(k) = 1$ for $k > 2k_F$, so that the the particles are uncorrelated except for the Pauli exclusion between states with $k < k_F$.

For a homogeneous system, one can Fourier transform this expression

$$g(r) = \frac{1}{N} \sum_k (S(k) - 1) exp(ikr) \tag{25}$$

to recover the same results as derived before for the exchange hole in real space. (Note: For an uncorrelated system $S(k) = 1$, $k \neq 0$, and $S(0) = N$, (self term). Some texts define S without the self term, so that $S(0) = 0$, e.g., Mahan, p. 74.)

Beyond Hartree-Fock: Correlations

In the class notes we give the main reasons why it is difficult to go beyond H-F. In finite systems, one finds the configuration-interaction expansion which grows exponentially with the number of particles. In condensed matter expansions formally diverge (Gellmann-Bruckner). This is easily seen in Jellium just by examining the integrals. What to do? This is the subject of the many-body theory of the course.

Conclusions

- Elementary excitations: Phonons and electrons

- Second quantization convenient for specifying hamiltonian and interactions

- Creation and annihilation operators defined to create and annihilate eigenstates of a single particle hamiltonian: harmonic phonons; non-interacting electrons

- Nuclear motion is a strongly interacting problem - the motion of nuclei is highly correlated - but in the harmonic approximation one can transform to non-interacting elementary excitations - phonons - a phonon is a collective excitation of the nuclei

- Interacting electron hamiltonian

- Structure factor and Exchange hole in Hartree-Fock approximation revisited in second quantization

- How to go beyond Hartree-Fock? Perturbation expansion in the interaction ($\propto e^2$) formally diverges - can be summed in a convergent way - leads to non-analytic behavior (as it must!)

- Gell-Mann Brueckner results; Wigner interpolation formula; improved results